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SKERRATT-LOVE, Katrina Leng-Hong

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Phosphate solubility and its effects on US radioactive waste glass properties

Katrina Leng-Hong Skerratt-Love

A thesis submitted in partial fulfilment of the requirements of
Sheffield Hallam University
for the degree of Doctor of Philosophy

May 2023

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Abstract

The Hanford Site in Washington State, USA is a decommissioned nuclear production site, home to 250 000 m³ of radioactive waste which is stored in 158 steel tanks, initially only for short term use and now subject to extensive and widespread corrosion problems. Numerous tanks are leaking radioactive 'sludge' containing a complex mixture of many elements of the periodic table. In an effort to clean up the waste, vitrification implementing a borosilicate glass composition was selected in 1989 as a means of safer disposal. However, previous research has identified that the final vitrified waste form may still be susceptible to leaching, leading to the potential release of radionuclides and other toxic components into groundwater in geological repositories. One potentially problematic component of the waste arises as a result of pre-processing: phosphorus compounds. Phosphorus pentoxide (P₂O₅) is poorly soluble in borosilicate glass systems, with concentrations >3.2 mol% (>4.5 wt%) potentially leading to phase separation that can affect melt viscosity and chemical durability. These are of particular importance because an overly viscous melt will be unpourable and may damage the melter if the increase in viscosity is due to the presence of crystallites and/or salt accumulation; and poor chemical durability could result in the leaching of radionuclides within geological repositories, ultimately resulting in groundwater contamination. Hence, it is important to establish the effects of different levels of P₂O₅ on the properties of radioactive waste borosilicate glasses.

This research investigated the effects of doping and altering the P₂O₅ content on the structure and properties of borosilicate glass compositions based on Hanford high level waste (HLW), low level activity waste (LAW), and immobilised low level activity waste (ILAW). X-ray fluorescence (XRF) spectroscopy and Inductively Coupled Plasma Optical Emission spectroscopy (ICP-OES) were used to analyse the chemical composition. X-ray diffraction (XRD) was used for crystalline phase identification and to confirm the amorphous nature of the glasses, where crystalline phases were quantified using Rietveld analysis and visually imaged using scanning electron microscopy (SEM). Glass structure was analysed using Raman spectroscopy, ⁵⁷Fe Mössbauer spectroscopy, X-ray absorption near edge structure (XANES) spectroscopy, and magic angle spinning nuclear magnetic

resonance (MAS-NMR) spectroscopy. The rheological behaviour of melts was investigated using high temperature viscosity (HTV) measurements, whilst glass chemical durability was analysed using the 7-day product consistency test (PCT) method B, and the thermal properties were determined using differential thermal analysis (DTA) and dilatometry.

The main findings were that simple sodium borosilicate glasses had a solubility limit of between 2.7 ± 0.02 and 4.0 ± 0.01 mol% P_2O_5 . When glass compositions were further complicated with additions of other oxides to more accurately represent Hanford HLW and LAW glass waste forms, the solubility limits of P_2O_5 were lower: between 0.69 ± 0.03 and 1.19 ± 0.00 mol% P_2O_5 for the HLW glasses, and 1.86 ± 0.00 and 2.04 ± 0.02 mol% P_2O_5 for LAW glasses. When P_2O_5 was added to a ILAW simulant glass its solubility was $>0.71 \pm 0.03$ mol%. When the solubility limit was exceeded in these glass systems, nucleation-type phase separation and crystallisation occurred, producing phosphate-based crystal phases. Whilst the additions of P_2O_5 did not seem to increase the solubility of other components, in particular sulphate (SO_4^{2-}), it did lead to the suppression of crystallisation in the heat treated HLW glasses. The structural analysis of the simple sodium borosilicate glasses doped with P_2O_5 provided an insight into the effects of P_2O_5 whilst its behaviour could be inferred in more complicated glasses. P_2O_5 initially entered the borosilicate glass structure as ultraphosphate (Q^3_P) but changed to orthophosphate (Q^0_P), pyrophosphate (Q^1_P), and metaphosphate (Q^2_P) as a function of the P_2O_5 concentration, where the lack of change in the boron (3+) tetrahedral ion, boron (3+) trigonal ion ($^{[3]}B^{3+}$: $^{[4]}B^{3+}$) ratio with increasing P_2O_5 content suggested that the phosphorus (P^{5+}) was potentially entering the $^{[4]}B$ sub-network, but where its oxygen (O^{2-}) was supplied by the silicate network, causing the non-bridging oxygens (NBØs) on the silicon (Si^{4+}) to transform into bridging oxygens (BØs) resulting in its re-polymerisation, as evidenced by the decrease in the Q^3_{Si} and increase in Q^4_{Si} units.

These glass systems provided a guide to the maximum P_2O_5 contents that can be present in the vitrified waste to avoid any potentially undesirable effects of phase separation and / or crystallisation. Insights into the structural changes and crystallisation behaviour of these glass systems, caused by altering their compositions, can be used to help inform crystallisation discriminators

(parameters determining crystallisation tolerances) used to limit the waste loading of glasses prepared from Hanford wastes with high P_2O_5 contents.

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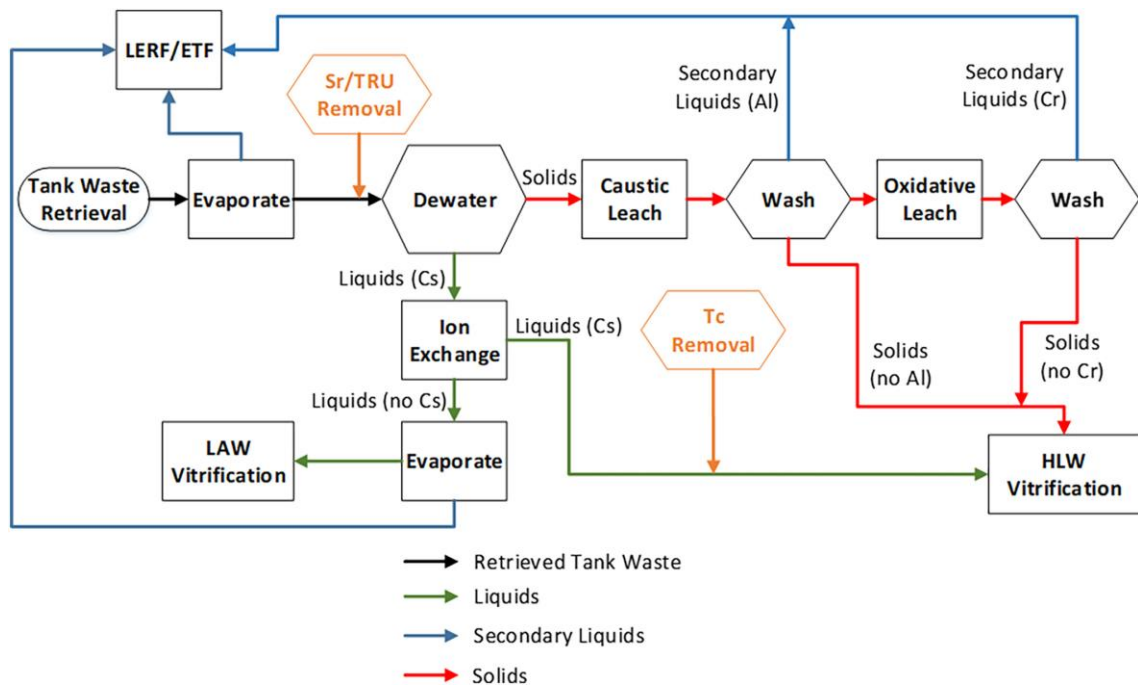
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Chapter 1: Introduction

The Hanford Site in the USA is a decommissioned nuclear site that was used for the production of plutonium during the Cold War and World War II. The production processes left behind solid and liquid wastes that posed, and continue to pose, an environmental risk including to the Columbia River. The waste was initially stored in 177 underground storage tanks, where 149 were single-shell tanks and 28 were double-shell tanks ranging in capacity with an overall total of 250 000 m³ (Colburn & Peterson, 2021; Wells et al., 2011). In 1989, the US Department of Energy (DoE), the Environmental Protection Agency (EPA), and the Washington State Department of Ecology entered the Tri-Party Agreement (TPA), for the comprehensive clean-up of the Hanford Site (Anderson, 2022). This clean-up process will use vitrification to convert complex mixtures of radioactive liquid, solid and sludge waste into a glass (Wells et al., 2011). Vitrification was selected as a means of making the disposal of the waste safer because it encases the harmful radioactive nuclides, preventing them from leaching into underground water aquifers or rivers.

The complication with the Hanford tank waste is its variation from tank to tank as a result of purification processes (Colburn & Peterson, 2021). Hanford wastes contain the majority of elements from the periodic table, where a variety have been identified as problematic components, for example, elements from pre-processing procedures e.g., P, metals (Al, Bi, Cu, Na, Fe, Si and others), anionic species, actinides, Cs, Sr, Te, and organics (Colburn & Peterson, 2021). Before the waste is vitrified, it will undergo pre-treatment at the waste treatment plant (WTP), where it will be retrieved and evaporated to meet the incoming waste acceptance criteria. The pre-treatment can be expressed via a flowsheet published by Colburn and Peterson (2021):



Term	Meaning
LERF	Liquid Effluent Retention Facility
ETF	Effluent Treatment Facility
Sr	Strontium-90
TRU	Transuranic isotopes
Tc	Technitium

Figure 1 - Baseline treatment flowsheet for Hanford Tank waste taken from (Colburn & Peterson, 2021) with copyright permission from Johnson Wiley and Sons (License number: 5612431462656)

The vitrification process outline was briefly described by Goel et al. (2019): (i) the pre-processed waste is mixed with glass forming oxides and other chemicals, (ii) the mixture of glass forming chemicals, waste and ware are fed into the joule-heated ceramic melter, (iii) the waste mixture is heated to convert it into a melt, (iv) the melt is then poured into steel canisters, (v) treatment of off-gases from the melting procedure, and (vi) the canisters are then left to cool ready for storage and disposal in either shallow land burial sites or deep geological repository (Goel et al., 2019).

As the different Hanford tank waste compositions are so complex, it is difficult to characterise the effects of the final vitrified form compositions on wasteform structures and properties. Hence, many studies have investigated identified problematic components e.g., Fe (Ahmadzadeh et al., 2020; Goel et al., 2019; McCloy & Schuller, 2022) and Mo (McCloy et al., 2019; McCloy & Schuller, 2022;

McKeown et al., 2017), in an attempt to understand their effects on the final vitrified forms. P_2O_5 and sulphate (SO_3) are other troublesome components present in the Hanford Site wastes that are to be converted into vitrified waste forms. The P_2O_5 in the waste originates from the bismuth phosphate, reduction and oxidation (REDOX), and plutonium uranium extraction (PUREX) processes used for plutonium extraction from irradiated uranium (Delegard & Jones, 2015). P_2O_5 can be problematic because it is poorly soluble in alkali borosilicate glass systems, with concentrations >4.5 wt% P_2O_5 potentially leading to phase separation (McCloy & Vienna, 2010; Schuller et al., 2008): this can affect melt viscosity and chemical durability (Schuller et al., 2008). In some Hanford waste glasses, P_2O_5 will be present at levels that can impact the melter performance and glass properties (Bingham et al., 2017; Mysen et al., 1981). Phase separation can be undesirable because it can lead to phases with different chemical and mechanical properties, which may increase the leachability of radionuclides in the waste glass, and hence reduce the integrity of the glass. SO_3 , like P_2O_5 , originated from the PUREX process and spent ion exchange resins, and is a known problematic component because of its limited solubility in borosilicate melts (Backnaes & Deubener, 2011; Jin et al., 2019; McKeown et al., 2001, 2004a) leading to a reduction in the waste loading capabilities of the final vitreous form (Peeler et al., 2015). In earlier work the SO_3 limit was set to 0.44 to 1.0 wt% to avoid potential salt accumulation which is highly corrosive to the waste melters (Jin et al., 2019; Skidmore et al., 2019).

The aim of this research was to characterise the effects of P_2O_5 on physical and thermal properties of glasses i.e., viscosity, glass transition temperature (T_g) and structure. In alkali and alkaline earth silicate glasses, phosphate units do not fully incorporate into the silicate network, but instead form phosphate-rich regions with low degrees of connectivity, forming pyrophosphate (PO_4^{3-}) and orthophosphate ($P_2O_7^{4-}$) units (Plodinec, 2000). P^{5+} has a strong ability to scavenge charge-balancing modifier cations from the silicate network, which increases the degree of silicate network polymerisation (Cheng, 2014). In borate and silicate glass systems the extent of miscibility gaps can be influenced by glass modifiers and can be discussed in terms of their polarising power (Taylor, 1990). Polarising power is expressed Z/r , where Z is the ionic charge and, r , is the ionic radius (Calahoo & Wondraczek, 2020). In general, the greater the polarising power of the metal cation the stronger the attraction between it and non-bridging oxygens

(NBØ), and hence the greater the tendency towards clustering of these particles and the occurrence of phase separation (Taylor, 1990). Phase separation in and of itself is not problematic, however, above approximately 4.5 wt% P_2O_5 the vitrified waste ceases to be homogeneous and instead becomes heterogeneous comprising for example, areas of amorphous and crystalline structures.

The output from the research is intended to inform processes which increase the solubility limit of P_2O_5 in relevant radioactive waste simulant compositions with the desired outcome of increasing waste loading capabilities of vitreous wasteforms produced at the Hanford WTP.

1.1 Aims

The aims of the project were as follows:

- Understand the effects of varying P_2O_5 on glass composition, properties, and structure.
- Identify and characterise phase separation / crystallisation in relevant glasses.
- Support increasing waste loading of current high-level activity and low-level activity wasteforms produced at the WTP, Hanford site.

1.2 Scope of the Thesis

Chapter 2 - Literature Review

This review evaluates relevant literature and is split into four main sections: (i) Glass formation theory; (ii) Glass composition, structure, and composition; (iii) Radioactive waste vitrification and the Hanford site; and (iv) P_2O_5 and SO_3 solubility in relevant glasses.

Chapter 3 - Experimental Methodology

The experimental methodology chapter discusses the glass synthesis and subsequent analysis techniques used to evaluate the composition, structure, and properties. For each technique used, the relevant theory about it will be discussed, after which this is followed by the parameters used for each technique in relation to the glass samples measured. The techniques used were X-ray Powder Diffraction (XRD), X-ray Fluorescence Spectroscopy (XRF), Inductively Coupled Plasma Optical Emission spectroscopy (ICP-OES), Back scattered

Scanning Electron Microscopy / Electron Dispersive Spectroscopy (BS SEM-EDS), Raman spectroscopy, Mössbauer spectroscopy, solid state Magic Angle Spinning Nuclear Magnetic Resonance (MAS NMR), Fe K-edge X-ray Absorbance Near Edge Spectroscopy (XANES), Product Consistency Test method B (PCT-B), Differential Thermal Analysis (DTA), Dilatometry, High Temperature Viscosity (HTV), and density.

Chapter 4 – Results

The results chapter is divided into five sub-chapters relevant to each glass series studied. Each sub-chapter follows the experimental parameters used, results and discussion relevant to each technique used, and a bullet pointed summary of key findings. The sub-chapters follow the order of the simplest compositional series to the most complex: NBSP, NBSiS-P, HLW, LAW, and ILAW.

Chapter 5 – Discussion

The discussion chapter re-states the main aims and objectives of the thesis, and discusses the glasses studied further in relation to these. The chapter divides the main discussion points in relation to the glass composition, structure, and properties. The chapter then discusses the impacts of this work and its findings in relation to the Hanford site.

Chapter 6 – Conclusions & Future Work

This chapter summarises the main findings of the thesis and suggests future research needed to progress this work further.

Chapter 2: Literature Review

2.1 Glass Formation

2.1.1 Introduction

Glass has existed for many thousands of years, with synthetic (human-made) artefacts being found and dated to about 3100 BC (Desoki, 2019). Natural occurring glass, e.g., obsidian, was used before people learned how to make it, with its uses including components for weapons e.g., spear heads and as cutting tools (Tsampiri, 2018). However, despite its wide usage and long history, the science behind the origin of glass formation remains a fundamental issue in glass science (Hu & Tanaka, 2020). Theories have been formulated to aid in the understanding of the glass structure and explain the different properties, but there is still much to discover. In order to understand why and how vitrification is used to dispose of radioactive waste, it is pertinent to understand the current and accepted theories surrounding glass.

2.1.2 The Definition of Glass

There have been several different definitions of glass in glass science, for example the description by Eduardo Mari in the paper by Zanotto (2017) stating that glasses are '*amorphous solids that are obtained by fast cooling a molten mass averting its crystallisation*' or the definition by Arun K Varshneya where '*Glass is a solid having a non-crystalline structure, which continuously converts to a liquid upon heating*' (Varshneya, 2013; Zanotto, 2017). A quantitative definition of glass was proposed in 1975 by Alfred R. Cooper and Prabhat K. Gupta: '*Glass is an isotropic material with relaxation time $\gg 10^3$ s and $\chi \sim 1$* ', where χ was defined as a normalised correlation range. Zero was a dilute gas and number close to one was for a new normal liquid or a glass (Cooper & Gupta, 1975; Zanotto, 2017). Copper and Gupta (1975) declared that this parameter allowed for a distinct difference between polycrystalline and non-crystalline materials (Zanotto, 2017). A proposed improvement on previous definitions of what is a glass was '*Glass is a non-equilibrium, non-crystalline state of matter that appears solid on a short time-scale but continuously relaxes towards the liquid state*' (Zanotto, 2017).

2.1.3 Glass Formation Theories

The earliest and most simple theory of glass formation was based on the observation by Goldschmidt (1926) stating that glasses of the general formula R_nO_m form the most easily when there is a radius ratio of the cation, R , to the oxygen ion which lies between 0.2 and 0.4 (Shelby, 2005; Wright, 2014). Goldschmidt only believed that melts containing tetrahedrally-coordinated cations could form glasses during cooling because radius ratios only tended to produce cations surrounded by four oxygen ions in the form of a tetrahedron (Goldschmidt, 1926; Shelby, 2005; Wright, 2014). Zachariasen (1932) then published a paper that expanded on Goldschmidt's model. His idea was that after melting and cooling, silicate crystals form glasses instead of recrystallising, and that they have a network as opposed to closely-packed structures (Shelby, 2005; Varshneya & Mauro, 2019; Wright, 2014). These structures then contain tetrahedra connected at all four corners, as opposed to crystals, however, the networks are not periodic and symmetrical like in a crystal (Shelby, 2005; Varshneya & Mauro, 2019; Wright, 2014). Instead, these networks extend in all three dimensions, where it was established that the formation of the vitreous network is a necessity for glass formation (Shelby, 2005; Varshneya & Mauro, 2019; Wright, 2014). Therefore, Zachariasen's theory can be summarised in three points: (i) the material will contain a high proportion of cations, surrounded by either O triangles or O tetrahedra, (ii) these polyhedra are only connected by their corners, and (iii) some of these O atoms are linked to only two cations and, therefore, do not form additional bonds with other cations (Shelby, 2005; Varshneya & Mauro, 2019; Wright, 2014; Zachariasen, 1932). Zachariasen's theory is the basis for the Random Network Theory and is the most widely accepted theory used today.

Zachariasen's model, the Random Network Theory, explains the structure of vitreous silica, however, Warren (1941, 1942) proposed an extension that described the structure of alkali silicates (Figure 2) (it can also be applied to alkaline earth silicates), and is hence known as the Zachariasen-Warren model. The Zachariasen-Warren random network model states that when a silicate glass contains an alkali or alkaline earth, the total number of O atoms are greater than the number of Si atoms, where each Si is tetrahedrally bonded to four O atoms, and where part of the O's have to be bonded to two Si atoms and the other to one Si atom (Warren, 1941, 1942). The alkali cations are assumed to randomly

occupy spaces within the rings of Si-O tetrahedra in the glass (Warren, 1941, 1942). When monovalent alkali cations are added, each causes a bridging oxygen (BØ) bond to become a non-bridging oxygen bond (NBØ), where these NBØs become charge balanced by the alkali cations, where the cations act as network modifiers (Warren, 1941, 1942; Wright, 2014).

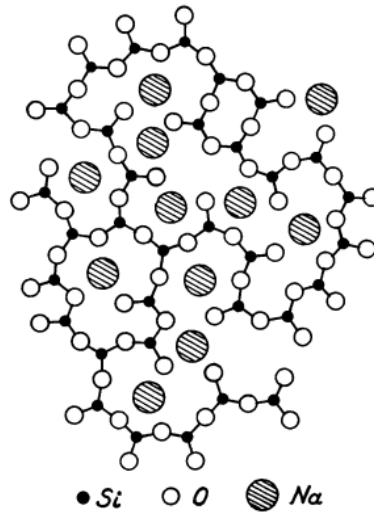


Figure 2 – Two dimensional example of the structure of an alkali silicate taken from (Warren, 1941) with copyright permission from Johnson Wiley and Sons (License number: 5612440965142)

Greaves (1985) introduced a modified random network (MRN) model for the structure of melts and glasses proposing that modifiers e.g., Na₂O broke inter-tetrahedral bonds, segregating into clusters before forming continuous channels, where the overall structure now consisted of two interlacing sublattices (Figure 3). The network regions would be constructed from network formers and inter-network regions comprised of modifiers, where ionic transport will be supported by the modified regions in the MRN.

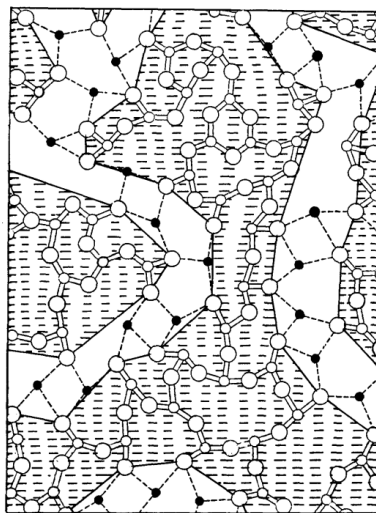


Figure 3 – A modified random network (MRN) for a “2-dimensional” oxide glass (Greaves, 1985) with copyright permission from Elsevier (License number: 5624891135958)

2.1.4 Nature of Glass Components

In order to understand the glass structure and its properties, it is pertinent to understand what the components of the glass are and what their role is in the structure. Zachariasen categorised oxides that constitute the glass structure into three groups, (i) network formers, (ii) modifiers, and (iii) intermediates. Examples of network formers are B_2O_3 , SiO_2 , GeO_2 , P_2O_5 , and As_2O_3 , (Smallman & Bishop, 1999; Zachariasen, 1932), where the modification of the glass properties can be induced by the addition of network modifiers i.e., alkali and alkaline-earth cations e.g., MgO , Li_2O , BaO , CaO , Na_2O , SrO , and K_2O (Jiusti, Zanotto, et al., 2020; Smallman & Bishop, 1999). Network intermediates can act as both network formers or modifiers depending on the composition and melting conditions e.g., Al_2O_3 , Sb_2O_3 , ZrO_2 , TiO_2 , PbO , BeO , V_2O_5 and ZnO (Smallman & Bishop, 1999).

Oxide based glasses are formed from network formers which are linked by $B-O$ s via covalent $-O-$ linkages (Edén, 2012; Greaves & Sen, 2007; Yu et al., 2019). Network modifiers de-polymerise the network by converting the $B-O$ s into $NB-O$ s, where this then alters the chemical and physical properties of the glass e.g., T_g (Edén, 2012; Greaves & Sen, 2007; Yu et al., 2019). Hence, it is important to understand the structural role an oxide has, and if it is a modifier, its distribution amongst the network forming species within the glass structure.

The oxides studied in this thesis can be categorised into the three main groups as seen in Table 1.

Glass Former	Glass Intermediate
SiO ₂	Fe ₂ O ₃
B ₂ O ₃	TiO ₂
P ₂ O ₅	ZrO ₂
Glass modifier	Al ₂ O ₃
Na ₂ O	Cr ₂ O ₃
Li ₂ O	SnO ₂
CaO	MgO
K ₂ O	SO ₃
	V ₂ O ₅

Table 1 - Glass oxide components used in making of thesis glasses

The glass modifiers Na₂O, Li₂O, CaO, and K₂O de-polymerise the glass structure, resulting in lowering of the T_g (Grund Bäck et al., 2019). Additions of Na₂O reduces the melting temperature (Goj et al., 2020), Li₂O reduces the melt viscosity (Li et al., 2022; Wallenberger et al., 2008), CaO decreases the melt viscosity but increases the melt density or density of the glass (Kraxner et al., 2008), and K₂O prevents crystallization and promotes the formation of glass (Ahmadi Mooghari et al., 2012). The potential effects of glass intermediates vary depending on their oxidation state, if they are a multivalent species, where this can dictate their role in the glass structure, and their concentration in the glass in comparison to the other components. Fe₂O₃ can be present as both Fe³⁺ (network former) and Fe²⁺ (network modifier). Fe³⁺ can lead to the strengthening of the glass structure, leading to an initial decrease in the dissolution rate of the glass due to the presence of [FeO_{4/2}]⁻ units compensated by one Na⁺ cation (Brossel et al., 2022). TiO₂, ZrO₂, and SnO₂ are opacifiers, where they have a tendency to promote the occurrence of phase separation (Vogel, 1994). TiO₂ and ZrO₂ are also nucleating agents, which can cause partial crystallisation of the glass (Achigar et al., 2021; Fernandes et al., 2013; Soleimanzade et al., 2014). TiO₂ is a multivalent species, present as both Ti⁴⁺ (network former) and Ti⁶⁺ (network modifier) (Mysen & Neuville, 1995; Nienhuis et al., 2020). SnO₂ is also used as a firing agent to reduce bubble formation in the glass melt (He et al., 2021). Al₂O₃ is a homogeniser and has been reported to prevent phase separation of B and Si sub-networks, where it can link Si and B units together when acting as a glass former (Bruns et al., 2020; Chen et al., 2022). Cr₂O₃ and V₂O₅ are both multivalent species and are nucleating agents that can impact the crystallisation and forming behaviour of the glass (McKeown et al., 2011; S. Zhang et al., 2020), where Cr₂O₃ can be present as Cr³⁺ (network former) and Cr⁶⁺ (network modifier) (Hansen et al., 2022; McKeown et al., 2011; Zhang et al., 2020), and V₂O₅ can be present as

V^{5+} (network former), and V^{3+} and V^{4+} (intermediates) (Lu et al., 2019; Smith-Gray et al., 2021). SO_3 can be present as S^{6+} and S^{4+} where it can be added to glass melts as a fining agent for accelerating melting and homogenising the melt (Lenoir, Grandjean, Dussossoy, et al., 2008). However, in nuclear waste, if the concentration of $SO_4^{2-} > 2$ wt% it results in the formation of a gall layer, which removes radioactive fission products from the glass matrix (Lenoir, Grandjean, Dussossoy, et al., 2008; Manara et al., 2007). MgO is also a nucleating agent promoting the formation of crystals (Soleimanzade et al., 2014). The overall effects of the oxides on properties e.g., thermal, rheological, chemical, and physical depend on the glass composition and structure. In this thesis, the main glass composition investigated was borosilicate glass.

2.1.5 Borosilicate Glass

Borosilicate glass is the main candidate chosen to vitrify the Hanford Site's radioactive waste as it has demonstrated better chemical durability compared to silicates, a testament to borosilicate's potential longevity (Plodinec, 2000). These glasses have shown an ability to dissolve a variety of different radioactive wastes at a lower temperature compared to similar silicate glass compositions not containing boron (Manaktala, 1992; Ojovan & Lee, 2005; Plodinec, 2000; Raj & Kaushik, 2009).

The simplest form of a borosilicate glass used to understand waste vitrification is $Na_2O-B_2O_3-SiO_2$ (McGrail et al., 2001; Nishi et al., 2019) with additive additions e.g., Li_2O , CaO , Al_2O_3 , ZnO etc. (Ali et al., 2022; Bruns et al., 2020; Motokawa et al., 2022; Rautiyal et al., 2021). Adding alkali and alkaline-earth oxides to a borosilicate glass system reduces the glass' formation temperature, leading to retention of volatile nuclides e.g., Ru and Cs (Vaishnav, 2018). Adding these alkali oxides also alters the structure, potentially forming NBØs (Mascaraque et al., 2019; Parkinson et al., 2007), altering leaching rates and glass durability (Lonergan & Neeway, 2017; Vaishnav, 2018). However, durability improves with low concentrations of Al_2O_3 (Kim et al., 2020), as AlO_4 tetrahedra cause the Na^+ ions to act as charge compensators *versus* being located at the NBØ matrix sites (Mascaraque et al., 2019; Vaishnav, 2018). Using borosilicate glass is further limited by its poor solubility of platinoids and high oxidation state cations e.g. Cr^{6+} and Mo^{6+} (Chen, 2012; Liu et al., 2022; Prakash et al., 2019).

2.1.5.1 Applying Glass Formation Theory

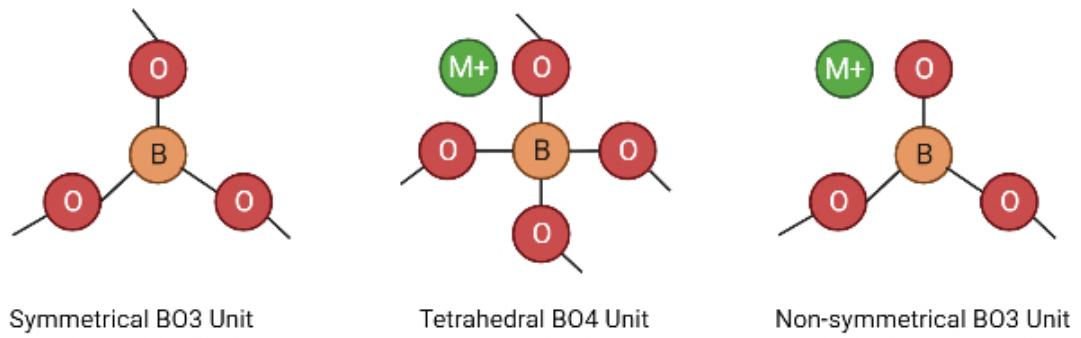


Figure 4 - Possible borate units that can be present in a borosilicate glass
modified from (Vaishnav et al., 2018)

The previously discussed structural theories (Random network theory and Zachariasen-Warren Model) cannot be applied to borosilicate glasses because boron exists as both 3-coordinate trigonal and 4-coordinate tetrahedral units in a glass network, whereas silica can only exist as a 4-coordinate state (Bray, 1985b; Wright & Dalba, 2010). As the B enters the silicate network the immediate-range network forming units further complicate the glass structure (Stone-Weiss et al., 2020). When alkali atoms are added to vitreous B₂O₃, they initiate the conversion of symmetrical trigonal BO₃ units into charged tetrahedral BO₄ units, instead of leading to the formation of NBØs as in silicate glass systems (Vaishnav, 2018; Wright & Dalba, 2010), increasing the polymerisation of the boron network and partially reducing the CTE. Adding more modifier oxides drives the conversion of BO₄ units to BO₃ units with an NBØ associated with the alkali cation, and is formally known as the 'boron-anomaly' (Uhlmann & Shaw, 1969; Vaishnav, 2018).

2.1.5.2 Structure of Borate and Borosilicate Glass

The structure of borate glasses have been studied extensively, where vitreous boron oxide consists mainly of boroxol rings, where the rings are formed of triangularly coordinated boron (Konijnendijk & Stevels, 1975). When a modifier is added to a borate glass, the modifier can act in two ways: (i) form four-coordinated boron (BO₄⁻) unit (reaction 1) or (ii) by forming NBØs (reaction 2) (Konijnendijk & Stevels, 1975; Padmaja & Kistaiah, 2009). These processes are characterised by reactions 1 and 2, where A₂O is the modifier oxide and A⁺ is the modifier ion (Padmaja & Kistaiah, 2009):



According to Krogh-Moe (1969), in Konijnendijk and Stevels (1975), $\text{Na}_2\text{O}-2\text{B}_2\text{O}_3$ glass compositions with <20 mol% Na_2O , contains both boroxol and tetraborate units, whilst compositions with 20–30 mol% Na_2O contain tetraborate and diborate units. Krogh-Moe (1969) further suggested a structural model, proposing that sodium borate glasses possessed a random network of large borate units comprising (i) boroxol ring, (ii) pentaborate, (iii) triborate, and (iv) diborate units (Figure 5) (Ota et al., 1990), similar to crystalline sodium borates (Konijnendijk & Stevels, 1975; Krogh-Moe, 1969). This model, potentially applicable to other alkali borate systems, was confirmed by Raman spectroscopy (Konijnendijk & Stevels, 1975; Krogh-Moe, 1969). Bray (1999) in Padmaja and Kistaiah (2009) inferred the existence of $^{[3]}\text{B}$ and $^{[4]}\text{B}$ units in ^{11}B NMR spectra of vitreous B_2O_3 . Raman spectroscopy of alkali oxide doped borate glasses showed characteristic Raman bands at $740\text{--}780\text{ cm}^{-1}$, assigned to boroxol rings converting to other ring-like structures comprising four-coordinated boron (Kamitsos et al., 1987; Osipov & Osipova, 2010; Padmaja & Kistaiah, 2009).

0-20 mol% R_2O	20-35 mol% R_2O	35-40 mol% R_2O
Boroxol groups	Tetraborate groups	Diborate groups
Tetraborate groups	Diborate groups	Metaborate groups
Loose BO_3 triangles	Loose BO_3 triangles	Pyroborate groups
Loose BO_4 Triangles	Lose BO_4 tetrahedra	Orthoborate units
		Loose BO_3 triangles with three $\text{B}\emptyset$ s
		Loose BO_3 triangles with a $\text{NB}\emptyset$

Table 2 - The presence of borate groups in alkali borate glasses in several composition areas, modified from (Konijnendijk & Stevels, 1975)

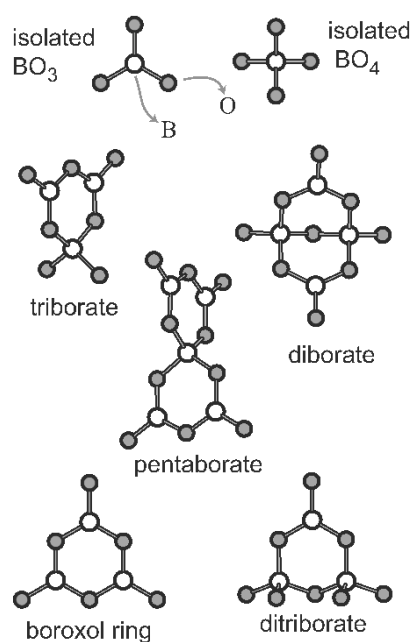


Figure 5 - Structural diagrams of superstructural units taken from (Šipr et al, 2007) with copyright permission from AIP Publishing (License number: 5625260583204)

Borosilicate glass composition is widely used commercial glass system, employed in labware, and kitchenware such as Pyrex (Phillips & Kerner, 2008; Smedskaer et al., 2014), and is a popular choice of composition for the vitrification of nuclear waste by countries such as the UK, USA, India, and France (Raj & Kaushik, 2009; Sobret, 1993). It is a glass system that contains substantial amounts of SiO_2 and B_2O_3 as glass network formers, where glass modifiers e.g., Na_2O and K_2O are added to alter glass properties. Its structure and properties are determined by the $\text{M}_2\text{O}/\text{B}_2\text{O}_3$ (M = alkali / alkaline earth) and the $\text{B}_2\text{O}_3/\text{SiO}_2$ ratio (Ehrt, 2000; Pacaud et al., 2017). Yun and Bray (1978) suggested from NMR data that the structural units in an $\text{Na}_2\text{O}-\text{B}_2\text{O}_3-\text{SiO}_2$ glass included (i) boroxol rings, (ii) diborate units, (iii) metaborate units, (iv) loose BO_4 units, (v) pyroborate units, (vi) orthoborate units, (vii) loose BO_3 units, and (viii) Si_3O_{10} units (Ota et al., 1990; Yun & Bray, 1978). The structural model of sodium borosilicate glasses presented by Yun and Bray (1978), that was later corrected by Yun et al. (1979). These models were further updated by Dell et al. (1983) where they proposed the following: (i) that Na_2O forms $^{[4]}\text{B}$ units regardless of the amount of Si present. (ii) The $^{[3]}\text{B}$ and $^{[4]}\text{B}$ units at $R = 5$ ($R = \text{Na}_2\text{O}/\text{B}_2\text{O}_3$) are arranged in diborate groups. When $0.5 \leq R \leq R_{\text{max}} = 1/2 + 1/16 K$ the Na_2O combines with some of the diborate groups forming reedmergnerite units. (iii) When $R_{\text{max}} \leq R \leq R_{\text{Di}} = 1/2 + 1/4 K$ additional Na_2O is absorbed by the reedmergnerite units forming

NBØ's on the silica tetrahedra, causing de-polymerisation of the glassy network. Manara et al. (2009b) revised the previous Yun, Bray and Dell structural models of borosilicate glasses, where they used more recent experimental data obtained from Raman spectroscopy to propose a more general formula for R where depolymerisation begins upon further additions of modifier content to the glass: $R = 0.5 + K / 2N$, where N is the average number of SiO₂ units included in reedmergnerite and danburite-like structures, and $K = [\text{SiO}_2]/[\text{B}_2\text{O}_3]$.

2.1.6 Phase Separation

Phase separation can occur naturally or be induced synthetically in materials e.g., polymers and glass. Phase separation is of particular interest when investigating the effects of P₂O₅ because of its recorded occurrence in radioactive waste glasses and its impacts on glass structure and melter properties. Phase separation has been reported in array of glass systems e.g., silicate and borates. To understand the potential effects of phase separation on the glass systems in this thesis, an understanding of how and why it occurs is needed based on available literature.

2.1.6.1 Thermodynamics and Kinetics of Phase Separation

Phase separation is a process involving the separation of a single phase into a multi-phase system, and has been observed in glass systems and other condensed matters e.g., polymers, metals and semi-conductors, and liquid systems and melts (Shelby, 2005; Tanaka, 1996). Immiscibility phenomena can be represented by solubility curves in an isobaric temperature-composition diagram, where the composition of both stable coexisting phases are plotted as functions of temperature (Figure 6) (Vogel, 1994).

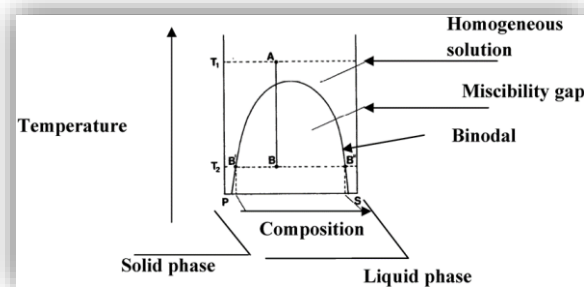


Figure 6 - Basic temperature – composition diagram with miscibility gap (El-Gendi, 2015). Originally published in InTech. Under CC BY 4.0 licence.

Available from: doi: 10.5772/60419

Graphically, phase separation is confined within the region of composition and temperature in the phase diagram known as the immiscibility gap (Taylor, 1990). As the temperature increases the miscibility gap decreases, where the temperature at which the gap disappears (above which all liquid compositions are homogeneous) is known as the consolute temperature, T_c (Taylor, 1990). Phase separation can be a stable phenomenon in the melt, e.g., in alkaline-earth borate, borosilicate, and silicate systems. However, in other systems phase separation is a metastable sub-liquidus process, meaning the critical miscibility temperature, T_b , lies between the liquidus temperature, T_L , and the glass transition temperature, T_g (Taylor, 1990).

Phase separation is usually initiated by the instantaneous temperature change from the initial to the final target temperature (Tanaka, 1996). The phases become thermodynamically unstable with their final state being identifiable in the miscibility gap (Smolders et al., 1971). The temperature below which any given composition becomes immiscible is termed the critical miscibility temperature T_b (Taylor, 1990).

The viability of phase separation happening increases at lower temperatures in the concentration region because the temperature dependant entropy, $(-T\Delta S_m)$ is not high enough to overcome the positive enthalpy of mixing (ΔH_m) (Yadav, et al., 2017) (Figure 6). When Gibbs free energy increases the system becomes stable i.e., the system is metastable with respect to small fluctuations of the composition. When the curvature is negative the spontaneous on set of spinodal decomposition occurs, and when it is positive, with a large enough fluctuation in

composition, nucleation and growth occurs. Gibbs free energy (ΔG) is calculated by the following equation (Eq 1) (Shelby, 2005):

$$\Delta G = \Delta H_m - T\Delta S_m \quad (1)$$

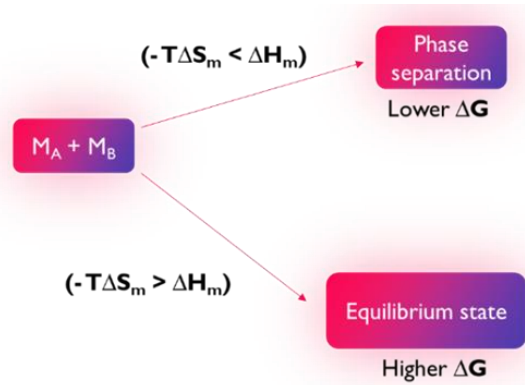


Figure 7 - Diagram showing how Gibbs free energy can be calculated

Phase separation can occur via two mechanisms in a glass melt, (i) spinodal decomposition and (ii) nucleation and growth (Figure 8). Spinodal decomposition is where the system quickly transitions from a stable region to an unstable spinodal phase region; this typically results in a three-dimensionally interconnected morphology consisting of two immiscible phases (Goldstein, 1965; Shelby, 2005; Suzuki & Tanaka, 2012). The nucleation-growth mechanism results in a morphology consisting of isolated spheres of the equilibrium composition randomly distributed through the matrix of another equilibrium composition (Shelby, 2005; Shepilov, 1996). Figure 8 demonstrates the evolution of potential morphologies obtained after different processes and different steps of equilibrium in free-energy at a temperature above the immiscibility temperature (McCloy & Schuller, 2022). L0 is a liquid of composition A, L1 is a liquid composition with initial crystallisation, where the precipitated crystals can act as nucleating agents promoting liquid-liquid phase separation (McCloy & Schuller, 2022). In borosilicate glass systems, phase separation can be exhibited as opalescence, appearing blueish to milky white in reflected light (Taylor, 1990).

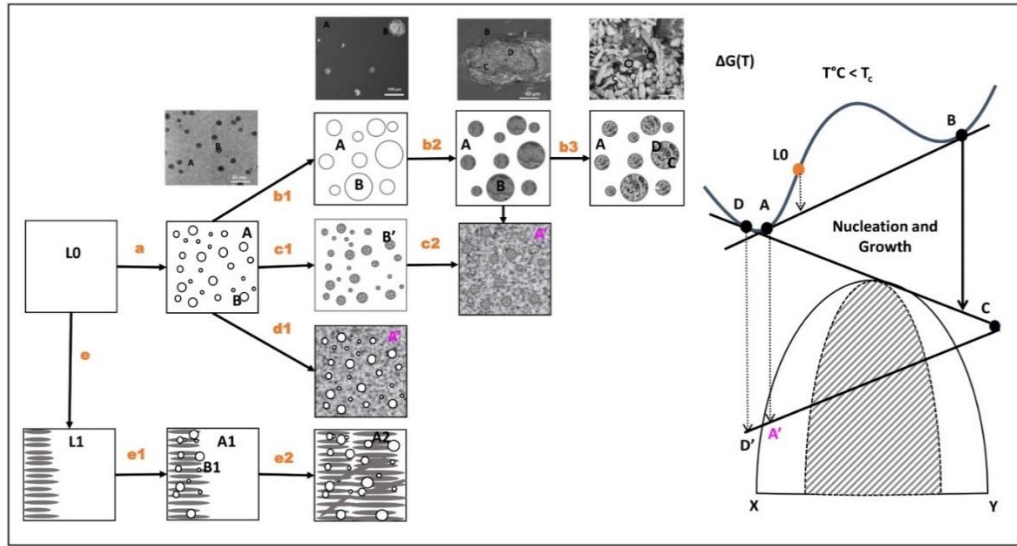


Figure 8 - Possible phase separation and crystallization mechanisms obtained by nucleation and growth processes in nuclear and industrial wastes. Taken from work by (McCloy & Schuller, 2022). Originally published in Comptes Rendus Geoscience. Under CC BY 4.0 licence. Available from: DOI: 10.5802/crgeos.111

In binary and tertiary borate and silicate glass systems the extent of miscibility gaps influenced by glass modifier cations can be discussed in terms of their polarising power (Taylor, 1990), where it is a parameter expressed as Z/r , where Z is the metal cation charge and r is the radius (Brooker & Bredig, 1973; Morozov et al., 2009). In general, the greater the polarising power of the metal cation the stronger the attraction between it and NBO_3 s, and hence the greater tendency towards clustering of these particles and occurrence of phase separation (Block & Levin, 1957; Sreenivasan et al., 2020; Taylor, 1990).

M^+ : Cs < Rb < K < Na < Li $\text{M}^{+/2+}$: Li^* (monovalent) < Pb $\approx$ Ba < Sr < Ca < Mg $\approx$ Zn

2.1.6.2 Theory of Phase Separation

2.1.6.2.1 Nucleation and Growth, and Spinodal Decomposition Mechanism

The rate of nucleation, J , according to classical theory of homogenous nucleation, is given by equation 2 (Craievich et al., 1983):

$$J = A \exp[-(\Delta G_D + W^*) / k_B T] \quad (2)$$

Where A is a constant, ΔG_D is the activation energy for atomic transport across the interface, W^* is the free energy of formation of a critical nucleus, k_B is the Boltzmann constant, and T is the temperature.

It should be noted that nucleation and growth could occur in the spinodal region of the miscibility gap, however nucleation is more likely to occur outside of the spinodal and closer to the bimodal instead (Craievich et al., 1983).

Cahn (1961) developed the linear quantitative theory of spinodal decomposition, where it predicted the exponential growth of a scattered peak characteristic of a phase separated region caused by periodic concentration fluctuations (Kyu & Saldanha, 1988). However, the Cahn theory does not apply to early stages of phase separation, hence, the development of newer theories using a statistical thermodynamic approach (Kyu & Saldanha, 1988), such as by Langer (1973), Binder (1978), and Stauffer (1994). The Cahn theory was developed to study low molecular weight binary materials but has since been used to mathematically model phase separation in unstable regions, where the theory adds a correction to the homogeneous free energy function to account for the spatial inhomogeneity (Kyu & Saldanha, 1988).

Morphology is not the only criteria which can decide the mechanism by which phase separation occurs, as the work by Seward et al. (1968) examined thin films of BaO-SiO₂ and found that compositions near the centre of the miscibility gap were fine isolated droplets in the early stages (Craievich et al., 1983; Seward et al., 1968). However, at a later stage, two interconnected phases were observed instead of isolated droplets, indicating nucleation and intersecting growth when the composition is within the spinodal region (Craievich et al., 1983; Seward et al., 1968). There are difficulties in conclusively establishing which mechanism has occurred, and observations by Seward et al. (1968) are insufficient. An attempt to overcome these difficulties and distinguish between nucleation and growth and spinodal decomposition, Srinivasan et al. (1976) tried to use replica electron microscopy and suggested that the volume fraction V_f for nucleation and growth should increase with time, and for spinodal decomposition the volume fraction should decrease with time (Craievich et al., 1983). The replica electron microscopy methodology has been criticized by Uhlmann and Kolbeck (1976), Burnett and Douglas (1971), and Tomozawa and Doremus (1979), as uncertainties could arise from etching conditions (Craievich et al., 1983). Tomozawa and Doremus (1979) measured properties such as chemical durability and viscosity as a function of the heat treatment time, where phase separation

occurred inside of the spinodal region, where the gradual composition variations indicated that spinodal decomposition was taking place.

2.1.7 Summary

A glass can be defined as a non-crystalline state of matter, wherein fast cooling of a liquid results in an amorphous material, but upon heating relaxes back to its liquid state. The main accepted theory that describes the glass structure is the Zachariasen-Warren model, but this is only applicable to silicates and not borosilicate glasses because boron can exist as both 3-coordinate trigonal units and 4-coordinate tetrahedral units in a glass network, whereas silica can only exist as a 4-coordinate state. Instead, the structure of a borosilicate glass can be determined by structural analysis techniques such as Raman spectroscopy and MAS-NMR, where characteristic intensities have been identified by literature. Phase separation is usually initiated by the instantaneous temperature change from the initial temperature to the final target temperature, with its viability of occurring increasing at lower temperatures. Phase separation in glasses occurs via two mechanisms, nucleation and growth, and spinodal and decomposition. The nucleation-growth mechanism results in a morphology that consists of isolated spheres of the equilibrium composition randomly distributed through the matrix of another equilibrium, whilst spinodal decomposition has a morphology that is three-dimensionally interconnected and consisting of two immiscible phases. The presence of certain cations in the glass system can contribute to increasing the likelihood that phase separation occurs.

2.2 Glass Compositions, Structure, and Properties

2.2.1 Glass Compositions

The glass in this study is based on a $\text{Na}_2\text{O-B}_2\text{O}_3\text{-SiO}_2\text{-xP}_2\text{O}_5$ system, to which additional oxides are added to simulate the vitrified waste; these oxides have the undesirable effect of complicating the analysis of the glasses.

The $\text{Na}_2\text{O-B}_2\text{O}_3\text{-SiO}_2$ glass system constituents of three binary systems ($\text{B}_2\text{O}_3\text{-SiO}_2$, $\text{Na}_2\text{O-B}_2\text{O}_3$, and $\text{Na}_2\text{O-SiO}_2$) which are prone to immiscibility, where the ternary system $\text{Na}_2\text{O-B}_2\text{O}_3\text{-SiO}_2$ exhibits an immiscibility dome (Vogel, 1994). The $\text{Na}_2\text{O-B}_2\text{O}_3\text{-SiO}_2$ glass system has been reported to be susceptible to phase separation (Charles, 1964; Scholes & Wilkinson, 1970; Schuller, 2020; Shepilov

et al., 2007; Yazawa et al., 2000), where heat treatment of the melts structurally alters the separated phases present (Vogel, 1994).

The $\text{Na}_2\text{O}-\text{B}_2\text{O}_3-\text{SiO}_2-x\text{P}_2\text{O}_5$ glass system is categorised as a mixed glass former (MGF) system (Tricot et al., 2020), identified to be silica, boron, and phosphorus. The sodium is a network modifier that can also act as a charge compensator to the different glass formers in the system. There have been some reported studies on phosphate-doped alkali borosilicate glasses (Cheng, 2014; Krishnamurthy et al., 2020; Muñoz et al., 2006; Munoz et al., 2007; Prasad et al., 2019), however, the effects of P_2O_5 on the structure of these glasses and its subsequent effects on the physical and chemical properties, are still poorly understood especially when applied to radioactive waste vitrification technology.

2.2.2 Glass Structure

In order to understand the effects of P_2O_5 on the structure of glass, it is pertinent to establish the effects it is having on the properties. Spectroscopic techniques and molecular dynamic modelling have been previously used to investigate the local environment surrounding the phosphorus in different oxide glasses (Krishnamurthy et al., 2020; Ohtsuki et al., 2011; Stone-Weiss et al., 2020). In this study, the glasses were structurally analysed using Raman spectroscopy, X-ray absorbance near edge spectroscopy (XANES), Mössbauer spectroscopy, and solid-state magic angle spinning nuclear magnetic resonance spectroscopy (MAS NMR).

2.2.2.1 Raman Spectroscopy

2.2.2.1.1 Q^n Species

In this investigation, the glasses measured by Raman spectroscopy contained silicon, boron, phosphorus, and iron in tetrahedral coordination with respect to oxygen. To distinguish between these element specific tetrahedra, a nomenclature is needed in order to accurately describe them, the Q^n species.

Q^n notation is a common nomenclature used to express the concentration of bridging oxygens per tetrahedron by varying the subscript n , where $n = 0$ to 4. The elements that can form a tetrahedral unit are Si^{4+} , B^{3+} , P^{5+} , Ge^{4+} , Al^{3+} , Fe^{3+} , and Mg^{2+} (Shelby, 2005). A tetrahedron with four bridging oxygens has the Q value 4, hence Q^4 , while an isolated tetrahedron surrounded by non-bridging oxygens (NBØ) has the Q value of Q^0 (Navrotsky et al., 1985; Shelby, 2005). It is

assumed that vitreous silica consists of 100% Q^4 units where pairs of tetrahedra are connected together by shared BØs and that the addition of alkali oxides, expressed as R_2O where R is the cation, converts one BØ to two NBØs (Hannon et al., 2021; Shelby, 2005). When alkali oxides are added to the SiO_2 network, Si-O-Si linkages are broken forming terminal oxygen atoms belonging to only one Si atom; this is the formation of a Q^n species where $n < 4$ in the glass structure (Osipov et al., 2015). The concentration of different types of Q^n species is dependent on the concentration of the modifier oxides and types of alkali cations present (Figure 9) (Osipov et al., 2015).

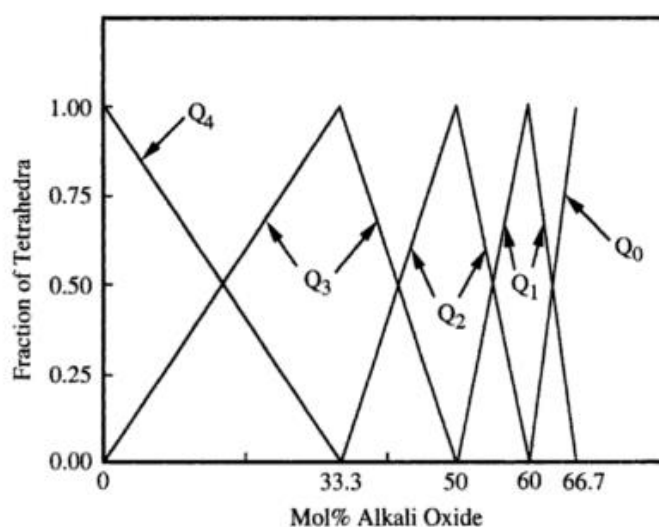


Figure 9 - Effect of alkali oxide concentration on the relative theoretical concentrations of Q_n units in alkali silicate glasses taken from (Shelby, 2005) with copyright permission from RSC (License number: 1391814-1)

2.2.2.1.2 Silicate Glasses

An adequate understanding of a glass and its melt compositions, and temperature dependencies is required to develop detailed information about its structure. It has been shown that a small number of co-existing structural units produce established numbers and positions within a Raman band (Mysen et al., 1982). For silicate glasses, it has been demonstrated that Si-O tetrahedra have varying numbers of BØ atoms (Osipov et al., 2015). The Si-O tetrahedra are called Q^n units, where $n = 0$ to 4 and is the number of BØ per SiO_4 tetrahedron (Figure 10) (Osipov et al., 2015). The Q^n species form a continuous random network of glass or silicon anions in a melt via the Si-O-Si linkages (Osipov et al., 2015). Raman bands of the Q^n species region can be difficult to interpret due

to the peak broadness, where they may also shift in frequency as a function of the polarisation of the relevant T–O bands (where T is a tetrahedral cation) (Mysen et al., 1982). These shifts may be induced by the type and abundance of polarising cations, the nature of the T cations, the distance between T–O linkages, the number of NBØs in a certain tetrahedron, and the angle of T–O–T (Mysen et al., 1982).

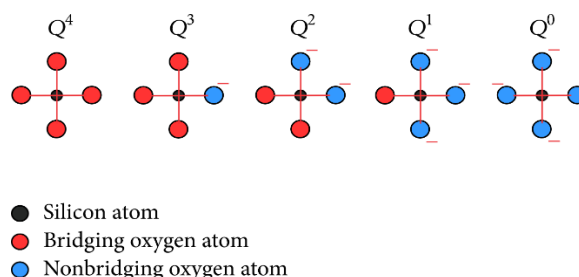


Figure 10 - Schematic of two-dimensional representation of the Q species taken from (Osipov et al., 2015). Originally published in International Journal of Spectroscopy. Under CC BY 3.0 licence. Available from: DOI: 10.1155/2015/572840

2.2.2.1.3 Borosilicate Glasses

Borosilicate glasses are systems containing two cationic formers (SiO_2 and B_2O_3), both of which can form their own anion groups when reacting with alkali metal oxides (Koroleva et al., 2011). Koroleva et al. (2011) used Raman spectroscopy to characterise and analyse a sodium borosilicate glass system ($x\text{Na}_2\text{O} \cdot x\text{B}_2\text{O}_3 \cdot (100 - 2x) \text{SiO}_2$, where $x \text{ mol\%} = 20, 25, 30, 25 \text{ and } 40$), where Raman spectroscopy identified three distinguishable regions in the spectra: 300–800, 800–1200, and 1200–1700 cm^{-1} . Manara et al. (2009) reported similar regions of 300–850, 850–1250, and 1250–1600 cm^{-1} . In the low frequency region, the intensities seen were attributed to the mixed bending and stretching modes of Si–O–Si units (Koroleva et al., 2011; Manara et al., 2009). Intensities in the region 850–1250 cm^{-1} varied depending on if the glass system was an alkali silicate, alkaline earth, or aluminosilicate, and whether they contained intensities associated with Si–O stretching in the different Q^n species, or vibrational stretching modes of Si–O (Manara et al., 2009). The 1250–1600 cm^{-1} region was assigned to the B–O stretching in the chain-type metaborate groups (Manara et al., 2009). Table 3 lists the main Raman shifts and their referenced associations, whereas Table 4 lists the characteristic ^{31}P , ^{29}Si , and ^{11}B NMR intensities and their referenced attributions.

Raman Shift (cm ⁻¹)	Association
450 (Manghnani et al., 2011)	Bending mode of Si-O-Si bond
480 – 490 (Kilymis et al., 2017; Manghnani et al., 2011; Mendoza et al., 2012)	Vibration of Si-O-Si and Si-O-B mode Mixed bending and rocking of the Si-O-Si angles
605 (Mendoza et al., 2012)	Si-O-Si bonds vibration in three membered [SiO ₄] rings
630 (Cheng, 2014)	BO ₄ tetrahedra bonded to silicate species
800 (Manghnani et al., 2011)	O-Si-O symmetric bond stretching
923 – 950 (Cheng, 2014; Kilymis et al., 2017; Manghnani et al., 2011)	Si-O stretching vibration with two NBØ atoms per silicon (Q ²)
1060 – 1070 (Cheng, 2014; Manghnani et al., 2011; Mendoza et al., 2012)	Si-O stretching in a tetrahedron with one NBØ per silicon (Q ³)

Table 3 - Characteristic Raman intensities based on literature

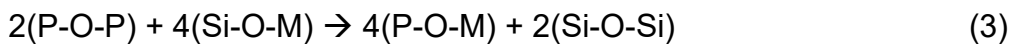
Species	NMR Intensity (ppm)	Association	Reference
¹¹ B	10 – 20	^[3] B	(Tricot et al., 2020)
	5 - 19		(Cheng, 2014)
	-5 - +5	^[4] B	(Tricot et al., 2020)
³¹ P	15	Monophosphate (PO ₄ ³⁻)	(Cheng, 2014; Muñoz et al., 2006)
	3	Diphosphate (P ₂ O ₇ ⁴⁻)	
	7.5	P-O-B	
²⁹ Si	-78 to -82.5	Q ¹	(Li et al., 2019; Zotov & Keppler, 1998)
	-80 to -87.5	Q ²	
	-93	Q ³	
	-104	Q ⁴	
	-111.6	Tridymite Si-O-Si	(Fyfe, 1990a, 1990b;
	-113.7	Cristobalite Si-O-Si	Malfait et al., 2008; van
	-113.1	Quartz Si-O-Si	Koningsveld, 1990)

Table 4 - Characteristic MAS NMR chemical shift intensities for ¹¹B, ²³Na, and ²⁹Si

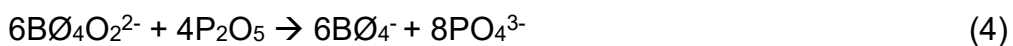
2.2.2.1.4 Phosphate Doped Glass Systems

In order to understand the effects of P_2O_5 on the structure of borosilicate glasses, it is pertinent to establish the effects it is having on the properties. Spectroscopic techniques and molecular dynamic modelling have been previously used to investigate the local environment surrounding the phosphorus in different oxide glasses (Krishnamurthy et al., 2020; Ohtsuki et al., 2011; Stone-Weiss et al., 2020).

It has been established that P_2O_5 often clusters together when it has exceeded a certain point, with a high tendency to phase separate/crystallise when introduced into silicate-based glass systems (Cheng, 2014; Krishnamurthy et al., 2020; Liu et al., 2011; Stone-Weiss et al., 2020). The competition between the glass formers in attracting the oxygen ions is what causes phase separation during cooling of the melt (Liu et al., 2011). In silicate melts, MAS-NMR and Raman spectroscopy studies have shown that P_2O_5 de-polymerises into orthophosphates (PO_4^{3-}) and pyrophosphates ($P_2O_7^{4-}$), forming P-O-B linkages ($P_2O_7^{4-}$ anions connected to $[^3]B$ and $[^4]B$ atoms), which are then counterbalanced by the re-polymerisation of the silicate network and its subsequent intermixing (Muñoz et al., 2006; Mysen, 1996; Stone-Weiss et al., 2020). The degree of polymerisation of the silicate network can be described by the following reaction in Eq 3 (Cheng, 2014):



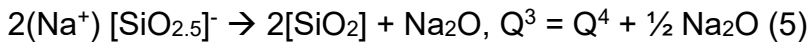
Gan & Hess (1992) investigated P and B speciation in $K_2O-B_2O_3-SiO_2-P_2O_5$ -doped glasses using ^{11}B and ^{31}P MAS-NMR. They showed that the coordination of the B is strongly regulated by the phosphate concentration, and that the fraction of BO_4 decreased with additions of 3 mol% P_2O_5 in the glass (Cheng, 2014; Gan & Hess, 1992). Similar work was also carried out by Bengisu et al. (2006) using $SrTiO_3$ -aluminoborate/aluminoborosilicate glasses with additions of P_2O_5 . They found that increased incorporation of P_2O_5 led to the increase in the BO_4 units at the expense of the BO_3 units, as indicated by Raman and Infra-Red (IR) spectroscopy (Bengisu et al., 2006; Cheng, 2014). These structural changes can be described in Eq 4 (Cheng, 2014):



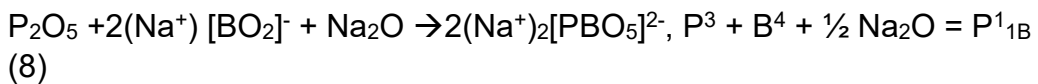
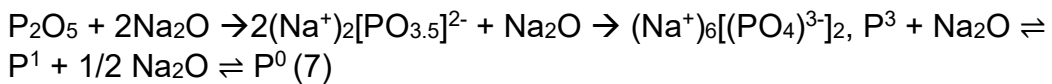
Where $\emptyset$ represents the BOs and the O^- represents the NBOs with respect to this particular equation.

Raman spectroscopy studies have revealed P-O stretching in PO_4^{3-} anions with a peak at 940-950 cm^{-1} and P-O stretching in $P_2O_7^{4-}$ anions with peaks at approximately 1000 cm^{-1} (Bih et al., 2013; Litasov & Podgornykh, 2017; Mysen, 1996, 1998). Cheng (2014) also implemented ^{31}P MAS-NMR and Raman spectroscopy on a sodium borosilicate glass system, reporting that as the P_2O_5 content increased and exceeded 3.0 mol%, borophosphate groups formed and increased in number at the expense of the ortho- and pyrophosphate groups (Cheng, 2014). The incorporation of P_2O_5 into the borosilicate glass network was strongly influenced by the distribution of NB $\emptyset$ s and alkali cations, where the phosphate speciation depended on the acid-base reactions of P_2O_5 with Na, B, and Al units, where the likelihood of a certain reaction could be predicted from the relative electronegativity of the components (Cheng, 2014). In this case, Na^+ is the most electropositive element and is the most likely to donate oxygen to electronegative cations, such as P_2O_5 , forming charged and isolated species (PO_4^{3-} and $P_2O_7^{4-}$). When there are not enough alkali cations to charge compensate the phosphorus, then P-O-Al or P-O-B linkages would occur (Cheng, 2014). These network speciation reactions can be summarized by the following equations (Cheng, 2014):

Metal Oxide Donor



Metal Oxide Acceptor



The alkali ions and NB $\emptyset$ s are released from the metal oxide donating borate and silicate sites to acidic metal oxides accepting phosphate sites (Cheng, 2014). Table 5 summarises the key Raman shift peaks and their referenced attributions for specific types of glass systems.

Glass system	Species	Peak Max. (cm ⁻¹)
Alkali silicate (Mysen, 1996)	P-O stretch in PO ₄ ³⁻	940
	P-O stretch in P ₂ O ₇ ⁴⁻	1000
	Q ³	1100
	Q ⁴	1150
Alkaline earth silicate (Yamashita et al., 2000)	PO ₃ ⁻	690, 1170, 1270
Borosilicate (Prasad et al., 2019b)	Mixed stretch-bend of Si-O-Si	602
	P-O stretch in PO ₄ ³⁻	950
	Si-O stretch	1076
Borosilicate (Cheng, 2014)	Si-O-Si stretch	574 - 559
	PO ₄ ³⁻ symmetric stretch	977 – 987
	P ₂ O ₇ ⁴⁻ symmetric stretch	1015 – 1021
	P-O-B vibrations	1085 – 1100
	P-O-Al vibrations	1055
Haplograntic aluminosilicate (Mysen, 1998)	AlPO ₄	1250
	P-O stretch in PO ₄ ³⁻	940
	P-O stretch in P ₂ O ₇ ⁴⁻	1000
	P-O stretch in berlinite (AlPO ₄)	1100
Phosphate minerals (Litasov & Podgornykh, 2017)	Symmetric stretch of P-O PO ₄ ³⁻	950 – 990
	Antisymmetric vibrations	1000 - 1050
Sodium Aluminosilicate (Ding et al., 2012)	PO ₄ ³⁻ symmetric stretch	936
	Si-O-NBØ stretch	1096
	P-O-P stretch	630
	PO ₄ ²⁻ symmetric stretch	1024
Meta- and per-aluminous sodium aluminosilicate (Lu et al., 2021)	Si-O-Si	450
	Si-O-Al	490
	Al-O-P	1070
Alkali - phosphate glasses (Bih et al., 2013)	Symmetric stretch of P-O-P	735
	P-O bending	925
	P-O stretch in PO ₄ ³⁻	950
	P-O stretch in PO ₃ ²⁻	1050
	(PO ₂) asymmetric vibrations	1100

Glass system	Species	Peak Max. (cm ⁻¹)
Meta- and per-aluminous system (Lu et al., 2021)	Si-O-Si	450
	Si-O-Al	490
	Al-O-P	1070
Alkali - phosphate glasses (Premila et al., 2020)	Asymmetric stretching of P-O in (Q ¹) P ₂ O ₇ ⁴⁻	1070

Table 5 - Characteristic Raman intensities for phosphate specific vibrations according to literature

2.2.2.1.5 Sulphate Doped Borosilicate Glasses

To better understand the effects of sulphate (SO₄²⁻) on the glass structure, relevant literature utilizing Raman spectroscopy have been reported by McKeown et al. (2001), Lonergan et al. (2020), Brendebach et al. (2009), Lenoir et al. (2010), Morizet et al. (2013), and Vaishnav et al. (2020). In a Raman spectrum, the increased presence of polar S-O bonds result in large Raman cross-sections and prominent lines in the spectrum (McKeown et al., 2001). These cross-sections result in sulphate peaks that are narrow but are superimposed over the broad borosilicate peaks (McKeown et al., 2001).

Studies by McKeown et al. (2001) and Lenoir et al. (2009) reported on key Raman shift intensities at 1100, 1000, 640 and 460 cm⁻¹. The 1000 cm⁻¹ was assigned to ν_1 the symmetric stretching mode of S-O, 460 cm⁻¹ was ν_2 assigned to the symmetric O-S-O bending modes, 1100 cm⁻¹ was ν_3 and assigned to the asymmetric S-O stretch modes, and 640 cm⁻¹ was ν_4 and assigned to the asymmetric O-S-O bend modes.

In a borosilicate glass, Lenoir et al. (2009) used Raman spectroscopy to ascertain the structure and quantify the sulphate solubility. The low-frequency region between 200-800 cm⁻¹ was attributed to vibrations involving BØs or the motions of Si against its tetrahedral cage with the slight displacement of its oxygen. The frequencies between 550-850 cm⁻¹ were characteristic of borate vibrations associated with ring breathing modes. The modes at 808 cm⁻¹ and 770 cm⁻¹ were associated with the ^[3]B and ^[4]B units, respectively.

A range of literature reported that the Raman shift band near 990 cm⁻¹ from Raman spectra performed on SO₄²⁻ containing glasses was attributable to the presence of S⁶⁺ in the form of a S-O stretch vibration (Brendebach et al., 2009;

Lenoir et al., 2010; Lonergan et al., 2020; McKeown et al., 2004; Morizet et al., 2013; Vaishnav et al., 2020). Table 6 summarises the key Raman shifts associated with SO_4^{2-} from the aforementioned glass systems.

Raman Intensity (cm^{-1})	Allocation
460	
(Lenoir et al., 2009; McKeown et al., 2001; Xu et al., 2020)	Symmetric O-S-O bending modes
640	
(Lenoir et al., 2009; McKeown et al., 2001; Xu et al., 2020)	Asymmetric O-S-O bending modes
990	
(Brendebach et al., 2009; Lenoir et al., 2009, 2010; Lonergan et al., 2020; McKeown et al., 2001; Morizet et al., 2013; Vaishnav et al., 2020; Xu et al., 2020)	S-O symmetric stretching modes within the sulphate tetrahedra
1000	
(Lenoir et al., 2009; McKeown et al., 2001)	Symmetric stretching mode of S-O
1100	
(Lenoir et al., 2009; McKeown et al., 2001)	Asymmetric S-O stretch modes

Table 6 – Summary table of key Raman intensities associated with sulphate species in glasses

2.2.2.2 MAS NMR

2.2.2.2.1 ^{11}B MAS NMR

Boron is a primary component in nuclear waste glasses that utilise a borosilicate glass system, where ^{11}B MAS NMR measurements are used to determine the ratio of three- and four-coordinated boron polyhedral structures (Kroeker, 2011). The ^{11}B unit exists as a tetrahedron with four B-Os, whilst the ^{10}B exists as a planar triangle with three B-O, and as a planar triangle with one B-O and two B-Os (Bril, 1976; Kroeker, 2011; Yadav & Singh, 2015). The ^{11}B MAS NMR provides quantitative information on the B coordination number (Angeli et al., 2010), where

acquisition of the spectra can provide accurate $^{13}\text{B}:$ ^{14}B ratios (Turner et al., 1986). However, the spectra are susceptible to second order quadrupolar broadening effects (Du & Stebbins, 2003; Kanehashi & Saito, 2002; Youngman, 2018).

In the literature, there have been extensive studies attempting to characterise B^{3+} in borosilicate and borophosphate based glass systems. Turner et al. (1986) used static ^{11}B NMR and ^{11}B MAS NMR to study borate and borosilicate minerals and borosilicate glass, in order to try and acquire accurate $^{13}\text{B}:$ ^{14}B ratios. The static ^{11}B NMR of three borates (kernite ($\text{Na}_2\text{B}_4\text{O}_6(\text{OH})_2 \cdot 3\text{H}_2\text{O}$), indierite ($\text{MgB}_3\text{O}_3(\text{OH})_5 \cdot (\text{H}_2\text{O})_4 \cdot (\text{H}_2\text{O})$), and borax ($\text{Na}_2\text{B}_4\text{O}_7 \cdot 10\text{H}_2\text{O}$)) resulted in diminished poorly resolved spectra due to the presence of B-H and B-B dipole-dipole interactions. ^{11}B MAS NMR of these borates, as well as danburite ($\text{CaB}_2\text{Si}_2\text{O}_8$), resulted in well-resolved spectra. Overall, it was reported that ^{11}B MAS NMR yielded reliable $^{13}\text{B}:$ ^{14}B ratios, where ^{13}B chemical shifts occurred in the range ~ 12.7 - 19.0 ppm, and ^{14}B chemical shifts occurred in the range ~ 3.3 - 2.0 ppm.

The application of ^{11}B MAS NMR has also been conducted by other researchers, for example a study by Angeli et al. (2010) where they reported that the B speciation for a SiO_2 - B_2O_3 - Na_2O - CaO - ZrO_2 glass system showed two different environments. The broadest peak was attributed to ^{13}B with two sites: BO_3 ring in boroxl rings and BO_3 non-ring in silicate units. Another study by Michaelis et al (2011) investigated borate rich K, Rb, and Cs borophosphate glasses, with $\text{B}_2\text{O}_3:\text{P}_2\text{O}_5$ ratio of 5, where the ^{11}B MAS NMR spectra exhibited a ^{13}B peak ranging 10-20 ppm and a ^{14}B peak ranging 0 to -4 ppm. The ^{13}B peak was also attributed to BO_3 ring and BO_3 non-ring, whilst the ^{14}B consisted of multiple peaks controlled by the degree of phosphate connectivity.

Carta et al. (2008) investigated the compositional effects on the structure of sodium borophosphate glasses in the system $40(\text{P}_2\text{O}_5)$ - $x(\text{B}_2\text{O}_3)$ -($60-x$)(Na_2O), where $10 \leq x \leq 30$ mol%. ^{11}B MAS NMR spectra of the samples showed a series of unresolved narrow bands in the region between 2 to -5 ppm, where chemical shifts in this region corresponded to ^{14}B coordination. In the $40\text{P}_2\text{O}_5$ - $10\text{B}_2\text{O}_3$ - $50\text{Na}_2\text{O}$ glass, peak deconvolution showed a band between 2 and -4 ppm may have had contributions from four overlapping peaks at 1, 0, -1, and -2 ppm. The resonances at -1, 0, and 1 ppm were assigned to $^{14}\text{B}_{1\text{P}}$, $^{14}\text{B}_{2\text{P}}$, and $^{14}\text{B}_{3\text{P}}$, respectively. There was also another band at 17 ppm identified in the $40\text{P}_2\text{O}_5$ - $30\text{B}_2\text{O}_3$ - $30\text{Na}_2\text{O}$ glass, which was assigned to BO_3 groups.

The observations noted in borophosphate systems have also been reported in phosphate doped borosilicate glasses. More recently, Krishnamurthy et al. (2020) investigated the network structure and dissolution behaviour of phosphate doped borosilicate glasses in the $\text{SiO}_2\text{-Na}_2\text{O-B}_2\text{O}_3\text{-Al}_2\text{O}_3\text{-P}_2\text{O}_5\text{-Cs}_2\text{O-MoO}_3$ glass system, where SiO_2 was incrementally substituted for P_2O_5 from 1 to 4 mol%. The ^{11}B MAS NMR spectra consisted of two main peaks centred at 15 and -2 ppm, which were attributed to planar BO_3 units and tetrahedral BO_4^- units, respectively. The two peaks were then deconvoluted into two distinct environments, where the BO_3 peak was decomposed into chemical shifts at 17 and 15 ppm, which were associated with BO_3 ring and BO_3 non-ring structures, respectively. The BO_4^- units were decomposed into overlapping sites with chemical shifts at -0.1 and -1.7 ppm, which were attributed to BO_4^- units with three and four Si neighbours, respectively.

Angeli et al. (2012) investigated the effects of temperature and thermal history on a borosilicate glass system ($63\text{SiO}_2\text{-17B}_2\text{O}_3\text{-17Na}_2\text{O-3Cs}_2\text{O}$), mol%. The study used a combination of solid-state MAS NMR and multiple quantum (MQ) MAS NMR. The ^{11}B MAS NMR spectra of the glasses showed a narrow BO_4^- peak at ~ 0 ppm. This peak had several sites underlying it, however, it was difficult to deconvolute the specific site contributions. Hence ^{11}B MQMAS NMR was employed to resolve these contributions by discriminating between a B atom surrounded by four Si atoms (-2 ppm), and a B atom surrounded by one B atom and three Si atoms (0 ppm). At 10 ppm there were two other contributions, which were attributed to a BO_3 unit that was either a ring-type in boroxol rings, both BO_3 and BO_4 (BO_3 ring) or non-ring type. The combination of MAS and MQMAS NMR suggested that the distribution of the two sites was attributed to the BO_4 site surrounded only by Si atoms and the BO_4 site surrounded by one B atom and three Si atoms.

Bradt Müller et al. (2019) reported on the structural characterisation of B containing glassy and semi-crystalline borosilicate $(\text{SiO}_2)_{0.49-x}(\text{CaO})_{0.258}(\text{Na}_2\text{O})_{0.233}(\text{P}_2\text{O}_5)_{0.017}(\text{B}_2\text{O}_3)_x$ ($x = 0, 0.01$ and 0.05) by multinuclear NMR for ^{29}Si , ^{31}P , and ^{11}B . The ^{11}B MAS NMR spectra showed two distinct line shapes corresponding to two different components, where the peaks centred at values between 17.9 and 19.0 ppm were attributed to either $[\text{B}]$ units bearing either a single $\text{NB}\emptyset$ and two $\text{NB}\emptyset$ (metaborate-type $\text{B}^{(2)}$ unit) or two $\text{NB}\emptyset$ s

and one B^Ø atom (pyroborate-type, B⁽¹⁾ unit), whilst the peaks centred at values between -1.0 and -0.1 ppm, were attributed to ^[4]B units.

A more recent study conducted by Stone-Weiss et al. (2020) combined MAS NMR techniques, molecular dynamic (MD) simulations, and density functional theory (DFT) calculations to build a model describing the potential short-to-medium range structure of glasses in the Na₂O-P₂O₅-B₂O₃-SiO₂ system. Three distinct baseline glasses with the following compositions were selected: (mol%) (i) 25Na₂O-30B₂O₃-45SiO₂ (R = 0.83 (peroboric)), (ii) 25Na₂O-25B₂O₃-50SiO₂ (R = 1 (metaboric)), and (iii) 25Na₂O-20B₂O₃-55SiO₂ (R = 1.25 (peralkaline)), where P₂O₅ varied between 0-9 mol%. The ¹¹B MAS NMR spectra of all glasses showed two main features, a peak at ~14 ppm attributed to ^[3]B, and a sharper peak at about 0 to -2.5 ppm, associated with ^[4]B. As the P₂O₅ content increased a moderate decrease in the fraction of ^[4]B units occurred, due to the need of anionic phosphate species needing to be charge compensated. The subsequent chemical shift of the feature near 0 ppm and -2.5 ppm was attributed to the formation of either multiple ^[4]B-O-P linkages, ^[4]B-O-Si, or a combination of both. ¹¹B{³¹P} rotational-echo double-resonance (REDOR) NMR experiments concluded that only the ^[4]B units were involved in the B-O-P linkages, due to ^[4]B species exhibiting strong dephasing compared to ^[3]B units.

Raskar et al. (2008) studied sodium borophosphate glasses in the (NaPO₃)_{1-x}(B₂O₃)_x, (0.0 ≤ x ≤ 0.3) glass system, where ¹¹B spectra of the samples when x ≤ 0.2 exhibited a single sharp peak centred near -3.0 ppm, which was attributed to ^[4]B units. When x = 0.3 the ^[4]B resonance broadened, implying the presence of multiple ^[4]B_{xP} species, where xP represents the phosphorus species. The spectrum also showed a second peak centred near 17.1 ppm, assigned to ^[3]B units.

Table 7 is a summary of referenced glass systems and their NMR attributions specific to ¹¹B.

Glass Composition	Assignment	NMR parameters	
	$B_0 = 11.7 \text{ T}$	δ_{iso} (ppm)	C_q (MHz)
(61-x)SiO ₂ -17B ₂ O ₃ -18Na ₂ O-4CaO-xZrO ₂ (Angeli et al., 2010)	BO ₃ rings	17.8	2.6
	BO ₃ non-ring	15	2.65
	BO ₄ (1B, 3Si)	0.2	0.44
	BO ₄ (0B, 4Si)	-1.4	0.24
40P ₂ O ₅ -10B ₂ O ₃ -50Na ₂ O (Carta et al., 2008)	^[4] B _{1P}	-1	
	^[4] B _{2P}	0	
	^[4] B _{3P}	1	
40P ₂ O ₅ -30B ₂ O ₃ -30Na ₂ O	BO ₃	17	
58.5SiO ₂ -N18.2a ₂ O-16.3B ₂ O ₃ -4.0Al ₂ O ₃ -xP ₂ O ₅ -3.0Cs ₂ O, where SiO ₂ was incrementally substituted for P ₂ O ₅ from 1 to 4 mol%. (Krishnamurthy et al., 2020)	BO ₃ ring	17	
	BO ₃ non-ring	15	
	BO ₄ (1B, 3Si)	-0.1	
	BO ₄ (0B, 4Si)	-1.7	
63SiO ₂ -17B ₂ O ₃ -17Na ₂ O-3Cs ₂ O, mol% (Angeli et al., 2012)	BO ₃ rings	17.9	2.56
	BO ₃ non-ring	14.9	2.7
	BO ₄ (1B, 3Si)	0	0.58
	BO ₄ (0B, 4Si)	-1.7	0.19
Na ₂ O-P ₂ O ₅ -B ₂ O ₃ -SiO ₂ 25Na ₂ O-30B ₂ O ₃ -45SiO ₂ (R = 0.83 (peroboric)), (ii) 25Na ₂ O-25B ₂ O ₃ -50SiO ₂ (R = 1 (metaboric)), and (iii) 25Na ₂ O-20B ₂ O ₃ -55SiO ₂ (R = 1.25 (peralkaline)) (Stone-Weiss et al., 2020)	BO ₃	14	
	BO ₄ (1B, 3Si)	0	
	BO ₄ (0B, 4Si) or BO ₄ (0B, 4P)	-2.5	
Borosilicate ((SiO ₂) _{0.49-x} (CaO) _{0.258} (Na ₂ O) _{0.233} (P ₂ O ₅) _{0.017} (B ₂ O ₃) _x (x = 0, 0.01 and 0.05)) (Bradt Müller et al., 2019)	^[3] B(2) or ^[3] B(1)	17.9 to 19.0	

Table 7 - Summary table of characteristic ¹¹B MAS NMR intensities according to literature

2.2.2.2.2 ^{31}P MAS NMR

Phosphorus is a polyvalent oxide and network former, where P atoms are surrounded by four O atoms (Tricot et al., 2020). While the nature of P is similar to Si, due to its +5 charge, it does not have the same level of connectivity, where the formation of P=O linkages are not available to form P-O-P bonds, hence phosphorus can only create three P-O-P linkages leading to a maximum polymerisation of Q^3 (Tricot et al., 2020).

In order to investigate the phosphate network, ^{31}P MAS NMR is used to identify the phosphate units, the degree of phosphate de-polymerization, and provide further information pertaining to the nearest neighbouring network formers (Michaelis et al., 2011). Previous literature has also investigated phosphorus' role in mixed network former glass compositions, such as borophosphate and borosilicate glasses (Angeli et al., 2012; Carta et al., 2008; Krishnamurthy et al., 2020; Michaelis et al., 2011; Muñoz et al., 2006; Ohtsuki et al., 2011; Rinke & Eckert, 2011; Stone-Weiss et al., 2020; Zielniok et al., 2007), to establish the speciation of phosphate units and whether linking of the phosphorus network and other polyhedral networks has preferential linkages or not (Rinke & Eckert, 2011).

Muñoz et al. (2006) investigated the speciation of phosphorus in sodium phospho-borosilicate glasses ($\text{RNa}_2\text{O-B}_2\text{O}_3\text{-KSiO}_2\text{-xP}_2\text{O}_5$ ($0.5 < \text{R} < 2$; $0.86 < \text{K} < 3$)) by ^{31}P , ^{11}B , ^{29}Si , and ^{23}Na NMR, ^{31}P double quantum (DQ) MAS NMR, and transfer of populations under double resonance (TRAPDOR) NMR between ^{31}P and ^{11}B . In the glasses where 3.0 mol% P_2O_5 was added, the P_2O_5 formed isolated PO_4^{3-} , $\text{P}_2\text{O}_7^{4-}$ anions, and $\text{P}_2\text{O}_7^{4-}$ anions connected to $^{[3]}\text{B}$ and $^{[4]}\text{B}$ units. The ^{31}P MAS NMR spectra of the sodium borosilicate glasses with 3.0 mol% P_2O_5 all showed resonances centred at -7.5, 3 and 15 ppm. The 3 and 15 ppm resonances were attributed to $\text{P}_2\text{O}_7^{4-}$ (diphosphate) and PO_4^{3-} (monophosphate) species, respectively. The -7.5 ppm resonance was attributed to phosphates bonded to borate units (P-O-B). When the phosphate content was increased the amplitude of the PO_4^{3-} and $\text{P}_2\text{O}_7^{4-}$ resonances decreased, with an increase in the P-O-B resonance. The ^{31}P DQ MAS NMR spectrum did not show PO_4^{3-} resonances meaning that these species were dispersed throughout the glass network. However, the spectrum did show the $\text{P}_2\text{O}_7^{4-}$ resonance located diagonally on the MAS dimension at -2.5 ppm and the P-O-B species located diagonally on the MAS dimension at -8.5 ppm. There were also two diagonally correlated pairs at

3.5 and -7 ppm, and 0.5 and -9 ppm in the MAS dimension, which were correlated to the proximity of $P_2O_7^{4-}$ to the borate units, to which they were likely bonded together.

Another study that investigated a series of similar compositions in the Na_2O - P_2O_5 - B_2O_3 - SiO_2 system was by Stone-Weiss et al. (2020), as mentioned earlier. ^{31}P MAS NMR spectra of all the glasses showed three main features: a low intensity feature at 1~6 ppm attributed to P^0 units, a strong peak centred between 1 to 4 ppm attributed to P^1 units, and a broader peak centred between -5 and -10 ppm attributed to P^2 units. The peralkaline glasses ($R > 1$) showed a slight increase in the intensity of the broad peak between -5 and -10 ppm, as the concentration of the P_2O_5 content increased from 1 to 3 mol%. These same glasses showed the narrowing of the P^0 and P^1 peaks and narrowing of the P^0 peak as the concentration of the P_2O_5 content increased from 1 to 3 mol%. These changes in the peaks may be indicative of the development of a more ordered phosphate environment, especially as some glasses showed evidence of the Na_3PO_4 crystal phase in XRD patterns. It was also found that in all the glasses studied, the P^1 peak shifted to lower frequencies with increased P_2O_5 content. Overall, the ^{31}P MAS NMR spectra were fitted with six Gaussian contributions, where component one was attributed to $P^1_{1B(IV)}$, component two was P^1_{1P} , component three was $P^{(2)}_{2B}$, components four and five were $P^{(2)}_{1B,1P}$ and $P^{(3)}_{2B,1P}$, and component six was isolated monophosphate (P^0) or $P^{(2)}_{2P}$ chain phosphate species, with no linkages to B.

Ohtsuki et al. (2011) investigated phase separation in borosilicate glasses containing P, where the composition of the base glass was 10 Na_2O -40 B_2O_3 -50 SiO_2 (mol%). ^{31}P MAS NMR spectra before and after heat treatment were collected, where one glass with the composition 10 Na_2O -40 B_2O_3 -47 SiO_2 -3 P_2O_5 exhibited a peak at ~ -14 ppm, which was assigned to either pure Q^2_p unit, a Q^2_p unit connected to one $^{[4]}B$ or a Q^3_p unit connected to one $^{[4]}B$. The spectra of this glass before and after heat treatment saw no changes in the PO_4 glass network.

Cheng et al. (2014) investigated the structure of the glass system xP_2O_5 - yAl_2O_3 - $(100-x-y)(Na_2O \cdot B_2O_3 \cdot 2SiO_2)$ and $y=0, 3, 6, 12$ mol% using multi-nuclear MAS NMR. The ^{31}P MAS NMR spectra of the P_2O_5 -doped borosilicate glasses displayed three main resonances at 15, 3, and -7 ppm, where the intensity of the 15 and 3 ppm decreased in intensity with increasing P_2O_5 content. The

resonances at 15 ppm and 3 ppm were attributed to PO_4^{3-} and $\text{P}_2\text{O}_7^{4-}$ species, respectively. Whilst the peak at -7 ppm was attributed to the P-O-B units.

A study by Rinke and Eckert (2011) utilised ^{31}P MAS NMR to investigate sodium borophosphate glasses in the system $(\text{Na}_2\text{O})_x(\text{BPO}_4)_{1-x}$ ($0.25 \leq X \leq 0.55$). Glasses with $0.25 \leq X \leq 0.45$ exhibited a spectral component at ~ -18 to -21 ppm, which had been mainly attributed to $\text{P}^{(3)}_{2\text{B}}$, but there were also minor contributions from $\text{P}^{(3)}_{1\text{B}}$ and $\text{P}^{(3)}_{3\text{B}}$. For glasses with $X \geq 0.35$, there was one spectral feature that had been deduced to be the overlapping chemical shift contributions from $\text{P}^{(2)}_{1\text{B}}$ and $\text{P}^{(3)}_{3\text{B}}$ (-9 and -10 ppm). For glasses where $x = 0.45$ and 0.50 , $\text{P}^{(2)}_{1\text{B}}$ and $\text{P}^{(2)}_{2\text{B}}$ were the dominating species, where there was a spectral component near -5 to -7 ppm accounting for both species.

Zielniok et al. (2007) also studied a sodium borophosphate glass system $((\text{Na}_2\text{O})_{0.4}[(\text{B}_2\text{O}_3)_x(\text{P}_2\text{O}_5)_{1-x}]_{0.6})$ using solid-state NMR to investigate the structure-property correlations. The ^{31}P MAS NMR spectra exhibited two main spectral features at -12.8 and -5.4 ppm which were attributed to $\text{P}^{(2)}_{1\text{B}}$ and $\text{P}^{(2)}_{2\text{B}}$ units, respectively. There was also a third feature that may have represented superimposed signals from a mixture of different species, such as in the sample where $x = 0.2$, where a peak observed at -20.3 ppm compromised of signals from both $\text{P}^{(2)}$ and $\text{P}^{(3)}_{2\text{B}}$ units. At higher B contents where $x > 0.7$, the spectra showed peaks near 3 and 10 ppm, which were assigned to $\text{P}^{(1)}$ and $\text{P}^{(2)}$ species, respectively.

Raskar et al. (2008) studied sodium borophosphate glasses in the $(\text{NaPO}_3)_{1-x}(\text{B}_2\text{O}_3)_x$, ($0.0 \leq x \leq 0.3$) glass system. ^{31}P MAS NMR of pure NaPO_3 glass ($x = 1$) exhibited one spectrum feature centred at -19.2 ppm, which was attributed to $\text{P}^{(2)}$ (metaphosphate-type) units. Additions of B_2O_3 led to the appearance of two new spectral features at ~ -11 and -30 ppm, which were attributed to $\text{P}^{(2)}_{1\text{B}}$ and could have arisen from a mixture of $\text{P}^{(3)}_{1\text{B}}$ or BPO_4^- like domains.

Krishnamurthy et al. (2020) investigated the network structure and dissolution behaviour of phosphate doped borosilicate glasses in the $\text{SiO}_2\text{-Na}_2\text{O-B}_2\text{O}_3\text{-Al}_2\text{O}_3\text{-P}_2\text{O}_5\text{-Cs}_2\text{O-MoO}_3$ glass system, where SiO_2 was incrementally substituted for P_2O_5 from 1 to 4 mol%. The ^{31}P MAS NMR spectra of the glasses containing the lowest P_2O_5 content had three peaks centred at 15.8, 3.4, and -6.6 ppm. These peaks were fitted where the chemical shifts at 15.8 ppm and 3.4 ppm were

attributed to ortho- (P^0) and pyro- (P^1) phosphate species. The peak centred at -6.6 ppm was attributed to metaphosphate (P^2) species where one or two of the neighbouring species may have been a borate unit. At 3.0 mol% P_2O_5 the spectra evidenced two distinct peaks that occur in the P^1 region (+5 ppm) and may have been due to the clustering of the poorly crystalline $Na_4P_2O_7$ phase. At 4.0 mol% P_2O_5 the concentration of the P^1 species and $Na_4P_2O_7$ increased at the expense of P^0 units.

As mentioned above, the study by Bradtmüller et al. (2019) reported on the structural characterisation of boron-containing glassy and semi-crystalline Bio silicate by multinuclear NMR. The ^{31}P MAS NMR spectra showed that they were dominated by a broad Gaussian line shape centred at 8.5 ppm, which was attributed to the fully de-polymerised $P^{(0)}$ units. There was also evidence of a minor contribution centred at 1.2 ppm, which was assigned to $P^{(1)}$ units.

Table 8 summarises the key ^{31}P referenced NMR assignments in relation to the aforementioned literature.

Composition	Assignment	NMR Parameters
		$B_0 = 11.7\text{ T}$ $\delta_{iso}\text{ (ppm)}$
RNa ₂ O-B ₂ O ₃ -KSiO ₂ -xP ₂ O ₅ (0.5 < R < 2; 0.86 < K < 3)) x = 3.0 mol%, (Muñoz et al., 2006)	PO ₄ ³⁻ (P^0)	15
	P ₂ O ₇ ⁴⁻ (P^1)	3
	P-O-B	-7.5
25Na ₂ O-30B ₂ O ₃ -45SiO ₂ (R = 0.83 (peroboric)), (ii)	P^0	16
25Na ₂ O-25B ₂ O ₃ -50SiO ₂ (R = 1 (metaboric)), and	P^1	1 to 4
(iii) 25Na ₂ O-20B ₂ O ₃ -55SiO ₂ (R = 1.25 (peralkaline)) (Stone-Weiss et al., 2020)	P^2	-5 to -10
10Na ₂ O-40B ₂ O ₃ -47SiO ₂ -3P ₂ O ₅ (Ohtsuki et al., 2011)	Q ² _p or Q ² _P connected to one ^[4] B, or Q ³ _P connected to a ^[4] B unit	14
58.5SiO ₂ -18.2Na ₂ O-16.3B ₂ O ₃ -4.0Al ₂ O ₃ -xP ₂ O ₅ - 3.0Cs ₂ O, where SiO ₂ was incrementally substituted for P ₂ O ₅ from 1-4 mol%.	PO ₄ ³⁻ (P^0) P ₂ O ₇ ⁴⁻ (P^1) P^2	15.8 3.4 -6.6

(Krishnamurthy et al., 2020)

$x\text{P}_2\text{O}_5 - y\text{Al}_2\text{O}_3 - (100-x-y) (\text{Na}_2\text{O} \cdot \text{B}_2\text{O}_3 \cdot 2\text{SiO}_2)$ and $y=0, 3, 6, 12.$ (Cheng, 2014)	$\text{PO}_4^{3-} (\text{P}^0)$	15
	$\text{P}_2\text{O}_7^{4-} (\text{P}^1)$	3
	P-O-B	-7
$40(\text{P}_2\text{O}_5)-x(\text{B}_2\text{O}_3)-(60-x)(\text{Na}_2\text{O})$ ($10 \leq x \leq 30$ mol%) (Carta et al., 2008)		
40P ₂ O ₅ -10B ₂ O ₃ -50Na ₂ O	P ¹ _(0B)	0.9
	P ² _(1B)	-9.8
	P ² _(0B)	-14.9
40P ₂ O ₅ -15B ₂ O ₃ -45Na ₂ O	P ¹ _(0B)	0.4
	P ² _(1B)	-10
	P ² _(0B)	-17.9
40P ₂ O ₅ -20B ₂ O ₃ -40Na ₂ O	P ² _(0B)	-11.4
	P ³ _(1B) , P ³ _(2B)	-18.4
	P ² _(0B)	-11.2
40P ₂ O ₅ -25B ₂ O ₃ -35Na ₂ O	P ³ _(1B) , P ³ _(2B)	-19.7
	P ³ _(1B) , P ³ _(2B)	-20.7
$(\text{Na}_2\text{O}) x(\text{BPO}_4)1-x$ ($0 \leq x \leq 0.2$)		
x = 0.25 (lowest)	P ³ _(2B)	-21
	P ⁴ _(4B)	-30.3
x = 0.55 (highest)	P ⁰	15.1
	P ¹ _(0B) + P ¹ _(1B)	3.1
(Rinke & Eckert, 2011)	P ² _(1B) + P ² _(2B)	-4.8
$(\text{NaPO}_3)1-x (\text{B}_2\text{O}_3)x$ ($0 \leq x \leq 0.3$)		
x = 0 (lowest)	P ¹ _(0B)	-19.2
	P ² _(1B)	-10.6
x = 0.15 (middle)	P ² _(0B) + P ³ _(2B)	-18.2
	P ⁴ _(4B)	-27.9
x = 0.30 (highest)	P ² _(1B)	-10.4
	P ² _(0B) + P ³ _(2B)	-17.8
(Raskar et al., 2008)	P ⁴ _(4B)	-24.8
$(\text{Na}_2\text{O})0.4[(\text{B}_2\text{O}_3)x(\text{P}_2\text{O}_5)1-x]0.6$ (Zielniok et al., 2007)		

x = 0	P ²	-22.7
	P ³	-32.3
x = 0.5	P ³ _(3B) + P ² _(2B)	-8.5
	P ³ _(2B)	-19.2
	P ⁰	15.6
x = 0.9	P ¹ _(1B)	5.3
	P ² _(2B)	-5.4
Borosilicate ((SiO ₂) _{0.49-x} (CaO) _{0.258} (Na ₂ O) _{0.233} (P ₂ O ₅) _{0.017} (B ₂ O ₃) _x (x = 0, 0.01 and 0.05)) (Bradt Müller et al., 2019)	P ⁰	8.
	P ¹	51.2

Table 8 - Summary table of characteristic ³¹P MAS NMR intensities according to literature

2.2.2.2.3 ²³Na MAS NMR

Sodium, while added to glasses as a network modifier, can and does act as a charge balancer for different Qⁿ species that have anionic charges, e.g., BO₄⁻ (Martineau et al., 2010). It has been previously proposed that Na⁺ in SiO₂-B₂O₃-Na₂O glass systems predominantly associates itself with ^[4]B tetrahedra, where the increase in the Na content leads to the conversion of ^[3]B to ^[4]B units until the maximum is reached (Yu et al., 2017). However, in similar glass systems that contain P₂O₅, when there is not enough alkali content available to charge compensate the most electronegative anionic species (P₂O₅), other bonding occurs instead, e.g., P-O-B (Cheng, 2014).

As mentioned earlier, investigations by Stone-Weiss et al. (2020) investigated the short-to-medium range structure of bioactive glasses in the Na₂O-P₂O₅-B₂O₃-SiO₂ glass system. The ²³Na MAS NMR spectra of these glasses showed that the isotropic chemical shift was dependent on the distribution of Na among the phosphate, silicate, and borate structural units, as its charge compensates these anionic species. The overall ²³Na MAS NMR chemical shift behaviour moved to more negative values upon the increase of x, reflecting the importance of the Na and P interactions, and subsequent decrease in the importance of ^[4]B-Na and Si³-Na interactions. It was also found through MD simulations that the NBØs surrounding the Na ions increased with increasing P₂O₅ content, suggesting that Na gradually shifts from its role as a charge compensator linked to B-bonded BØ species, to being a charge compensator of anionic NBØs linked to phosphate

species instead. Hence, Na preferentially links to phosphate over other network forming units in its second order coordination shell.

The study by Muñoz et al. (2006), as mentioned previously, investigated a $\text{RNa}_2\text{O}-\text{B}_2\text{O}_3-\text{KSiO}_2\text{x}-\text{P}_2\text{O}_5$ glass system ($0.5 < \text{R} < 2$; $0.86 < \text{K} < 3$), where it was reported that a decrease in the chemical shift of the ^{23}Na spectra was an indication that Na^+ ions moved from a charge compensator position for BO_4^- to a non-bridging position instead.

A study by Rinke and Eckert (2011) used ^{23}Na MAS NMR to investigate sodium borophosphate glasses in the system $(\text{Na}_2\text{O})_x(\text{BPO}_4)_{1-x}$ ($0.25 \leq \text{X} \leq 0.55$) to establish the local Na environment. It was found that at high Na contents there were positive chemical shift values, reflecting the strong interaction of the Na ions with BO_3 s that were associated with P^1 units. When $x = 0.25$ and 0.30 , there was an indication for a preference of Na^+ cations to charge compensate P^2 and B^4 species, however, when $x \geq 0.33$ the charge compensation of borate units had been exhausted, and therefore an anionic compensation hierarchy was followed $\text{B}^4 \rightarrow \text{P}^2 \rightarrow \text{P}^1$.

2.2.2.2.4 ^{29}Si MAS NMR

Krishnamurthy et al. (2020) investigated phosphate doped borosilicate glasses in the $\text{SiO}_2\text{-Na}_2\text{O-B}_2\text{O}_3\text{-Al}_2\text{O}_3\text{-P}_2\text{O}_5\text{-Cs}_2\text{O-MoO}_3$ glass system, where the ^{29}Si MAS NMR spectra displayed a broad peak typical of silicate glasses. The chemical shifts of the Q^3 and Q^4 species were determined to be -93 and -102 ppm, respectively. When the SiO_2 was replaced by P_2O_5 , the broad peak moved towards more negative frequencies, suggesting that there was an increase in the Q^4 speciation.

The study by Muñoz et al. (2006) investigated the speciation of P in sodium phospho-borosilicate glasses, where the ^{29}Si NMR spectra presented resonances that were centred with a more negative chemical shift. The lower resonance was indicative of the degree of polymerisation of the silicate network increasing, due to the increased proportions of Q^3 and Q^4 tetrahedra or the decreased connectivity between silicates and BO_3 and BO_4 species.

Angeli et al. (2012) reported a distinct lack of variation in the ^{29}Si MAS NMR spectra of the borosilicate glass with nominal mol% composition $63\text{SiO}_2\text{-17B}_2\text{O}_3\text{-17Na}_2\text{O-3Cs}_2\text{O}$, which was attributed to the presence of a B atom as the second

neighbour to the Si atom, causing the spectral line to shift in the direction associated with de-polymerisation. The peak situated at ~ -90 ppm was assigned to $\text{Si}(\text{Q}^3)$ and $\text{Si}(\text{Q}^4)\text{-BO}_4$ units, whilst the peak at ~ -100 ppm was assigned to fully polymerised $\text{Si}(\text{Q}^4)$ units and $\text{Si}(\text{Q}^4)\text{-BO}_3$ non-ring units.

Similarly, the ^{29}Si MAS NMR spectra from the study by Stone-Weiss (2020) of three base glasses with the compositions (mol%) (i) $25\text{Na}_2\text{O}\text{-}30\text{B}_2\text{O}_3\text{-}45\text{SiO}_2$ ($R = 0.83$ (peroboric)), (ii) $25\text{Na}_2\text{O}\text{-}25\text{B}_2\text{O}_3\text{-}50\text{SiO}_2$ ($R = 1$ (metaboric)), and (iii) $25\text{Na}_2\text{O}\text{-}20\text{B}_2\text{O}_3\text{-}55\text{SiO}_2$ ($R = 1.25$ (peralkaline)) exhibited a broad peak centred approximately at -92 ppm, which shifted towards lower frequencies with increased P_2O_5 content. The spectra had poorly resolved line shapes, which made it difficult to deconvolute the Si speciation from the MAS NMR spectra alone. However, it was suggested that Si^4 species connected to a mix of ^{13}B and ^{14}B may be present, as well as Si^3 units. The shift trend exhibited in the ^{29}Si MAS NMR spectra may have been due to a decrease in the Si-B network connectivity, as well as reflect a reduction in the presence of Si^3 units, or a subsequent increase in Si-O-P linkages. The reduction of Si^3 units was attributed to the competition between SiO_2 and P_2O_5 in attracting network modifiers and/ or the charge sharing between P and B units in P-O- ^{14}B linkages where there was a distinct lack of network modifiers. Hence, the distribution of Si in the glasses was predominantly as Si^4 species and Si^3 species, with small amounts of Si^2 species. As the P_2O_5 content increased in the glass, the silicate network became more polymerized, indicating the transfer of Na^+ ions toward the anionic phosphate units. However, there were also small amounts of ^{13}B units connected to Si^3 and Si^4 species and P ($x \leq 0.2$ mol%) that were second neighbours to Si^4 species.

Bradt Müller et al. (2019) also used ^{29}Si MAS NMR to study a borosilicate glass, where the glasses that contained B, were deconvoluted into two line shapes, with components centred near -80 and -90 ppm, which corresponded to $\text{Si}^{(2)}$ and $\text{Si}^{(3)}$ sites, respectively.

Table 9 summarises the characteristic ^{29}Si MAS NMR intensities according to literature.

Composition	Assignment	NMR parameters
	$B_0 = 11.7 \text{ T}$	δ_{iso} (ppm)
58.5SiO ₂ -N18.2a ₂ O-16.3B ₂ O ₃ -4.0Al ₂ O ₃ - xP ₂ O ₅ -3.0Cs ₂ O, where SiO ₂ was incrementally substituted for P ₂ O ₅ from 1 to 4 mol%.	Q ³	-93
(Krishnamurthy et al., 2020)	Q ⁴	-102
63SiO ₂ -17B ₂ O ₃ -17Na ₂ O-3Cs ₂ O, mol%	Si(Q ³) and Si(Q ⁴)-BO ₄	-90
(Angeli et al., 2012)	Si(Q ⁴) units and Si(Q ⁴)-BO _{3 non-ring}	-100
25Na ₂ O-30B ₂ O ₃ -45SiO ₂ (R = 0.83 (peroboric)), (ii) 25Na ₂ O-25B ₂ O ₃ -50SiO ₂ (R = 1 (metaboric)), and (iii) 25Na ₂ O-20B ₂ O ₃ - 55SiO ₂ (R = 1.25 (peralkaline) (Stone- Weiss et al., 2020)	Si(Q ⁴) connected to a mixture of [³ B and [⁴ B, and Si(Q ³)	-92
Borosilicate		
((SiO ₂) _{0.49-x} (CaO) _{0.258} (Na ₂ O) _{0.233} (P ₂ O ₅) _{0.017} (B ₂ O ₃) _x (x = 0, 0.01 and 0.05))	Q ²	-80
(Bradtmüller et al., 2019)	Q ³	-90

Table 9 - Summary table of characteristic ²⁹Si MAS NMR intensities according to literature

2.2.2.3 Mössbauer Spectroscopy

In 1958, Rudolf Mössbauer discovered a phenomenon whereby he observed the strange temperature dependence for the absorption cross-section of the 129 KeV γ -ray absorption produced by the decay of ¹⁹¹Ir (G. Williams, 1990). At low temperatures the absorption cross-section increased which contradicted the previous expectation that at lower temperatures the thermal absorption and emission profiles should reduce, leading to a decrease in the degree of overlap and hence a decrease in the absorption cross-section (G. Williams, 1990). This phenomenon can be explained in terms of the number of nuclei that become

frozen in the lattice as the temperature decreased. These frozen nuclei have no thermal motion and are unable to recoil, meaning that they will emit or absorb γ -rays with an specific energy equivalent to the nuclear transition energy (G. Williams, 1990).

Mössbauer spectroscopy uses the Doppler effect, which was discovered by Christian Doppler in 1842, and is when the frequency of any harmonic wave motion at a receiver differs from the frequency at its source whenever the receiver, the source, or both are in motion relative to each other (Joseph, 2014).

The Mössbauer effect has been detected in 72 isotopes of 42 different elements such as Ni, Zn, Sn, Cs, La etc. (Gütlich et al., 2012). Due to certain criteria, namely the suitable lifetime of the nuclear excited state, accessibility, transition energy, and handling, only 20 elements can be studied by Mössbauer spectroscopy, e.g., Fe, Ni, Sn, Sb, Ag, and W (Bianchi et al., 2021; Gütlich et al., 2012). The most widely studied element is ^{57}Fe due to its low gamma-ray energy and long-life excited state (Bianchi et al., 2021; Gütlich et al., 2012). ^{57}Fe was studied via Mössbauer spectroscopy in this thesis to investigate its oxidation state and local structural environment.

Both Fe^{2+} and Fe^{3+} are distinguishable by Mössbauer spectroscopy, as they have different characteristic isomer shifts (δ) and quadrupole splitting (Δ) of the low-spin states. The low-spin state of Fe^{2+} and quadrupole splitting tends to be lower in low spin Fe^{2+} compounds than Fe^{3+} . An example of low-spin δ for Fe^{2+} compounds are $\delta = -0.1$ to 0.2 mm/s with $\Delta = -0.2$ to 1.9 mm/s, whilst typical high-spin δ for Fe^{3+} compounds are $\delta = 0.9$ to 1.3 mm/s with $\Delta = 2.0$ to 2.7 mm/s at room temperature. Table 10 summarises the Mössbauer characteristic δ and Δ of ^{57}Fe according to literature.

Fe Coordination	Glass system	Isomer / chemical shift, δ (mm/s)	Quadrupolar splitting, Δ (mm/s)	Reference
Fe ²⁺	Silicate	0.5	2.00	(Mysen, 1987)
	Borosilicate	0.68 – 0.78	2.04 – 2.31	(Eremyashev et al., 2014)
Fe ³⁺	Silicate	0.19 – 0.30	-	(Mysen, 1987)
		0.4 – 0.9	-	(Pathak et al., 2010)
		0.28 – 0.32	-	(Pathak et al., 2010)
	Borosilicate	0.24 – 0.27	0.89 – 0.96	(Eremyashev et al., 2014)

Table 10 - Summary table of characteristic chemical shift and quadrupolar splitting of ⁵⁷Fe according to literature

It has been reported that additions of Fe to borosilicate glasses enters the glass system as a network-former and/or modifier, which has seen the conversion of [BO_{4/2}] to BO₃ structural units (Cizman et al., 2017). Furthermore, Fe²⁺ cations that are mostly sixfold coordination occupy interstitial sites near BO₃ groups as network modifiers, whilst Fe³⁺ cations are four-coordinated and seem to substitute with Si in the glass network as network formers (Cizman et al., 2017; Cochain et al., 2008). Typical values of Fe³⁺ tetrahedrally coordinated to oxygen in silicate glasses are between 0.20-0.32 mm.s⁻¹, compared to a range of 0.35-0.55 mm.s⁻¹ when octahedrally coordinated (Johnson & Johnson, 2005). The data range for Fe²⁺ has been observed to be between 0.90-0.95 mm.s⁻¹ when tetrahedrally coordinated and 1.05-1.10 mm.s⁻¹ when octahedrally coordinated (Johnson & Johnson, 2005).

It is possible to quantitatively measure the redox ratio of the Fe²⁺ and Fe³⁺ ions by comparing absorption area ratios if the recoil free fraction ratio, *f*, is assumed

to be 1, which may not be the case for all systems (Bingham, 2001). It should also be noted that for low Fe content, the analysis needs to be conducted at a very low temperature of $\geq 10\text{K}$ (Bingham, 2001). The Fe atoms in different local environments and oxidation states absorb at different energies (Bingham, 2001; Scrimshire, 2019; Vaishnav, 2018). Fe^{2+} compounds show a larger isomer shift than Fe^{3+} compounds due to extra 3d electrons in Fe^{2+} that further shield the $3s^2$ electrons from the nucleus (Williams, 1990).

2.2.2.4 X-ray Absorption Near-Edge Structure (XANES) Spectroscopy

X-ray absorption near-edge structure (XANES) spectroscopy is a synchrotron radiation technique that provides information on the local electronic and geometric structure (DeBeer, 2011; Henderson et al., 2014).

A synchrotron is a type of circular charged particle accelerator, where the magnetic field and frequency are varied to maintain a synchronous particle at a constant orbit radius (Balerna & Mobilio, 2015). Synchrotron generate intense collimated electromagnetic radiation ranging from infrared to X-ray wavelengths (Sutton & Newville, 2014). A synchrotron consists of five main components: the electron source, booster ring, storage ring, radio frequency (RF) supply, and beamlines (Figure 11) (Bharti & Goyal, 2019). In a synchrotron, electrons are firstly accelerated by either a microtron or a linear accelerator to a few hundred MeV in energy (Bharti & Goyal, 2019). The electrons are then injected into a circular accelerator to increase their energy in order to approach the main storage ring electron energy, called the booster ring (Bharti & Goyal, 2019). The electrons are then intermittently transferred to the main storage rings from the booster ring when the storage ring current drops by $\sim 70\%$ in order to maintain the beam current (Bharti & Goyal, 2019). The storage ring is the main component of a synchrotron, where electrons travel in a closed path under a magnetic field, where the magnets comprise of a set of bending (dipole), quadrupole and sextuple magnets, called a magnet lattice (Balerna & Mobilio, 2015; Bharti & Goyal, 2019). These magnets force the electrons to follow a set closed path (Bharti & Goyal, 2019). As the electrons are accelerated in a circular path they lose energy, which is then emitted as radiation (Balerna & Mobilio, 2015). The electrons radiate at frequencies in the electromagnetic spectrum i.e., UV, visible, and X-rays (Bharti & Goyal, 2019). The energy lost is fully regained by the electrons passing through the RF cavities (Balerna & Mobilio, 2015).

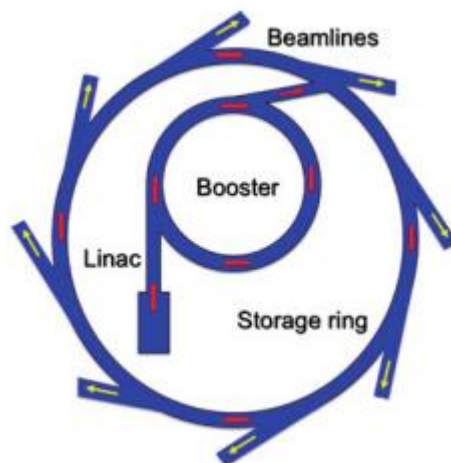


Figure 11 - Schematic planar view of a synchrotron radiation facility (Balerna & Mobilio, 2015) with copyright permission from Springer Nature (License number: 5624870049197)

In XANES, a photon is used to excite an electron from its core state to an empty state, where the photon energy has to be equal to or higher than the binding energy of the electron core energy level (Henderson et al., 2014). Therefore, the energy of an absorption edge corresponds to the core energy level, which is characteristic for a particular element, and hence can be used as a characterisation technique (Henderson et al., 2014).

In this thesis, XANES was used as a complimentary technique to Mössbauer spectroscopy to characterise Fe in the SCPD-HLW/LAW glasses, and the ILAW glasses, due to Fe being present in two valence states (Fe^{2+} and Fe^{3+}), whose proportional content is dependent on the melting temperature and glass composition (Husain et al., 2018). Table 11 summarises the referenced Fe K-edge XANES energy range and pre-edge centroid energy for Fe^{3+} and Fe^{2+} .

Element of interest	Oxide	K- edge (eV)	Reference	Pre- edge centroid energy (eV)	E ₀ (eV)	Reference
Fe ³⁺	Fe ₂ O ₃	7112	(Alderman et al., 2017; Kim et al., 1998; Rogantini et al., 2018; Simon et al., 2021)	7113.5	7123.41	(Husain et al., 2018)
				-	7125.3	(Latif et al., 2018)
				7114.62	-	(Berry et al., 2003)
				7113.25	-	(Río et al., 2005)
				-	7127	(Li et al., 2016)
Fe ²⁺	FeO	-	-	7112.45	-	(Wilke et al., 2001)
				7117.0	-	(Nie et al., 2016)

Table 11 - Fe K-edge XANES referenced energy range and pre-edge centroid energy for Fe³⁺ and Fe²⁺

2.2.3 Glass Properties

2.2.3.1 Crystallisation Behaviour

A study by Lu et al. (2021) investigated the structural and crystallization behaviour of phosphorus in meta- and per-aluminous sodium aluminosilicates glasses and its correlation with crystallization behaviour. The additions of Al₂O₃ in binary alkali silicate glass systems impacts the solubility and structural role of P₂O₅, of which this is particularly evident in per-aluminous silicate melts and glasses, where the solubility of P₂O₅ increases with an increase in Al₂O₃ content (Lu et al., 2021; Wolf

& London, 1994). The role of P_2O_5 can act as either a network former or a network modifier in de-polymerized $Na_2O-Al_2O_3-SiO_2$ glasses based on the Na/Al ratio (Lu et al., 2021). The dependence of the structural role of P_2O_5 on the alkali-to-alumina ratio in silicate glasses has been used to encourage crystallization in the per-alkaline composition $Li_2O-Al_2O_3-SiO_2$ system, where P_2O_5 concentrations ranging between 1-10 mol% induced phase separation by the removal of Li^+ ions from the silicate glass network (Lu et al., 2021). As a result, $3Li^+(PO_4)^{3-}$ units were formed and upon heating crystallised to form Li_3PO_4 crystals which acted as nucleation sites for the nucleation and growth of Li_2SiO_3 and $Li_2Si_2O_5$ crystals (Lu et al., 2021; Marcial et al., 2018). However, in metaluminous glass systems, this was not the case with the formation of $NaPO_3$, where it potentially acted as a nucleation site for the crystallization of an alkali aluminosilicate phase or the formation of $AlPO_4$, resulting in the glass matrix having a lower Al^{3+} content, thus suppressing crystallization (Lu et al., 2021). In the metaluminous glasses ($P_2O_5 \leq 15$ mol%) approximately 95% of the phosphate units were Q^0_{mAl} units, where m refers to the number of Al atoms connected to each $[PO_4]^{3-}$ tetrahedron (Lu et al., 2021). Nepheline was repressed in these metaluminous glasses due to the formation of Al-O-P linkages leading to the reduction in Si-O-Al in the glass (Lu et al., 2021).

2.2.3.2 Thermal Properties

Several studies have explored the effect of P_2O_5 on thermal properties of silicate, borosilicate, and aluminoborosilicate glasses, e.g., Bingham (2004) and Bingham and Hand (2007). Bingham (2004) commented that 0.4 wt% P_2O_5 in a soda-lime silicate glass system had no effect on the viscosity, CTE or T_g , but at 1.0 wt% P_2O_5 saw a reduction in the T_{liq} and increase in the T_d . Whilst Bingham and Hand (2007) found that additions of P_2O_5 to a $SiO_2-Al_2O_3-B_2O_3-MgO-CaO-Na_2O$ glass system also saw no notable change in the CTE, T_d , or T_g . However, there was a reported increase in the T_{liq} with increasing P_2O_5 content, contradicting what was previously stated by Bingham (2004). Another study by Muñoz et al. (2006) commented that the additions of P_2O_5 (3 mol%) led to an increase in the T_g when there was less than 38% P-O-B groups relative to the number of phosphate species, and decreased when there was more than 38%, as shown in Figure 12. A study by Cheng (2014) also reported that the T_g of a sodium borosilicate glass

system initially increased with the addition of 1 mol% P_2O_5 , after which further additions saw the T_g decrease.

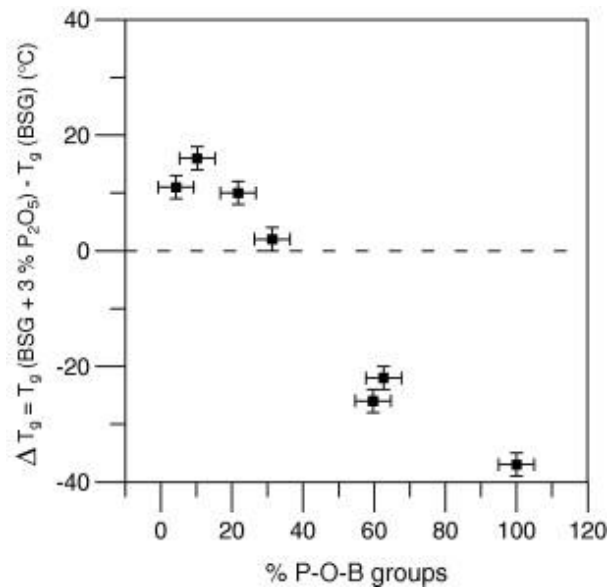


Figure 12 - Temperature difference between the T_g of the borosilicate glasses with and without 3 mol% P_2O_5 calculated from the P-O-B percentage measured by the deconvolution of ^{31}P NMR spectra taken from (Muñoz et al., 2006) with copyright permission from Elsevier (License number: 5621801319505)

The relationship between the structure and properties in borosilicate glasses has been discussed by Cheng (2014), whereby they commented that the T_g was sensitive to changes in the degree of connectivity, with the decrease in T_g potentially being a result of an increase in the fraction of NBØs in the silicate network, whilst the increase may have been a result of the conversion of $[^3]B$ to $[^4]B$ units.

2.2.3.3 Rheological Properties

Toplis and Dingwell (1996) reported that depending on the type of composition of the glass melt i.e., perkaline or metaluminous, depended on the effect additions of P_2O_5 had on the viscosity. The most perkaline composition showed a linear increase in the viscosity at 4.9 mol% P_2O_5 , but when the P_2O_5 content increased to 6.0 mol% there was a decrease in the viscosity, implying that the maximum viscosity occurred between 5.0 and 6.0 mol% P_2O_5 . The metaluminous compositional melt viscosity moved at lower P_2O_5 content.

Wang et al. (2018) studied the role of P_2O_5 additions on the viscosity of $CaO-SiO_2-Al_2O_3-Na_2O-P_2O_5$ melts, where they reported that the viscosity generally

increased with decreasing temperature. They also observed that the viscosity of the samples increased with increasing P_2O_5 additions, which agreed with other literature cited in their report i.e., Sun et al. (2014), who had reported that additions of P_2O_5 to a $CaO-SiO_2-Al_2O_3-MgO-TiO_2-P_2O_5$ melt showed an increasing basicity and viscosity with increasing P_2O_5 content. Zhang et al. (2016) in Wang et al. (2018) also observed that the viscosity increased with increasing P_2O_5 content in a $FeO-SiO_2-V_2O_3-CaO-P_2O_5$ melt.

2.2.3.4 Chemical Durability

Determining and understanding the long term behaviour of a vitreous waste form is of particular importance because some radionuclides have half-lives that extend to millions of years (10^3-10^6 years) (Thorpe et al., 2021) and require geological disposal, yet current lab investigations are of a relatively short time period (Ma et al., 2017). Hence, the development of reliable durability assessment models based on agreed upon mechanisms are needed in order to control the long-term dissolution behaviour of the glass (Ma et al., 2017). There are a variety of standard methods employed to determine the glass dissolution such as the single-pass flow through (ASTM C1662) and materials characterisation centre tests 1-4 (ASTM C1220) (Thorpe et al., 2021). However, the method used in this thesis was the product consistency test – Method B as described in ASTM C1285.

Chemical durability can be described by different theories, with the surface complexation theory stating that the dissolution rates of oxides and silicates are controlled by the breaking of the metal-oxygen framework bonds (Carroll et al., 1994). These are accelerated by the adsorption of OH^- and H^+ at the surface, where the pH of the solution correlates to the H^+ , with its adsorption leading to an increase in acidity and its desorption in an alkaline solution (Carroll et al., 1994). Hence, the greater number of non-bridging silanol bonds, the less durable the glass due to durability being controlled by the polymerization reactions at the glass-solution interface (Carroll et al., 1994).

The dissolution kinetics of a glass in a static closed system begins with the glass being in contact with water, followed by a release of alkaline elements such as Na^+ and Ca^{2+} , a process which is limited by the diffusion rate through the glass layer (Piovesan et al., 2018). At the same time, the glass network undergoes hydrolysis leading to the release of network forming and modifying elements

(Piovesan et al., 2018). This stage is known as the initial dissolution period (stage 1) and continues to occur as long as there is no feedback effect from dissolved elements (Ferrand et al., 2021; Piovesan et al., 2018). Based on the release rates, there are another two stages: residual dissolution (2) and resumption of glass alteration (3) (Ferrand et al., 2021). Residual glass dissolution is where the glass dissolution rate is so many magnitudes lower than the initial dissolution rate, and resumption of glass alteration occurs under specific conditions i.e., high pH/ and or high temperatures (Ferrand et al., 2021). The stages of glass dissolution are characterized in Figure 13.

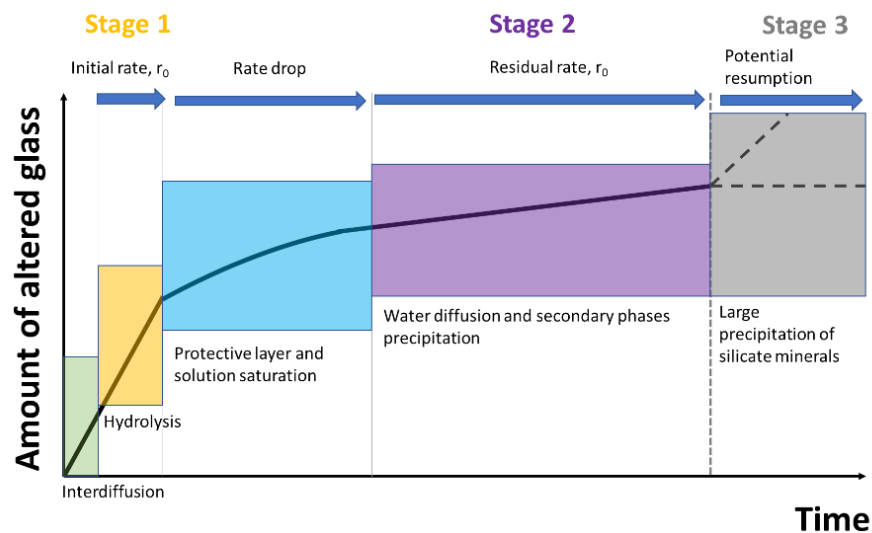
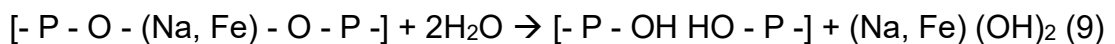


Figure 13 - Schematic of dissolution kinetics of glass modified from (Harrison, 2014)

Bunker et al. (1984) devised a general description of the dissolution reactions between phosphate glasses and water (Eq 9) (Bunker et al., 1984; Ma, 2014). The first stage of dissolution is controlled by the diffusion of ions through the hydrated layer back into the solution. Water hydrates the phosphate anions by reacting with metal (Na, Fe) - O-P bonds linked to neighbouring P-anions (Bunker et al., 1984; Ma, 2014):



Phase separation may cause changes in properties of the glass including its chemical durability, where durability deteriorates when type A or B phase separation occurs, wherein by type A is spinodal decomposition and type B is nucleation and growth with the more durable phase dispersed in the less durable phase (Taylor et al., 1987). To this degree, the microstructure is an important

factor with these changes, e.g., if there is glass-in-glass phase separation this produces continuous immiscible regions wherein leach paths exist for the least durable phase leading to the degradation of the glass (Arbab et al., 2007). A borosilicate glass that is phase separated often consists of a silica-rich phase and a less durable borate-rich phase (Arbab et al., 2007). The addition of divalent metal oxides (RO) ($R = \text{Mg, Ba, Ca} \dots$) to borosilicate glasses increases the extent of phase separation and ultimately becomes detrimental to the chemical durability of the glass. Arbab et al. (2007) reported that the most detrimental oxide to the chemical durability of an alkaline borosilicate glass opacified by P_2O_5 was ZnO (containing 6 wt%). However, glasses containing CaO generally showed a better chemical durability due to the formation of apatite crystals.

Cheng et al. (2017) investigated the dissolution behaviour in alkaline solutions of a borosilicate glass with and without P_2O_5 . They reported that the breakdown of the silicate network of the glasses in an alkaline solution was encouraged by the increase in the solubility of silicate anions and the catalytic effects of OH^- ions. The dissolution behaviour exhibited in both the sodium borosilicate (NBS) and NBS-3P in Ca-free solution was typical of an alkaline attack of a silicate and borosilicate glass network. They noted that when Ca^{2+} ions were introduced into the alkaline solution the dissolution rate reduced by a factor of 10 when compared to the Ca^{2+} free solutions, supporting previous studies that observed the inhibition effects of the Ca^{2+} ions when in solution. When 3.0 mol% P_2O_5 was added to the borosilicate glass, Ca-P rich particles formed on the glass surface, with XRD and Raman data confirming that these particles were hydroxyapatite (Hap). The formation of Hap was limited by the release of orthophosphates because of the passivity of the C-S-H gel. The presence of P_2O_5 in the glass did not majorly influence C-S-H formation and the inhabitation effect on the glass dissolution.

Krishnamurthy et al. (2020) investigated the dissolution behaviour of P_2O_5 -doped borosilicate glass and commented that the elemental release rate decreased as the P_2O_5 content increased from 1.0 to 4.0 mol%, suggesting that solely phosphate species were not responsible for the degradation of the durability of the glasses. The phase separated phosphate-rich regions suffered from a lower durability and were hence, more accessible to the solvent resulting in its dissolution.

2.2.4 Summary

The effects of P_2O_5 on the structural, thermal, and rheological properties are dependent on the composition to which it is being added, and the subsequent ratios of the other components, where the base glass composition may already be susceptible to immiscibility based on its position in the $Na_2O-B_2O_3-SiO_2$ ternary phase diagram. The composition will then affect the overall structure, where increasing additions of P_2O_5 alters the structure by its strong ability to attract charge compensating cations that may have previously been acting as glass modifiers. The origin of the NBØs and BØs and how the ratio between them is being affected, dictates the polymerisation behaviour of the glass structure, which in turn affects the properties of the glass. The effects of P_2O_5 can be measured and analysed structurally using Raman, Mössbauer, XANES, and MAS NMR spectroscopy, whereas the properties of interest such as T_g , rheology, crystallisation behaviour, and chemical durability can be measured using DTA, Dilatometry, viscosity, XRD, and PCT, respectively.

2.3 Radioactive Waste Vitrification and the Hanford Site

2.3.1 Nuclear Waste Generation and Sources

The sources of radioactive waste are an accumulation of agricultural, medical, industrial, and human wastes that contain naturally occurring radionuclides. However, what is deemed as a controllable radioactive material is determined by each individual country, and hence their classification as radioactive wastes (Sutherland, 2008). The accumulated amount of radioactive waste can pose health and environmental risks, where there is the potential for radiation to be released into the surrounding environment where the waste is stored and disposed of (European Environmental Agency, 2013). The result of the release of radionuclides into the environment, could in extreme cases, lead to short- or long-term genetic mutations, as witnessed at Chernobyl (European Environmental Agency, 2013; Lazjuk et al., 1998), where increased levels of radioactivity can then pass through the food chain and affect human food sources (European Environmental Agency, 2013).

Since the growing urgency to address climate change, there has been a global increase in projected growth for nuclear power and the construction of new nuclear power plants by countries e.g., China (Massachusetts Institute of

Technology, 2011). Reactor wastes are a product from the worldwide use of uranium in energy production in nuclear power reactors which require the nuclear fuel cycle (Sutherland, 2008). The nuclear fuel cycle involves the mining of uranium and ends with the production of nuclear waste. The spent nuclear fuel waste, that which is not reprocessed, needs to be disposed of and stored in geological repositories to reduce the radioactivity and decay-heat for between 40 to 60 years (Massachusetts Institute of Technology, 2011).

2.3.1.1 Re-processing of Spent Nuclear Fuel

Most countries who utilise nuclear technology have generated HLW from nuclear weapons programs and/or commercial nuclear power usages (Jantzen, 2011). The Plutonium and Uranium Extraction (PUREX) process is the main separation process used for spent fuel in most active fuel cycle programs (Jantzen, 2011). The UK and France reprocess spent fuel from other countries using the PUREX process for electricity, where they recover Pu and U (Jantzen, 2011). The Hanford Site in Washington State, US, also utilised the PUREX process, as well as two other methods i.e., Bismuth Phosphate Process (BPP) and Reduction-Oxidation (REDOX) process (Tedeschi & Wheeler, 2013).

BPP was a reprocessing method based upon the precipitation and solid-liquid phase separation of spent nuclear fuel to separate Pu (Schwantes & Sweet, 2012). The spent fuel was dissolved in nitric acid, where the uranium ions were placed in a solution with added sulphate to stabilise the ions, while Pu^{4+} was reduced and co-precipitated with the fission products from U using bismuth phosphate (Schwantes & Sweet, 2012). After the phase separation and dissolution of the solid phase products, the Pu^{4+} is stabilised in solution by oxidation to Pu^{6+} with sodium dichromate, while the fission products are precipitated with bismuth phosphate again (Schwantes & Sweet, 2012; Zentner et al., 2005). The cycle of reducing, precipitating, phase separation, dissolution, and oxidation is repeated many times to increase the effectiveness of Pu separation. However, there are three main issues with this process: (i) it leaves valuable uranium in the process waste after plutonium recovery, (ii) it is inefficient as a 'batch' process and, (iii) it requires large quantities of processed chemicals, and produces large amounts of waste of approximately 10, 000 gallons per metric ton of U processed (Zentner et al., 2005)

The PUREX process is a method that uses solvent extraction to perform separations and is capable of recovering Pu in a continuous extraction (Paulenova & Vandegrift, III, 2013; Schulz et al., 1987; Simpson & Law, 2010). This method produces less waste than the BPP. Spent fuel is dissolved in nitric acid, where dissolution occurs, after which the plutonium and uranium nitrates are transferred into their organic phases (Simpson & Law, 2010). The fission products are removed from the aqueous phase (Paulenova & Vandegrift, III, 2013; Schulz et al., 1987; Simpson & Law, 2010). The plutonium is then separated from the uranium in another solvent extraction process (Paulenova & Vandegrift, III, 2013; Schulz et al., 1987; Simpson & Law, 2010). The PUREX process involves the removal of fuel cladding through a combination of chemical and mechanical processes, followed by the fuel being dissolved in nitric acid, resulting in a solution that is then combined with a tri-butyl phosphate (TBP) solution in refined kerosene (Paulenova & Vandegrift, III, 2013; Schulz et al., 1987; Simpson & Law, 2010). The TBP solution extracts the uranium and plutonium nitrates, leaving behind the fission products and other nitrates (Paulenova & Vandegrift, III, 2013; Schulz et al., 1987; Simpson & Law, 2010). The chemical conditions are then altered so that plutonium and uranium are re-extracted into a fresh aqueous phase (Simpson & Law, 2010; Zentner et al., 2005). The first solvent extraction cycle removes the fission products from the uranium and plutonium, while the second cycle decontaminates the aqueous phase further (Paulenova & Vandegrift, III, 2013; Schulz et al., 1987; Simpson & Law, 2010). The uranium and plutonium are then separated from each other in a similar extraction process (Paulenova & Vandegrift, III, 2013; Schulz et al., 1987; Simpson & Law, 2010).

The REDOX process also relied upon oxidation changes to separate Pu from U and was conducted by employing a continuous solvent extraction process (Delegard & Jones, 2015). This process extracted Pu from U from dissolved irradiated fuel and then separated them into acid hexavalent uranium (U(VI)) and plutonium (Pu(VI)) using the methyl isobutyl ketone (MIBK) (Delegard & Jones, 2015). When using MIBK, Pu(VI) can be extracted but Pu(III) is not, hence why strong ionic bonds are needed to force the Pu(VI) and U(VI) into the organic phase (Delegard & Jones, 2015). Low/zero – HNO_3 concentrations were used alongside $\text{Al}(\text{NO}_3)_3$ as a salting agent to increase the ionic strength of the aqueous phase and drive U and Pu into the organic phase (Delegard & Jones, 2015). The

Pu and U(VI) treated in the REDOX plant were then treated with sodium dichromate ($\text{Na}_2\text{Cr}_2\text{O}_7$) to oxidise the Pu to Pu(VI) oxidation state (Delegard & Jones, 2015). The solution was then boiled to remove the fission product Ru, as it was difficult to separate it from the U and Pu during the REDOX process (Delegard & Jones, 2015). The sodium dichromate oxidises the ruthenium-to-ruthenium tetroxide, which is very volatile and is turned into an off gas which is then captured (Delegard & Jones, 2015). The Pu and U are separated from each other by stripping away the organic phase, where the two separate streams are then purified (Delegard & Jones, 2015).

2.3.2 Nuclear Waste Classification

There are six classifications of radioactive waste in accordance to the outline proposed by the IAEA safety standards (International Atomic Energy Agency & IAEA, 2009) (Appendix: IAEA radioactive waste classification), where the type of waste dictates the depth at which the waste is disposed (Ojovan & Steinmetz, 2022): Exempt waste (EW), Very Short Lived Waste (VSLW), Very Low Level Waste (VLLW), Low Level Waste (LLW), Intermediate Level Waste (ILW), and High Level Waste (HLW).

The USA use different classification schemes (Table 12), where there is the High-Level Waste (HLW), Spent Nuclear Fuel (SNF), and low and intermediate level waste which is divided further into four sub-classifications: Low-Level Waste (LLW), Mixed Low-Level Waste (MLLW), Immobilised Low-Activity Waste (ILAW), and Transuranic (TRU) Waste (Lowenthal, 1997; U.S. Department of Energy, Richland Operations Office, 2004).

Type of Waste	Description
High-Level Waste (HLW)	Radioactive waste that is highly radioactive and is a result of reprocessing of spent nuclear fuel, including liquid waste produced from the re-processing of solid material, and other highly radioactive material (Lowenthal, 1997).
Spent Nuclear Fuel (SNF)	Irradiated fuel that has been retrieved from nuclear waste, where the contained elements have not been separated by reprocessing.

Low-Level Waste (LLW)	Radioactive waste that is not HLW, SNF, TRU, by-product material (as defined under the Atomic Energy Act of 1954 (42 USC 2011)), or naturally occurring radioactive material. LLW has a range of forms, radionuclide concentrations, and hazards. LLW can range in radionuclide concentrations but can be disposed of in shallow land disposal sites.
Mixed Low-Level Waste (MLLW)	LLW that contains both radionuclides subject to the Atomic Energy Act of 1954, and a hazardous chemical component subject to the Resource Conservation and Recovery Act (RCRA) (42 USC 6901) or applicable Washington State Dangerous Waste Regulations.
Immobilised Low-Activity Waste (ILAW)	Solidified LAW from the treatment and immobilization of Hanford tank wastes. LAW is the waste that remains after separating from high-level waste (HLW) as much of the radioactivity as possible, and that when solidified may be disposed of as LLW in the near surface facility.
Transuranic Waste (TRU)	TRU is radioactive waste containing more than 100 nanocuries (3700 becquerels) of alpha-emitting ions, except for the following: HLW; waste that the Secretary of Energy has determined, with the concurrence of the Administrator of the Environmental Protection Agency, does not need the degree of isolation required by the 40 CFR 191 disposal regulations; waste that the Nuclear Regulatory Commission has approved for disposal on a case-by-case basis in accordance with 10 CFR 61; After DOE (2001c.).

Table 12 – Classifications of USA Radioactive Waste sourced and modified from (Lowenthal, 1997; U.S. Department of Energy, Richland Operations Office, 2004)

HLW and SNF are stored either dry or underwater, where most spent fuel is stored underwater, where the water acts as a radiation shield, keeping the SNF at an acceptably low temperature (International Atomic Energy Agency (IAEA), 2003). Storage of some waste is above ground or at shallow depth, where some containers are stored inside another structure, often built from concrete due to its ability to provide acceptable radiation shielding (The International Atomic Energy Agency (IAEA), 2003). However, in some instances, some storage may be in the

ground, a few meters below the surface (The International Atomic Energy Agency (IAEA), 2003). Once securely stored, the waste needs to be disposed of in a way that will isolate the waste from the environment that would affect life.

2.3.3 Nuclear Waste Immobilisation and Disposal

Radioactive waste needs to be immobilized such that it is a chemically inert and leach resistant solid material that can be easily stored or disposed of (Donald, 2010). Storage of waste allows for the decay of radioactivity and heat, allowing for safer handling and further reprocessing. Disposal solutions of the waste seek to be environmentally safe and publicly acceptable, where near surface and deep geological disposal are the most favoured solutions depending on the type of waste i.e., LLW / ILW and HLW. Disposal of the waste means that there is no foreseeable use for it, where no future action will be taken with the exception of environmental monitoring.

The immobilisation of the waste can either be by its '*dissolution at an atomic scale within a host lattice, or by encapsulation into an inert matrix*' (Donald, 2010). Candidate materials considered for the immobilisation need to have the following desirable properties (Donald, 2010; Raj & Kaushik, 2009; Vaishnav, 2018):

- High waste capacity to accommodate the variety of harmful chemicals and radionuclides.
- High chemical durability and low leachability
- Low forming temperatures.
- High thermal stability due to heat produced from radioactive decay.
- Utilise available production technology to reduce cost.

Depending on the type of waste, glasses, ceramics, glass-ceramics, and concrete have been utilised for immobilisation. However, in this thesis glass compositions specific to The Hanford Site have been studied and so shall be considered in further detail. The Hanford Site utilised borosilicate glass as the inert matrix to vitrify its waste, however, other countries have employed other glass compositions such as silicate, aluminoborosilicate, and phosphate (Marasinghe et al., 2000; Nascimento et al., 2005; Varitis et al., 2017). The main processes implemented to immobilise nuclear waste are calcination, bituminization, and vitrification.

Calcination is a process used to remove volatile components from the nuclear waste, and is when matter is heated in either the absence or presence of limited O to a temperature that is below its melting point (Fuks et al., 2022). Calcination takes place in a calciner, where the off-gas produced is purified and released into the atmosphere, where the remaining solid calcine is gathered, stored, and processed (Fuks et al., 2022). The processed calcine is then transformed into a glassy material or diluted into an insoluble matrix (Fuks et al., 2022).

Bituminisation is a process that allows solid and liquid radioactive waste to be formed into a solid block (Fuks et al., 2022; International Atomic Energy Agency, 1993). Bitumen is a thermoplastic that is formed by mixing different '*high molecular weight hydrocarbons that are soluble in carbon disulphide*' (Fuks et al., 2022). Bitumen is used as a matrix for radioactive waste (Fuks et al., 2022), where there are two types of bituminization processes: (i) batch and (ii) continuous (Fuks et al., 2022).

Vitrification is the transformation of liquid and chemical waste into a non-crystalline amorphous solid to stabilise radioactive waste before it is stored, and is currently employed by the USA, Japan, France, UK, Slovakia, India, Russia, and South Korea (Gin et al., 2013). The borosilicate glass system has been the main composition used for vitrification processes, however, phosphate based compositions have also been implemented by Russia (Fuks et al., 2022). France, for example, implemented a two-step vitrification process for HLW using borosilicate and aluminosilicate glass systems, where calcining was followed by melting in an induction heated melter (Fuks et al., 2022). The Hanford Site LAW stored in underground tanks will be filtered to remove solids and then processed through ion exchange columns to remove Cs (Dixon et al., 2019). These pre-treatment processes will allow the waste to be transferred to the Hanford tank waste treatment and immobilisation plant facility, where it will be immobilised into a glass by mixing the waste with glass forming chemicals (GFCs) to form a slurry that is then fed into a Joule heated ceramic lined electric melter for vitrification (Dixon et al., 2019).

2.3.3.1 Immobilisation

2.3.3.1.1 Borosilicate Glass

The choice of waste form for nuclear waste immobilisation is dependent on the simplicity and reliability of current available technology, which may have advantages over more complex and novel technology (Ojovan & Batyukhova, 2007). There are a variety of materials available for immobilisation of the waste, such as glass, glass-ceramics, crystalline ceramics, concrete, and glass composite materials (Ojovan & Batyukhova, 2007). However, the two most widely used glass types for nuclear waste immobilisation are borosilicate and phosphate glasses. The compositions can be tailored to allow for *'easy melting, avoidance of phase separation and uncontrollable crystallisation, and acceptable chemical durability'* (Ojovan & Batyukhova, 2007).

The advantage of using a borosilicate glass as a host matrix is its ability to be able to incorporate a variety of fission products, its low formation temperature below 1200°C leading to the extension of the melter life, its resistance to degradation induced by radiation, and its resistance to leaching in an aqueous environment (Plodinec, 2000). Borosilicate glasses have also shown to be as durable as aged basalts, which provides an indication of their potential longevity (Plodinec, 2000).

2.3.3.2 Disposal

There have been various methods proposed for the disposal of immobilised nuclear waste, such as the indefinite storage at secure facilities, disposal of sealed canisters into the sea, burial of waste in natural and underground salt cavities, disposal in space, and burial between tectonic plates (Donald, 2010; Internationale Atomenergie-Organisation, 2011). The type of radioactive source (^{125}I , ^{192}Ir , ^{90}Sr , ^{137}Cs , ^{238}Pu , ^{239}Pu etc.) dictates the type of storage i.e., decay in storage, near surface disposal, near surface disposal at a greater depth and/or barriers, and geological disposal at 200-1000 metres (IAEA, 2005). Geological disposal utilises multiple barriers to isolate the radioactive waste, where the radioactive waste is contained deep underground. The multiple barriers are the solid waste form itself, the waste container, and the material placed around the waste container known as a buffer or backfill (Ojovan & Steinmetz, 2022; Radioactive Waste Management, 2017).

Some example disposal options used by some countries include France, where geological disposal was used as waste storage and has been planned to begin in 2025 for ILW and 2070 for HLW, where HLW will be encapsulated in carbon steel overpacked canisters, which are placed in clay boreholes (Gin et al., 2013). The UK currently stores vitrified HLW in engineered containers located at various nuclear waste facilities around the country, categorised as surface storage, such as Sellafield in Cumbria (Radioactive Waste Management, 2017). Surface storage is not a permanent solution, whereas geological disposal is a widely accepted method of disposing of HLW waste (Radioactive Waste Management, 2017). The Hanford Site will use surface storage for LAW (Office of River Protection, 2020) and use geological disposal for their vitrified HLW (Ryan & Freedman, 2016).

2.3.4 Brief History of The Hanford Site

The Hanford site is located north-northwest of the Yakima and Columbia Rivers that run through the Tri-cities in Washington State in the US, and currently hosts different decommissioning facilities, underground waste storage tanks, and construction of waste treatment and immobilization plants. It was established in WW2 for the production of Pu for atomic weapons for the Manhattan Project, where Hanford was tasked with constructing nuclear reactors, managing fuel facilities and chemical separation facilities (Fehner & Gosling, 2012; Gephart & Lundgren, 1995; Harvey, 2000; Lichtenstein, 2004).

Three chemical separation processes were used to recover Pu from spent nuclear fuel (SNF): (i) BPP, (ii) REDOX process and (iii) PUREX process (Tedeschi & Wheeler, 2013). All three processes operate on the principle of changing the oxidation state of Pu, which allows the selective decontamination and separation from elements with a similar chemistry (U), corrosion constituents, and process chemicals (Goel et al., 2019). With the end of the Cold War and signing of the Tri-party Agreement in 1989, the mission focus of The Hanford Site was shifted to developing new waste treatment and disposal technologies, and characterisation and clean-up of the contamination caused by the historical operations (Department of Energy, 2021). The Tri-Party Agreement was a clean-up and compliance agreement signed by the U.S. Department of Energy (DOE), the U.S. Environmental Protection Agency, and the State of Washington Department of Ecology (Black, 1995).

In 1995, The Hanford Site was identified to contain ~61 million gallons, later amended to 56 million gallons (~212 million litres), of radioactive and hazardous chemical waste that has been historically stored in 177 underground steel tanks (Gephart & Lundgren, 1995; Goel et al., 2019; Niles, 2014). According to the Hanford Annual Site Environmental Report (2021), there are currently 353 metric tons of solid mixed waste and 585 metric tons of solid radioactive waste generated at The Hanford Site.

2.3.4.1 Types of Waste at the Hanford Site

The Hanford tank waste consists of insoluble sludge, water-soluble salts, aqueous liquids, and vapours, as a result of processing chemicals and fission/activation products. The primary and secondary waste types from individual tanks (Table 79 and Table 80 in Appendix 8.3) can be categorized based on the Hanford tank farm they originated i.e., A, AN, AP, AW, AY, AX, AZ, B, BX, BY, C, S, SX, SY, T, TX, TY, and U (Cragnolion et al., 1997; Peterson, 2022; Wells et al., 2011).

The Hanford tank waste has a distinct composition when compared to other DOE processing facilities, due to being the only facility to use bismuth phosphate, REDOX, and the U extraction processes (Colburn & Peterson, 2021). The waste also contains Al from the de-cladding processes, and Na(OH) and NaNO₃ which were added to increase the pH and inhibit corrosion of the steel tanks (Colburn & Peterson, 2021). As a result of the production and waste-minimization processes used at the Hanford Site, the tank wastes contain a mixture of Na, nitrates, carbonates, Al, phosphates, sulphates, Bi, Si, U, Zr, Cr, and oxalates (Colburn & Peterson, 2021; Kupfer et al., 1999; Pabalan et al., 2001).

Based on the Hanford tank waste, there are two different main types of radioactive waste, LAW and HLW. The HLW is a result of reprocessed spent nuclear fuel (SNF), including directly re-processed solid material from liquid waste containing fission product (International Atomic Energy Agency, 1992). The HLW exists mostly as a salt cake and sludge that is rich in Na and Al oxides, hydroxides and nitrates with strong concentrations of transition metal oxides, e.g., Fe₂O₃ and MnO (Goel et al., 2019; Peterson et al., 2018). The LAW is a result of reprocessed SNF and constitutes ~90% volume of the Hanford tank inventory (Goel et al., 2019).

2.3.4.2 Proposed Clean-up Process

2.3.4.2.1 Pre-treatment of Waste

The Hanford waste is pre-treated to reduce the volume of waste and subsequent canisters produced at the Hanford WTP (Colburn & Peterson, 2021). The HLW tank waste will be evaporated, where wastes with high complexant concentrations will require additional co-precipitation to remove ^{90}Sr and transuranic species. The waste solids are then separated by liquid filtration through crossflow filters, where the solids are caustic washed to remove Al and then oxidative leached to remove Cr, after which the solids are transferred to the HLW melter (Figure 1). The LAW is separated from the remainder of the waste by pumping it through a cross-flow filter to remove any solids (Pabalan et al., 2001), where the filter permeate is sent on for further treatment via ion exchange to remove soluble fission products, ^{137}Cs and ^{99}Tc , by using SuperLig 644 and 639 (Carreon et al., 2002; Pabalan et al., 2001), respectively, before going to the LAW facility (Figure 14) (Colburn & Peterson, 2021; Pabalan et al., 2001).

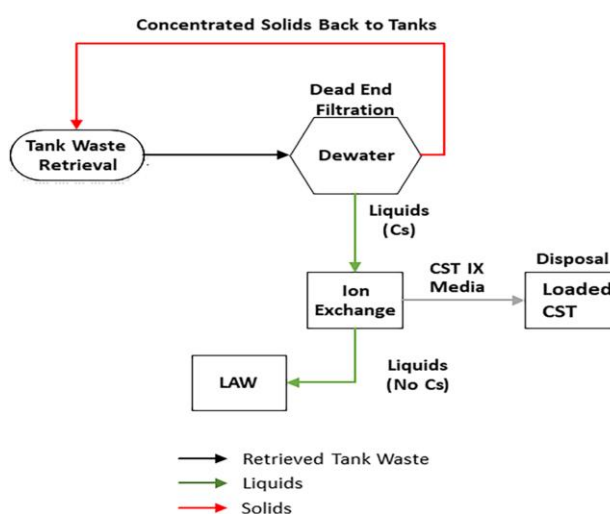


Figure 14 – Direct Feed LAW Pre-treatment flowsheet for Hanford tank waste taken from (Colburn & Peterson, 2021) with copyright permission from Johnson Wiley and Sons (License number: 5612431462656)

2.3.4.2.2 Glass Compositions

Numerous waste-free glass compositions have been investigated regarding their processing temperatures, quality of the vitrified form, and waste loading capabilities (Manaktala, 1992). However, only a few compositions have been considered and adapted for use on a larger scale, where glass frits typically used for HLW and LAW are based on the Na_2O - B_2O_3 - SiO_2 ternary system, where there

may be additions of other components e.g., Li_2O , K_2O , TiO_2 , CaO etc. (Manaktala, 1992). In addition to borosilicate glass, there are other glass systems being researched for their potential viability i.e., Iron phosphate where it has a high tolerance for waste components e.g. sulphates, halides, and heavy metals (Ray & Ray, 2013; Kim & Day, 2003; Ray et al., 2018; Sevigny et al., 2012), lanthanide borosilicate where it is devoid of alkalis and has increased PuO_2 waste loading capacity (Darab et al., 2022; Ebert, 2006; Grambow, 2019), aluminosilicate (Zhao et al., 2020), and phosphate (Xu et al., 2015) glasses.

2.3.4.2.3 Vitrification

The proposed clean-up process at the Hanford Site will use a process called vitrification (as described in 2.3.3). The specific parameters used by the Hanford Site will vitrify the waste into a borosilicate glass by heating a mixture of waste and glass-forming additives to a temperature as high as 1150°C using a single-stage vitrification process with a joule-heated ceramic lined melter (JHCM) (Figure 15), (Goel et al., 2019; Hrma, 2002; Kelly, 2011; Smith et al., 1990).

The vitreous product contains the waste contaminants in its macro- and microstructure (Donald, 2010). The DOE are currently building a Tank Waste Treatment and Immobilisation plant (WTP) that will cover approximately 67 acres and exceed the cost of \$17 billion at The Hanford Site to separately vitrify the LAW and HLW into borosilicate glass (Goel et al., 2019).

Due to the radioactive liquid waste having different components, it is difficult to predict how these will interact with each other and what effects they will have on the melt properties e.g., viscosity, the glass structure, and its properties. The step-by-step process by which the radioactive waste is vitrified into a borosilicate glass is outlined by (Goel et al., 2019).

Some of the issues that can arise from the vitrification process are associated with the throughput rate, which is defined as $[waste\ throughput\ rate] = [waste\ loading\ in\ glass] \times [glass\ melting\ rate]$ because it directly influences the life cycle of the nuclear waste clean-up (Goel et al., 2019; Kim, 2015). Another concern is the creation of a cold cap on the molten glass that is produced when a slurry is charged from the top of the JHCM (Hrma & Kruger, 2008; Lee et al., 2020) (Figure 15). The cold cap is made from a reaction layer and foam layer and can affect the

melting rate of the melt and it covers 90 – 95% of the melt surface (Guillen et al., 2019).

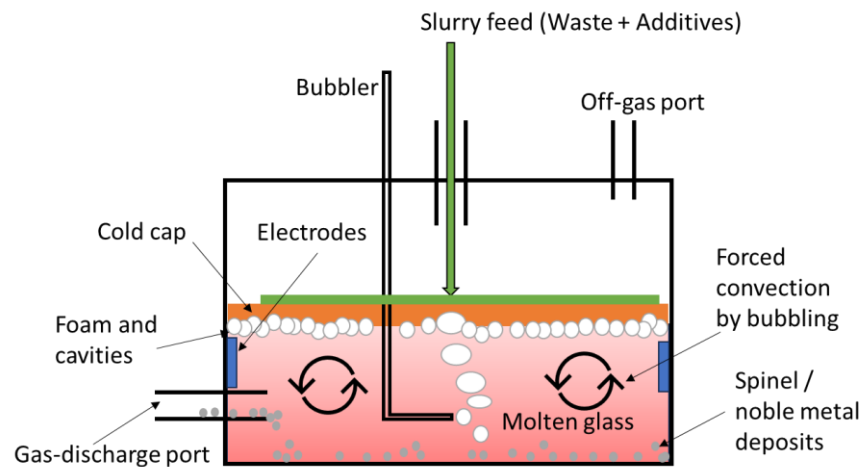


Figure 15 – Schematic cross section of JHCM in HLW glass melter modified from (Goel et al., 2019)

2.3.4.3 Current Hanford Site Objectives

The current mission of The Hanford Site is focused on environmental restoration of contaminated areas, decontamination and decommissioning of Hanford Site facilities, waste management, and research and development of waste management technologies and related scientific and environmental research (Department of Energy, 2021).

The Hanford Site's strategic vision for 2021-2031 is the complete start-up of the WTP LAW facility and commencement of LAW tank waste treatment by the end of 2023. Some of the Key regulatory milestones for 2023 outlined for between 2021-2031 are for the Liquid Effluent Retention Facility (LERF) and Effluent Treatment Facility (ETF) upgrades to be complete to support the DFLAW hot commissioning by April 2023, and the completion of LAW Facility hot commissioning and the beginning of the production-scale tank waste disposition by the end of 2023 (Department of Energy, 2021). This will then be followed by the transfer of Cs and Sr capsules to dry storage and complete soil remediation and 324 building demolition in 2025, complete single-shell tank retrievals from A/AX farms, and removal of all mixed waste containers stored at the central waste storage complex outside Areas A and B in 2026 (Department of Energy, 2021). As of December 2022, it was reported in a public press release that the Hanford Site had treated a significant amount of tank waste in their caesium removal

system, where they are preparing for 24/7 operations to treat waste from the underground tanks through the direct-feed-low-activity-waste program. This program will directly feed the treated waste to the Waste Treatment and Immobilisation Plant (Conrad, 2022).

2.3.5 Summary

In summary, radioactive waste is an environmental risk where there have been various methods discussed and implemented by different countries to try and safely dispose of it, such as calcination, bituminization, and vitrification. The Hanford Site waste was a product of Pu and U extraction processes used during WW2 and The Cold War, where the original waste was stored in single and double-shell steel tankers. The proposed method of disposal of the radioactive waste was to mix it with glass forming additives, where the final waste form was vitrified. This vitrified form would be stored in canisters and disposed of via geological disposal, where its radioactivity will dictate how deep underground it is stored.

2.4 P₂O₅ and SO₃ Solubility in Borosilicate Glasses

2.4.1 Introduction

This section will evaluate literature that has determined P₂O₅ solubility and phase separation, as well as those that have assessed the effects of sulphate (SO₃) in different glass systems to aid in the wider understanding of its effects on Hanford radioactive waste glasses. This is due to both P₂O₅ and SO₃ having been described as troublesome components in the Hanford waste glasses, affecting the waste loading capabilities amongst other properties. Studies have investigated attempting to increase the solubility limit of P₂O₅ and SO₃ individually, with P₂O₅ potentially being a candidate to increase the solubility of SO₃, however, very little research has explored this. Hence, why there will be a results sub-chapter in this thesis looking at the effects of P₂O₅ on the solubility limit of SO₃ in borosilicate glass (*Section 4.2*).

At the Hanford Site, P₂O₅ originates in the waste streams from the Pu and U extraction processes. The concentrations of P₂O₅ varies across different radioactive wastes stored at The Hanford Site. The wastes of particular interest for this study are Hanford intermediate low-level activity waste (ILAW) glasses 32, 35 and 36 (Gervasio et al., 2018), because of their high P₂O₅ concentration

and differences in composition, as stated in Table 13. These compositions will be used to develop a full simulant composition on which tests will be conducted.

Oxide (Mass fraction)	ILAW-Glass32	ILAW-Glass35	ILAW-Glass36
Al ₂ O ₃	0.0553	0.0906	0.0553
B ₂ O ₃	0.06	0.06	0.06
CaO	0.0683	0.0479	0.0824
Cl	0.0002	0.0003	0.0002
Cr ₂ O ₃	0.0015	0.006	0.0006
F	0.0032	0.0029	0.0031
Fe ₂ O ₃	0.0298	0.0058	0.0072
K ₂ O	0.0007	0.0005	0.0004
Li ₂ O	0	0	0.0117
MgO	0.0002	0.0087	0.035
Na ₂ O	0.26	0.252	0.1851
P₂O₅	0.0312	0.0324	0.0340
SO ₃	0.0052	0.0153	0.0175
SiO ₂	0.3842	0.3789	0.4384
SnO ₂	0.0275	0.0119	0
TiO ₂	0.0049	0.005	0.0009
V ₂ O ₅	0	0.0138	0
ZrO ₂	0.0675	0.0675	0.0675
Minors	0.0003	0.0005	0.0007
SUM	1.0000	1.0000	1.0000

Table 13 - ILAW compositions containing P₂O₅ taken from (Gervasio et al., 2018)

2.4.2 P₂O₅ Solubility in Borosilicate Glasses

In a borosilicate glass system there is competition for the structural network former role between Si, B and P causing one or more of the three tetrahedral units to phase separate (Charles, 1964; Jantzen et al., 2000; Muñoz et al., 2008). The (PO₄)³⁻ will separate first in the borosilicate glass with any accompanying charge balancing cations (Jantzen et al., 2000). The tendency for phase separation can be anticipated by the strong field strengths of the glass formers, $P^{5+} = 2.1$, $[^3]B^{3+} = 1.63$, $Si^{4+} = 1.57$ and $[^4]B^{3+} = 1.34$ (Jantzen et al., 2000), hence phase separation occurs in all known binary systems with these glass formers e.g., B₂O₃ – P₂O₅ (Jantzen et al., 2000; Muñoz et al., 2008). If the difference in field strength between the major network formers exceeds 0.3, then the phase separation will be of a crystalline nature as oppose to an amorphous one (Jantzen et al., 2000). Hence phase separation in a phosphate based system will exhibit crystalline or partially crystalline phase separation (Jantzen et al., 2000). A peroboric glass (Na/B < 1) can incorporate up to 5-7 mol% P₂O₅, whilst metaboric and perkalkine glasses are limited to 4-5 mol% P₂O₅ and 3 mol%, respectively (Stone-Weiss et al., 2020). When perkalkine glasses contain >3 mol% P₂O₅ they show evidence of the crystalline phase Na₄P₂O₇ (Stone-Weiss et al., 2020). The solubility of P₂O₅ is not as limited in aluminosilicate glasses when compared to silicate glasses, because Al can have a four-fold coordination that uses the net charge from the double-bonded O (AlO₄) (Langowski, 1996). Al tetrahedra have a net negative charge, whilst the PO₄ tetrahedra have a net positive charge, meaning that the two structures together can form Al-O-P bonds which are similar to Si-O-Si bonds (Langowski, 1996). Hence, if the molar ratio of P/Al is near or <1 then it is possible to incorporate a larger concentration of P₂O₅ into the silicate glasses (Langowski, 1996). However, the introduction of an alkali ion in an aluminosilicate glass can compete with the AlO₄ tetrahedra, reducing the amount of P₂O₅ that can be incorporated into said glass, leading to phase separation (Langowski, 1996). Studies carried out at PNNL on HLW based compositions reported that phase separation was caused by the accumulation of ≥1.5 wt% sulphate (gall) (Langowski, 1996). Krishnamurthy et al. (2020) reported that up to 3.0 mol% P₂O₅ could be added to an aluminoborosilicate glass before phase separation occurred. However, at 4.0 mol% P₂O₅ the glass exhibited the beginnings of clustering in the form of a partially ordered sodium-phosphate phase as NMR defects, even though visually the glass appeared translucent and

XRD patterns and SEM images showed no features (Krishnamurthy et al., 2020).

Table 14 contains a list of relevant borosilicate compositions and their P₂O₅ solubility limits.

P ₂ O ₅ (wt%)	B ₂ O ₃ (wt%)	xM ₂ O or xMO (wt%) (M = Alkali/ alkaline earth metal oxide)	SiO ₂ / B ₂ O ₃ (wt%)	Major alkali	P ₂ O ₅ solubility limit (wt%)	Crystal phase	Glass/ melt Temp (°C)	Reference
Borosilicate glasses containing Li₂O								
≥ 2.6	7.2	~ 16	7.64	Na ₂ O + Li ₂ O	2.5 – 3	Li ₃ PO ₄	DWPF 165 @ 1150°C	(Jantzen, 1986)
3.33 - 7.33	13.06 – 13.63	10.92 – 11.15	3.83	Na ₂ O + Li ₂ O		Li ₃ PO ₄ + Cr ₂ O ₃ + AlPO ₄	PFP waste @ 1150°C	(Langowski, 1996)
1.94 – 4.0	5.68 – 10.65	15.83 – 25.74	3.56 – 8.09	Na ₂ O + Li ₂ O	> 2.6	8 with Li ₃ PO ₄ + 3 with SiO ₂ or silicate	11 M-area MLLW glasses various temperatures	(Jantzen et al., 2000)
Borosilicate glasses without Li₂O								
2.68 – 5.05	17.6 – 19.5	16 – 17.66	3.06 – 3.47	Na ₂ O		SiO ₂ (cristobali te + tridymite)	Na ₂ O–B ₂ O ₃ – SiO ₂ ~ 1150 1150°C	(Cozzi, 1998)
~3	5	20.33	11.36	Na ₂ O + CaO + K ₂ O		Na ₃ PO ₄ and Na ₂ Ca ₄ (P O ₃) ₂ SiO ₄	LLW @ 1300°C	(Crichton et al., 1995)
~2.5	17	6.5	4.16	Na ₂ O + CaO		Ca ₃ (PO ₄) ₂	Common Pyrex	(Vogel & Jeffery, 1989)

~3 mol%	40 mol%	6 – 10 mol%	47 – 50 mol%	Na ₂ O	3.0 mol%	AlPO ₄	Na ₂ O–B ₂ O ₃ – SiO ₂ @ 1400°C	(Ohtsuki et al., 2011)
1 – 6 mol%	19.4 – 60 mol%	19.4 – 29.7 mol%	37.6 – 60 mol%	Na ₂ O	3.0 mol%	Na ₄ P ₂ O ₇	Na ₂ O–B ₂ O ₃ – SiO ₂ @ 1200 to 1500°C	(Muñoz et al., 2008)

Table 14 - Phase separation of different glass systems based on results reported by Jantzen et al. (2011)

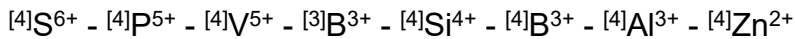
2.4.3 Sulphate Solubility in Borosilicate Glasses

The origins of SO₃ in the Hanford waste glasses include, but are not limited to, the PUREX process and spent ion exchange resins (Bingham et al., 2017). SO₃ is a known problematic component in the LAW and to a smaller extent in the HLW, because of its limited solubility in borosilicate melts (Jin et al., 2019). SO₃ was believed to have been removed in the pre-treatment of HLW prior to vitrification, and hence, SO₃ loading in the HLW glasses was not considered to be a problem (Goel et al., 2019). Waste loading of SO₃ in the LAW glasses has been mostly pushed by its solubility in the melt, with excess SO₃ forming an alkali and alkali-earth sulphate molten salt layer that accumulates on the surface of the melt (Bingham et al., 2017; Goel et al., 2019; Jin et al., 2019; Lenoir et al., 2010; McKeown et al., 2001). The molten salt layer has been associated with problems in melter performance because of its high corrosion behaviour segregation in the WTP melters (Goel et al., 2019; McKeown et al., 2001; Skidmore et al., 2019), which in turn impacts the waste throughput, glass production rate, and operation time (Brendebach et al., 2009). The salt layer also acts as pathway for radionuclides i.e., Cs and Tc to be released into the environment upon contact with water (Bingham et al., 2017; Jin et al., 2019; Vaishnav et al., 2020).

In early work, the solubility limit of SO₃ was set to between 0.44 wt% and 1.0 wt% so that salt accumulation could be avoided (Jin et al., 2019). The solubility of SO₄²⁻ in HLW implemented by Savannah River National Laboratory (SRNL) was to be 0.40 wt% to avoid segregation of the sulphate in the salt layer (Billings & Fox, 2010). This limit was later increased to 0.60 wt% after the processing of more recent tank sludge (Billings & Fox, 2010). However, a study by Vienna et al. (2014a) commented that the allowable concentration of SO₃ may range from 0.37 to over 2.05 wt% depending on the composition of the melter feed. More recently,

SO₃ solubility in borosilicate glasses has been successful, where Xu et al. (2020) reported a LAW SO₃ solubility of 0.15–1.83 wt%. In silicate melts, the primary form of sulphate ions are isolated tetrahedra associated with either alkali or alkaline earth ions (Vienna et al., 2014).

Literature has supported the addition of low strength cations that are large and basic, e.g., Na, Mg, and Ca as a means of increasing SO₃ capacity in a silicate or borosilicate glass system (Bingham et al., 2017; Brendebach et al., 2009). Lenoir et al. (2010) and Manara et al. (2007) suggested that the SO₃ solubility increased when the alkaline content increased, that is to say when the glass network became more de-polymerised. The components that increase the SO₃ solubility the most are Li₂O>V₂O₅>CaO ≈ P₂O₅ > Na₂O ≈ B₂O₃>K₂O, while the components that decrease the SO₃ solubility are Cl>Cr₂O₃>Al₂O₃>ZrO₂≈ SnO₂>others ≈ SiO₂ (Vienna et al., 2014). However, Manara et al. (2007b) commented that the capacity of a vitreous matrix to incorporate sulphates depended on the compatibility between the crystallo-chemical parameters of the sulphates and the cations present in the glass. These parameters are the Dietzal field strength, the cation oxygen binding energy, the strength of the bond, and the size and polarisation of the polyhedrons. Hence, with these parameters in mind, the cations present in a glass can be distributed in the following series:



Where the prefix superscripts in square brackets represent the cation coordination. The closer the single network modifier, the closer the ions in the series, and the better the compatibility for the incorporation/formation in the glass. For example, sulphate and phosphate tetrahedra have a better compatibility than silicate tetrahedrons (Manara et al., 2007).

It has been theorised that in order to increase the sulphate capacity in a melt, the thermodynamic solubility needs to be increased. Vienna et al. (2014) suggested from their model that there was a constant improvement for sulphate solubility with a P₂O₅ concentration of up to 3.0 wt%, and with Na₂O and B₂O₃ moderately improving this. Figure 16 is a response-trace plot that shows the effects of separate components, compositional changes on the predicted SO₃ solubility. The centre of the plot is the average composition of the test data used to fit the model (Vienna et al., 2014).

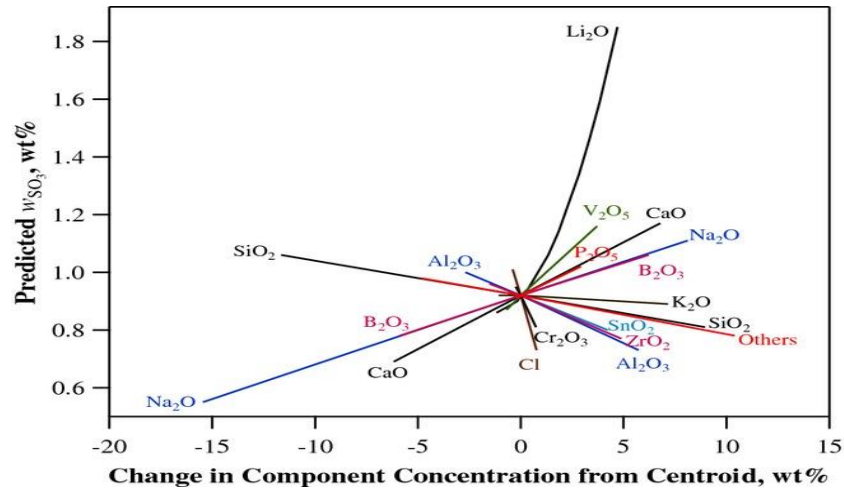
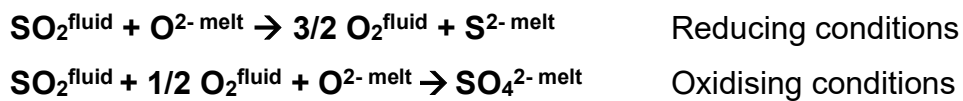


Figure 16 - Effects of component concentration changes on predicted sulphur at the composition region centroid taken from (Vienna et al., 2014) with copyright permission from John Wiley and Sons (License number: 5612430609759)

Also increasing the free volume aids in SO_3 incorporation, because it exists as an isolated unit that stays in the interstitial spaces within the network, hence increasing the network connectivity lowers the amount of interstitial space, thus reducing SO_3 incorporation (Manara et al., 2007; Xu et al., 2020). Manara et al. (2007) reported that the creation of suitable voids in the glass network can increase the kinetics of SO_3 incorporation and increase its solubility.

Fincham and Richardson (1954) cited by McKeown et al. (2004) mentioned that the incorporation of SO_3 in silicate melts can be explained in terms of the two-species model (sulphate and sulphide) from the study by Fincham and Richardson. It states that under oxidizing conditions sulphate is the dominant species, because as the O^{2-} fugacity decreases, the SO_4^{2-} solubility decreases until the sulphide (S^{2-}) becomes the dominant species (Fincham & Richardson, 1954; Lenoir et al., 2010; McKeown et al., 2004). Hence, under oxidising conditions, S is dissolved in a silicate glass system as a sulphate (SO_4^{2-}), and in reducing conditions as a sulphide (S^{2-}) (Morizet et al., 2013). The dissolution of SO_3 can be summarised by two chemical reactions (Morizet et al., 2013):



Therefore, the SO_3 REDOX state plays an important role in the determination of the sulphate solubility (Lonergan et al., 2020). Manara et al. (2007) proposed a general formula (Eq 10) for sulphate activity in a borosilicate glass based on Pinet

and Di Nardo, where f_a is the fugacity of the gaseous species α , f_{SO_2} and f_{O_2} is the dependence on the gaseous atmosphere, where NBØ is the non-bridging oxygens, and BØ is the bridging oxygens:

$$a_{SO_4^{2-}} \propto \frac{f_{SO_2} [NBØ]^2 \sqrt{f_{O_2}}}{[BØ]} \quad (10)$$

In order to determine solubility in glasses, there have been different methodologies described in the literature as summarised below:

Lenoir et al. (2009) described removing the molten salt layer on top of the samples, before the glasses were washed with hot DI water for an hour, so that only the glass remained, with SO_3 salt having been dissolved in the water.

Jin et al. (2019) described a method for determining SO_3 solubility in glass, known as the crucible saturation method. The glass was crushed and sieved, where a calculated amount of Na_2SO_4 was added to the powdered glass. The glass mixture was re-melted, crushed, sieved, and then dissolved in DI water to remove excess salt for chemical analysis. Skidmore et al. (2019) also utilized this methodology, in addition to filtering the saturated glass using a centrifugal filter.

2.4.4 Summary

Both P_2O_5 and SO_3 are deemed to be problematic components in Hanford waste streams depending on the compositions of the glass host matrices. The literature has suggested that P_2O_5 may potentially increase the solubility of SO_3 , however, this is dependent on the REDOX behaviour of the glass melt, and how the S, as either sulphide or sulphate, is incorporated into the glass melt. In order to determine the SO_3 solubility in a lab setting, several approaches have been described in the literature with studies by PNNL implementing the crucible saturation method.

Chapter 3: Experimental Methodology

3.1 Introduction

The compositions in Table 15 are based on a borosilicate glass, and is the compositional system selected by the Hanford site to vitrify their radioactive waste.

The compositions of the LAW and HLW samples in this study are simulants of fully vitrified waste streams as provided by the Office of River protection (ORP) and The Hanford Tank Waste Treatment and Immobilization Plant (Vit Plant). Within these compositions three main series of samples were investigated:

Series 1: Sodium boro-silicate glasses comprising P_2O_5 and/or S (NBSP, NBSi-S and NBSiS-P) based on compositions reported in prior studies by (Vienna & Kim, 2008) (Kruger et al, 2013), (Kruger & Matlack, 2005), (Kruger et al, 2010), and (Muller et al, 2016),

Series 2: Alumina boro-silicate glasses at both high level and low level of waste (SCPD-HLW and -LAW), and doped with P_2O_5 , based on the same compositional sources as series 1,

Series 3: A fully immobilised LAW (ILAW) simulant whose composition was based on three specific glasses reported by Gervasio et al.(2018).

Sample naming Conventions:

The sodium borosilicate glasses are named sodium-borosilicate-phosphorus doped (NBSP), sodium-borosilicate-sulphur doped (NBSi-S), and sodium-borosilicate-sulphur and phosphorus doped (NBSiS-P). When the samples become more complex, they are named simple-complex-phosphate-doped with respect to the high-level or low-level activity-based compositions (SCPD-HLW and SCPD-LAW). The LAW radioactive simulant with the most complex composition has the nomenclature full-simulant-phosphorus (FS-P) or ILAW, interchangeably.

Non-bridging oxygens will be shorted to NBØ and bridging oxygens shortened to BØ, unless otherwise stated in the text.

3.2 Raw Materials and Batching

The raw materials used in batching the different glass systems used high purity oxides, carbonates, and sulphates. Prior to weighing, each raw material was dried in an oven at 100°C for 24 hours to remove any hydration, except for H₃BO₃ because of its low decomposition temperature (it is stored at room temperature). The raw materials were weighed in accordance with the batch calculations on an electric balance with an accuracy of 0.01 g. The weighed chemicals are then transferred from weighing boats to plastic zip lock bags and shaken before being milled in a steel mill for 30 seconds at 700 RPM to ensure a homogenous powder mixture. The mixture was then transferred to a crucible and placed in an electric furnace and ramped at a slow rate until it reached the desired melting temperature. The size of the crucible varied depending on the volume of the glass batch.

Raw Material	Oxide (mol %)	Sample series					
		NBS-P	NBSi-S	NBSi-P	SCPD-HLW	SCPD-LAW	ILAW simulant
SiO ₂	SiO ₂	52.47 –	54.56	51.77 –	46.64	44.94	44.60 –
		55.81	–	54.56	–	–	45.30
			55.26		46.06	46.09	
2(H ₃ BO ₃)	B ₂ O ₃	15.30 –	15.91	15.10 –	12.32	9.04 –	5.77 –
		16.28	-	15.91	–	9.27	5.86
			16.12		12.16		
Na ₂ CO ₃	Na ₂ O	26.23 –	27.28	25.88 –	12.94	19.52	25.09 –
		27.91	–	27.28	-12.78	-	25.48
			27.63			20.02	
(NH ₄ , H ₂ PO ₄)	P ₂ O ₅	0.00 –	-	0.00 –	0.00 –	0.00 –	0.00 –
		6.00		5.00	1.25	2.50	1.53
(Al(OH) ₃)	Al ₂ O ₃	-	-	-	7.78 -	5.15 -	4.40 –
					7.77	5.29	4.47
CaCO ₃	CaO	-	-	-	5.59 -	12.40	7.90 –
					5.66	-	8.02
						12.72	

NaCl	Cl	-	-	-	-	-	0.04 –
							0.05
Cr ₂ O ₃	Cr ₂ O ₃	-	-	-	-	-	0.12
NH ₄ F	F	-	-	-	-	-	1.08 –
							1.10
Fe ₂ O ₃	Fe ₂ O ₃	-	-	-	5.86 -	1.65 -	0.60 –
					5.79	1.69	0.61
K ₂ CO ₃	K ₂ O	-	-	-	-	-	0.04
Li ₂ CO ₃	Li ₂ O	-	-	-	8.60 –	4.80 -	0.87 –
					8.71	4.93	0.89
MgCO ₃	MgO	-	-	-	-	-	2.43 –
							2.47
			1.00				
CaSO ₄	SO ₃	-	–	2.25	-	-	1.06 –
			2.25				1.08
SnO ₂	SnO ₂	-	-	-	-	-	0.58 –
							0.59
TiO ₂	TiO ₂	-	-	-	-	-	0.58 -
							0.06
V ₂ O ₅	V ₂ O ₅	-	-	-	-	-	0.17
ZrO ₂	ZrO ₂	-	-	-	-	-	3.67 –
							3.72

Table 15 – Compositional range of glass systems studied

3.3 Melting Conditions

Table 16 documents the melting conditions for each specific glass system. Some of the glasses were air quenched because of the requirements needed for a characterisation technique or because of the presence of molten salt layers from the presence of sulphur. Some glasses were melted, air quenched, milled, and re-melted to create homogenous glasses.

	NBS-P	NBSi-S	NBSiS-P	SCPD- HLW	SCPD- LAW	ILAW simulant
crucible	Pt with 10% Rh	Alumina	Alumina	Alumina	Alumina	Alumina
Melting temperature (°C)	1150	1150	1150	1150	1150	1150
Temperature ramp rate (°C)	5	5	5	5	5	5
Dwell time (h)	1	3	3	3	3	3
Double melt	Yes	No	No	No	No	Yes
Air quenched	Yes	Yes	Yes	No	No	No
Pour conditions	Melt is poured into a pre- heated mould	Melt is poured into a mould	Melt is poured into a mould	Melt is poured into a mould	Melt is poured into a mould	Melt is poured into a mould
Furnace type (melting)	Electric in air	Electric in air	Electric in air	Electric in air	Electric in air	Electric in air
Annealing temperature (°C)	500	-	-	480	480	480
Dwell time (h)				2	2	
Furnace type (annealing)	Electric in air	Electric in air	Electric in air	Electric in air	Electric in air	Electric in air
Washed and heated in DI water	No	Yes	Yes	No	No	No

Table 16 - Melting conditions of different glass systems

3.3.1 Centreline Cooling Curve (CCC) Heat Treatments

In the steel canisters into which Hanford HLW glasses will be poured, the melt is expected to cool slowly from the melter operating temperature of 1150°C to ambient

temperatures (Marcial et al., 2020). The centreline of the canister is where it is expected that crystallisation will occur and be at its greatest, where cooling is slowest (Simmons et al., 1974). In the case of HLW glasses, it has been shown that the cooling regime promotes crystallisation of aluminosilicate phases such as nepheline and spinel (Christian, 2015; Marcial et al., 2020; McClane et al., 2019; Reynolds & Hirma, 1996; Rodriguez et al., 2011). The presence of nepheline is problematic in HLW glass because it can decrease the chemical durability of the final immobilized vitrified form by removing Si and Al from the glass network (Christian, 2015; Marcial et al., 2020; McClane et al., 2019; Reynolds & Hirma, 1996; Rodriguez et al., 2011), whilst spinel crystallisation during melting may cause shorting of electrodes and block the melter discharge port (Lonergan et al., 2022; Reynolds & Hirma, 1996). In order to replicate the behaviour of the slowest cooled area in the canister, the CCC thermal profiles (Table 17 and Table 18) were developed by SRNL (Gervasio et al., 2021; Russell et al., 2018) to model the worst-case scenario for the occurrence of crystallisation. The HLW (Russell et al., 2018) CCC regime was performed on the NBSP samples and HLW0.00 and HLW1.25, whilst the LAW (Gervasio et al., 2021) CCC regime was performed on the NBSP samples and LAW0.00-2.25 samples. The samples were then analysed using XRD and SEM/EDS to establish the crystalline phases present.

Segment	Start Temperature (°C)	Stop temperature (°C)	Rate (°C/min)	Dwell (min)
1	1150	1150	0	30
2	1150	1114	Furnace quench	-
3	1114	1000	-7.1	-
4	1000	900	-1.8	-
5	900	825	-0.6	-
6	825	775	-0.3	-
7	775	725	-0.2	-
8	725	600	-0.1	-
9	600	0	-0.1	-

Table 17 - LAW centreline canister cooling schedule taken from (Gervasio et al., 2021)

Segment	Start Temperature (°C)	Stop temperature (°C)	Rate (°C/min)	Dwell (min)
1	1150	1150	0	30
2	1150	1050	Furnace quench	-
3	1050	980	1.6	-
4	980	930	0.8	-
5	930	875	0.6	-
6	875	825	0.4	-
7	825	775	0.3	-
8	775	725	0.3	-
9	725	400	0.3	-
10	400	0	Furnace quench	-

Table 18 - HLW centreline canister cooling schedule taken from (Russell et al., 2018)

3.4 Compositional Characterisation

3.4.1 X-ray Fluorescence (XRF) Spectroscopy

X-ray fluorescence (XRF) is a spectroscopic technique that is used for the non-destructive chemical analysis of a sample to establish its composition. It analyses trace elements and compares them to various standards, with a measured value being produced from the statistical computation of all the results.

XRF spectroscopy works by bombarding a sample with X-rays, which excites the sample causing it to generate X-ray fluorescence photons (Uo et al., 2015). These X-rays come from individual electrons out of the atom of a specific element, in particular the K and L inner atomic shells, resulting in a vacancy in that shell that is then filled by an electron from a higher energy shell (Figure 17) (Schlotz & Uhlig, 2006). The excess energy released by the electrons is emitted as X-ray fluorescence radiation, which is characteristic to a particular element like that of a fingerprint (Uo et al., 2015). The intensity of the radiation is proportional to the concentration of the element(s) in the sample (Schlotz & Uhlig, 2006).

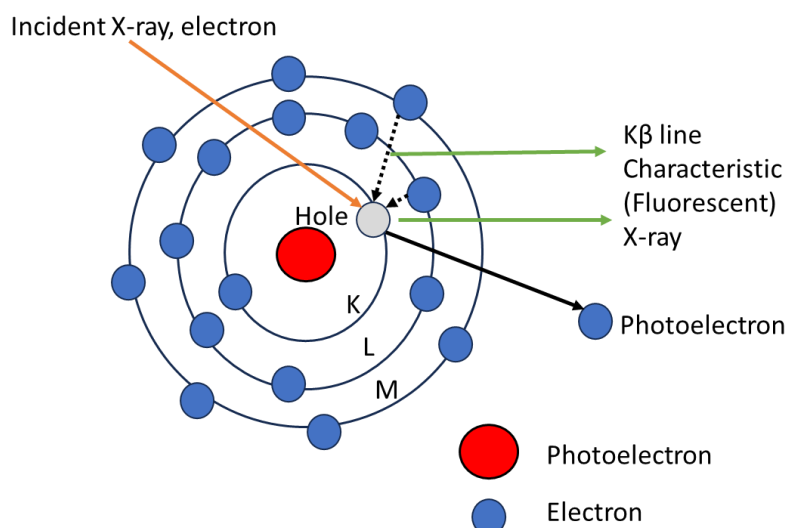


Figure 17 - The mechanism by which characteristic X-rays are generated, modified from (Uo et al., 2015)

XRF is used to determine the elements quantitatively and qualitatively by measuring the characteristic radiation released (Schlotz & Uhlig, 2006). Calibration standards whose elemental concentrations are known are used to generate calibration curves, which are then used to calculate concentrations from sample spectra. XRF is limited by its ability to detect whether certain elements are present in the sample or not i.e., lighter elements e.g., B and Li due to having low energy levels that struggle to escape from the sample without re-absorption, and where fluorescent X-rays that do escape from the sample being too diminished and having greatly reduced penetrating power, which struggle to reach the instrument, where XRF is unable to quantitatively estimate the elemental concentration (Bickford et al., 1995).

3.4.1.1 Sample Preparation

XRF samples were made by mixing approximately 1.000 g of sample powder with 10.000 g of lithium tetraborate fusion flux in a platinum crucible, before being placed in the LeNeo automatic fusion system at 1065°C for 20 minutes, before being poured and cooled, producing fused beads. The lithium tetraborate flux is doped with 0.5% lithium iodide as an anti-cracking agent.

3.4.1.2 Analysis

The XRF results were analysed at Sheffield Hallam University and were collected using a PANalytical MagiX PRO XRF spectrometer using an Rh anode X-ray tube. The XRF data were analysed using a modified version of the OXI program

as outlined by Bell et al. (Bell et al., 2020) and Giles et al. (Giles et al., 1995). The XRF results analysed by Glass Technology Services were collected using a Bruker S4 Pioneer spectrometer using an Rh anode X-ray tube, where the XRF data was analysed using a modified oxide program as part of the onboard Bruker software EVAL Spectra Plus. The results provided were calculated but did not comment on B or Li due to being too light to be measured. However, their nominal contents can be incorporated into the analysed composition giving an estimation of the full composition. To obtain a more accurate value for B and Li, inductively coupled plasma optical emission spectroscopy (ICP-OES) would need to be used. The results were processed and analysed using Microsoft Excel and OriginPro software.

3.4.2 X-ray Powder Diffraction (XRD)

3.4.2.1 Theory

Powder X-ray Diffraction (XRD) is a destructive technique used to analyse a material's phase composition and structure. The XRD pattern generated is characteristic to the sample, where analysis of the pattern will provide a fingerprint, like XRF, of the crystalline phases present in the sample (Ermrich & Oppen, 2013). If the sample is wholly amorphous or with crystalline components too low to measure, then the pattern will exhibit a broad peak and is termed '*X-ray amorphous*'. The resulting XRD pattern are then compared against standard reference patterns from the International Centre for Diffraction Data (ICDD) Powder Diffraction File (PDF) (Gates-Rector & Blanton, 2019) to allow for identification (Ermrich & Oppen, 2013).

X-rays are high energy short-wavelength beams of electromagnetic radiation and are either characterised by photon energy or wavelength (Leng, 2013). X-rays are produced by high-speed electrons that are accelerated by a high-voltage field colliding with a metal target. The deceleration of said electrons on the metal target enables the kinetic energy of the electrons to be converted into the X-ray radiation energy (Leng, 2013). The wavelength of the X-ray radiation (λ) is related to the acceleration electron voltage (V) by the following equation (Eq 11) (Leng, 2013):

$$\lambda = ((1.2398 * 10^3) / V) * 10 \text{ (Å)} \quad (11)$$

X-rays are usually generated by X-ray tubes but can also be generated by other methods e.g., synchrotron radiation. Synchrotron radiation is the electromagnetic

radiation emitted when charged particles are accelerated in a curved pathway (Balerna & Mobilio, 2015; Sutton & Newville, 2014).

The X-ray tube contains a source of electrons and two metal electrodes in a vacuum tube. The voltage across the electrodes draws the electrons to the anode (target) and the X-rays produced at the point of impact on the anode surface radiates in all directions (Leng, 2013). The X-ray radiation generated from the X-ray tube has a range of wavelengths, with the intensity maxima being the characteristic X-rays. The single-wavelength (monochromatic) X-ray radiation is generated by filtering out other radiations from the spectrum (Leng, 2013). When the incident electron beam has enough energy to excite an electron in the inner shell of an atom, another electron from an outer shell will be promoted and fill its place. The released electron will emit a characteristic X-ray with a specific wavelength or a photon with a specific energy (Figure 18 and Figure 19) (Leng, 2013). The wavelength of the photon depends on the atomic number Z using the Moseley law (Ermrich & Oppen, 2013): $1/\lambda \sim Z^2$.

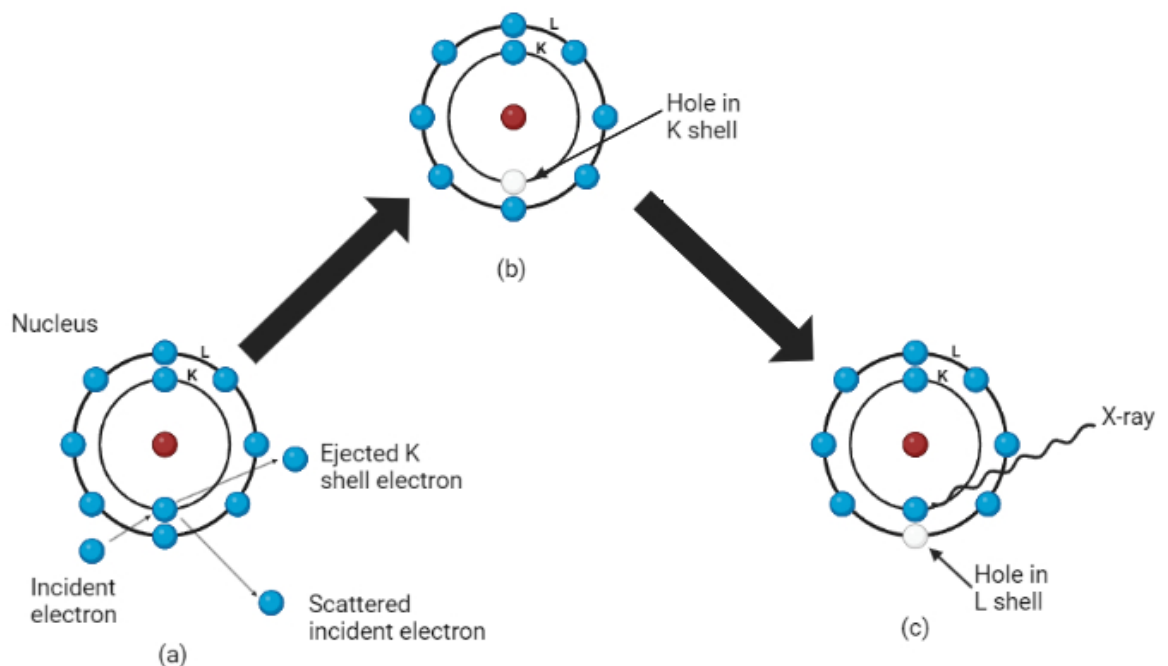


Figure 18 - Process of the inner-shell ionisation and the subsequent emission of a characteristic X-ray modified from (Suryanarayana & Norton, 1998)

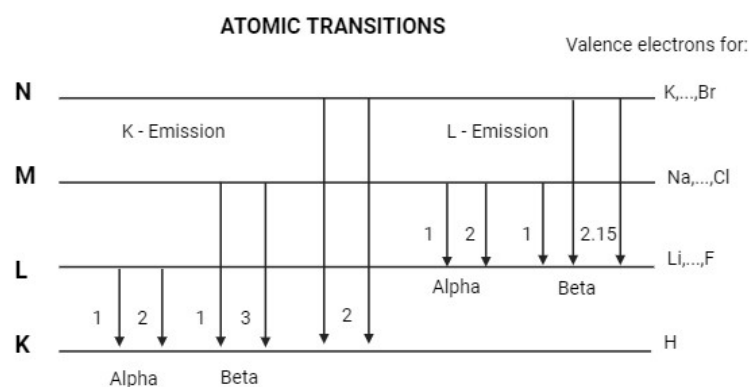


Figure 19 – Atomic transitions diagram modified from (Schlotz & Uhlig, 2006)

When the X-rays from the target sample are analysed, they are found to consist of a mixture of different wavelengths with varying intensity depending on the tube voltage and material (Table 19) (Cullity, 1956). The X-ray tube itself delivers characteristic wavelengths of its anode material, and said radiation is superimposed on the white radiation (Ermrich & Oppen, 2013). When the voltage is increased the intensity of the subsequent wavelengths increases as well. The primary monochromators have either one or two crystals positioned in the beam path so that when the incident beam hits the lattice plane it fulfils the Bragg equation, where the resultant beam is diffracted and highly monochromatic (Ermrich & Oppen, 2013). Figure 20 shows a basic schematic of the set-up of an XRD beam path.

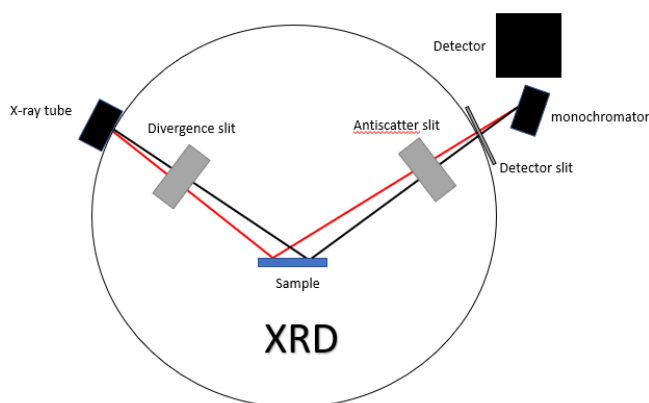


Figure 20 – Example of a simple beam path setup for XRD

Anode	Wavelength (Å)			K β filter
	K α_1	K α_2	K β	
Co	1.789	1.7929	1.6208	Fe
Cu	1.5406	1.5444	1.3922	Ni

Table 19 – Wavelengths used for XRD and attenuation filters for K β filters
(Ermrich & Oppen, 2013)

3.4.2.1.1 Rietveld Refinement Analysis

The Rietveld refinement method was developed and reported by Hugo M. Rietveld, where he refined a crystal structure by using not only single Bragg reflection intensities but by also using a group of overlapping diffraction intensities by profile refinements (Rietveld, 2014; Runčevski & Brown, 2021). The full implementation of the method was published in the seminal paper '*A Profile Refinement Method for Nuclear and Magnetic structures*' (Rietveld, 1969) where the method was mainly used to refine structures from data obtained by fixed wavelengths (Rietveld, 2014). The Rietveld method is a quantitative phase analysis technique, where it employs a whole-pattern fitting approach, and can be applied to a quantifiable crystalline phase with a known crystal structure (Djerdj, 2019). If amorphous material is present then a known reference standard is used in order to quantitatively calculate the phase contents, and can be added as either an internal standard or external standard (measured out separately) (Djerdj, 2019).

3.4.2.1.2 Lattice and Crystal Structures

There are seven crystal systems (Table 20), and these are listed in order of increasing symmetry, where triclinic cell has the lowest symmetry and the cubic cell has the highest symmetry (Suryanarayana & Norton, 1998). If lattice points were put at the corners of each unit cell of the seven crystal systems, you get different point lattices, where there are 14 possible lattices (Suryanarayana & Norton, 1998) (Figure 21) (Table 21).

System	Relationship among lattice parameters
Triclinic	$a \neq b \neq c, \alpha \neq \beta \neq \gamma \neq 90^\circ$
Monoclinic	$a \neq b \neq c, \alpha = \gamma = 90^\circ; \beta \neq 90^\circ$
Orthorhombic	$a \neq b \neq c, \alpha = \beta = \gamma = 90^\circ$
Tetragonal	$a = b \neq c, \alpha = \beta = \gamma = 90^\circ$
Hexagonal	$a = b \neq c, \alpha = \beta = 90^\circ; \gamma = 120^\circ$
Rhombohedral or Trigonal	$a = b = c, \alpha = \beta = \gamma \neq 90^\circ$
Cubic	$a = b = c, \alpha = \beta = \gamma = 90^\circ$

Table 20 – The seven crystal systems (Suryanarayana & Norton, 1998)

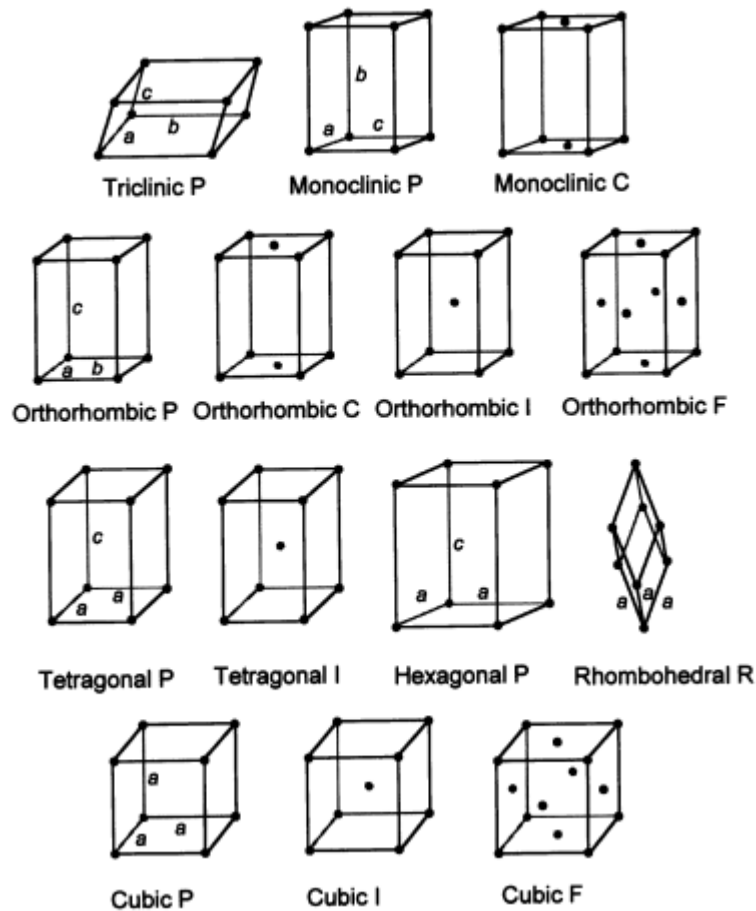


Figure 21 – The 14 Bravais lattices (Suryanarayana & Norton, 1998) with copyright permission from Springer Nature (License number: 5624870762883)

Symbol	Meaning
P	Primitive or simple cell, where there is a lattice point at each corner.
F	Face-centred cell, where the lattice point is centred on each face as well as on the corners of a unit cell.
I	Body-centred cell, where the lattice point is in the centre of a unit cell as well as the corners of the unit cell.
A, B or C	Base-centred cell, where the lattice points are centred on opposite faces of a unit cell as well as at the corners.

Table 21 - Lattice symbols and their meanings (Suryanarayana & Norton, 1998)

Different crystal planes and lattices (*Figure 22*) are described using Miller indices (Suryanarayana & Norton, 1998).

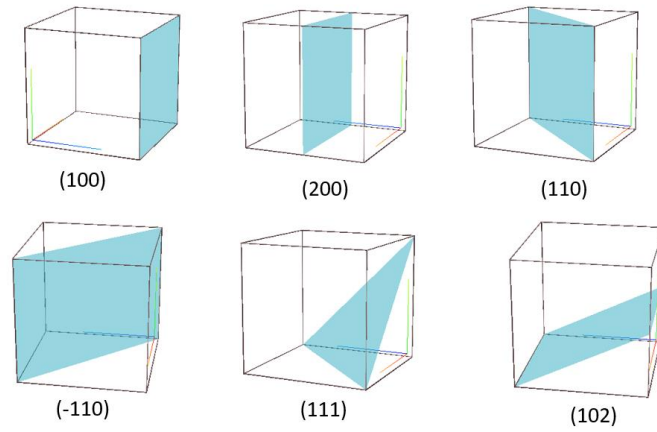


Figure 22 – Example of different lattice planes with Miller indices

3.4.2.1.3 Diffraction Geometry

Lattice planes are points in a crystal lattice where the arrangement of the particles are in numerous planes running in different directions through lattice points, either vertically, horizontally, or diagonally (Schlotz & Uhlig, 2006). All the planes running parallel to the lattice planes are at defined distances from each other and this distance is called lattice plane distance, d , (Schlotz & Uhlig, 2006). When X-ray light parallel to the lattice plane strikes, every particle then acts as a scattering centre and emits a secondary wave (Schlotz & Uhlig, 2006). These secondary waves combine with the reflected waves (Schlotz & Uhlig, 2006). The reflected waves interfere with each other, and cancellation can occur if the amplification condition is not met correctly, “*phase difference = a whole multiple of the wavelength ($= n$)*”, resulting in a wavelength that is not amplified (Schlotz & Uhlig, 2006). For a defined wavelength and lattice plane distance, with a specific angle, the Bragg angle, Bragg’s law is formed (Eq 12) (Figure 23) (Bell, 1998; Schlotz & Uhlig, 2006).

Bragg’s law:

$$\lambda = 2d_{hkl} \sin(\Theta) \quad (12)$$

Where d is the Lattice interplanar spacing of the crystal. It is dependent on the crystal size and symmetry of the unit cell, Θ is the X-ray incidence angle (Bragg angle), λ is the Wavelength of the characteristic X-ray in nm, L is the Average crystallite size, K is the constant related to the crystallite shape and is normally 0.9 assuming the crystalline shape is spherical, and β is the diffraction profile in 2Θ (width of Bragg peak) (Scherrer, 1918).

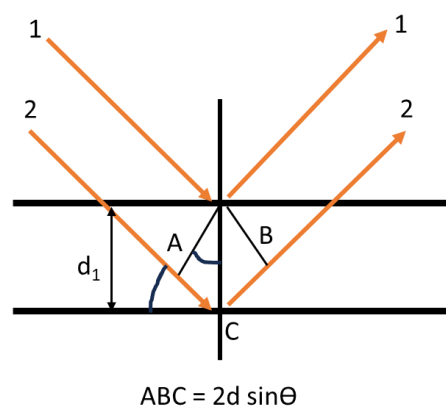


Figure 23 – Bragg's law diagram modified from (Schlotz & Uhlig, 2006)

Using Bragg's law (Figure 23), if the angle θ is measured, the wavelength can be determined, and hence the chemical elements. If the lattice plane distance or wavelength is known then the crystalline structure can be determined, hence, quantitative, and qualitative techniques that determine the chemical elements (XRF) and crystalline structure (XRD), depending on if it is the wavelength or $2d$ -value that is identified via the measurement of the angle θ (Schlotz & Uhlig, 2006). Different lattice planes will give peaks in the powder diffraction at different angles.

Amorphous materials, such as glass, show a broadly centred peak, which is also the strongest peak seen in its crystalline diffraction pattern of the same composition (Suryanarayana & Norton, 1998).

3.4.2.2 Sample Preparation

Solid samples in this study were powdered in a Retsch PP40 vibration mill inside a grinding cup with hardened steel rings for one minute at 700 RPM. The powders were then pressed into powder specimen holders and mounted on a reflection-transmission spinner stage. Rietveld analysis samples were prepared by mixing ~0.20 g of sample powder with 0.50 g of pure Si powder in a mortar and pestle.

3.4.2.3 Analysis

XRD patterns were recorded using either a Bruker D8 Advance diffractometer (PNNL), PANalytical X'Pert PRO diffractometer and a PIXCEL-1D area detector (SHU) or Empyrean (SHU). The Bruker D8 Advance diffractometer used $\text{CuK}\alpha$ X-rays with a step size of $0.015^\circ 2\theta$, scan step time of 177 seconds, and were measured between 5° and $70^\circ 2\theta$. The PANalytical X'Pert Pro diffractometer used $\text{CuK}\alpha$ X-rays and a with a step size of 0.013; scan step size of 199 seconds and were measured between 5° and $80^\circ 2\theta$. The Empyrean used $\text{Co K}\alpha$ X-rays and

a step size of $0.013^{\circ}2\theta$, scan step time 457 seconds, and were measured between 5° and $80^{\circ}2\theta$. Rietveld analysis used the PANalytical X'Pert Pro diffractometer, where it had a step size of $0.0131^{\circ}2\theta$; scan step time of 448.855 seconds; and were measured between 5° and $80^{\circ}2\theta$. The XRD traces were analysed using HighScore Plus to obtain XRD patterns that best matched the crystalline peaks in the samples, as well as to refine the profile parameters for Rietveld analysis.

3.5 Structural Characterisation

3.5.1 Scanning Electron Microscopy / Electron Dispersion Spectroscopy (SEM/EDX)

3.5.1.1 Theory

Scanning electron microscopy (SEM) allows for the observation and subsequent characterisation of organic and inorganic materials on a nanometre and micrometre scale, hence its use in obtaining three dimensional images of surfaces and topological characteristics (Goldstein et al., 2008). It works by a specimen being under vacuum and being exposed to a high-energy electron beam. Low-energy secondary electrons are then emitted from the area where the electron beam is focused (Ratner, 2004). The intensity of said secondary electron emission is a function of the atomic composition of the sample (Ratner, 2004). Non-conductive samples are coated in a thin layer of an electrically grounded layer of metal e.g. gold or carbon to minimize the negative charge accumulation from the electron beam, but this layer is thick enough in order that electrons that are emitted from the sample beneath cannot penetrate it (Ratner, 2004).

Electron Dispersive X-ray Spectroscopy (EDS) is a chemical microanalysis technique used in conjunction with SEM. EDS detects X-rays that are emitted from a sample when it is bombarded by an electron beam in order to characterise its elemental composition (Materials Evaluation and Techniques Inc, 2014). When electrons bombard the sample, electrons are ejected from the atoms on the samples surface, resulting in electron vacancies that are filled by electrons from a higher energy state, as a result an X-ray is emitted (Materials Evaluation and Techniques Inc, 2014). The EDS detector measures the relative abundance of these emitted X-rays versus their energy (Materials Evaluation and Techniques

Inc, 2014). The optical arrangement of SEM consists of an electron gun and electromagnetic lenses and apertures (Figure 24) (Leng, 2013).

The advantages of using SEM with EDX spectroscopy is that it is a rapid and an inexpensive approach to characterise topological features, providing a qualitative elemental analysis of the sample.

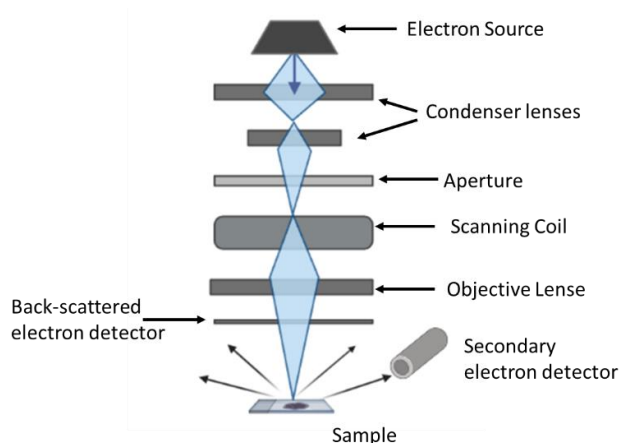


Figure 24 - Schematic diagram of SEM modified from (Joshi & Bhattacharyya, 2008)

3.5.1.2 Sample Preparation

The samples were either sliced using a diamond saw then mounted using crystal epoxy onto a metal base so that they could be ground down using sandpaper and water, or they were suspended in epoxy resin and hardener and then ground down and polished. They were ground down using grit sizes: 60mm, 240mm, 320mm, 600mm, 800mm, 1200mm and then polished using a series of polycrystalline diamond slurry suspension at sizes 15 μ m, 9 μ m, 3 μ m and 1 μ m. The samples analysed in the US at PNNL were covered in a 2 nm coating of Iridium or carbon because the samples themselves were non-conductive.

3.5.1.3 Analysis

Images were achieved with EDX mapping using a JEOL JSM-Field emission SEM with JEOL PC-SEM v.2.1.0.9 software to drive the microscope and image the samples. The samples analysed at Sheffield Hallam University were mounted in graphite epoxy and secured to an SEM stub before being carbon coated in a EMITECH K950X, as well as being applied with silver dag to ensure the samples were conductive. Images were achieved with EDX mapping using an FEI Quanta 650 with the analysis software Aztec.

3.5.2 Raman Spectroscopy

3.5.2.1 Theory

Raman spectroscopy is used as a structural analysis tool and was developed by Sir C. V. Raman and Kirishnan in 1928 (Yadav & Singh, 2015). In the latter's study, they commented that Raman intensity is 10^{-6} to 10^{-9} times less than Rayleigh scattering and that a low intensity of this magnitude can be produced by lasers (Yadav & Singh, 2015). When laser light is incident to a vibrating molecule, the energy of the photons may change (Yadav & Singh, 2015). The excited molecules or atoms return to different states, and the change in energy between the original state and new state gives rise to the shift of the emitted photon. The excited molecule or atom goes to a higher or lower frequency than the original state and this phenomenon is known as the Stokes Raman scattering or anti-Stokes Raman scattering, or Stokes shift or anti-Stokes shift, respectively, for short (Yadav & Singh, 2015). Raman shifts are unique depending on which atoms and molecules are being investigated, e.g., orthophosphates' Raman shift will differ from pyrophosphates' (Yadav & Singh, 2015). Figure 25 displays a basic diagram of the principles of Raman spectroscopy.

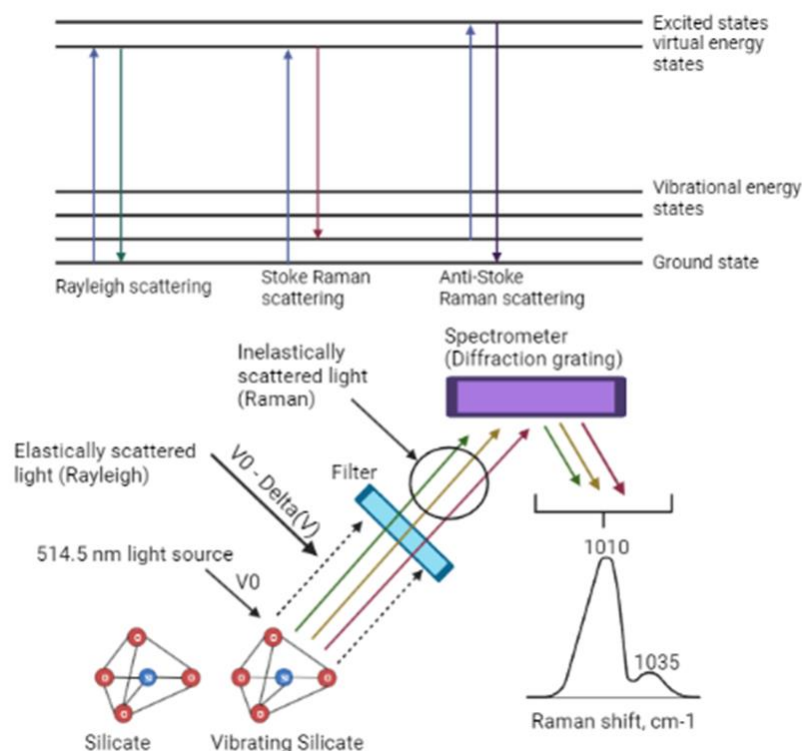


Figure 25 - A diagram showing the principles of Raman modified from (Yadav & Singh, 2015)

The advantage of Raman spectroscopy is that it provides information about surfaces, and can provide data from the interior of the sample (Atalla et al., 1992). Regarding glassy materials, Raman spectroscopy is used to determine their structure, dynamics, and structural environment; it is a complimentary technique to infrared (IR) spectroscopy, NMR spectroscopy, and XRD (Yadav & Singh, 2015).

Raman spectroscopy provides information on vibrational frequencies and band intensities, which is similar but not identical to IR spectroscopy (Atalla et al., 1992). The difference being that for a molecule to be IR-active it needs to change its dipole moment, which is accompanied by a vibrational transition, whereas to be Raman-active, there needs to be a change in the molecular polarizability during its transition (Atalla et al., 1992). What this means is that polar bond systems with a high dipole that show a strong IR frequency can be seen easily, e.g., NaCl with a dipole 9.000 D (Bastos & Leite, 2017), whilst a highly covalent molecule can be seen easily in a Raman spectra, e.g., CS₂ (Atalla et al., 1992).

Another advantage of Raman spectroscopy is that it can be used to study heterogenous samples. IR spectroscopy struggles to do this due to Rayleigh scattering (an oscillating dipole moment that emits with the frequency of an incident field) of infrared photons, with the degree of Rayleigh scattering being dependent on the refractive indices (Atalla et al., 1992; Hotokka, 2008). The variation in the refractive indices' wavelength in regions of strong IR absorption is difficult to distinguish between, due to molecular absorption caused by Rayleigh scattering (Atalla et al., 1992). Raman spectroscopy can distinguish between the Rayleigh scattering of different atoms and molecules and, hence can distinguish variations in refractive indices in heterogenous samples (Atalla et al., 1992).

3.5.2.2 Raman Data Pre- and Post-processing

After spectra are collected via Raman spectroscopy, they need to be pre-processed to reduce any irrelevant and random variations in the data. This is often achieved through removing spikes, caused mostly by cosmic rays, by reducing and/or removing them by performing multiple accumulations. The Raman data needs to be smoothed to reduce noise by using multiple methods including using an average, moving average, moving polynomial, or Fourier filter. The background of the Raman spectra produced by fluorescence can be removed, followed by normalization of the spectra, removing systematic

differences caused by changes in the laser power and depth of focus. There are two normalization methods: (i) minimum/maximum and (ii) vector normalization. The data is then long-corrected using the Neuville and Mysen correction method (Eq 13) which corrects the data for temperature and frequency dependent scattering intensity before statistical analysis (Neuville & Mysen, 1996).

$$I = I_{obs} \cdot [V_0^3 [1 - \exp(-hcv/kT)]v/(v_0 - v)^4] \quad (13)$$

Where h is the Planck constant, k is the Boltzmann constant, c is the speed of light, T is the absolute temperature, V_0 is the wavenumber of the incident laser light, and v is the measurement of the Raman shift.

3.5.2.2.1 Peak Fitting Profiles

The mechanisms that cause spectral line broadening are (i) natural broadening, (ii) pressure or collision broadening, and (iii) thermal Doppler broadening (Yuan & Mayanovic, 2017). Natural broadening relates to the lifetime of the excited state and uncertainty of its energy, and hence the frequency (Heisenberg uncertainty principle), where it produces a Lorentzian profile (Yuan & Mayanovic, 2017). Pressure and collision broadening are where the energy levels of an atom are perturbed by other atoms close by (Yuan & Mayanovic, 2017). The thermal Doppler broadening is where the frequency shift of an emitted photon from the Doppler effect depends on the velocity of the atom(s), producing a Gaussian profile (Yuan & Mayanovic, 2017). Other factors that can affect the broadening mechanisms are the bond length and angles, hydrogen bonding, and heterogeneity in solids e.g., crystal lattice defects (Yuan & Mayanovic, 2017). Glasses often have broad Raman peaks and are best fitted with Gaussian profiles, while mineral crystals have sharp and narrow Raman peaks and are best fitted with Gaussian-Lorentzian or Voigtian Profiles (Yuan & Mayanovic, 2017).

Gaussian (Eq 14) and Lorentzian (Eq 15) functions both have symmetrical profiles and are characterised by their peak intensity (a_0), peak centre position (a_1), peak width (a_2) and full width half-maximum (FWHM). They are expressed by the following equations (Yuan & Mayanovic, 2017):

$$\text{Gaussian (G): } y = a_0 \exp \left[-\ln 2 \left(\frac{x-a_1}{a_2} \right)^2 \right] \quad (14)$$

$$\text{Lorentzian (L): } y = a_0 \left[1 + \left(\frac{x-a_1}{a_2} \right)^2 \right]^{-1} \quad (15)$$

For symmetric bands that cannot utilise the Gaussian or Lorentzian profile alone, a sum of the convolution of both functions can be used or a Voigtian profile. The Gaussian-Lorentzian function and Voigtian function are as expressed by the Equations 16 and 17 (Yuan & Mayanovic, 2017):

Gaussian – Lorentzian (GL Sum):

$$y = a_0 \left\{ a_0 \exp \left[\ln 2 \left(\frac{x-a_1}{a_2} \right)^2 \right] + (1 - a_3) \left[1 + \left(\frac{x-a_1}{a_2} \right)^2 \right]^{-1} \right\} \quad (16)$$

Voigtian (V):

$$y = a_0 \int_{-\infty}^{\infty} \frac{\exp(-t^2)}{a_3^2 + \left(\frac{x-a_1}{a_2} - t \right)^2} dt / \int_{-\infty}^{\infty} \frac{\exp(-t^2)}{a_3^2 + t^2} dt \quad (17)$$

Where a_0 is the peak intensity, a_1 is the peak position, a_2 is the FWHM, and a_3 is the degree of Lorentzian (0) and Gaussian (1) for Eq 16, and where a_0 is the peak intensity, a_1 is the centre position, a_2 is the Gaussian width, and a_3 is the Ratio of Lorentzian and Gaussian widths for Eq 17.

3.5.2.3 Sample Preparation

The glass samples were prepared by grinding with sandpaper at grades P240 to P1200 to achieve a flat surface.

3.5.2.4 Analysis

The Raman system used for all samples except the quenched NBSP samples was a Thermo DXR2 Raman spectrometer with a wavelength of 532 nm at Sheffield Hallam University. The samples had an exposure of 15 seconds at 200 accumulations with a laser of 10mW using a 50µm slit and a magnification of 10x. The quenched NBSP samples were analysed using a Renishaw CCD Camera Raman spectrometer with a wavelength of 514.5 nm at the University of Sheffield. The samples had an exposure of 10 seconds at 3 accumulations with a laser power of 100% using a 2400 L/mm grating and a magnification of 50x. The spectra were corrected using the onboard sonic ray removal application. The samples had readings taken at three different locations in order to calculate an average value. The spectra were then corrected for temperature and excitation line effects using the Neuville and Mysen correction method (Eq 15) (Neuville & Mysen, 1996).

3.5.2.5 Peak Fitting Actual Sample Data

The raw Raman data obtained in this study were first corrected using a polynomial baseline for each spectrum that was then subtracted from the original data. The resulting spectrum was then devoid of any effects caused by fluorescence. The spectra data was then normalised between the values of 0 and 1 in Microsoft Excel using the minimum/maximum normalization technique. The Raman spectra were then deconvoluted using OriginPro software using the peak analysis application. The spectra were then deconvoluted using the Gaussian response function with a Fourier filtering algorithm.

3.5.2.6 Raman Difference Spectroscopy

The normalized Raman spectra were used to determine the Raman Difference Spectra (RDS). This was done by subtracting two Raman spectra, where the first contained a common main component in both the spectra (Moguš-Milanković et al., 2001). The bands intensity can be positive or negative depending on the original band intensity (Moguš-Milanković et al., 2001). RDS is often employed to measure frequency changes, where small frequency shifts between two similar spectra results in the Raman difference signal resembling the first derivative curve (Durig & North Atlantic Treaty Organisation, 1980; Laane, 1983).

3.5.3 ⁵⁷Fe Mössbauer Spectroscopy

3.5.3.1 Theory

Mössbauer spectroscopy is a structural analysis technique that provides information about the structure, electronic, and magnetic properties within a material. It gives quantitative information on hyperfine interactions, which are the small energies produced from the interaction between the nucleus and its neighbouring electrons (Fultz, 2011). There are three types of hyperfine interactions (Figure 26): the isomer shift (IS) from the electron density at the density, the nuclear quadrupole splitting at the gradient of the electric field (EQS), and the hyperfine magnetic field (HMF) from the unpaired electron density at the nucleus (Fultz, 2011). These hyperfine interactions are then used to determine the spin and valence of the resonant atom. The isomer shift is a result of the change in the electrostatic interaction between the nucleus and its orbital electrons during γ -ray transition.

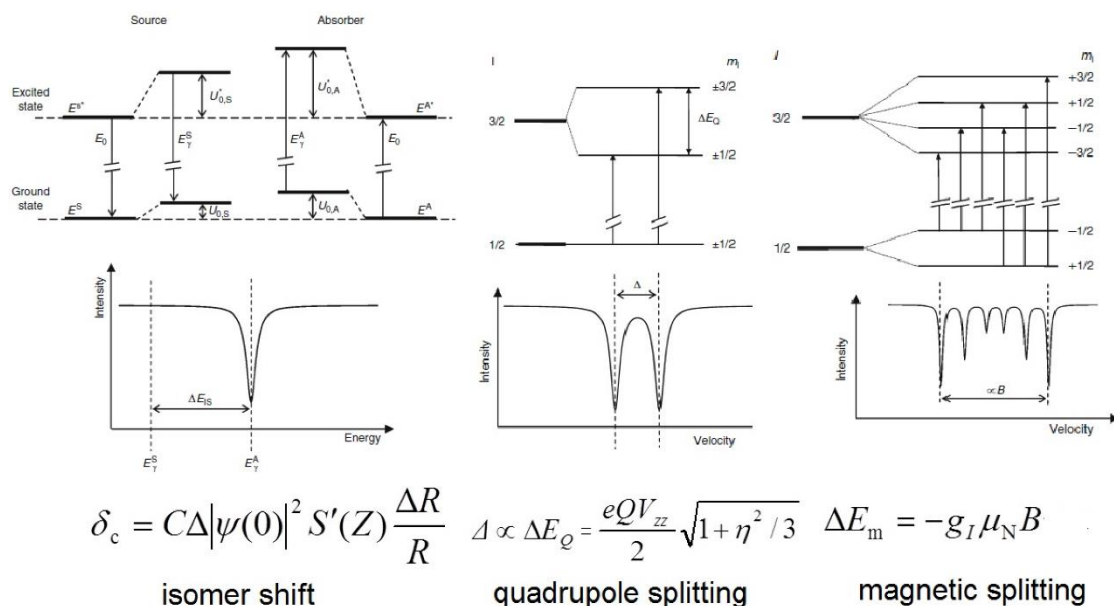


Figure 26 - Energy level diagrams for hyperfine interactions at $3/2 \rightarrow 1/2$ nuclear spin transition and a schematic representation of the corresponding Mossbauer parameters in the spectrum taken from (Kuzmann et al., 2021). Originally published in *Molecules*. Under CC BY 4.0 license. Available from: doi: <https://doi.org/10.3390/molecules26041062>

Mössbauer spectroscopy uses the Doppler effect to tune the energy of the incident radiation, producing a spectrum of the intensity of γ -ray absorption versus the energy of a specific resonant nucleus e.g., Fe or Co (Fultz, 2011; Kaščáková, 2014). By comparing the spectrum with a known reference, such as α -Fe, it is possible to obtain information about the bonding, valency, and coordination (Bingham, 2001). Once the spectrum has been measured, it is then fitted with a Lorentzian (Eq 18) line shape representing Fe^{2+} and Fe^{3+} (Bingham, 2001; Perepelitsa, 2007).

$$L(E) = \frac{I_0 \left(\frac{\Gamma}{2}\right)^2}{(E - E_0)^2 + \left(\frac{\Gamma}{2}\right)^2} \quad (18)$$

Where E_0 is the energy, I_0 is the intensity, and Γ is the full-width half-maximum.

Room temperature Mössbauer spectroscopy of iron (^{57}Fe) will be used in this thesis to provide information on the isomer or centre shift (δ), line width (Γ), paramagnetic hyperfine splitting (hfs), and quadrupole splitting (Δ), to indicate the environment and subsequent coordination of the Fe present in the complex borosilicate glasses (Bingham, 2001). The Fe content has been kept constant

upon P₂O₅ additions, so it will be interesting to see if there has been an effect on the speciation and role of Fe in the network, or if any change has occurred at all.

3.5.3.2 Sample Preparation

The glass samples were milled using a vibration mill at 700 RPM for one minute using a hardened steel milling set. The powdered samples were then mixed out with pure graphite powder to assist in spreading the sample evenly across the diameter of the sample holder to ensure there is enough of the resident isotope to enable a spectrum to be collected. Graphite powder was used because it is inert to gamma rays. The effective thickness of an absorber (t_A) needs to be considered to calculate the ideal ⁵⁷Fe concentration. When $t_A > 1$ saturation effects occur distorting the absorption line shapes, and when $t_A < 1$ the data collection time is increased beyond the optimum and intensities are small (Rancourt et al., 1993; Williams, 1990).

The effective thickness of an absorber (t_A) can be defined as

$$t_A = \beta \eta f_A \sigma_0 \quad (19)$$

Where β is the multiplicity of the absorber spectrum (typically taken as 1), η is the number of resonant nuclei per cm⁻², f_A is the recoil-free fraction of absorber, and σ_0 is the maximum absorption cross section (cm²). In order to set the ideal value of 1, f_A is taken as 0.7, σ_0 is for ⁵⁷Fe is taken as 2.56×10^{-18} cm² (Rancourt et al., 1993). Using these constants, η can be calculated as follows:

$$\eta = \frac{t_A}{f_A * \sigma_0} \quad (20)$$

$$\eta = \frac{1}{0.7 * (2.56 * 10^{-18})}$$

$$\eta = 5.580 \times 10^{17} \text{ } ^{57}\text{Fe per cm}^2$$

This value can be converted from number of atoms to a mass by:

$$\frac{(5.580 * 10^{17}) * 57}{(6.022 * 10^{23})} = 5.282 \times 10^{-5} \text{ grams of } ^{57}\text{Fe per cm}^2 \quad (21)$$

The natural abundance of ⁵⁷Fe/Fe is 2.14% of the total iron content (Rancourt et al., 1993), where the value can be converted to the mass of total iron by:

$$\frac{(5.282 * 10^{-5}) * 100}{2.14} = 2.47 \times 10^{-3} \text{ grams pf iron per cm}^2 \quad (22)$$

Based on these equations, the mass of total iron needed per cm² can be derived, where the area of the absorber disks is kept constant, and only the iron content of the material being tested is needed. For example, if a sample had a total iron content of 6 wt%, the needed sample mass loading can be calculated as follows (Scrimshire, 2019):

$$2.47 \times 10^{-3} \text{ grams per iron per cm}^2 \times \text{area of absorber} \times (100/\text{Fe}\%) \quad (23)$$

The data was collected at 297 ± 2 K (room temperature) using the spectrometer Janis CCS-850 10 K cryocooler that uses a SeeCo W304 drive unit and SeeCo 45431 Kr proportional counter, with a velocity range of ± 6 mm/s (Figure 27). The spectrometer used a ⁵⁷Co source in a Rh matrix.

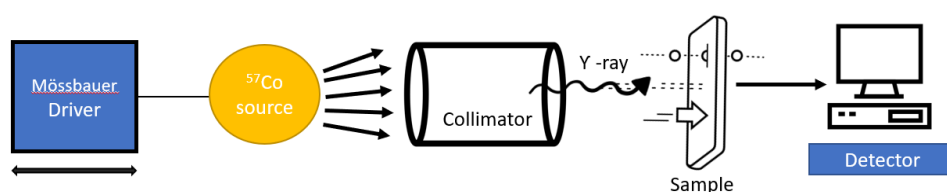


Figure 27 - Simple diagram explaining the Mössbauer equipment setup

3.5.3.3 Analysis

The spectra collected for the samples were analysed using the software Recoil (Lagarec & Rancourt, 1998) and were, fitted with two different line fitting parameters – Lorentzian and xVBF, respectively. Lorentzian uses doublets with adjustable line widths (Rancourt, 1994), whilst xVBF fits every iron site with a Gaussian distribution with an independent isomer shift and quadrupole splitting (Stoch & Stoch, 2015).

3.5.4 Magic-Angle Spinning Nuclear Magnetic Resonance (MAS NMR) Spectroscopy

3.5.4.1 Theory

Nuclear magnetic resonance (NMR) is a spectroscopic technique that focuses on the interactions between isolated spin pairs of the element studied providing information about the structure (Chen, 2014). Atomic nuclei with odd mass nuclei have fractional spins, even mass nuclei comprised of odd numbers of protons and neutrons have integral spins, and even mass nuclei comprised of even numbers of protons and neutrons have zero spin (Figure 28) (Chen, 2014).

Solid state NMR suffers from two drawbacks, low sensitivity and resolution (Polenova et al., 2015). Magic Angle Spinning (MAS) NMR addresses these issues by rapidly rotating the sample around an axis of 54.74° (Alia et al., 2009; Andrew et al., 1958; Martin et al., 2005) with respect to the static magnetic field i.e., the magic angle. This method suppresses chemical shift broadening (Alia et al., 2009), resulting in the averaging of the anisotropy of nuclear reactions where the frequency depends on the orientation in accordance with a second order Legendre polynomial, $P_2\cos(\theta)$ (Martin et al., 2005; Polenova et al., 2015).

The basis of NMR is in the nuclei possessing both angular momentum and magnetic moments (Drain, 1957). When a charged particle has any form of motion, a magnetic dipole, when placed in a magnetic field, results in a magnetic moment μ (Gerothanassis et al., 2002). The nuclei of natural occurring isotopes of most elements have an angular momentum or spin of total magnitude $h = \sqrt{I(I+1)}$, where h is the reduced Planck constant and I is the nuclear spin momentum (Akitt & Mann, 2000). I can either have a value of an integral or half an integral (Akitt & Mann, 2000). Quadrupolar nuclei have a spin value that is $>1/2$, whilst isotopes have a spin value that is $1/2$ (Chen, 2014). When the atomic number or atomic mass is an odd value, or when both are an odd value, the nucleus has a magnetic spin (Lambert et al., 2018). However, if the atomic mass and atomic number are even then there are no magnetic properties and the spin value is 0 (Lambert et al., 2018).



Figure 28 - 3 classes of nuclei spin

When the nuclei are in a magnetic field B_0 , the interaction between the magnetic moment of the nuclei and the magnetic field causes an atomic beam to split, creating quantifiable energy levels with different spin orientations that are separated by the energy difference ΔE (Eq 24) (Vaishnav, 2018). This is known as the '*Zeeman effect*' (Ozerov & Vorobyev, 2007; Vaishnav, 2018). The energy

difference that occurs between the spin states is related to the Larmor frequency (Figure 29) (Eq 24 and 25) (Lambert et al., 2018).

$$\Delta E = h\omega_0 = h\nu_0 = \gamma \beta_0 h \quad (24) \quad \omega_0 = \gamma \beta_0 \quad (25)$$

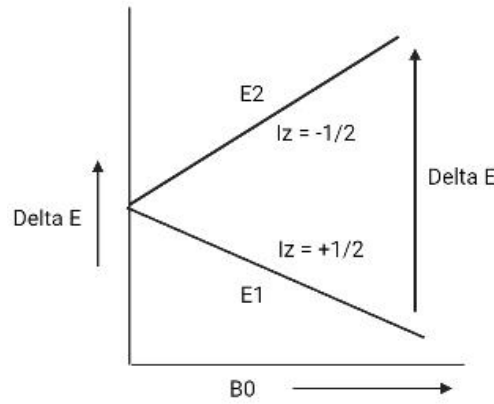


Figure 29 - The energy difference between the spin states and the energy difference as a function of the external field modified from (Lambert et al., 2018)

When in a magnetic field the electrons surrounding the nucleus produce a secondary field, where this has the potential to affect the total field at the nucleus and change the resonance frequency of the nucleus (Duer, 2002). The interaction of this secondary field with the nucleus is known as the shielding interaction (Duer, 2002). The frequency shift in an NMR spectrum is called the chemical shift (Duer, 2002). The chemical shift (Eq 26) is characterised as the difference in the parts per million between that of the resonance frequency of the observed proton and the tetramethylsilane hydrogens (TMS) (Karunakaran et al., 2018). TMS are an internal reference compound for ^1H NMR used for its strong and sharp resonance line from its twelve protons. The use of TMS does not interfere with other resonances.

$$\Delta = \frac{(\sigma_R - \sigma_C) \times 10^6}{(1 - \sigma_R)} \quad (26)$$

Where σ is the chemical shift, σ_R is the frequency of the compound, σ_C is the frequency of the reference, and $1 - \sigma_R$ is the spectrometer frequency.

By measuring the chemical shift it is possible to study the local electron environment (Vaishnav, 2018). There are also other anisotropic interactions besides the Zeeman effect and magnetic electron shielding that occur, where these result in a broad and featureless peak in the NMR spectra that is hard to analyse (Vaishnav, 2018). The NMR spectrum plots the magnetic field strength

on the X-axis and absorption on the Y-axis, with the different NMR absorptions pertaining to the chemical shifts δ .

A typical solid-state NMR spectrometer contains an energy source, signal detector, and data processor, with the specific components being a probe, magnets, shims, amplifier, console, transmission electronics, and a computer (Li, 2012).

3.5.4.2 Sample Preparation

The glass samples were milled in a tungsten carbide mill for 10 seconds at 700 RPM. The sample powders were then weighed, bagged, labelled, and sent to Dalhousie University, Canada Solid State NMR facilities, respectively for testing, where the samples underwent MAS NMR spectroscopy.

3.5.4.3 Instrument Parameters

The NMR analyses for ^{11}B , ^{31}P , ^{29}Si and ^{23}Na MAS NMR were carried out on spectrometers at NMR-3 at Dalhousie University. NMR analyses of ^{11}B MAS NMR were conducted on a Bruker Advance NMR spectrometer with a 16.4T magnet (224.67 MHz ^{11}B Larmor frequency) using a probe head with rotors of 2.5 mm diameter. The ^{11}B MAS NMR spectra were accumulated using a single pulse with length of 0.53 μs corresponding to a 15° pulse angle in the nearly cubic environment of NaBH_4 . The spectra were accumulated at 20 kHz MAS frequency accumulating at least 64 scans. The ^{31}P MAS NMR analyses were carried out on a combined Tecmag/Bruker NMR spectrometer with a 9.4 T magnet (162.02 MHz ^{31}P Larmor frequency) using a probe head with rotors of 2.5 mm diameter. The ^{31}P MAS NMR spectra were accumulated using a single pulse with either a 90° or a 10° angle with a pulse length of 4.2 μs and 0.5 μs , respectively. For the final spectra, a 10° pulse angle excitation was used at 20-21 kHz MAS frequency accumulating up to 8600 scans. The ^{31}P MAS NMR signal of $\text{NH}_4\text{H}_2\text{PO}_4$ served as a secondary chemical shift standard at 0.81 ppm relative to aqueous 85% H_3PO_4 . The ^{29}Si MAS NMR analyses were carried out on a Bruker Advance NMR spectrometer with a 16.4T magnet (139.1 MHz ^{29}Si Larmor frequency) using a probe head for rotors of 4 mm diameter. The ^{29}Si MAS NMR spectra were accumulated using a single pulse with length of 0.77 μs corresponding to a 10° angle, with a pulse repetition of 5 seconds. Up to 12000 scans were accumulated at 10.0 kHz MAS frequency. A small pulse angle was chosen to circumvent the very long spin lattice relaxation times. The ^{29}Si MAS NMR signal of solid Kaolin

(Al₂Si₂O₅(OH)₄) served as chemical shift standard at -90.9 and -91.4 ppm as secondary reference against TMS. The ²³Na MAS NMR analyses were carried out on a Bruker Advance NMR spectrometer with a 16.4T magnet (185.2 MHz ²³Na Larmor frequency) using a probe head with rotors of 2.5 mm diameter. The ²³Na MAS NMR spectra were accumulated using a single pulse with length of 0.42 µs corresponding to a 15° angle in the cubic environment of solid NaCl. The final spectra were accumulated at 20 kHz MAS frequency accumulating 1024 scans. The ²³Na MAS NMR signal of solid NaCl served as chemical shift standard at 0.0 ppm.

3.5.4.4 Analysis

The data was analysed using Bruker TopSpin 4.1.1 software and was fitted using Gaussian lines on DmFit at Dalhousie University, before being plotted in the OriginPro software package. The spectra were then interpreted in accordance with literature.

B and P centres were determined using ¹¹B and ³¹P MAS NMR results to evaluate the amount of O available for Si, where the distribution between Q⁴_{Si} and Q³_{Si} could be estimated. The uncertainties were calculated using the uncertainty propagation for a function f(x, y, ...), with parameter uncertainties x, y which is calculated using the formula of functions (Eq 27):

$$\Delta(f) = \sqrt{\left(\frac{\partial f}{\partial x}\right)^2 (\Delta(x))^2 + \left(\frac{\partial f}{\partial y}\right)^2 (\Delta(y))^2} \quad (27)$$

3.5.5 X-ray Absorption Spectroscopy (XAS)

3.5.5.1 Theory

X-ray absorption spectroscopy (XAS) is an investigative technique that probes the local geometric and electronic structure (DeBeer, 2011; Guda et al., 2021; Henderson et al., 2014). In XAS a photon is absorbed resulting in an excited core electron being promoted to an unoccupied state, providing detailed information on the local electronic structure of a specific element (DeBeer, 2011; Henderson et al., 2014; Lee et al., 2013).

The XAS edge is a result of a core electron absorbing energy that is equal or greater than its binding energy (DeBeer, 2011). The edges are labelled in accordance with the shell that the electron originates from, e.g., a K-edge

corresponds to the 1s core level (DeBeer, 2011; Yano & Yachandra, 2009). The K-edge has high energies and the L and M edges have lower energies, meaning that high vacuum conditions are needed (DeBeer, 2011; Yano & Yachandra, 2009). During an XAS experiment, the absorption coefficient μ is monitored as a function of energy, with the resultant spectrum being divided into two regions (*Figure 30*): the X-ray absorption near edge (XANES) region, and the extended X-ray absorption fine structure (EXAFS) region (DeBeer, 2011). The edge can be characterised by the sudden sharp discontinuity or increase in absorption resulting from the ionization of the core electron (DeBeer, 2011). The pre-edge is the lower energy region of the edge and contains the transitions of photoelectrons to unoccupied orbitals (DeBeer, 2011). The ionised electron is then released into the continuum to interact with neighbouring atoms (DeBeer, 2011). As this photoelectron is deflected off potential neighbouring atoms, an interference pattern is developed and is known as the EXAFS region (DeBeer, 2011; Yano & Yachandra, 2009). The edge region provides information about the electronic structure, with the K-edge's intense edge feature being a result of an electric dipole transition occurring from 1s to 4p (DeBeer, 2011). The edges are often used as a '*fingerprint*' of the local geometric and electronic structure, whilst the EXAFS region provides information pertaining to the number and type of ligands surrounding the photoabsorber (DeBeer, 2011; Kuzmin & Chaboy, 2014).

In the XANES region of spectra for a single element, the photoelectrons populate unoccupied states above the potential μ . The scattered wave causes the density of the final state of the element to change, meaning the shape of the absorption edge is different in different chemical environments (DeBeer, 2011).

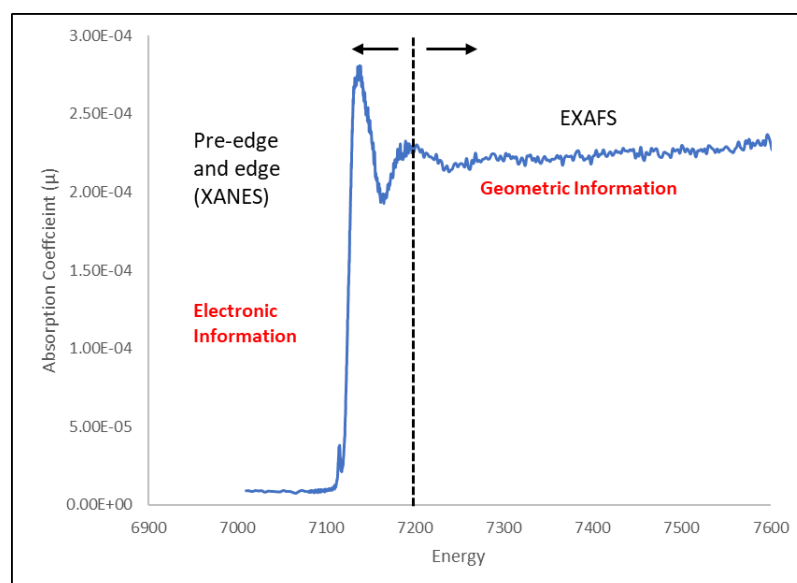


Figure 30 - The XANES and EXAFS regions of an XAS spectrum modified from (Brendebach et al., 2009)

The XAS experiments carried out in this thesis were collected from two synchrotron beamlines: Diamond Light Source, Oxfordshire, UK - B18 and European Synchrotron Radiation Facility (ESRF), Grenoble, France - BM28 XAS beamlines.

The advantages of using XANES is that it is a relatively non-destructive technique that is element specific and suitable for samples that are paramagnetic (contain iron) that cannot be structurally analysed using NMR. It is highly sensitive to an element's local environment i.e., valence and coordination.

3.5.5.1.1 XAS Detection Modes

In transmission mode X-rays in the synchrotron pass by the monochromator, where the intensity (I_0) is measured inside an ionisation chamber utilising a grid covered in a thin metallic foil, that absorbs part of the photons or a photodiode (de Groot et al., 1997). The X-rays interact with the sample and the intensity produced is measured with a second ionization chamber or photodiode (de Groot et al., 1997).

Both total electron yield (TEY) and fluorescence yield (FY) detection modes are by-products of the absorption process and are commonly used to measure X-ray absorption (Achkar et al., 2011; Gudat & Kunz, 1972; Jaklevic et al., 1977). Both modes indirectly measure $\mu(E)$ and are used in the soft X-ray energy region between 2.1-6.0 KeV (Zheng et al., 2011). The absorption of X-rays causes the emission of electrons from the sample that are proportional to the absorption

coefficient from the photoelectrons and Auger electrons (Krause & Oliver, 1979; Reusch, 2020). The collection of these electrons is known as TEY (*Figure 31*) and is measured with electron multipliers (Krause & Oliver, 1979). FY is proportional to the absorption coefficient as valence electrons emit photons in order to fill core spaces left by said absorption (Reusch, 2020). *Table 22* is a summary table of key elemental K-edge values in accordance with literature.

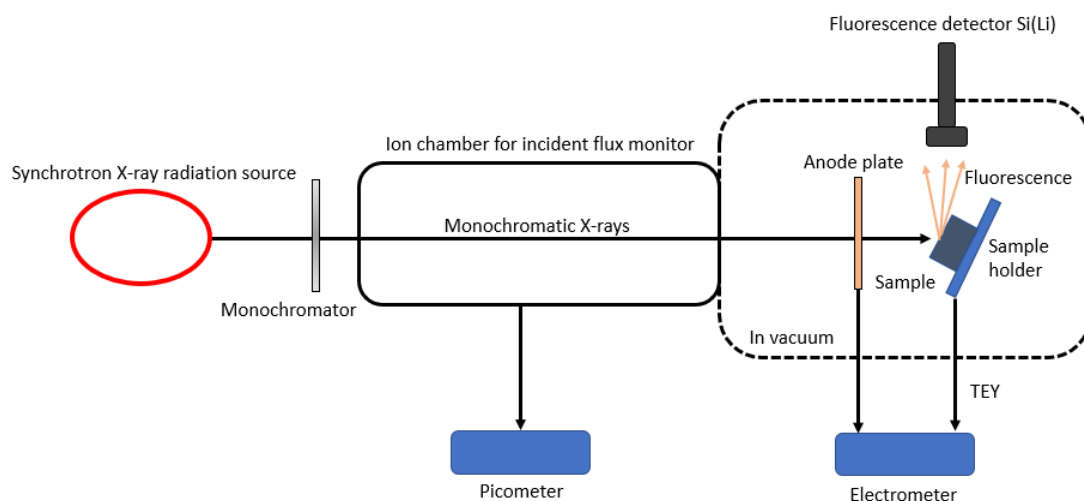


Figure 31 - Schematic diagram of TEY mode for XANES measurements based on (Zheng et al., 2011)

Element	K-edge (eV)	References
P	2130 – 2150	(Nicotra et al., 2016)
B	193.6 – 200	(Xu & Peak, 2007) (Fleet & Muthupari, 1999)
Si	1832.8 – 1842.8	(Moulton et al., 2018)
Na	1065 - 1125	(Neuville et al., 2004) (Henderson et al., 2014)
Ca	4020 - 4100	(Henderson et al., 2014)
Al	1545.8 – 1560.8	(Moulton et al., 2018)
O	514.3 – 524.3	(Moulton et al., 2018)
Fe	7112 - 7113	(Wilke et al., 2001)

Table 22 - Summary table of key elemental edge values based on literature

3.5.5.1.2 Fe K-edge

The redox chemistry of Fe shows that it can form oxidation states between Fe^{2+} to Fe^{6+} but is mostly found as ferrous Fe^{2+} and ferric Fe^{3+} . The Fe K absorption

edge is comprised of the following features (Berry et al., 2003): $1s \rightarrow 3d$ (pre-edge), $1s \rightarrow 4s$ (shoulder), and $1s \rightarrow 4p$ (edge crest).

The pre-edge region of the XAS spectra consists of $1s \rightarrow 3d$ energy transitions that are sensitive to the metal coordination number and symmetry, and is dependent on systems that have 3d holes caused by multiple splitting from electron-electron repulsion and ligand field effects (Budi et al., 2019). In order to estimate the Fe^{2+}/Fe^{3+} ratio the position of the centroid and integrated intensity of the pre-edge feature in Fe K-edge of Fe-bearing minerals can be used (Gaur & Shrivastava, 2015). The pre-edge shifts to higher energy with increasing $Fe^{3+}/\Sigma Fe$ (Berry et al., 2003). The reference spectra produced from Fe-bearing minerals help to determine the oxidation state and coordination number at the pre-edge feature. For example, Magnetite (Fe_3O_4) crystallises in an inverse spinel cubic structure, in which Fe^{2+} ions are on octahedral sites and the Fe^{3+} ions are equally divided between octahedral and tetrahedral sites (Berry et al., 2003; Okudera et al., 2012).

3.5.5.1.3 B18: Diamond XAS Beamline

The B18 beamline is an XAS spectrometer (Figure 32) built for general use on a variety of samples and to complement the more specialised I18 and I20 beamlines. The B18 beamline was built on a bending magnet and has an energy range (2-35 keV covering K-edges P to I and L_{III} -edges from Y to U) that will overlap with ranges from I18 and I20 (Dent et al., 2009). The beamline's optical design is based on three components: a collimating mirror, a fixed-exit double crystal monochromator, and a double toroidal focusing mirror (Dent et al., 2009). There is also a pair of harmonic rejection mirrors for low energy operations (Dent et al., 2009). The bending magnet source has a 3 mrad beam fan that allows the collection of two separate beam fans in a horizontal plane, each 0.9 mrad wide (Dent et al., 2009). The two beam fans follow different optical paths that are focused at 37.5 m from the source, resulting in an improvement in the stability and a reduction in the number of alignment operations needed (Dent et al., 2009). After the front-end, the white beam is collimated by a flat, cylindrical bent mirror at a fixed incidence angle of 2.3 mrad. This mirror is coated with two strips of Cr and Pt, one for each beamline branch. The monochromator is a bounce-down, double crystal fixed exit unit, hosting two directly water cooled flat crystal sets, (Si (111) and Si (311) cut) in a vacuum (Dent et al., 2009, 2013). The monochromator

Bragg axis operates between 6° to 70° and is driven by a water-cooled brushless DC motor, with a speed of 1 deg/s (Dent et al., 2009). This means that the beamline can acquire full QXAFS spectra in the full energy range of the monochromator, with acquisition times of a few seconds to several minutes, hence giving it a distinct advantage over older EXAFS set-ups that utilise step-scan acquisition strategies (Dent et al., 2013).

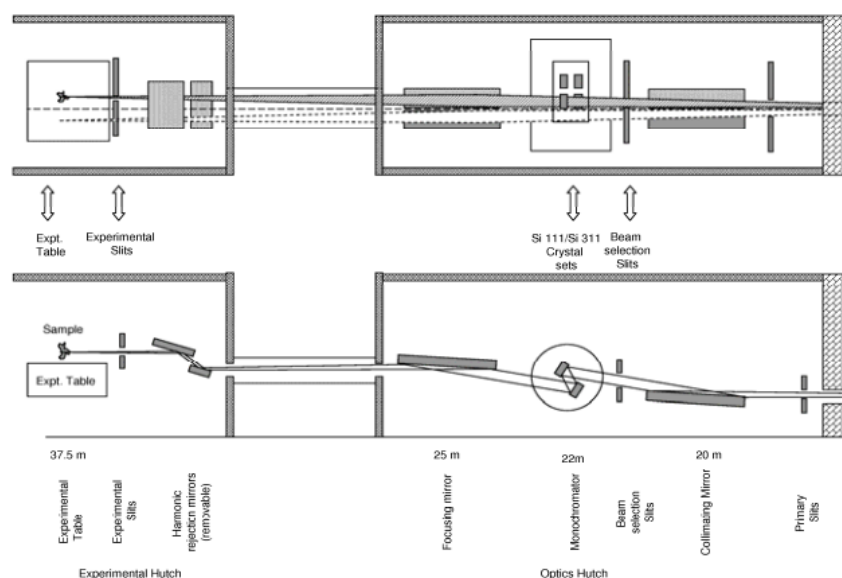


Figure 32 - B18 Optical lay-out taken from (Dent et al., 2013). Originally published in Journal of physics by IOP Under CC BY 4.0 licence. Available from: <https://doi.org/10.1088/1742-6596/190/1/012039>.

The ESRF XMaS BM28 beamline uses a copper micro-focus tube (Jarratt, 2021). The electron beam spot size is approximately $50 \mu\text{m}$, with an electron beam energy of 40 KeV. It is based on a bending magnet, where the X-ray source is located 2.7 m upstream (Jarratt, 2021). The source itself is a 0.86 Tesla short bend that provides more flux at higher energies (Jarratt, 2021). The optical configuration uses a Si (111) monochromator and a toroidal mirror in a 1:1 optical geometry (Jarratt, 2021). Downstream of the monochromator is the toroidal mirror that focuses the beam onto the sample (Jarratt, 2021). There are also two flat harmonic rejection mirrors and a phase retarder (Jarratt, 2021). In order to focus the beam, the toroidal mirror geometry has been kept the same, but the mirror coating and angles of incidence have been changed (Jarratt, 2021). The mirror coating material was changed to Pt for the higher X-ray energies; however, a second mirror needed to be introduced with a Cr coating to maintain a clean energy spectrum across the energy range 2.035 to 40 KeV (Jarratt, 2021). The

incident angle of the two mirrors is identical at 2.5 mrad, as this is the best compromise between the delivered flux for both the low and high energies (Jarratt, 2021).

3.5.5.2 Sample Preparation

Samples were prepared by milling glass in a tungsten carbide mill at 700 RPM for two minutes. 180 mg of sample and 30 mg of cellulose acetate were measured and mixed in a mortar and pestle, before being transferred to a 10 mm ejectable pellet die. The samples were pressed using 5 tonnes of force for two minutes in a Specac manual hydraulic press. Three pellets per sample were made alongside standards to measure the Fe K-edge. Table 23 and Table 24 summarise the XAS element specific edge energies and beamline specific parameters, respectively.

3.5.5.3 Instrumental Parameters

Element	Sample series	Energy range (eV)	K-edge (eV)	L ₁ -edge (eV)	L _{2,3} -edge (eV)	Notes
P	NBSP,		2130			Results were collected from B07 (Diamond)
	SCPD-HLW/LAW	75 - 200	– 4042	189	130 - 150	Data collected had poor resolution and could not be analysed
B	NBSP, SCPD-HLW/LAW	100 - 950	187	-	-	Samples did not run due to postal issues
Na	NBSP	950 - 1425	1071	620	750 - 760	Samples did not run due to postal issues
Fe	SCPD-HLW/LAW, ILAW	6962 - 7212	7112	844.6	706.8 – 719.9	Results were collected from BM28 (ESRF) and B18 (Diamond)

Table 23 - XAS element specific edge energies

Beamline	Samples measured	Mode	Parameters
B18 (Diamond)	SCPD-HLW	Fluorescence	Step size: 0.30 eV
	SCPD-LAW	Transmission	Sample angle: 45°
	ILAW		Energy range: 6900 – 8350 eV
BM28 (ESRF)	SCPD-HLW		Step size: 0.35 eV
	SCPD-LAW	Fluorescence	Sample angle: 45°
			Energy range: 7010 – 7300 eV

Table 24 - Beamline specific parameters

3.5.5.4 Analysis

3.5.5.4.1 Corrections and Data Processing

Prior to analysis of the data, it needs to be corrected in order to remove glitches and can include removal of the pre-edge background, self-absorption effects, and normalization of the edge jump to one (Henderson et al., 2014). The background of the edge under the pre-edge features needs to be removed by fitting a polynomial which reproduces a smooth slope prior to the pre-edge, e.g., a spline, Gaussian or Lorentzian function (Henderson et al., 2014). In order to reduce the XANES data correctly the data needs to be processed, as explained by Newville (2014) (correction steps are in Appendix 8.5).

3.5.6 Atom Probe Tomography (APT)

3.5.6.1 Theory

Atom Probe Tomography (APT) is a technique that provides a 3D elemental and isotropic analysis of a sample at the sub-nm resolution, where it chemically maps individual atoms in the X and Y axis, and models the Z axis (Reddy et al., 2020; Zhang et al., 2018).

An APT sample must be prepared by focus ion beam into a sharp needle with a tip radius of 50-100 nm, after which an electric field is concentrated and applied to the sample tip. APT is a destructive technique to the sample, where it produces a sample specific data set that combines time-of-flight mass spectrometry with nanoscale 3D spatial coordinates, producing a large atomic point cloud (Figure 33) (Reddy et al., 2020). The reconstruction algorithms assume the trajectory of the ions throughout the field evaporation process, however, the assumption is

one of the main sources of error as the material may contain phases that evaporate at different rates under the applied electric field (Fletcher et al., 2020). This non-uniform evaporation rate, assumed sample surface geometry, and altered trajectory taken by the evaporated field ion results in the distorted APT reconstructions observed as density fluctuations within the 2D ion positions and 3D reconstruction (Fletcher et al., 2020). APT was utilized to attempt to construct a 3D model of the onset of phase separation in the NBSP glass system (Appendix: Atom Probe Tomography).

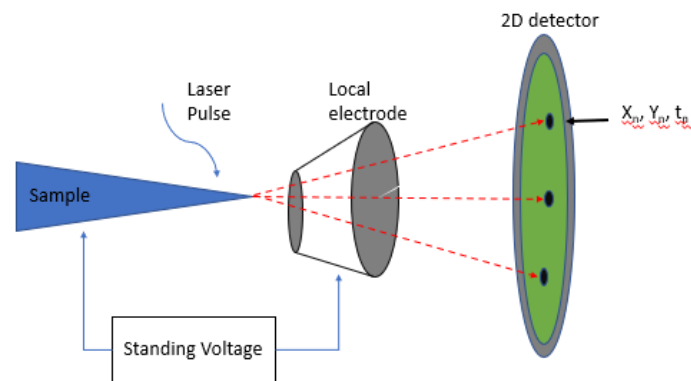


Figure 33 - Basic APT experimental setup

3.5.6.2 Sample Preparation

The samples were prepared by cutting a thin piece of glass from the bulk sample using a diamond saw to a thickness of ~ 1.0 mm with a length and width of ~ 5.0 mm. The sample was then ground using silicon carbide paper with grit sizes P120-P1200 and then polished using CeO_2 solution until a mirror finish was achieved. The sample was then coated in a thin layer of carbon and mounted onto an SEM stub using silver dag to ensure the sample was conductive. The samples were then sent to the University of Oxford to be prepared into their final form using a focus ion beam (FIB). This technique uses a Ga ion beam to cut the conical shape which is then extracted by a micromanipulator tool and positioned on individual Si microtip coupon posts, where the sample is then milled into a needle-shape geometry radius of ~ 50 - 100 nm (Figure 34) (Halpin et al., 2019).

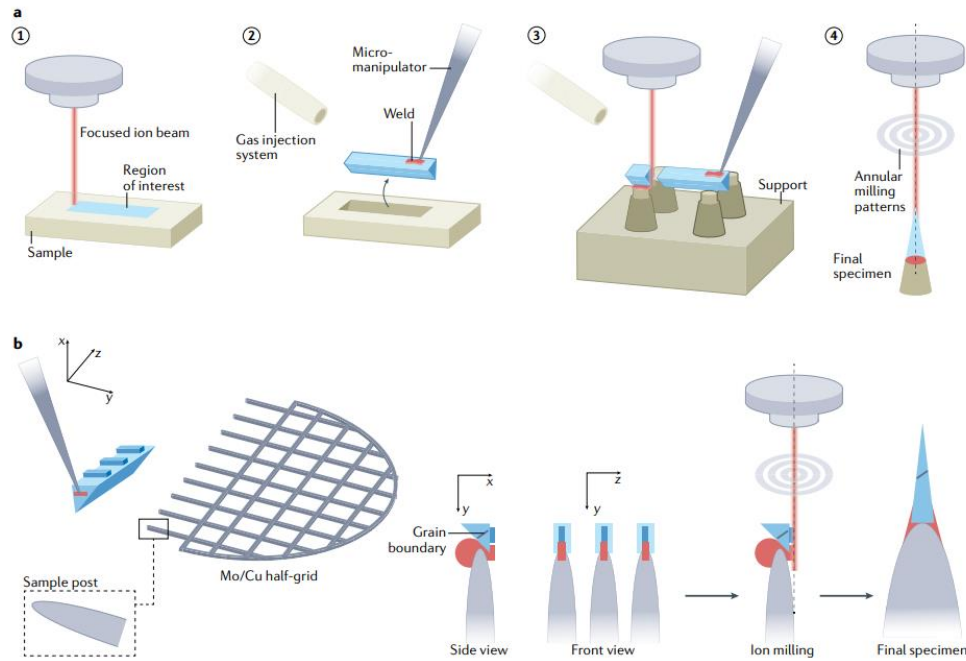


Figure 34 - Schematic on how an APT sample is prepared by APT taken from (Gault et al., 2021). with copyright permission from Spring Nature (License number: 5622030165026)

3.5.6.3 Experimental Parameters

APT and FIB were conducted at the University of Oxford by Prezema Klups and Dr Paul Bagot through the Henry Royce Institute and NNUF access schemes. The samples were prepared using a ZEISS Crossbeam 540 FIB and a CAMECA LEAP 5000 XR APT. APT was conducted at a temperature of 45K, with a pulse energy of 200 pJ, a pulse frequency of 200 Hz, and a detection rate of 0.20%.

3.5.6.4 Analysis

There were two main stages to the data processing and analysing of the APT data: (i) the 3D reconstruction of the sample using the chemistry and coordination of each atom recorded, and (ii) the extraction of useful information from the reconstructed image, e.g., identifying crystallisation, phase separation, and clustering (Zhang et al., 2018). The 3D reconstruction of the sample was created by Prezema Klups using the 3Depict software package. The 3D reconstructions, elemental atom maps, and proxygrams of isosurfaces (these can be found in Appendix 8.7) were then analysed with the assistance of Prezema Klups to identify real and imaginary features in the NBSP3.0 and 4.0 samples.

3.6 Thermal Characterisation

3.6.1 Differential Thermal Analysis (DTA)

3.6.1.1 Theory

Differential thermal analysis (DTA) is a thermal analysis technique where there are two cavities with attached thermocouples, which are often made from Pt. One cavity is filled with an inert standard, while the other holds the sample. The sample and inert reference sample are heated in a furnace at a specified rate of increasing temperature. The temperature difference between the thermocouples results in an increase in the thermal electromotive force proportional to the difference, producing an exothermic reaction with the inverse polarity of the electromagnetic force (e.m.f), resulting in an endothermic reaction. As a result, a thermogram is produced showing the thermal events the sample underwent, e.g., T_g and T_m (Herold & Plan Je, 1948; McConnel & Earley, 1951).

The T_g is a phenomenon that occurs in some crystalline and amorphous solids. When these solids are heated, melted, and quench cooled, instead of being allowed to crystallise they are instead converted into an amorphous solid that appears like a glass (Jadhav et al., 2009). The T_g is the temperature below which a solid stays in a glassy state and above which will go to a viscous liquid form (Jadhav et al., 2009). T_g can be determined from measurements of the temperature dependence of either the thermal expansion coefficient (CTE) or the heat capacity during the reheating of a glass (Shelby, 2005). T_{rg} is the reciprocal value of the reduced T_g , where $T_{rg} = T_g/T_m$, and is understood to be the measure of easiness by which a glass forms (Kozmidis-Petrović, 2010).

Glass stability (GS) is the resistance of a glass to devitrification upon heating (Kozmidis-Petrović, 2010). There are several parameters used to estimate this stability and are based on characteristic temperatures from when a glass is heated: T_g , T_x (onset temperature of crystallisation), T_c (maximum crystallization temperature), and T_m (melting temperature) (Kozmidis-Petrović, 2010). In order to quantitatively characterise the thermal stability and glass forming ability (GFA) two criterions can be used: the Hruby parameter (K_H) and a reduced glass transition temperature ($T_{rg} = T_g/T_m$), respectively (Sharda et al., 2017). The reduced glass transition temperature indicates the ease at which a glass forms, with the value of T_{rg} remaining constant and equal to 2/3 (Sharda et al., 2017).

Hruby parameter (K_H) is expressed as (Sharda et al., 2017):

$$K_H = \frac{T_c - T_g}{T_m - T_c} \quad (28)$$

Where $T_c - T_g$ is the nucleation process, $T_m - T_c$ is the Growth process, and K_{gl} is the Maximum thermal stability and glass forming ability.

However, it has been proposed by Jiusti et al. (2020) that the best glass stability parameter is the $K_w = (T_c - T_g) / T_m$ parameter, proposed by Weinberg, which includes a normalization of the ΔT_g (T_c) = $T_c - T_g$ by T_l (Jiusti, Cassar, et al., 2020; Kozmidis-Petrović, 2010). Larger values of the K_H and K_w implies a high thermal stability of the glass regarding devitrification. Angell (1995) proposed a classification scheme based on a glass-forming-liquid's fragility, which is a measure of how '*rapidly the relaxation dynamics of a material slow down upon approaching the T_g* ' (Ciarella et al, 2019). Glass-forming-liquids can be distinguished into three groups depending on the degree of fragility: strong glass formers, fragile glass formers, and intermediate glass formers (Biswas et al., 2006). "Strong" glass formers are when the relaxation-time growth near T_g obeys the Arrhenius law, whereas the relaxation time for "fragile" glass formers increases unexpectedly upon cooling (Ciarella et al, 2019).

3.6.1.2 Sample Preparation

The quenched NBSP solid samples with masses below 0.1000 grammes were heated up to 625°C and 1160 °C at a rate of 10°C/min, respectively on a SDT Q600 V20.9 build 20. The annealed NBSP, LAW, HLW, and ILAW samples with masses below 0.1000 grammes were heated up to 1150°C at a rate of 10°C/min on a TA Instruments SDT650 (Discovery Series - Serial Number 0650-0655), TRIOS Software (Version 5.3.0.4815).

3.6.1.3 Analysis

The DTA traces produced were initially analysed using the SDT Q600 V20.9 build 20 analysis software to establish the T_g onset. The exported raw data was then processed in Microsoft Excel and then analysed and plotted in the OriginPro software. The traces were used to establish the first derivative to establish the T_g onset and midpoint, as well as the T_c and T_m .

3.6.1.4 Dilatometry

3.6.1.4.1 Theory

Dilatometry is a thermal analysis technique and is used to measure volume changes (Rocha et al., 2009). A connecting rod dilatometer uses a furnace and transfers the thermal expansion to a strain gauge, which measures the change (Figure 35) (Rocha et al., 2009). The rod itself is exposed to the same temperature as the sample and expands, hence this change needs to be considered in the results (Rocha et al., 2009). Dilatometry can be used to determine the T_g onset and midpoint, softening temperature (T_d) and the thermal expansion. Thermal expansion is where there is a change in the matter's volume in response to temperature changes (Rocha et al., 2009). The ratio between this expansion and the change in temperature is called the linear coefficient of thermal expansion (CTE) (Ding et al., 2020; Rocha et al., 2009). Volume expansion occurs when the energy stored between the atoms of a solid sample begin to change with temperature. As the stored energy increases the distance between the atoms increases and a volume expansion occurs in the sample (Rocha et al., 2009). There are different coefficients of thermal expansion and they can be defined as the following (Rocha et al., 2009):

Linear thermal expansion:
$$\alpha_L = \frac{1}{L_0} \left(\frac{\partial L}{\partial T} \right) \quad (29)$$

Area thermal expansion:
$$\alpha_A = \frac{1}{A_0} \left(\frac{\partial A}{\partial T} \right) \quad (30)$$

Volumetric thermal expansion:
$$\alpha_L = \frac{1}{V_0} \left(\frac{\partial V}{\partial T} \right) = \frac{1}{\rho_0} \left(\frac{\partial \rho}{\partial T} \right) \quad (31)$$

Where L_0 , A_0 , V_0 , ρ_0 , T correspond to the length, area, volume, density, and temperature of the sample, respectively. For isotropic materials: $\alpha_A = 2\alpha_L$ and $3\alpha_v = 3\alpha_L$.

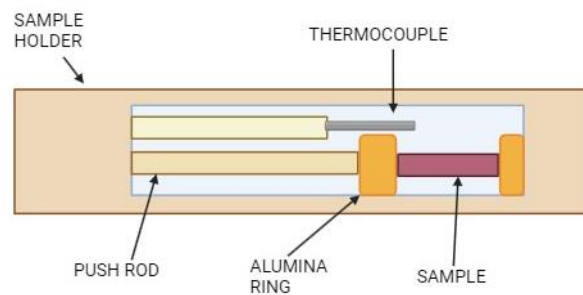


Figure 35 - Push rod dilatometer set-up

3.6.1.5 Sample Preparation

The samples are cut into a monolith with dimensions 5.00 x 5.00 x 25.00 mm using a diamond saw and then are ground using grit sizes of P80, P120 and P240.

3.6.1.6 Analysis

The samples were heated up to 800°C at a rate of 10°C/min using the NETZSCH DIL 402SE dilatometer. The raw data was initially analysed by the NETZSCH Proteus software to establish the T_g , CTE and T_c . The raw data was then analysed further to establish the aforementioned parameters as well as the T_g onset and midpoint with better accuracy using the OriginPro software.

3.7 Rheological Characterisation

3.7.1 High Temperature Viscosity (HTV)

3.7.1.1 Theory

Viscosity is a material property used to measure a fluids resistance to flow (Wedgewood, 2019). Viscosity of liquids is determined by the collision of particles and the force fields which determines the molecule interactions (Messaâdi et al., 2015). There are two types of viscosity: (i) shear flow and the (ii) extensional flow (Malvern, 2016). Shear flow is when the fluid components shear past one another, whilst extensional flow is where the fluid components flow away from another or towards each other (Malvern, 2016). HTV is the experimental technique used to determine the rheological properties of a material, and is defined as the analysis of flow and deformation of the material through the interrelationship between deformation, force, and time (Malvern, 2016).

There are several theories for estimating viscosity (Messaâdi et al., 2015), among which there is the distribution function theory proposed by Kirkwood et al. (1950), the molecular dynamic approach as reported by Cummings and Evans (1992), and the reaction rate theory by Eyring (1935). Data in literature has shown that liquid viscosity decreases with absolute temperature in a non-linear and concave manner when empirical and semi empirical methods are used near or above the boiling temperature (Messaâdi et al., 2015).

3.7.1.1.1 Newton's Law of Viscosity

Newton's law of viscosity defines what the relationship is between the shear stress and shear rate of a fluid experiencing mechanical stress (George & Qureshi, 2013). The ratio of the shear stress to shear rate is constant for a given pressure and temperature, and is defined as the coefficient of viscosity or simply viscosity (George & Qureshi, 2013). Viscosity can be calculated from the following equation (Eq 32) (Ślęzak, 2015):

$$\text{Viscosity (Pa.s)} = \frac{\text{Shear stress}}{\text{Shear rate}} = \frac{\tau}{\dot{\gamma}} \quad (32)$$

A Newtonian fluid can be characterised by the linear relationship between the applied shear stress and rate of shear, demonstrated in the following equation (Eq 33) (Chhabra, 2010):

$$\sigma_{yx} = \frac{F}{A} = \eta \dot{\gamma}_{yx} \quad (33)$$

Non-Newtonian behaviour can be grouped into three main categories:

1. Systems where the value of $\dot{\gamma}$ at a certain point within the fluid is determined by the current value of σ : these substances are known as purely viscous, generalised Newtonian fluids (GNF) or time-dependant (Chhabra, 2010).
2. Systems where the relationship between σ and $\dot{\gamma}$ show further dependence on the duration of shearing and the kinematic history are known as time-dependant-fluids (Chhabra, 2010).
3. Systems that exhibit a mixture of viscous fluid behaviour and of an elastic solid-like behaviour, for example a class of materials that show partial elastic recovery, creep recoil etc. These are called visco-elastic or elastic-viscous fluids (Chhabra, 2010).

3.7.1.1.2 Fragility

By plotting viscosity in the logarithmic scale against the T_g/T , liquids can be classified into fragile and strong glasses (Bellissard & Egami, 2018), as suggested by Angell (1996). In a strong glass e.g., a silica glass, the Arrhenius temperature dependence goes above the T_g up to very high temperatures, showing nearly Arrhenius-type behaviour in the transverse T_g ($1/T_g$), which is

defined as 10^{12} P.s (Bellissard & Egami, 2018; Huang & McKenna, 2001). Angell plots have become a common method for representing the temperature dependence of viscosity (Huang & McKenna, 2001).

The non-Arrhenius version of fragility is expressed in terms of the Vogel-Tammann-Fulcher (VTF) equation (Eq 34) (Huang & McKenna, 2001):

$$\tau(T) = \tau_0 \exp [B / (T - T_\infty)] \quad (34)$$

Where τ_0 , B and T_∞ are positive constants.

The definition of fragility is the gradient of the viscosity curve at the T_g on a reduced temperature scale. Fragility can be calculated by differentiating the VTF equation (Eq 35), where T is the absolute temperature (Huang & McKenna, 2001; Toplis et al., 1997):

$$\text{Fragility} = m = \left. \frac{d(\log_{10} \dot{\eta})}{d(T_g / T)} \right|_{T=T_g} = \frac{B_{TVF}}{T_g (1 - C_{TVF} / T_g)^2} \quad (35)$$

A low m value generally implies a broader T_g range, whereas a high m value often indicates super Arrhenius behaviour associated with “fragile” glass formers (Ciarella et al, 2019).

3.7.2 Sample Preparation

The Rheometer used pre-air quenched glasses that were then crushed into small pieces.

3.7.2.1 Analysis

The Rheology of the glass melts used quenched glass samples using an Anton Paar modular compact rheometer, MCR 502. Viscosity values were collected at four different temperatures to build a profile, $8.18\text{E-}04$ (1/T) K, $7.5\text{E-}04$ (1/T) K, $7.03\text{E-}04$ (1/T) K, and $6.5\text{E-}04$ (1/T) K. The shear rate vs shear stress plots were produced by a MATLAB script developed by Dr Jaime George using the rheology raw data. The viscosity data was then plotted in the OriginPro software.

3.8 Chemical Characterisation

3.8.1 Chemical Durability via Product Consistency Test Method B

3.8.1.1 Theory

One of the most important issues facing the safe disposal of vitrified nuclear waste, is the corrosion of the glass by groundwater or meteoric water in long-term storage over geological time scales (up to 10^6 years) (Geisler et al., 2015). When glass comes into contact with flowing or stagnant groundwater, then corrosive gases, vapours, or aqueous solutions can form as a result of chemical reactions occurring at the glass-water interface, which is dependent on the glass composition, pH of the solution, and temperature of the surrounding environment (Jain, 2012). The chemical durability of nuclear waste glasses is an important parameter in understanding two aspects: (i) the ability to predict glass durability in order to produce glasses that meet specific leaching criteria, and (i) the ability to predict long-term ($>10,000$ years) dissolution behaviour of the glasses (Jain, 2012). In most studies investigating glass break down by aqueous solution, a nano- to micro-porous corrosion layer forms on the surface of the glass, which has the potential to affect the long-term reactivity of the glass (Geisler et al., 2015).

The leaching behaviour of glass can be described by a model, wherein by a glass sees an infinite supply of water under-saturated in dissolution products and the mass loss is kinetically limited by the maximum rate which is determined by the hydrolytic destruction of the glass network (Chick & Turcotte, 1983).

3.8.1.1.1 Product Consistency Test (PCT)

Product consistency test (PCT) is a method used to measure the chemical durability of homogeneous, phase separated, vitrified, glass-ceramic glasses and waste forms, or combinations thereof, by measuring the concentrations of species in the test solution under certain controlled conditions (ASTM International, 2021). There are two variations of PCT, A and B, where PCT-A consists of a 7-day test at 90°C , with specific conditions for the particle size distribution, test vessel material, and leachant composition (Backhouse, 2018). Whilst PCT-B allows for variation in the temperature, particle size distribution, vessel material, and duration (Backhouse, 2018). In this thesis, PCT-B was used

on the SCPD-HLW, SCPD-LAW and ILAW simulant series, in accordance with ASTM C225-85 standard.

3.8.1.2 Sample Preparation

The samples were first crushed and then milled using a tungsten carbide mill forming a powder. The powder was then sieved using mesh sizes -100 to +200 to obtain the particle size between 75 and 150 μm . Then 20 g of powder was taken to be cleaned using ethanol to dissolve any secondary phases, before being placed in a beaker to be further washed using ~50 ml of DI water in an ultrasonic cleaner. This was performed twice before the water was decanted. Ethanol was then added to the beaker and the sample before it was placed in the ultrasonic cleaner again for a further two minutes, after which the ethanol was decanted. The beaker with the cleaned glass was then placed into a drying oven at $90 \pm 10^\circ\text{C}$ to dry overnight. The dried powders were then placed in a HDPE vessel with 20ml of DI water and placed in a drying oven at $90 \pm 10^\circ\text{C}$ for 7 days, along with a blank sample. Once the vessels were removed and cooled to ambient temperature, they were weighed to establish the weight loss, with $\geq 5\%$ mass loss meaning the vessel was invalid. The leachate pH was tested three times per vessel to establish an average, where the final value was recorded before adding HNO_3 to prevent hydrolysis of heavy metal cations. The acidified leachate solution was then drawn for cation analysis using ICP-OES. The glass powder was dried in an oven at $90 \pm 10^\circ\text{C}$ to dry overnight before being analysed by XRD to identify secondary precipitates. These procedure were conducted in accordance to ASTM C225-85 standard (ASTM International, 2021).

3.8.1.3 ICP

3.8.1.3.1 Analysis

The normalised concentration of the solution and normalised elemental mass loss are calculated using the procedure and equations stipulated in the ASTM C1285 -14 (ASTM International, 2021).

3.8.1.4 Dissolution Rate Calculations

Standard deviation of the blank concentrations:

$$\sqrt{\frac{\sum (c_i(l) - c_i(blank))^2}{m}} \quad (36)$$

Where S is the standard deviation of the blank concentrations, $C_i(\text{blank})$ is the average blank concentration, g/L , $C_i(i)$ is the concentration observed in the i^{th} blank, and m is the number of replicate blank vessels.

$$\text{Corrected leachate concentration: } c_i(\text{sample}) = \left(\frac{c_i(n) \cdot V_f(n)}{v_i(n)} \right) - c_i(\text{blank}) \quad (37)$$

Where $C_i(n)$ is the observed concentration in the test with the n^{th} sample, g/L , $V_f(n)$ is the final volume of leachate measured in the test with n^{th} sample replicate, L , $V_i(n)$ is the Initial volume of leachate in the test with N^{th} sample replicate, and $C_i(\text{blank})$ is the average blank concentration, g/L .

$$\text{Normalised concentration: } NC_i = \frac{C_i(\text{sample})}{f_i} \quad (38)$$

Where NC_i is the normalised concentration, g/L , $NC_i(\text{sample})$ is the concentration of element “I” in the solution from the test sample, g/L , and f_i is the mass fraction of element “I” in the unleached sample, g/g_{glass} .

$$\text{Normalised elemental mass loss: } NL_i = \frac{C_i(\text{sample})}{(f) \cdot \left(\frac{SA}{v} \right)} \quad \text{or} \quad NL_i = \frac{NC_i}{\left(\frac{SA}{v} \right)} \quad (39)$$

Where NL_i is the Normalised elemental mass loss, $g_{\text{wasteform}}/m^2$, $C_i(\text{sample})$ is the concentration of element “I” in solution, g/L , f_i is the Mass fraction of element “I” in the unleached samples, g/g_{glass} , and SA/V is the surface area divided by the leachate volume, m^2/L .

3.9 Physiochemical Characterisation

3.9.1 Density and Molar Volume

3.9.1.1 Theory

Density is a physical characteristic of a material and is the value equal to the ratio between the mass of substance to its volume and is measured in g/cm^3 . Relative density is a value that is calculated from the ratio between the substance of interest and a reference substance (Varshneya, 2013). Measuring the density of glass is most commonly achieved by weighing the selected piece of glass in air and then dividing this weight by the buoyancy when suspended in water (Varshneya, 2013). The buoyancy, according to the Archimedes’ principle, equals the weight of the displaced liquid, which if it is water, equals the volume (Varshneya, 2013). Hence, if ω_a is the weight of the specimen in air, and ω_b is the weight of the specimen in water, then the buoyancy is $\omega_a - \omega_b$ and the density is

$\rho = \omega_a / (\omega_a - \omega_b)$ (Varshneya, 2013). The standard test method using buoyancy to measure density is described in the ASTM C693-93 (Figure 36). Density of glasses is sensitive to the composition and can increase with the addition of network modifying cations, (lightest) $\text{Li} < \text{Na} < \text{K} < \text{Rb} < \text{Cs} < \text{Ag} < \text{Ti}$ (Heaviest) (Varshneya, 2013). The density of a glass can be calculated according to ASTM C693-93 (Appendix 8.4).

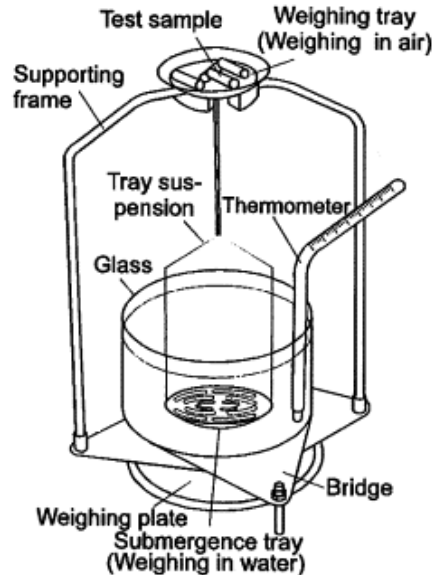


Figure 36 - Density Buoyancy example diagram taken from (Rabier et al., 2006). with copyright permission from Elsevier (License number: 5624850136615)

The density can then be used to calculate the molar volume and atomic packing factor. The molar volume (Eq 40) is the volume occupied by one mole of an element or chemical compound and is calculated by dividing the molar mass by the density (Chanshetti et al., 2011). The atomic packing factor (Eq 41) is calculated by multiplying the volume of atoms in a unit cell by the volume of a unit cell, where packing is assumed to be by hard spheres (Xu et al., 2020).

$$V_m = \text{Molar mass of sample (M)} / \text{Density } (\rho) \quad (40)$$

$$\text{APF} = \text{volume of atoms in unit cell} / \text{Volume of unit cell} \quad (41)$$

The theoretical density can be calculated using the following equation (Eq 42):

$$\text{Density } (\rho) = nA / V_c N_A \quad (42)$$

Where n is the atoms per unit cell, A is the atomic weight (g/mol), V_c is the Volume per unit cell ($\text{cm}^3/\text{unit cell}$), and N_A is Avogadro's constant (6.023×10^{23} atoms/mol).

3.9.2 Sample Preparation

There is no sample preparation needed for this technique, where the only parameter is that the sample is solid, non-porous, and does not dissolve in water.

3.9.3 Analysis

The sample density is taken independently three times to calculate an average density value. The molar mass (M) is calculated by multiplying the molecular mass of the glass and multiplying it by the amount of moles in the glass and dividing it by 100.

Chapter 4: Results

4.1 NBSP Glass Series

4.1.1 Introduction

This glass series is a simplification of Hanford radioactive waste glasses as the original compositions were far too complicated, with many components, to allow any meaningful structural analysis, e.g., by Raman spectroscopy. To understand the effects that P_2O_5 has on an alkaline borosilicate glass, a simple glass system was needed, hence sodium borosilicate was selected. The NBSP glasses have a constant molar concentration between $Na_2O:B_2O_3:SiO_2$ with varying P_2O_5 content and were characterised in order to determine the effects of P_2O_5 on the compositional, thermal, rheological, physio-chemical, and structural properties. The undoped base glass had the nominal composition $27.9Na_2O-16.3B_2O_3-55.8SiO_2$, which lays outside the immiscibility region in the $Na_2O-B_2O_3-SiO_2$ ternary phase diagram.

4.1.2 Experimental Procedures

Seven sodium borosilicate glasses were prepared, with a P_2O_5 undoped base glass and corresponding incrementally P_2O_5 doped samples (Table 25). 100 g batches of the NBSP glasses were prepared by using the melting-annealing and melting-quenching methods using the precursors of SiO_2 , Na_2CO_3 , H_3BO_3 , and $NH_4H_2PO_4$. The precursors were weighed and transferred to a plastic tub that was thoroughly shaken to mix the contents, before being milled in an agate mill for one minute to achieve a homogenous mixture. The mixture was then placed in a 90%Pt-10%Rh crucible and heated in an electric furnace at $1150^{\circ}C$ for one hour, after which part of the melt was air quenched on a steel plate and left to cool to room temperature. The remainder of the melt was cast into a steel mould on a heated hot plate before being placed in an annealing furnace at $500^{\circ}C$ for one hour with a cooling rate of $1^{\circ}C/min$ to $25^{\circ}C$.

The samples were characterised for their bulk density, whilst the composition was analysed using XRF, SEM/EDS, and XRD as described in *Chapter 3: Experimental Methodology*. XRD patterns were recorded using two machines: (i) $CuK\alpha$ radiation on a Bruker D8 Advance diffractometer with step size of $0.015^{\circ}2\theta$; scan step time of 177 seconds; and were measured between 5° -

70°2 Θ . (ii) CuK α radiation on an X-PERT PRO diffractometer and a PIXCEL-1D area detector with step size of 0.0131°2 Θ ; scan step time of 448.855 seconds; and were measured between 5°-80°2 Θ . The XRD patterns were then analysed using HighScore Plus. The sample's thermal characteristics were measured using DTA and dilatometry, the rheological properties were measured in terms of its HTV, and structure was measured using Raman and MAS-NMR spectroscopy.

4.1.3 Results and Discussion

4.1.3.1 Visual Observations

The sample glasses (Figure 37) obtained after annealing resulted in bubbly, transparent, relatively homogeneous glasses with an amorphous structure as confirmed by XRD (Figure 40). However, increasing P₂O₅ content led to a decrease in the glass-forming abilities of the material, resulting in visually opaque samples (Figure 37 and Figure 38). Figure 38 does illustrate that the sample was not homogeneous due to the presence of opalescence in only part of the sample and not its entirety and may indicate heterogeneity in the glass composition or a temperature gradient during annealing. Phase separation occurred visually at a macroscopic scale as opalescence above 4.0 mol% P₂O₅, which gives the impression of a bluish and creamy-white colour (Figure 37 and Figure 38). The occurrence of opalescence is due to the presence of one or more secondary phases with a different refractive index to the bulk glass matrix, and as a result they act as scattering centres (Lui et al., 2012). Opalescence often occurs as a bluish colour because the Rayleigh scattering associated with the size of the crystalline particles is smaller than or similar to the minimum wavelength of visible light (Lui et al., 2012). Table 25 and Figure 39 present the nominal and analysed composition of the annealed and quenched NBSP samples, as measured by XRF.



Figure 37 - Annealed NBSP glass samples (0.0 (left) to 6.0 (right) mol (%) P_2O_5) with a ruler to act as a scale marker and visual guide of the level of opalescence in the samples

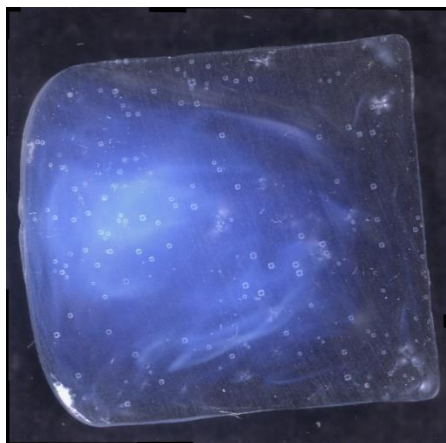


Figure 38 - Cross-section optical image of NBSP6.0 at x50 to illustrate opalescence

4.1.3.2 XRF

Table 25 contains the nominal, and XRF and ICP-OES analysed compositions of the annealed and quenched glass samples. While both sets of glasses have come from the same melt, it can be seen that there is a deviation in the contents of SiO_2 , Na_2O , and P_2O_5 , indicating that the melts had a degree of inhomogeneity. However, the analysis of the quenched samples was done as a precaution to better inform the effects of thermal treatment and resulting crystallisation behaviour.

Figure 39 plots the XRF and ICP-OES analysis results for the annealed samples, where the associated uncertainties are recorded in Table 25. ICP-OES was only used to measure the boron content of the annealed NBSP0.0, 3.0 and 4.0, due to equipment and time restraints, as they were the samples where the solubility limit was determined to be between. The analysed SiO_2 , Na_2O , and P_2O_5 contents varied between 50.7 and 57.4 mol%, 25.2 and 28.0

mol%, and 0.0 and 6.5 mol%, respectively. When compared to the nominal composition the SiO₂ content of NBSP0.0 and 5.0 were comparable within error, whereas NBSP1.0 and 2.0 were slightly higher, and NBSP3.0, 4.0, 5.5, and 6.0 were slightly lower. The Na₂O content of NBSP0.0, 1.0, 2.0, 3.0, 4.0, 5.0, and 6.0 were comparable to the nominal composition within error, whereas NBSP5.5 was higher by 3.44 mol%. The P₂O₅ content of NBSP1.0, 2.0, 3.0, 4.0, 5.0, and 5.5 were all comparable with the nominal composition within error, but the NBSP6.0 sample was slightly elevated by 0.5 mol%. The differences in measured concentration of XRF analysed components may be a result of the heat treatment of the glass, which part of the cooled glass melt was poured and analysed, i.e., from the top, middle or bottom of the crucible, or any uncertainties associated with preparation and analysis by XRF. Other sources of error may be due to the volatilisation of P₂O₅ and Na₂O during melting, the section of the sample used for the XRF fused bead, where samples with >3.0 mol% P₂O₅ presented evidence of phase separation and crystallisation, meaning the composition was not homogeneous throughout the sample. Another potential cause for fluctuations in the composition may be due to contamination from sample preparation.

The ICP-OES analysed B₂O₃ content of the NBSP0.0, 3.0, and 4.0 samples had a concentration of 16.3 ±0.01, 19.2 ±0.01, and 15.9 ±0.01 mol%, respectively. The NBSP0.0 content was comparable with the nominal content within error, whereas the NBSP3.0 sample was significantly higher by 3.41 mol%, where this may have been subject to contamination. The NBSP4.0 was marginally higher than the nominal content by 0.27 mol%. The variations in the B₂O₃ content of the samples measured by ICP-OES may be due to the sample not being homogeneous, where the sample used had a variation in composition to another section. Another source of uncertainty may be related to the ICP-OES technique, where signal drift, spectral interferences, or the inaccurate signal identification may affect the results.

Table 25 - Nominal vs. analysed glass compositions with associated errors

Oxides		Sample							
		NBSP0.0	NBSP1.0	NBSP2.0	NBSP3.0	NBSP4.0	NBSP5.0	NBSP5.5	NBSP6.0
Na₂O	Nominal (mol%)	27.91	27.63	27.35	27.07	26.79	26.51	24.56	26.23
	Analysed								
	Annealed by XRD (mol%)	28.2 ± 0.01	25.2 ± 0.01	26.7 ± 0.01	26.4 ± 0.01	27.53 ± 0.01	25.9 ± 0.01	28.0 ± 0.01	27.4 ± 0.02
	Analysed								
	Quenched by XRD (mol%)	28.4 ± 0.01	28.3 ± 0.01	27.7 ± 0.01	27.5 ± 0.01	27.2 ± 0.01	27.9 ± 0.01	28.1 ± 0.01	27.1 ± 0.01
B₂O₃	Nominal (mol%)	16.28	16.12	15.95	15.79	15.63	15.47	15.38	15.3
	Analysed								
	Annealed by ICP-OES (mol%)	16.3 ± 0.01	-	-	19.2 ± 0.01	15.9 ± 0.01	-	-	-
SiO₂	Nominal (mol%)	55.81	55.26	54.7	54.14	53.58	53.02	52.74	52.47

P₂O₅	Analysed								
	Annealed	55.5 ± 0.01	57.7 ±	55.2 ±	51.6 ±	52.5 ±	53.9 ±	50.9 ±	50.7 ±
	by XRD		0.01	0.01	0.01	0.01	0.01	0.01	0.01
	(mol%)								
	Analysed								
	Quenched	55.4 ± 0.01	54.6 ±	54.3 ±	53.7 ±	53.0 ±	51.5 ±	51.0 ±	52.0 ±
	by XRD		0.5	0.01	0.01	0.01	0.01	0.01	0.01
	(mol%)								
P₂O₅	Nominal	0.0	1	2	3	4	5	5.5	6
	(mol%)								
	Analysed								
	Annealed	0.0	1.0 ±	2.1 ±	2.7 ±	4.0 ±	4.9 ±	5.7 ±	6.5 ±
	by XRD		0.02	0.02	0.02	0.01	0.01	0.01	0.01
	(mol%)								
P₂O₅	Analysed								
	Quenched	0.0	1.1 ±	2.1 ±	3.0 ±	4.2 ±	5.2 ±	5.6 ±	6.2 ±
	by XRD		0.02	0.02	0.02	0.01	0.01	0.01	0.01
	(mol%)								

* B₂O₃ nominal values used, due to boron being undetected by the XRF spectrometer used, except for NBSP0.0, 3.0, and 4.0 for which ICP-OES analyses were used.

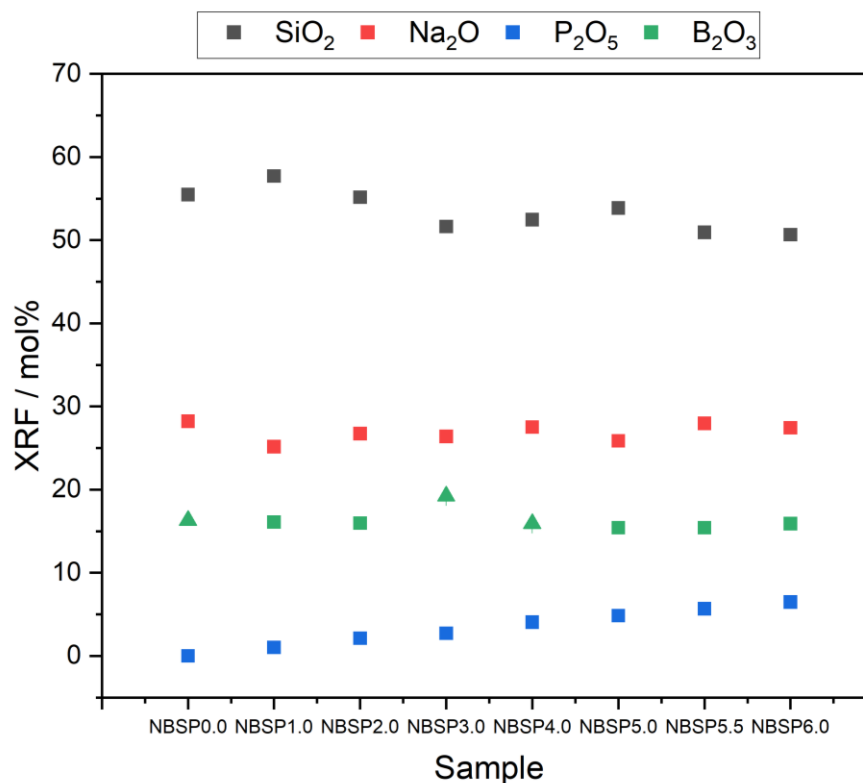


Figure 39 - Graphical representation of XRF results for annealed NBSP samples, where triangle markers represent B₂O₃ analysed by ICP-OES, where associated errors can be found in Table 25. Where error bars are present but are too small to be plotted.

4.1.3.3 X-Ray Powder Diffraction

4.1.3.3.1 Annealed

Figure 40 shows that samples NBSP0.0, 1.0, 2.0 and 3.0 were X-ray amorphous with no measurable crystallinity, whilst samples NBSP4.0, 5.0, 5.5 and 6.0 had measurable Bragg reflections and identifiable crystalline phases present within the amorphous material. Sample NBSP4.0 exhibited the crystalline phase sodium phosphate (Na₃PO₄, PDF#: 01-071-1918); sample NBSP5.0 had sodium phosphate (Na₃PO₄; PDF#: 01-071-1918) and (Na₄P₂O₇; PDF#: 01-073-5982); sample NBSP5.5 had sodium phosphate (Na₃PO₄; PDF#: 01-071-1918), (Na₄P₂O₇; PDF#: 01-073-5982) and cristobalite (SiO₂; PDF#: 01-074-9378); and sample NBSP6.0 had sodium phosphate (Na₃PO₄; PDF#: 01-071-1918) and (Na₄P₂O₇; PDF#: 01-073-5982). The crystal structure of the Na₃PO₄ was face centred cubic (fcc), where the phosphorus sites are fully occupied while the sodium and oxygen sites are only partially filled. The Na₄P₂O₇ possesses an orthorhombic crystal

structure where all its sites are fully occupied. The identification of a strong Bragg peak at $\sim 22^\circ 2\theta$ in NBSP5.5 was tentatively attributed to SiO_2 (visually verified) (cristobalite, PDF#: 01-074-9378).

As the P_2O_5 content of the samples increased, the glasses became increasingly crystalline, with a change in the nature of the phosphate phases present. At a lower P_2O_5 concentration there were orthophosphate Q_P^0 species, $[\text{PO}_4]^{3-}$, as indicated by the Na_3PO_4 phase in the NBSP4.0 sample. In sample NBSP5.0-6.0 there were Na_3PO_4 and $\text{Na}_4\text{P}_2\text{O}_7$ present, which introduced Q_P^1 pyrophosphate anions, $[\text{P}_2\text{O}_7]^{4-}$. However, the characteristic Bragg peaks associated with $\text{Na}_4\text{P}_2\text{O}_7$ occurred alongside Na_3PO_4 , increasing in relative intensity with increasing P_2O_5 content. The crystallisation of Na_3PO_4 and $\text{Na}_4\text{P}_2\text{O}_7$ is consistent with results for other relevant glasses in which Na_2O is present at high levels (> 20 mol%) (Achigar et al., 2021; Muñoz et al., 2008). Therefore, as the P_2O_5 content increases, the ratio of PO_4^{3-} to $\text{P}_2\text{O}_7^{4-}$ anions changes in favour of the pyrophosphate cations ($\text{P}_2\text{O}_7^{4-}$). However, this increase means that more Na^+ ions are needed to charge compensate the P^{5+} anions, resulting in the increase in the ratio of 3-coordinated boron ($^{[3]}\text{B}$) to 4-coordinated boron ($^{[4]}\text{B}$), and subsequent increase in the degree of polymerization of the silicate network through the conversion of $\text{NB}\emptyset\text{s}$ to $\text{B}\emptyset\text{s}$ (Krishnamurthy et al., 2020; Muñoz et al., 2008; Wang & Cheng, 2016). If this were the case, T_g could be expected to change. The transition of orthophosphate to pyrophosphate with increasing P_2O_5 content is, therefore, due to the clustering observed as the sodium phosphate crystal phases where the ratio of orthophosphate to pyrophosphate increased with increasing P_2O_5 content; this was the case in both the quenched and annealed glasses.

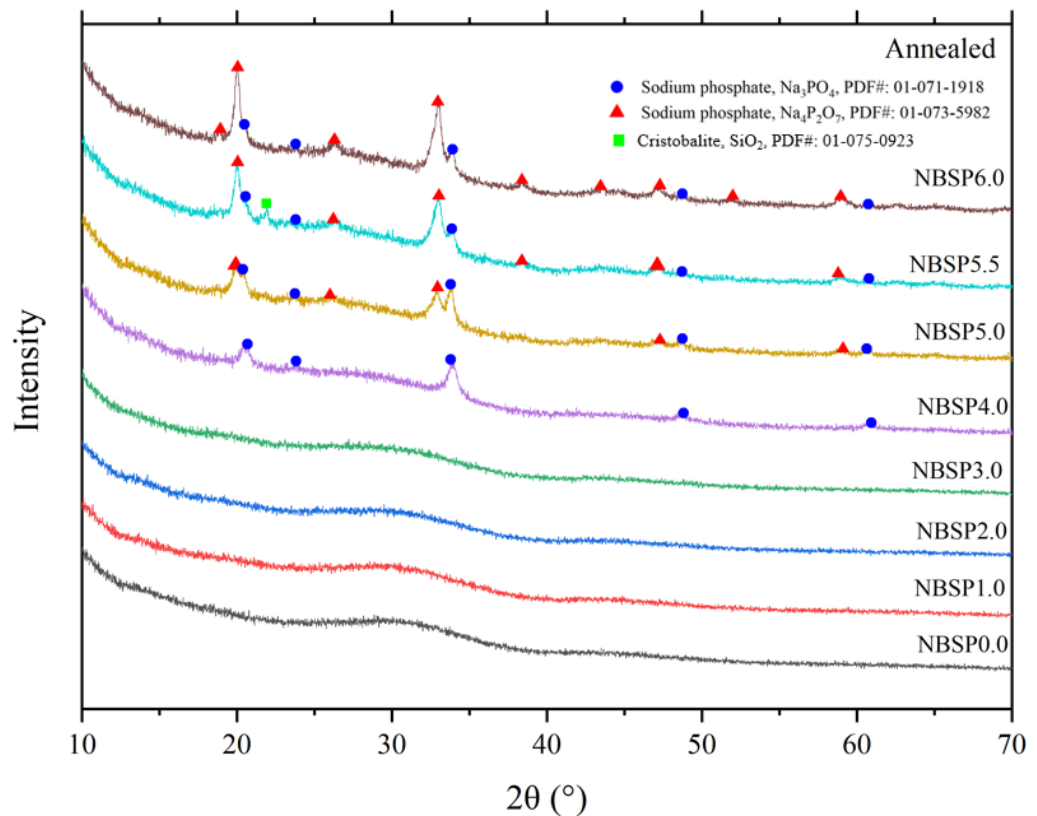


Figure 40 - XRD patterns of annealed NBSP glass samples with identified crystalline phases

4.1.3.3.1.1 Rietveld Analysis

As seen in the XRD patterns (Figure 40), as the P_2O_5 content increased, the quantity of crystalline material increased in the samples. Figure 41 showed that between 0.0 and 3.0 mol% P_2O_5 , the samples were 100 wt% X-ray amorphous, however, upon the addition of 4.0 mol% P_2O_5 there was the presence of approximately 12.4 wt% Na_3PO_4 (PDF#: 00-031-1318; space group: Fm-3m (Palazzi et al., 1971)). Further additions of P_2O_5 saw a reduction in the Na_3PO_4 content (13.16 to 2.13 wt%) and subsequent occurrence and increase in $Na_4P_2O_7$ (PDF#: 04-018-4331; space group: P212121 (Leung & Calvo, 1972)) between 0.0-23.31 wt%, and an overall reduction in the amorphous material from 100.00 to 74.56 wt%. The Rietveld analysis did not provide any evidence on the presence of identifiable cristobalite peaks, as suggested by XRD.

Sample	Na ₃ PO ₄ (%)	Na ₄ P ₂ O ₇ (%)	Amorphous (%)	Total
NBSP0.0	0.00	0.00	100.00	100.00
NBSP1.0	0.00	0.00	100.00	100.00
NBSP2.0	0.00	0.00	100.00	100.00
NBSP3.0	0.00	0.00	100.00	100.00
NBSP4.0	13.16	0.00	86.84	100.00
NBSP5.0	2.63	12.05	85.32	100.00
NBSP5.5	1.88	16.75	81.38	100.00
NBSP6.0	2.13	23.31	74.56	100.00

Table 26 - XRD Rietveld pro-rat'd wt% of the NBSP samples

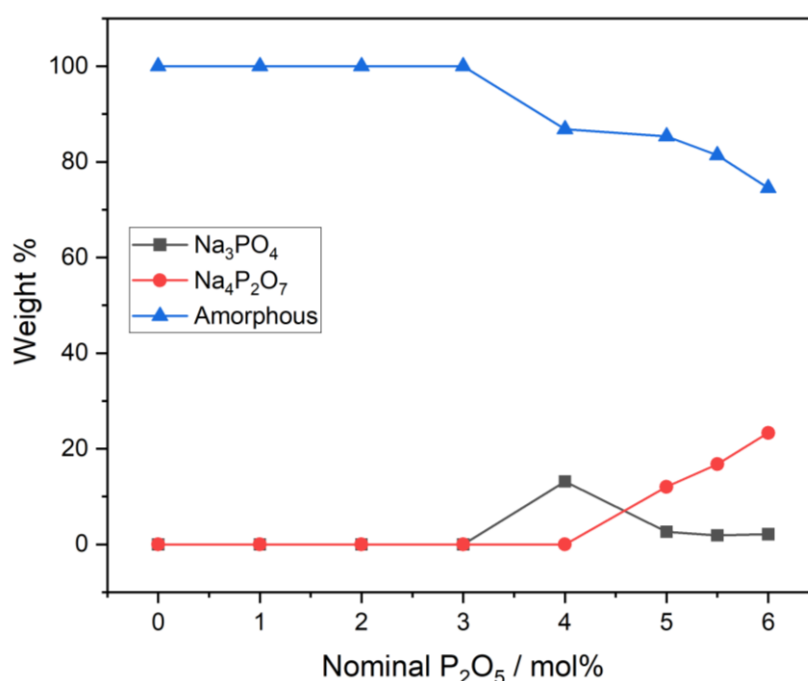


Figure 41 - Graphical representation of XRD Rietveld analysis of annealed NBSP samples

4.1.3.3.2 Quenched

Figure 42 shows the XRD patterns for the quenched samples, with NBSP1.0, 2.0 and 3.0 being shown as X-ray amorphous with no measurable crystallinity. Samples NBSP4.0, 5.0, 5.5, and 6.0 had measurable Bragg peaks and identifiable crystalline phases present within the amorphous material. Sample NBSP4.0 showed evidence of a small Bragg reflection at $\sim 22^\circ 2\theta$. Although this was not positively identified, it is consistent with the peaks attributed to cristobalite (SiO₂; PDF#: 01-071-3839 (Barth, 1932)) for

the higher- P_2O_5 samples. Samples NBSP5.0, NBS5.5 and NBSP6.0 contained the phases sodium phosphate ($Na_4P_2O_7$; PDF#: 01-073-5982 (Leung & Calvo, 1972)) and cristobalite (SiO_2 ; PDF#: 01-071-3839). There was also a shoulder peak beside the characteristic $Na_4P_2O_7$ Bragg peak ($\sim 20^\circ 2\theta$) at $\sim 20.5^\circ 2\theta$, which when compared with the annealed samples correlated with an identified Na_3PO_4 Bragg peak. Hence, these peaks have been labelled as Na_3PO_4 . As the P_2O_5 content increased, the simultaneous presence of Na_3PO_4 and $Na_4P_2O_7$ characteristic Bragg peaks in the NBSP5.0-6.0 samples, visually saw an increase in the relative intensity of $Na_4P_2O_7$ peaks.

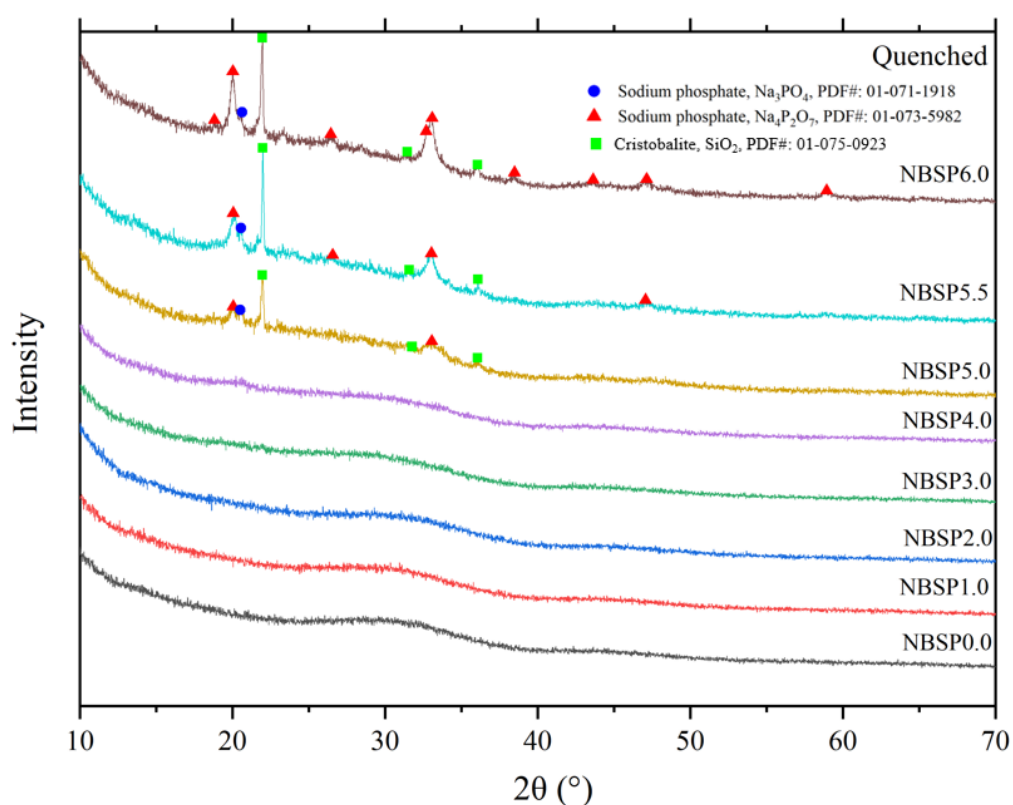


Figure 42 - XRD patterns of quenched, unannealed NBSP glass samples

4.1.3.3.3 Comparison of annealed vs air quenched samples

XRD was conducted on both the annealed and quenched samples to understand whether annealing the samples had any effect on the crystalline phases in comparison to air quenching. The quenched samples presented cristobalite in samples NBSP5.0, 5.5 and 6.0, while the annealed samples only presented cristobalite in sample NBSP5.5. Having cristobalite present in the annealed NBSP5.5 sample suggests that there was a small amount of

unmelted silica in the glass arising from imperfect melting of the raw materials, meaning that the glass may have needed to be heated at either a higher temperature and/or left to dwell longer to ensure all the silica had been incorporated into the melt. The presence of SiO₂ in the quenched samples also indicates that the point at which the glass was poured from has an impact on the crystallisation behaviour.

Glasses are non-equilibrium states of matter and move towards their equilibrium state when heated at a temperature below T_g . This phenomenon, which changes the glass properties, is referred to as structural relaxation (Kaur et al., 2018). During annealing, structural relaxation occurs, thermal stresses are removed, and the enthalpy of the glass reduces (Schawe & Wrana, 2020). Hence, the glasses were annealed at 500°C because this is the temperature just below the T_g , where literature showed that the T_g of the base glass was approximately 515°C (Akimov, 1989). The annealed samples have a lower threshold due to the annealing process having a slower cooling rate, where the structural relaxation of the glass subsequently leads to the nucleation and growth of crystals and/or phase separated droplets (Buff, 2016).

The heat treatment / thermal history of the glasses, whether annealed or quenched, has influenced the crystallisation behaviour, where the quenched glasses have X-ray measurable crystalline peaks at 5.0 mol% P₂O₅ as opposed to at 4.0 mol% P₂O₅ in the annealed glasses. Heat treatment (annealing) of a glass melt/matrix can have an effect on nucleation and crystallisation processes, where cooling at a constant rate or holding at a given temperature, in this case 500°C, can enable any nuclei present in the melt/matrix to grow until they have reached a critical size, at which point they are retained and allowed to develop, resulting in their precipitation as crystals (Liu et al., 2011; Ong et al., 2018; Sycheva, 2016). For example, formation and growth of a second, initially amorphous, phase and its growth during cooling of the melt and then heat treatment (annealing) at 500°C is consistent with heating at temperatures above the T_g of this second phase (theoretical T_g ~424°C based on the extrapolation of the nominal composition 75Na₂O-25P₂O₅ mol% (obtained from XRD showing Na₃PO₄ as the first crystalline phase that forms, and calculated for the 4.0 mol% P₂O₅ sample from the

SciGlass software database)) which has consequently placed the sample in a temperature regime (above T_g) whereby this second amorphous phase is capable of crystallisation. This could explain the presence of crystalline sodium phosphate (Na_3PO_4) at lower nominal P_2O_5 contents in the annealed (heat treated) glass samples compared to the quenched (unannealed and thus not heat treated) equivalent samples. This is an important finding as it illustrates the need for caution when investigating phase separation in glasses. It should also be noted that the cooling rate and temperature distribution of the quenched glasses are unknown, which could better inform the crystallisation behaviour. However, there have been some literature on broadly similar sodium borosilicate glass systems reporting cooling rates such as Yazawa et al. (1999), Angeli et al. (2012), and Peugeot et al. (2013) reported the values 600 K/min, 0.7×10^6 K/min, and 3.0×10^4 K/min, respectively.

4.1.3.3.4 CCC Heat Treated

Further to the finding that annealing can impact on phase separation / crystallization behaviour, in order to better understand the behaviour of the studied glasses under an imposed heat treatment regime relevant to nuclear waste vitrification, we have undertaken Canister Centreline Cooling (CCC) experiments. In the steel canisters into which Hanford HLW glasses will be poured, the melt is expected to cool slowly from the melter operating temperature of 1150°C to ambient temperatures (Donald, 2010; Marcial et al., 2020). The centreline of the canister is where it is expected that crystallisation will occur and be at its greatest, where cooling is slowest (Kim et al., 2003). In order to replicate the behaviour of the slowest cooled area in the canister, the CCC thermal profiles (Tables 2 and 3) were developed by Savannah River National Laboratory (SRNL) (Kruger et al., 2022; Russell et al., 2018) to model the worst-case scenario for the occurrence of crystallisation. Both HLW (Kruger et al., 2022) and LAW (Russell et al., 2018) CCC regimes were performed on all NBSP samples.

When the samples underwent the CCC heat treatment the sodium phosphate crystal phase transitions from a cubic structure in NBSP3.0, 4.0 and 5.0, to orthorhombic in NBSP5.0 and 5.5, to hexagonal in NBSP6.0. Interestingly, crystallinity occurred at a lower P_2O_5 content in the CCC regime treated glasses when compared to the annealed glasses, with X-ray crystallinity

observed on a macroscale in the NBSP4.0 sample and measurable in the NBSP3.0 sample. These phases have developed because they are closer to their high-temperature equilibrium, meaning that during the HLW CCC regime the samples were held at higher temperatures (e.g. $> 800^{\circ}\text{C}$) for considerably longer, allowing for the main phase nucleation sites to grow and crystallise (Kim et al., 2003).

Comparing the HLW CCC and LAW CCC NBSP glasses, both developed similar sodium phosphate crystalline phases with increasing P_2O_5 contents. The heat-treated samples demonstrated that the solubility limit of P_2O_5 / onset of crystallization does differ with heating regime. The precipitation of the cristobalite and tridymite could decrease the chemical durability of the glasses because they strip SiO_2 from the glass matrix and thus can affect the rate of glass dissolution in water (Kim et al., 2003; Riley et al., 2002). It should be noted that this data is limited in respect to the type and extent of crystallisation that the final Hanford glasses will exhibit, because of the reduced number of components in the studied glass system, and the overall composition. The P_2O_5 may interact and behave differently when in the presence of other cations other than Na, and with other glass formers and intermediates, e.g., Fe_2O_3 and Al_2O_3 . For example, a representative waste glass simulant composition reported by Achigar et al. (2021), in the SiO_2 - B_2O_3 - Al_2O_3 - Fe_2O_3 - Na_2O - Li_2O - CaO glass system, exhibited two different crystal phases, NaCaPO_4 and NaLi_2PO_4 , where phosphate crystallisation occurred at 3.2 mol% P_2O_5 . The NBSP HLW and LAW CCC heated glasses also exhibited sodium phosphate bearing crystal phases, where crystallisation occurred at 3.0 and 4.0 mol% P_2O_5 , respectively. Therefore, the solubility limit of P_2O_5 and crystallisation behaviour strongly depends on the composition and the abundance of each oxide present.

Figure 43 shows the XRD pattern for the HLW CCC NBSP glasses. Samples NBSP0.0, 1.0 and 2.0 were X-ray amorphous, whilst sample NBSP3.0 had evidence of some degree of crystallinity present within the amorphous material. As the P_2O_5 content increased, the samples gradually became more crystalline. Sample NBSP3.0 possessed sodium phosphate (Na_3PO_4 ; PDF#: 00-031-1318 (Palazzi et al., 1971)) but also presented a peak at $\sim 26^{\circ}2\theta$, which corresponds to the strongest intensity peak of quartz (SiO_2 , PDF#: 01-089-

1961), where its presence in this sample may be due to unmelted silica. Sample NBSP4.0 possessed sodium phosphate (Na_3PO_4 ; PDF#: 00-031-1318 (Palazzi et al., 1971)), sample NBSP5.0 possessed sodium phosphate (Na_3PO_4 , PDF#: 00-03-1318 and $\text{Na}_4\text{P}_2\text{O}_7$, PDF#: 04-018-433 (Leung & Calvo, 1972)) with evidence of the characteristic cristobalite peak at $\sim 23^\circ 2\theta$ albeit it was weak in intensity; sample NBSP5.5 possessed sodium phosphate (Na_3PO_4 , PDF#: 00-031-1318 and $\text{Na}_4\text{P}_2\text{O}_7$, PDF#: 04-018-4331) and cristobalite (SiO_2 , PDF#: 00-039-1425); and sample NBSP6.0 possessed sodium phosphate (Na_3PO_4 , PDF#: 00-031-1318 and $\text{Na}_4\text{P}_2\text{O}_7$, PDF#: 00-010-0187 (Visser & de Wolff, 1964)) and cristobalite (SiO_2 ; PDF#: 00-039-1425, (Wong et al., 1988)). The Na_3PO_4 exhibited a cubic structure, whilst $\text{Na}_4\text{P}_2\text{O}_7$ was either orthorhombic or hexagonal and SiO_2 was tetragonal.

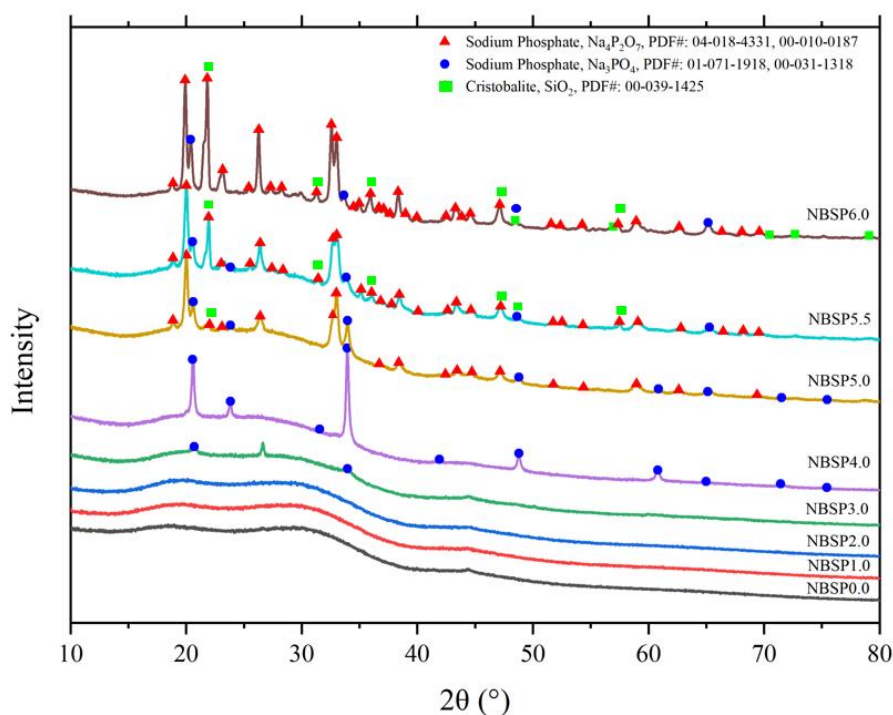


Figure 43 - XRD patterns for all samples and identified crystalline phases in NBSP0.0 to 6.0 for HLW CCC regime

Figure 44 shows the XRD patterns of the LAW CCC NBSP glasses. Samples NBSP0.0 to NBSP3.0 are shown to be X-ray amorphous. Like the HLW CCC NBSP glasses, as the P_2O_5 content increased the degree of crystallinity of the glasses increased. However, the “onset” of crystallinity occurred at higher P_2O_5 contents in the LAW CCC treated glasses than the HLW CCC treated glasses. Sample NBSP4.0 possessed Na_3PO_4 (PDF#: 00-031-1318 (Palazzi

et al., 1971)) and a weak intensity peak characteristic of cristobalite; NBSP5.0 possessed Na_3PO_4 (PDF#: 00-027-0771 (Palazzi et al., 1971)) and $\text{Na}_4\text{P}_2\text{O}_7$ (PDF#: 00-010-0187 (Visser & de Wolff, 1964)), NBSP5.5 and NBSP6.0 possessed $\text{Na}_4\text{P}_2\text{O}_7$ (PDF#: 04-018-4331 (Leung & Calvo, 1972)) and SiO_2 (cristobalite and tridymite) (PDF#: 04-008-4812 (Downs & Palmer, 1994) and 04-012-1333 (Hirose et al., 2005)). There was also evidence of similar characteristic Bragg peaks for Na_3PO_4 in the sample as the previous samples, but it was not officially identified using HighScore Plus because of their weak intensity and overlaps with other crystalline phases' peaks. Na_3PO_4 present in NBSP4.0, 5.0, and 5.5 had the same cubic crystal structure. $\text{Na}_4\text{P}_2\text{O}_7$ in NBSP5.0 had a hexagonal crystal structure, while in NBSP5.5 and 6.0 it had an orthorhombic structure. The SiO_2 in the NBSP6.0 sample was present as cristobalite and tridymite which had tetragonal and monoclinic crystal structures, respectively.

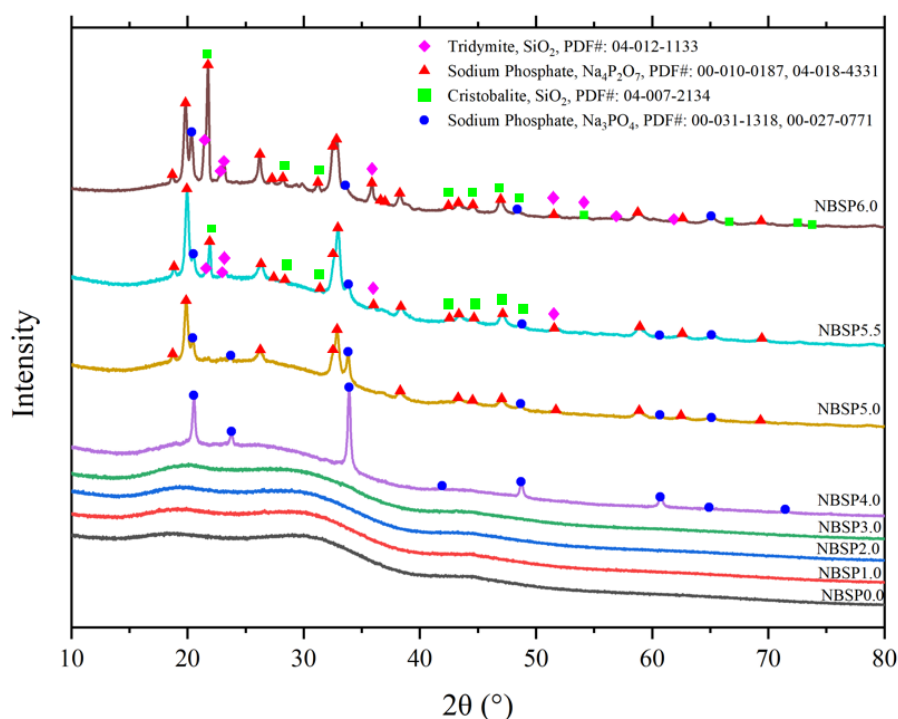


Figure 44 - XRD patterns for all samples and identified crystalline phases in NBSP0.0 to 6.0 for LAW CCC regime

4.1.3.4 DTA and Dilatometry

DTA and dilatometry were conducted on the annealed samples, where the following figures exhibit graphical representations of this data. Figure 45 shows the effects of increasing the P_2O_5 content on T_g (the onset T_g value) based on values from Table 27.

From analysing Figure 13, the DTA T_g onset exhibits little change, within error limits, between 0.0 and 2.7 mol% P_2O_5 , but not between 2.7 and 6.5 mol% P_2O_5 . Instead, there is decrease at 4.0 mol% P_2O_5 followed by a sharp increase at 4.9 mol% P_2O_5 through to 6.5 mol% P_2O_5 . The dilatometry T_g onset shows a similar trend as DTA where between 0.0 to 2.7 mol% P_2O_5 , the T_g onset is the same within error. However, this was followed by a sharp increase at 4.0 mol% P_2O_5 onwards, which is the same within error between 4.0 to 6.5 mol% P_2O_5 . The increase at 4.0 mol% P_2O_5 is in correspondence with the occurrence of sodium phosphate crystal phases which were confirmed by XRD patterns. Both sets of data follow a similar trend of an increase in the T_g onset with increasing P_2O_5 content.

The decrease of the T_g onset at 2.7 mol% P_2O_5 in the DTA data may suggest that the silicate network is becoming de-polymerised, resulting in an increase in NBØs in the glass network, and therefore, there may be more planar trigonal boron units in the system and that P_2O_5 may be promoting the formation of P-O-B species leading to a less connected network and, therefore, a decrease in T_g (Muller et al., 2016). There are not enough Na^+ ions to charge compensate the less polymerised phosphate units, hence the bonding of phosphate to a borate unit to form borophosphate species (Muller et al., 2016). However, to establish if this is the case, ^{31}P -NMR and ^{11}B -NMR would need to be conducted on the glasses. Moreover, there is a difference in behaviour observed between the DTA and dilatometry-measured samples.

T_g is sensitive to the degree of network connectivity in the glass system, and the increase in NBØs in the silicate network decreases it, but the conversion of planar trigonal $[^3]B$ to tetrahedral $[^4]B$ units increases T_g (Kruger et al., 2013; Muller et al., 2015). Between 0.0 to 2.1 mol% P_2O_5 the T_g increased then reduced at 2.7 mol%, before continuing to increase again up to 6.5 mol% P_2O_5 . This observed behaviour of the dual effect of P_2O_5 has been observed previously by other researchers such as Cheng (Cheng, 2004), who reported that for borosilicate glasses with the addition of 1.0 mol% P_2O_5 , T_g increased but after further additions T_g gradually decreased until the glass phase separated. The initial increase in T_g suggests this is a result of the increased polymerization of the silicate network, and that the re-polymerisation of the

network upon further additions of P_2O_5 is due to the NBØs and metal cations being scavenged to charge compensate the phosphate specific species in the glass network (Muller et al., 2016). The reduction in T_g in the DTA data may be evidence of the negative effect P_2O_5 can have on glasses, where there are not enough excess alkali cations to charge compensate the less polymerized PO_4^{3-} and $P_2O_7^{4-}$ units, and they instead form P-O-B linkages, however, the presence of the units needs to be confirmed using NMR (Kruger et al., 2013; Muller et al., 2015). O'Donnell et al. (2008) reported that P_2O_5 had this dual effect on bioactive glasses, stating that when the P_2O_5 content was increased, instead of the T_g increasing as expected, it decreased which contradicted the theory. They then commented on phosphate additions needing to be charge balanced by modifier cations such as sodium and calcium, which are taken from the silicate network, resulting in the re-polymerisation of the network.

Sample	DTA T_g onset (°C)	DTA T_g Mid- point (°C)	Dilatometry T_g onset (°C)	Dilatometry T_g Mid- point (°C)	T_d (°C)	(CTE) ((1/T) K)
NBSP0.0	515 ± 3	532 ± 3	512 ± 5	532 ± 5	550 ± 5	6.96 ± 0.2x10 ⁻⁶
NBSP1.0	519 ± 3	537 ± 3	508 ± 5	535 ± 5	550 ± 5	6.88 ± 0.2x10 ⁻⁶
NBSP2.0	523 ± 3	540 ± 3	514 ± 5	545 ± 5	551 ± 5	7.05 ± 0.2x10 ⁻⁶
NBSP3.0	518 ± 3	536 ± 3	509 ± 5	539 ± 5	550 ± 5	6.59 ± 0.2x10 ⁻⁶
NBSP4.0	509 ± 3	540 ± 3	525 ± 5	561 ± 5	570 ± 5	7.12 ± 0.2x10 ⁻⁶
NBSP5.0	520 ± 3	550 ± 3	530 ± 5	564 ± 5	575 ± 5	7.30 ± 0.2x10 ⁻⁶
NBSP6.0	540 ± 3	562 ± 3	535 ± 5	569 ± 5	581 ± 5	7.60 ± 0.2x10 ⁻⁶

Table 27 - Experimental DTA and dilatometry thermal properties

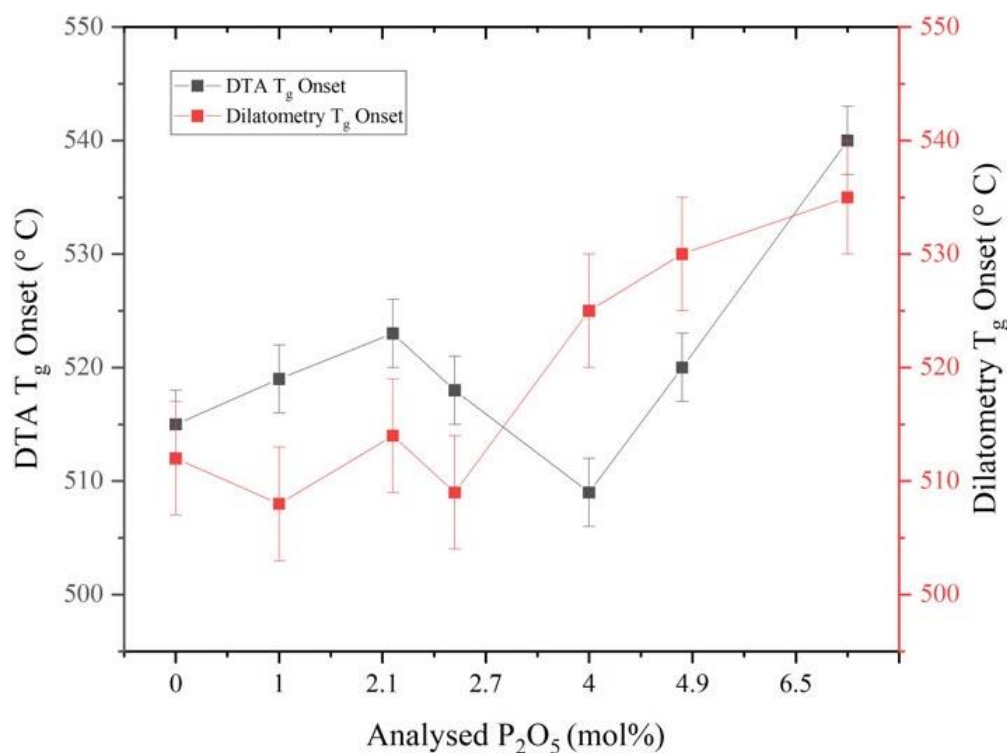


Figure 45 - DTA and dilatometric T_g onset temperatures as functions of analysed P₂O₅ content

Figure 46 shows the effects of increasing the P₂O₅ content has on the DTA T_g onset, T_d, CTE and viscosity at 950°C based on values from Table 5. T_d is constant between 0.0 and 2.7 mol% P₂O₅, within uncertainties, the same as the T_g onset. However, there is a sharp increase of 20 ± 5°C between 2.7 and 4.0 mol% P₂O₅, after which the increase between 4.0 and 6.5 mol% P₂O₅ is the same, within uncertainties. The CTE shows a decrease between 0.0 and 1.0 mol% P₂O₅. There is then an increase between 2.1 and 2.7 mol% P₂O₅ and between 2.7 and 4.0 mol % P₂O₅. The samples with 4.0 to 6.5 mol% P₂O₅ exhibit no further change in CTE, within uncertainties. The viscosity, exhibited via T_d, shows a general positive linear relationship with P₂O₅ content.

CTE can give qualitative information on glass structure, since CTE depends on the glass composition, thermal history, and temperature range of the dilatometry data from which it is extracted. The presence of asymmetrical units in the glass structure will lead to an increase in the CTE because they will cause anharmonic vibrations, while a more symmetrical network would lead to a decrease in the CTE (Klyuev, 2006). In Figure 46, the increase in the CTE between 2.0 and 3.0 mol% P₂O₅ and 2.7 and 4.0 mol% P₂O₅ may be indicative of the network de-polymerising due to the formation of “less-

symmetrical units” e.g., P-O-B and ^{31}B groups, which in turn indicates an increase in NBØ atoms present in the glass structure (Klyuev, 2006). Studies by Klyuev (2006) concluded, firstly, that if the CTE increased, then it was because there was an increase in the presence of NBØs. Secondly, that the glass network contained cations whose coordination numbers were changing within the temperature range that exceeded the lower T_g range, and lastly, that the glass structure contained layered or chain fragments that were linked together by Van der Waals bonds (Minami & Mackenzie, 1977). Therefore, there could be several reasons as to why the CTE increased in the dilatometry data. Minami & Mackenzie (1977) commented that a decrease in the cationic field strength led to the observed increase in CTE, because the CTE is controlled by the interactions between the cation and NBØs, hence the depolymerisation of the glass network (Minami & Mackenzie, 1977). Both Muñoz et al. (2008) and Kirkpatrick and Brow (1995) reported that P attracts Na^+ cations from the silicate sub-network, resulting in its subsequent re-polymerisation (Keyvani et al., 2011; Kirkpatrick & Brow, 1995). This structural change may then result in effects on thermal properties and chemical durability.

Based on the available data, it can be shown that the T_d is following a broadly similar trend to T_g onset, in that it is steadily rising with increased P_2O_5 content. The softening temperature ranges between 0.0 to 2.7 mol% P_2O_5 and 4.0 to 6.5 mol% P_2O_5 are the same within error, however, there is a notable increase between 2.7 and 4.0 mol% P_2O_5 . In phase separated glasses, the softening of the glass determines the value of T_d , which is controlled by the more viscous phase. If that phase is continuous, then the shift to a higher temperature is a result of the continuous high temperature phase (Cheng et al., 2017). According to Keyvani et al. (2011), the increase in T_g and T_d is a result of the increase in the viscosity. Therefore, this suggests that the glasses have begun to phase separate between 2.7 and 4.0 mol% P_2O_5 which affects T_d .

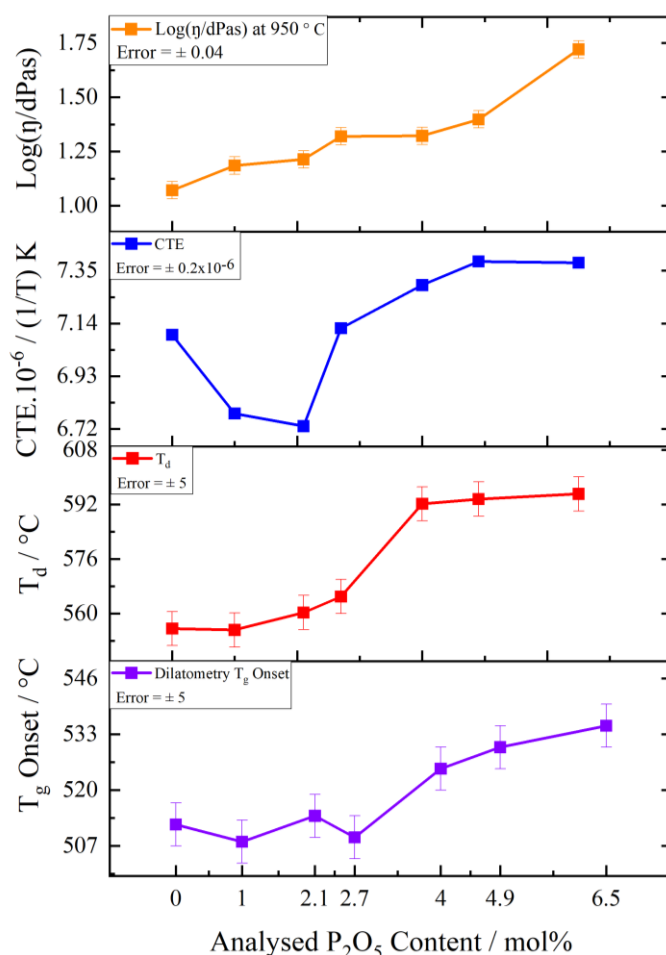


Figure 46 - Effects of increasing P₂O₅ content on viscosity at 950°C, coefficient of thermal expansion, T_g onset, and T_d dilatometric softening point

4.1.3.5 High Temperature Viscosity (HTV)

Figure 51 depicts a line graph illustrating the measured viscosity at several temperatures for each NBSP glass melt, highlighting the effect of increasing P₂O₅ content. The general trend is a linear positive correlation, in that for a given temperature, as the P₂O₅ content increases, the viscosity of the melt increases. The increase in viscosity as the P₂O₅ content increases is indicative that the silicate network is re-polymerising, which can also be seen increasing both T_g and T_d (Figure 46). The plot of the logarithm of viscosity versus the reciprocal of absolute temperature (1/T) produced a linear function (Figure 51), and data could be reliably fitted with the Arrhenius-type equation ($\ln(\eta) = \ln(A_s) + (E_a/R) \cdot (1/T)$), where (E_a/R) is the gradient of the straight line, and ($\ln(A_s)$) is equal to the intercept of the y-axis (Messaâdi et al., 2015). The methodology reported by Messaadi et al. (2015) was adopted, using both

linear least-squares fitting and graphical methods in the Excel work package to establish the Arrhenius activation energy (E_a/R) and entropic factor of Arrhenius ($\ln(A_s)$) as a function of P_2O_5 ; the values are presented in Table 6. The Arrhenius activation energy (E_a) ranged between 16.429-22.826 kJ.mol⁻¹, whilst the entropic factor of Arrhenius ($\ln(A_s)$) ranged between -10.94 to -14.74. The Arrhenius behaviour of the melts suggests that the increase in the P_2O_5 contents increased the activation energy for viscous flow due to the re-polymerization of the melt structure (Hrma & Kruger, 2016). The Vogel-Fulcher-Tammann (VFT) equation was not implemented on the viscosity data because it is used to fit data ranging between 10³-10¹³ Pa.s and fails when viscosity values are < 10² Pa.s (Colombani & Bert, 2004); the viscosity data in this investigation ranged between -0.08495 to 1.72102 Pa.s (Figure 51).

Figure 47 to Figure 50 illustrate the rheological behaviour of the glass melts, where a Newtonian fluid is when the viscosity is independent of the shear rate displaying a linear relation between shear rate and shear stress (Ovarlez, 2012), whilst a non-Newtonian fluid has a non-linear function of the shear rate (Eberhard et al., 2019). Figure 47 to Figure 50 present the viscosity behaviour of the glass melts at 950°C, 1050°C, 1150°C, and 1250°C with increasing nominal P_2O_5 content, respectively. At 0.0 mol% P_2O_5 , the glass melt behaves as a fully Newtonian liquid at 950 and 1250 °C. However, there is a slight discrepancy in the data at 1050 and 1150°C, when the shear rate was between 6.1-7.8 s⁻¹ and 12.2-12.9 s⁻¹, respectively. The graphical function was no longer linear, but instead exhibited a slight hysteresis loop, where this behaviour indicated that the glass melt was exhibiting shear thickening of the fluid. Shear thickening is when the viscosity of the liquid increases with an increase in shear stress at a constant shear rate (Holmes et al., 2005; Ovarlez, 2012). Such an effect can result in a jump in the shear stress on exceeding the “critical” shear rate, where the flow of the liquid becomes erratic, suggesting the formation and separation of stress supporting structures (Gunasekera et al., 2013; Izdebska & Thomas, 2016; Ovarlez, 2012). At 1.0 mol% P_2O_5 at 950°C (Figure 47) the data shows little variance in the shear stress when compared to 0.0 mol% P_2O_5 , however the shear stress does increase slightly above 300 Pa. It continues to behave as a Newtonian liquid at all temperatures. At 2.0 mol% P_2O_5 at 950°C (Figure 47) the data shows

little difference from 1.0 mol% P_2O_5 , exhibiting Newtonian behaviour at 950 and the following temperatures (Figure 47 to Figure 50). At 3.0 mol% P_2O_5 (Figure 47 to Figure 50) the graphs show an increase in the shear stress, reading approximately 400 Pa, where it then reduces slightly when the rate decreases, demonstrating slightly non-Newtonian behaviour. At 4.0 mol% P_2O_5 the melt viscosity decreases in shear stress from approximately 400 Pa to 20 Pa between 950 to 1250°C (Figure 47 to Figure 50), with some variance in the melt behaviour at 1050°C, where there is strong evidence of non-Newtonian behaviour. The non-Newtonian behaviour is characterised by the slight hysteresis loop approximately between 10-15 s^{-1} , which has been identified to correspond to thixotropic behaviour, where the viscosity of the fluid is dependent on the time of shear rate, where viscosity decreases with time (Eberhard et al., 2019). At 5.0 mol% P_2O_5 at 950°C (Figure 47) the shear stress has a value of 500 Pa with variance in the Newtonian behaviour at 1250°C (Figure 50). At 5.5 mol% P_2O_5 the shear stress increases to above 600 Pa with non-Newtonian behaviour being exhibited at 1150°C, specifically thixoplastic behaviour (Figure 49). Finally, at 6.0 mol% P_2O_5 the shear stress at 950°C increases to 1000 Pa with evidence of non-Newtonian behaviour, specifically thixoplastic behaviour, suggesting that as the P_2O_5 content increased the shear stress of the glass melts increased at 950°C, corresponding to the increase in the viscosity.

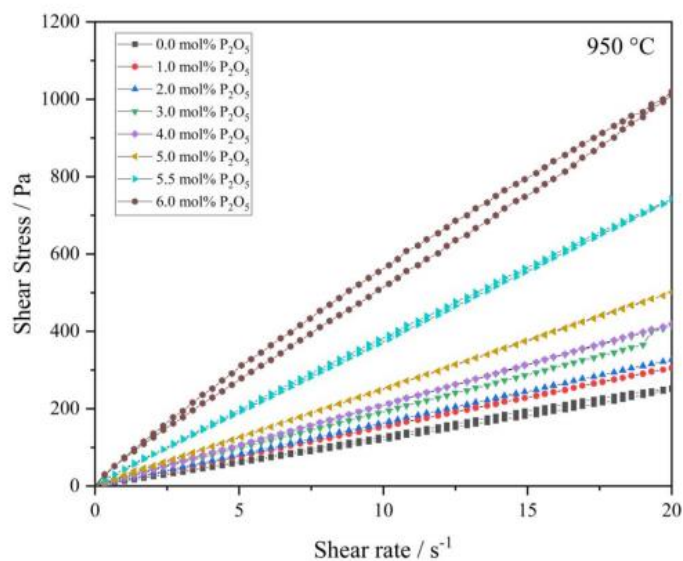


Figure 47 - Viscosity of NBSP samples at 950°C

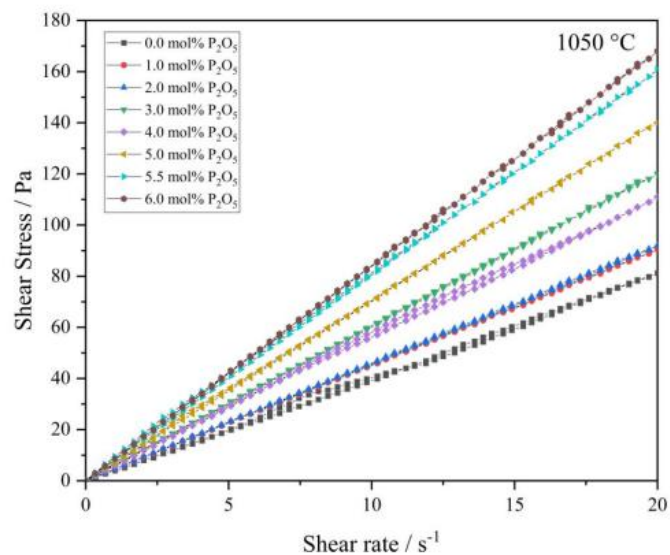


Figure 48 - Viscosity of NBSP samples at 1050°C

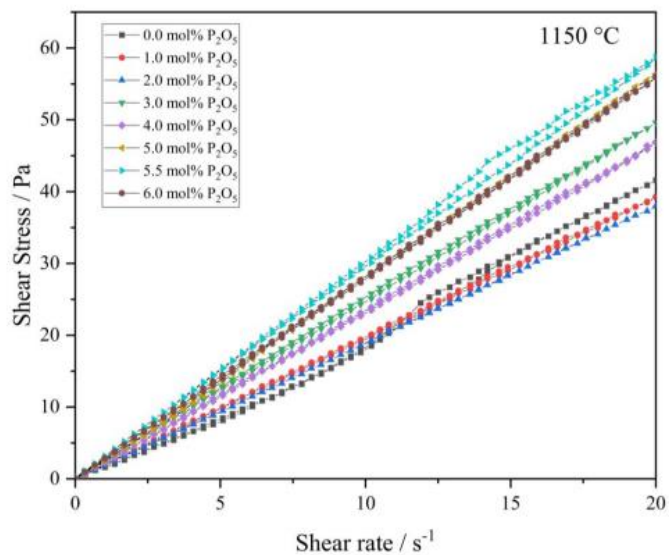


Figure 49 - Viscosity of NBSP samples at 1150°C

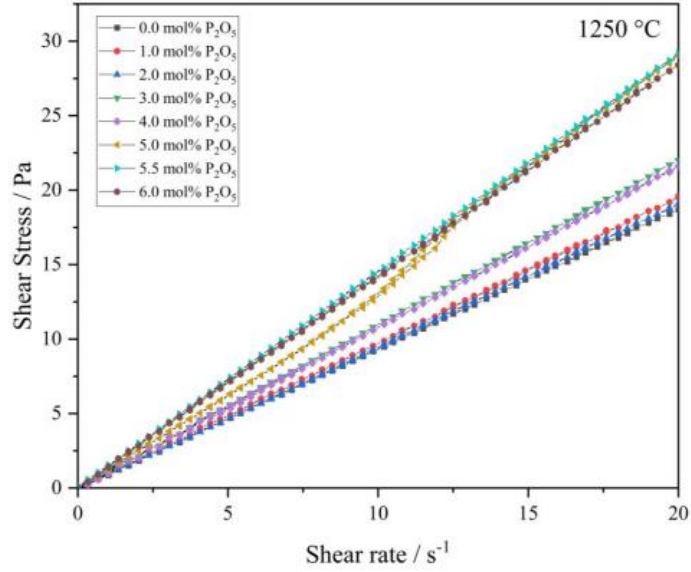


Figure 50 - Viscosity of NBSP samples at 1250°C

The viscosity of fluids is a measurement of its resistance to shear deformation, where the viscosity-temperature relationships determine the melting parameters, annealing temperatures, refining rate, and crystallization rate (Hrma & Kruger, 2016). Viscosity directly dictates the relaxation processes in amorphous materials, and is reliant on the glass composition (Hrma & Kruger, 2016). In this particular study, the experimental viscosity data will contribute to property-composition relationship models to provide potential glass compositions for application at the Hanford Waste Treatment and Immobilisation Plant and for waste streams high in P₂O₅ (Sadler, 1996). Previous authors have highlighted the importance of measuring the viscosity of glass melts to better inform not just processing properties, but to provide further information on a glasses' thermal properties such as T_g, and its structure (He et al., 2013; Hrma & Kruger, 2016; Mauro et al., 2009), especially as changes in the composition which may reduce structural connectivity reduce the melt viscosity and vice versa (Zhang et al., 2001).

A fluid's viscosity behaviour can be described as being a Newtonian fluid, which is characterised by the linear relationship between the applied shear stress and rate of shear, demonstrated in (Eq 43) (Trimble et al., 2016):

$$\sigma_{yx} = F/A = \eta \dot{\gamma}_{yx} \quad (43)$$

Where σ is the shear stress, which is defined as the applied force, F , acting over a given unit area, A . The shear viscosity, η , is defined as the coefficient

of proportionality between the shear rate and shear stress, whilst the shear strain, γ , is defined as the displacement gradient across the sample.

When the viscosity of fluid is not constant at a given temperature but instead relies on the rate of shear, the fluid is said to be non-Newtonian. A non-Newtonian fluid can be grouped into three main categories (Trimble et al., 2016):

1. Generalised Newtonian Fluids (GNF) / Time Dependant
2. Time-dependant Fluids
3. Visco-elastic Fluids

Reviewing the viscosity of the glass melts it can be determined that samples NBSP1.0 to NBSP3.0 and NBSP5.0 behaved entirely as Newtonian fluids at temperatures 950°C, 1050°C, 1150°C, and 1250°C, but samples NBSP0.0, NBSP4.0, NBSP5.5, and NBSP6.0 acted as non-Newtonian fluids depending on the temperature, and may in fact have been type-two non-Newtonian fluids ‘time-dependent fluids’, which show further dependence on the duration of shearing and the kinematic history; or type-3, which is a mixture of viscous fluid behaviour and an elastic-solid-like behaviour (Koroleva et al., 2011). However, the viscosity of the samples may have increased at higher P₂O₅ content at the expected Hanford Site melting temperature of 1150°C, the majority of the samples still displayed Newtonian behaviour except for NBSP0.0 and NBSP5.5.

It should be noted that phase separated systems under shear flow can have anisotropic morphological evolution, which can even induce ordering of the structure (Schuller et al., 2008). Zhang et al. (2001) found that in a binary system in which phase separation has occurred, the viscous phase is the minor phase and the viscosity of the bulk contribution differs from that of the interfacial contribution, leading to a reduction on the non-Newtonian behaviour. When this viscous phase is the major phase, the bulk concentration is comparable to that of the interfacial contribution and hence the non-Newtonian behaviour is instead strengthened (Zhang et al., 2001).

The differences in viscous flow observed here have most likely come from the differences in the local molecular environments around that of the flow species in the glass melt (Simmons et al., 1974). Simmons et al. (1974) proposed a

model that was based on the concept that the shear structural relaxation processes which control viscosity are dependent on the size and type of microstructure(s) present in the glass melt. If the system has an interconnected microstructure with different viscosities, then there are three types of viscosity behaviour that will follow depending on the microstructure size (Simmons et al., 1974). When there are small microstructures due to a space averaging within the relative size, this can lead to the molecules having their activation energies and relaxation times equivalent to each other, and therefore, the distributions are small, with expected viscosity behaviour. However, as the microstructure grows, the areas in the microstructure will differ leading to non-equivalent activation energies and relaxation times, where this broadening of the distribution of molecules and increase in viscosity are accentuated as the relative size grows (Simmons et al., 1974).

Therefore, considering this information and reviewing the viscosity results for the NBSP sample glass melts, the increase in viscosity may be a result, first of phase separation induced by the increase of the P_2O_5 content, and then, with decreasing temperature, with the presence of solid sodium phosphate crystalline phases acting as the major viscous phase with the bulk concentration being comparable to the interfacial contribution, and hence the non-Newtonian behaviour of the melt.

Temperature / (1/T) K	Log (η /dPas) $\pm$ 0.04							
	NBSP 0.0	NBSP 1.0	NBSP 2.0	NBSP 3.0	NBSP 4.0	NBSP 5.0	NBSP 5.5	NBSP 6.0
8.18E-04	1.0715	1.1855	1.2137	1.3202	1.3222	1.3984	1.5747	1.7210
7.56E-04	0.5547	0.6568	0.6639	0.782	0.7582	0.8616	0.9101	0.9250
7.03E-04	0.1893	0.286	0.2768	0.3754	0.3574	0.4325	0.4889	0.4693
6.57E-04	-0.085	-0.012	-0.024	0.0401	0.0316	0.0756	0.1642	0.1499

Table 28 - Viscosity of NBSP samples at different melting temperatures during heating cycle

Sample	E_a (kJ.mol ⁻¹)	Ln (A_s) (Pa.s)
NBSP0.0	16.429	-10.94
NBSP1.0	17.216	-11.42
NBSP2.0	17.815	-11.85
NBSP3.0	18.433	-12.08
NBSP4.0	18.541	-12.19
NBSP5.0	18.961	-12.32
NBSP5.5	20.242	-13.05
NBSP6.0	22.626	-14.74

Table 29 - Arrhenius parameters of the NBSP glass melts: Arrhenius activation energy (E_a (kJ.mol⁻¹)) and entropic factor of Arrhenius (Ln(A_s)/Pa.s) as a function of P₂O₅ content.

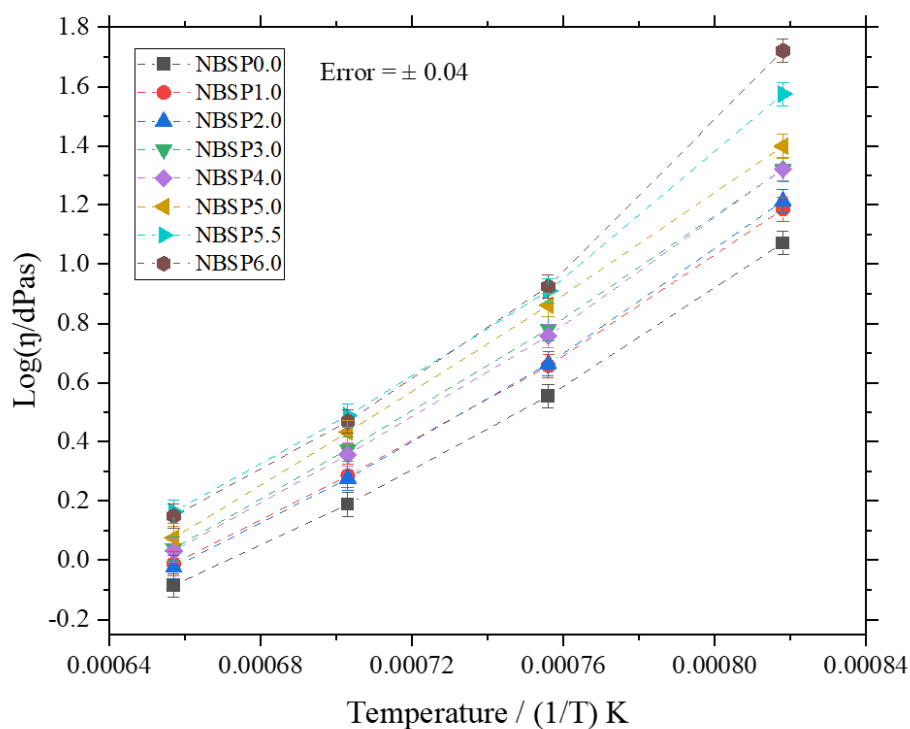


Figure 51 - Effects of temperature on log (viscosity) of NBSP samples at 8.18E-04 (1/T) K, 7.5E-04 (1/T) K, 7.03E-04 (1/T) K, and 6.5E-04 (1/T) K, with varying P₂O₅ content. The data is from a constant shear rate of 10 s⁻¹.

4.1.3.6 SEM/EDX

Figure 52 to Figure 56 show the backscattered SEM images of NBSP3.0, 4.0 5.0, 5.5 and 6.0 at a magnification of 60000x. NBSP0.0-2.0 were X-ray amorphous and so were not analysed using SEM. Sample NBSP3.0 displayed a fully amorphous matrix with no evidence of droplets or other characteristics associated with phase separation or crystallisation. Samples NBSP4.0-6.0 samples exhibited black droplets in a matrix of grey, with small lighter crystal clusters growing, showing the crystals growing from the droplets, however, without the use of EDS it cannot be confirmed what phases were present. EDS was not used because of the potential damage of the samples by beam damage. However, the formation of these $<1\text{ }\mu\text{m}$ relatively, uniformly separated droplets suggests that the glass composition is located in between the spinodal and binodal lines, where phase separation occurs as a nucleation-type mechanism (Koroleva et al., 2011). The increase in some of the droplets with 4.0-6.0 mol% P_2O_5 additions may have been produced by the Ostwald ripening mechanism due to a diffusion process (Schuller, 2020). The display of two different coloured droplets in the residual matrix (Figure 52 to Figure 56) may be an indication that they all have a different composition. The original base glass was determined to not be susceptible to immiscibility given its position in the $\text{Na}_2\text{O}_3\text{-B}_2\text{O}_3\text{-SiO}_2$ ternary phase diagram, and that the additions of P_2O_5 have enhanced the glasses susceptibility to phase separation and crystallization (Schuller, 2020).

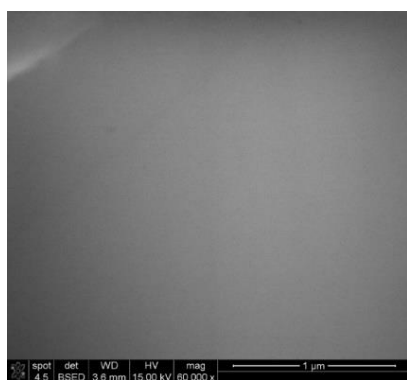


Figure 52 - Backscattered electron image of NBSP3.0 at a magnification of 60000x



Figure 53 - Backscattered electron image of NBSP4.0 at a magnification of 60000x

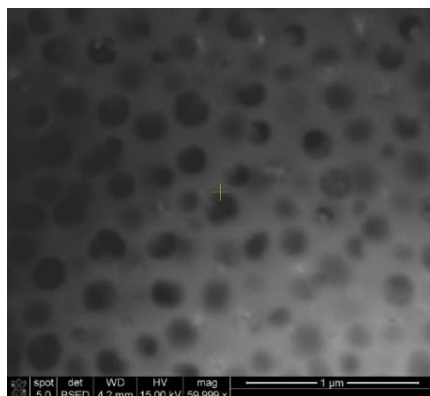


Figure 54 - Backscattered electron image of NBSP5.0 at a magnification of 60000x

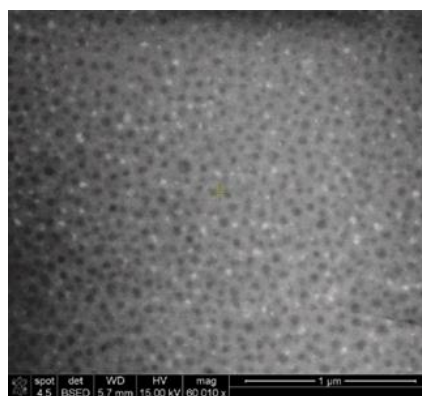


Figure 55 - Backscattered electron image of NBSP5.5 at a magnification of 60000x

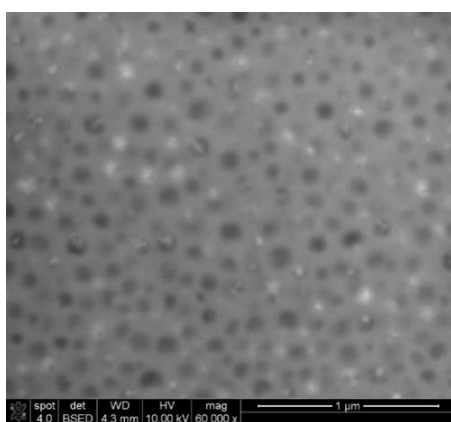


Figure 56 - Backscattered electron image of NBSP6.0 at a magnification of 60000x

The mixture of droplets seen in the SEM back scattered images (Figure 52 to Figure 56) may be indicative of liquid–liquid phase separation that may have occurred upon cooling, where one phase may have cooled before the other as the P_2O_5 content increased in the glass system. The black and grey dots in the matrix of lighter grey may have been nucleation sites for crystals with potentially different compositions. However, the exact mechanism by which phase separation occurred is currently unknown i.e., spinodal decomposition, nucleation and growth, or both. Visual inspection of the morphology postulates that the phase separation took place via the nucleation and growth mechanism, where said mechanism occurred at low supersaturations, near to the immiscibility limit. However, conclusively stating that the phase separation occurred by the nucleation and growth mechanism cannot be confirmed, as it is notoriously difficult to decide on the mechanism based solely on morphology. Seward et al. (1968) cited in Craievich et al. (1983) examined $BaO-SiO_2$ thin films, reporting

that compositions found near the centre of the miscibility gap presented fine isolated droplets, however, at a later stage two interconnected phases were observed indicating the intersecting growth when the composition was within the spinodal region. Vogel (1965) reported that the high cation field strength of P allows it to dominate the process in mixed glass systems, e.g., $\text{Na}_2\text{O-B}_2\text{O}_3\text{-SiO}_2\text{-P}_2\text{O}_5$, where it gathers alkali cations from the unmixed borosilicate phase and into an additional phosphate rich droplet phase (Langowski, 1996).

The relationship between crystallisation and liquid-liquid phase separation, or immiscibility is subtle, however, it is generally accepted that the origin of immiscibility and crystallisation in silicate solutions derives from the thermodynamic driving force (Deng et al., 2014). Studies by Uhlmann (1976) reported that local changes in the composition caused by phase separation phases:

1. can increase or decrease the thermodynamic driving forces of crystallisation.
2. can enhance the crystal nucleation through the existence of interfaces in the phase separated,
3. which results in one of the liquid phases having a higher atomic mobility than the present homogeneous phase,
4. providing a larger driving force for the nucleation or atomic mobility by the interfacial regions between the enriched separated component in one of the phases.

It should be noted that crystallisation itself is a two-step process: (i) the initial nucleation of the crystal followed by (ii) the growth of the nuclei by the addition of more atoms (Sycheva, 2016). There are also two types of nucleation: heterogenous and homogeneous. The first occurs when the nuclei form at an already pre-existing surface or interface, and the latter occurs when nuclei form spontaneously in the melt/matrix (Sycheva, 2016). When the crystals are small the positive surface energy term is dominant, making them unfavourable and re-dissolving back into the glass matrix (O'Donnell et al., 2008; Vogel, 1965). When these crystals are larger than the critical nuclear size, the bulk free energy dominates instead, meaning the nuclei are stable and grow in size (Sycheva, 2016). In heterogeneous nucleation, the crystal forms on an existing

interface/surface, while in homogeneous nucleation the interface that is being formed is between the melt/matrix and crystal (Sycheva, 2016). As a result, the combination of creating and eliminating interfaces leads to a reduction in the activation energy needed for crystallisation. Hence, heterogeneous nucleation is faster than homogeneous nucleation. Therefore, systems with more pre-existing interfaces e.g., phase separation, voids, and crystals will have a higher nucleation rate than a glass system without such interfaces (Sycheva, 2016). In summary, SEM has confirmed that the solubility limit of P_2O_5 in these glasses is between 2.7-4.0 mol% P_2O_5 , which is in agreement with XRD patterns (Figure 4).

4.1.3.7 Raman Spectroscopy

4.1.3.7.1 Annealed and Quenched Samples

Figure 57 and Figure 58 show the Raman spectra of the annealed and quenched NBSP glasses, respectively. Table 30 and Table 31 list the identified peaks in spectra for the annealed and quenched samples, and Table 32 lists the associations, according to literature, of the identified peaks. The spectra can be divided into three main regions: the low frequency region (200-800 cm^{-1}), the mid- frequency region (800–1200 cm^{-1}), and the high-frequency region (1200-1600 cm^{-1}). The glasses are sodium borosilicate glasses meaning that the glasses contain two medium range sub-networks associated with silica and boron, with sodium cations acting as either a modifier cation or charge compensator. The addition of P_2O_5 leads to the formation of a phosphorus rich sub-network, where discrete PO_4^{3-} and $P_2O_7^{4-}$ species form outside of the silicate network (Muller et al., 2016). Phosphorus scavenges metal cations and NBØs to charge compensate itself, leading to the re-polymerisation of the silicate network (Muller et al., 2016).

The base glass spectra of the annealed and quenched samples exhibited low intensity peaks at 495, 534/549, 630, and 729 cm^{-1} , an intense region between 800-1200 cm^{-1} with identified peaks at 935/937, 1000, 1026, 1075/1079, 1086, and 1109/1111 cm^{-1} , and a broader low intensity region between 1200-1600 cm^{-1} with identifiable peaks at 1315, 1330, 1469, and 1471 cm^{-1} .

When 0.0-3.0 mol% P_2O_5 was added to the annealed glasses, the peaks at

534 and 630 cm^{-1} increased in intensity before continuing to decrease in intensity upon further additions of P_2O_5 (4.0-6.0 mol%). As these peaks reduced, a peak at 729 cm^{-1} occurred at 5.0 mol% P_2O_5 and continued to increase in intensity up to 6.0 mol% P_2O_5 . The band at 935 cm^{-1} increased in its relative intensity between 0.0-3.0 mol% P_2O_5 , but reduced at 4.0 mol% P_2O_5 , before increasing to its highest relative intensity at 5.0 mol% P_2O_5 , before decreasing again at 5.5 mol% P_2O_5 . The peak at 1000 cm^{-1} was present at 2.0 and 4.0 mol% P_2O_5 and reduced in its relative intensity upon additions of ≥ 5.0 mol% P_2O_5 at the expense of the peak at 1026 cm^{-1} . The broad band with a peak at ~ 1076 cm^{-1} increased in intensity between 1.0 and 4.0 mol% P_2O_5 , but then reduced at 5.0 mol% P_2O_5 , after which there was a sharp peak at ~ 1086 cm^{-1} , which then completely reduced again at 6.0 mol% P_2O_5 . The peak at 1109 cm^{-1} only occurred in samples with ≥ 5.0 mol% P_2O_5 and whose relative intensity did not fluctuate that much with increasing P_2O_5 content. In the high frequency region (1200-1600 cm^{-1}), the base glass had two peaks identified at 1315 and 1471 cm^{-1} , where the additions of 1.0 mol% P_2O_5 saw the development of a third peak at ~ 1531 cm^{-1} . This peak shifted to higher and then lower frequencies upon the addition of 2.0 and 3.0 mol% P_2O_5 , respectively. At 4.0 mol% P_2O_5 , there were only two identifiable peaks centred at ~ 1311 and 1419 cm^{-1} . When 5.0–6.0 mol% P_2O_5 was added to the glass composition, there were still two peaks present, however, the peak that was at ~ 1419 cm^{-1} was replaced by a peak at ~ 1432 cm^{-1} .

In the quenched glasses, as the P_2O_5 content increased the bands at 495 and 549 cm^{-1} decreased in their relative intensities, whilst the peak at 630 cm^{-1} increased until 3.0 mol% P_2O_5 , before continuing to reduce in intensity from 4.0 mol% P_2O_5 onwards. The peak at 729 cm^{-1} occurred from 5.0 mol% P_2O_5 onwards, increasing in intensity with increasing P_2O_5 content. The peak at 935 cm^{-1} increased in its relative intensity between 0.0 and 5.0 mol% P_2O_5 , before decreasing at 5.5 and 6.0 mol% P_2O_5 . The band at 1000 cm^{-1} was present in the 2.0 and 4.0 mol% P_2O_5 doped samples, where it reduced in intensity at the expense of the peak at 1026 cm^{-1} upon additions of ≥ 5.0 mol% P_2O_5 . The broad peak at 1078 cm^{-1} decreased in intensity whilst the peak at 1026 cm^{-1} increased, with increasing P_2O_5 content. In the high frequency region (1200-1600 cm^{-1}), two discernible peaks were identified, where the

second peak moved to a lower frequency upon the addition of P_2O_5 . These peaks were centred at ~ 1330 and 1469 cm^{-1} in the base glass and at 1453 and 1469 cm^{-1} in the P_2O_5 doped samples.

The small band at 495 cm^{-1} could be associated with the vibrationally isolated Si-O-Si or Si-O-B mode of four-membered rings or SiO_4 tetrahedra with four B $\emptyset$ ions (Trimble et al., 2016). The bands at $534/549\text{ cm}^{-1}$ have been attributed to the symmetrical stretching and partial deformation vibrations of Si-O-Si bridges (Koroleva et al., 2011; McKeown et al., 2000). The band at 630 cm^{-1} , according to literature, is potentially caused by the breathing mode of B-O-Si(B) in reedmergnerite- and/or danburite- like rings with Na^+ ions instead of a Ca^{2+} ions acting as charge compensators for $^{[4]}\text{B}$ units (Angeli et al., 2012; Manara et al., 2009; Winterstein-Beckmann et al., 2014; Yadav & Singh, 2015), or by metaborate vibrations of the ring-type (Koroleva et al., 2011). The band at 729 cm^{-1} has been attributed to the symmetric stretching of P-O-P (Yadav & Singh, 2015) and occurs from 5.0 mol% P_2O_5 onwards in both the annealed and quenched samples and can be matched to the same peak in the $\text{Na}_4\text{P}_2\text{O}_7$ crystalline standard. The band at $935/937\text{ cm}^{-1}$ can be assigned to the formation of the stretching of a Q^0P unit, which is consistent with the peak in the Na_3PO_4 crystal standard spectra (Manghnani et al., 2011; McKeown et al., 2010; Taylor, 1990; Yadav & Singh, 2015; Yamashita et al., 1998). The bands at 1000 and 1026 cm^{-1} can be attributed to P-O symmetric stretching vibrations of the pyrophosphate Q^1P unit (Cheng, 2004; Gangadharan et al., 2002; Giacomazzi et al., 2017; Kiran et al., 2017; Lui et al., 2011; Rinke & Eckert, 2011; Taylor, 1990). The bands at 1078 cm^{-1} and 1086 cm^{-1} are in the region where Q^3 units are expected, and so have been assigned to the stretching of the NB $\emptyset$ of the Q^3 structural units in the silicate groups (Smedskjaer et al., 2011; Yadav & Singh, 2015). The bands at $1109/1111\text{ cm}^{-1}$ have been attributed to the combination of P-O stretching in $\text{P}^2_{(1\text{B})}$ (Minamf & Mackenzie, 1977), PO_2 vibrations of $\text{P}^{(2)}$ units connected to two boron's $\text{P}^2_{(1\text{B})}$ and PO_3 vibrations of $\text{P}^{(1)}$ species (Zielniok et al., 2007), and Si-O $^-$ stretching in Q^3 units (Kirkpatrick & Brow, 1995). The peaks centred at $\sim 1311/1315/1330$ and $1453/1469/1471\text{ cm}^{-1}$ could be attributed to loose $^{[3]}\text{B}$ units and $^{[3]}\text{B}$ units linked to $^{[3]}\text{B}$ units, respectively, whilst the peak at 1419 cm^{-1} can be attributed to $^{[3]}\text{B}$ units linked to $^{[4]}\text{B}$ units, and the peak at 1432 cm^{-1} can be attributed to $^{[3]}\text{B}$ units linked to

boroxol rings (Möncke et al., 2015; Seshadri et al., 2020).

The presence of the band at 630 cm^{-1} (reedmergnerite- and / or danburite-like rings) in both sets of glasses implies that the silicate and borate sub-networks are interconnected to some degree, but that the reduction in its intensity suggests that with increasing P_2O_5 content the silicate sub-network is re-polymerising and the borate sub-network is forming fewer Si-O-B linkages. The increase in the relative intensity of the peak at 1026 cm^{-1} at the expense and reduction in the band at $\sim 1000\text{ cm}^{-1}$ implies that there was an increase in the presence of pyrophosphate Q^1_{P} units, which is supported by the presence of sodium phosphate crystals in the XRD pattern (Figure 40) in samples with $\geq 5.0\text{ mol\% P}_2\text{O}_5$. The broad band with peaks centred at $\sim 1076/1078\text{ cm}^{-1}$ decreased as the relative intensity at $1026/1086\text{ cm}^{-1}$ increased, suggesting that as the P_2O_5 content increased, there was an increase in the presence of Q^1_{P} species at the expense of Q^3_{Si} species. Overall, additions of P_2O_5 have a dual effect of de-polymerising and re-polymerising the silicate and borate network, by scavenging metal cations (Na^+) and NBØs. Table 32 summarises the Raman shift peaks and their referenced attributions.

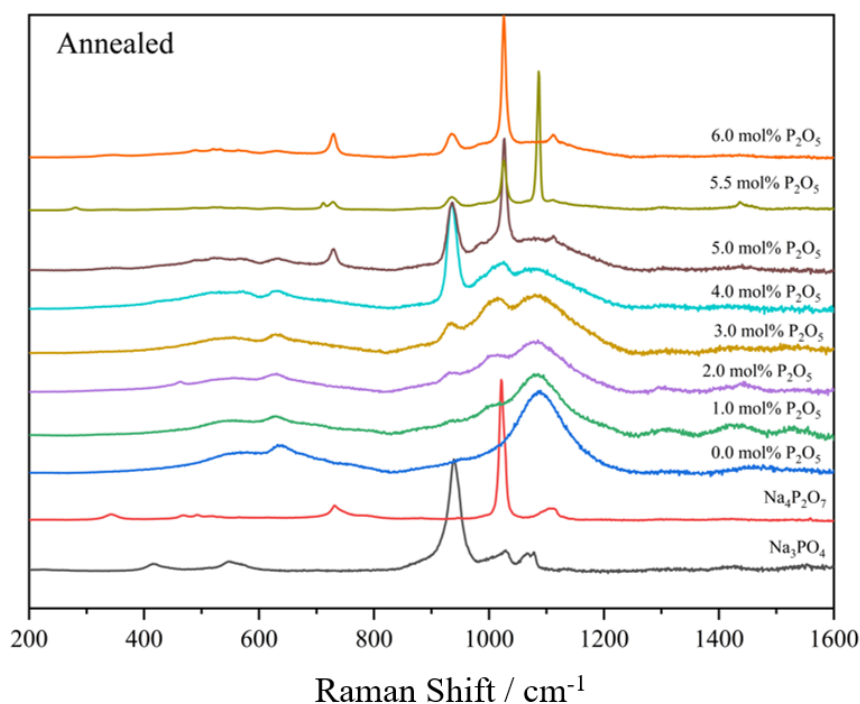


Figure 57 - Raman spectra of annealed NBSP glasses and sodium phosphate crystalline standards, Na_3PO_4 and $\text{Na}_4\text{P}_2\text{O}_7$

Sample	Raman Spectra band position (cm ⁻¹)
NBSP0.0	534, 630, 937, 1086, 1445
NBSP1.0	534, 630, 937, 1086, 1445
NBSP2.0	534, 630, 937, 1000, 1086, 1445
NBSP3.0	534, 630, 937, 1000, 1086, 1445
NBSP4.0	534, 630, 937, 1026, 1086, 1445
NBSP5.0	534, 630, 937, 990, 1026, 1086, 1109, 1445
NBSP5.5	534, 630, 729, 937, 990, 1026, 1086, 1109, 1445
NBSP6.0	630, 729, 937, 990, 1026, 1109, 1445
Na ₃ PO ₄	416, 548, 939, 1022, 1066
Na ₄ P ₂ O ₇	343, 733, 1022, 1111

Table 30 - Raman peak maxima in the annealed NBSP glasses from the Raman spectra

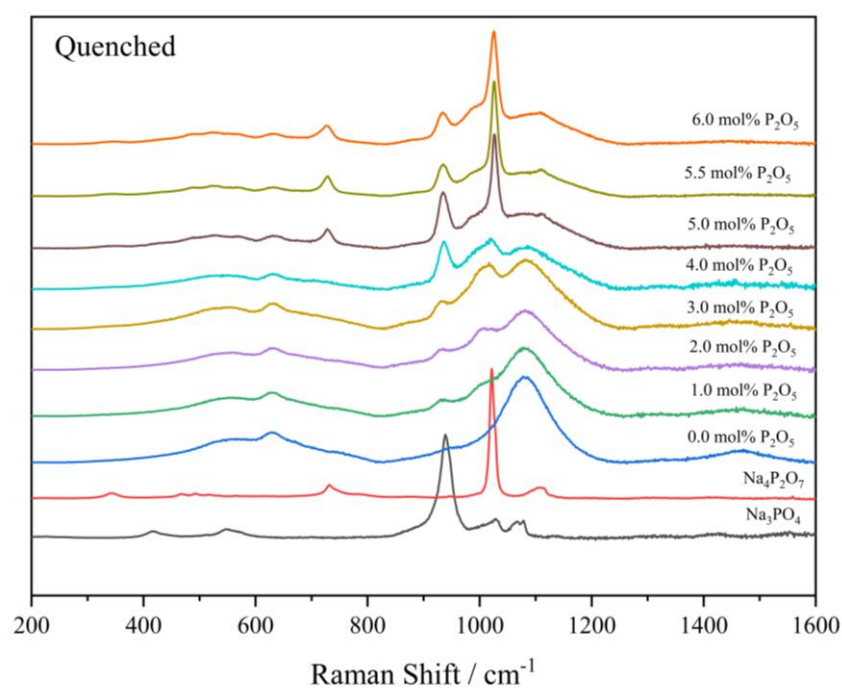


Figure 58 - Raman spectra of quenched NBSP glasses and sodium phosphate crystalline standards, Na₃PO₄ and Na₄P₂O₇

Sample	Raman spectral band position (cm ⁻¹)
NBSP0.0	495, 549, 630, 935, 1000 1078, 1472
NBSP1.0	495, 549, 630, 935, 1000, 1078, 1472
NBSP2.0	495, 549, 630, 935, 1000, 1078, 1472
NBSP3.0	495, 549, 630, 935, 1000, 1078, 1472
NBSP4.0	495, 549, 630, 935, 1000, 1078, 1472
NBSP5.0	495, 549, 630, 729, 935, 1000, 1026, 1078, 1111, 1472
NBSP5.5	495, 549, 630, 729, 935, 1000, 1026, 1078, 1111, 1472
NBSP6.0	495, 549, 630, 729, 935, 1000, 1026, 1078, 1111, 1472

Table 31 - Raman peak maxima in the quenched NBSP glasses from the Raman spectra

Raman shift (cm ⁻¹)	Attribution	Reference
534 (annealed) 549 (quenched)	Symmetrical stretching and partial deformation vibrations of Si-O-Si bridges	(Koroleva et al., 2011; McKeown et al., 2000)
629 (annealed) 628 (quenched)	Breathing mode of B-O-Si(B) in reedmergnerite- and / or danburite- like rings with Na ₂ O instead of CaO as a charge compensator for ^[4] B units Metaborate vibrations of the ring-type	(Angeli et al., 2012; Manara et al., 2009; Möncke et al., 2015) (Koroleva et al., 2011)
729 (annealed and quenched)	Symmetric stretching of P-O-P	(Yadav & Singh, 2015)
937 (annealed) 935 (quenched)	P-O stretching in PO ₄ ³⁻ Q ⁰ tetrahedra	(Manghnani et al., 2011; McKeown et al., 2010; Taylor, 1990; Yadav & Singh, 2015; Yamashita et al., 1998)

1000 (annealed and quenched)	P-O stretching in $P_2O_7^{4-}$	(Kiran et al., 2017; Muñoz et al., 2006; Taylor, 1990)
1026 (annealed and quenched)	P-O symmetric stretching vibrations of pyrophosphate ($P_2O_7^{4-}$) Q ¹ units	(Cheng, 2014; Gangadharan et al., 2002; Giacomazzi et al., 2017; Rinke & Eckert, 2011)
1086 (annealed) / 1078 (quenched)	Stretching of the NBØ of the Q ³ structural units in silicate groups	(Koroleva et al., 2011; McKeown et al., 2010)
1111 (quenched) / 1109 (annealed)	P-O stretching in $P_{(1B)}^{2-}$ PO ₂ vibrations of P ⁽²⁾ units connected to two borons $P_{(1B)}^{2-}$ and PO ₃ vibrations of P ⁽¹⁾ species Si-O ⁻ stretching in Q ³ units	(Raskar et al., 2008) (Zielniok et al., 2007) (Manara et al., 2009)
1445 (annealed) / 1472 (quenched)	BO ₃ units with one bridging bond of BO ₄ tetrahedra B-O(NBØ) stretch	(Seshadri et al., 2020) (Möncke et al., 2015)

Table 32 - Raman peak maxima with associated referenced assignments for the annealed and quenched NBSP samples

4.1.3.7.2 Raman Difference Spectra

Figure 59 shows the Raman difference spectra (RDS) of the annealed NBSP samples, with *Table 33* listing the key intensities and likely associations based on literature. The RDS are produced by subtracting the Raman spectrum for the base glass that is common to all the samples i.e., sodium borosilicate glass with 0.0 mol% P₂O₅, from the spectra for the other samples that contain P₂O₅, thereby presenting the effects of P₂O₅ additions in the y-axis. However, it should be noted that there are contributions from boron and silicate species, but these are being convoluted by the phosphate-specific intensities, hence other techniques such as MAS-NMR would be needed to establish the Qⁿ speciation of the borate and silicate units.

Detailed study of Raman spectroscopy data on various alkali and alkaline earth doped oxide glasses with similar glass formulations to the glasses in this study, have been reviewed to give details of the structural changes P_2O_5 can cause. Referring to the intensities produced by the RDS (Figure 59), the 729 cm^{-1} intensity has been associated with the symmetric stretching of P-O-P, whilst the 937 cm^{-1} intensity was associated with the symmetric stretching of the P-O bond isolated in the $PO_4^{3-} Q^0$ tetrahedra (Gangadharan et al., 2002; Manghnani et al., 2011; Mysen, 1998; Trimble et al., 2016; Yadav & Singh, 2015; Yamashita et al., 1998). However, Yadav et al. (2015) instead associated the intensities at approximately 940 cm^{-1} to be PO_2 symmetric stretching of NBØs in Q_0^1 units. Litasov et al. (2017) commented that the peak at 987 cm^{-1} could also be the symmetric stretching of P-O isolated PO_4^{3-} species as suggested by Mysen (1995; 1998) and Trimble et al. (2016). When referring to the XRD patterns for the annealed NBSP samples (Figure 40), orthophosphate and pyrophosphate species are present in the NBSP4.0, 5.0, 5.5 and 6.0 samples, evidenced by the occurrence of sodium phosphate crystals. Therefore, it is reasonable to assume that the Raman band at 937 cm^{-1} has been caused by the symmetric stretching of the P-O isolated in the $PO_4^{3-} Q^0$ tetrahedra. The 729 cm^{-1} and 937 cm^{-1} intensities can be further supported by comparing them with the Na_3PO_4 and $Na_4P_2O_7$ crystal phase standard Raman spectra seen in Figure 57, where the 729 cm^{-1} intensity is associated with $Na_4P_2O_7$ and 937 cm^{-1} with Na_3PO_4 . The intensity at $\sim 1000\text{ cm}^{-1}$ could either be attributed to the P-O stretching in $P_2O_7^{4-}$ or the stretching vibration of P-O in the $P(Q^1)$ chain (Mysen & Neuville, 1995; Mysen, 1998; Yadav & Singh, 2015). Support for this suggestion is evidenced by the occurrence of the pyrophosphate species as evidenced in the XRD patterns for samples NBSP5.5 and 6.0 as sodium phosphate crystals (Figure 40). The peak at 1026 cm^{-1} seen in samples NBSP5.0, 5.5 and 6.0 could either be attributed to the asymmetric stretching modes of Si-O-NBØ or the P-O symmetric stretching vibration of the pyrophosphate Q_1 unit (Gangadharan et al., 2002; Giacomazzi et al., 2017). However, this band only occurs in the amorphous-

crystalline phase separated samples (samples NBSP5.0 to 6.0). The 1026 cm^{-1} intensity is most likely the result of the P-O symmetric stretching vibration of the pyrophosphate Q_1 unit in the sodium phosphate crystals, especially when compared with the $\text{Na}_4\text{P}_2\text{O}_7$ Raman spectrum, which has the characteristic peak at $\sim 1029\text{ cm}^{-1}$. The intensity at 1114 cm^{-1} seen in NBSP5.0, 5.5 and 6.0 can be attributed to $\text{Na}_4\text{P}_2\text{O}_7$ when compared to the $\text{Na}_4\text{P}_2\text{O}_7$ Raman spectrum in Figure 58. The intensity at 1109 cm^{-1} seen in NBSP5.0, 5.5 and 6.0 may be attributed to the P-O stretching in $\text{P}^{2(1\text{B})}$ units (Raskar et al., 2008; Zielniok et al., 2007). The Raman intensity at 1445 cm^{-1} seen in all spectra, from samples NBSP0.0 to 6.0, can be assigned to BO_3 units with one bridging bond of a BO_4 tetrahedron (Seshadri et al., 2020). Table 33 summarises the key Raman shifts identified by the Raman difference spectra with referenced associations.

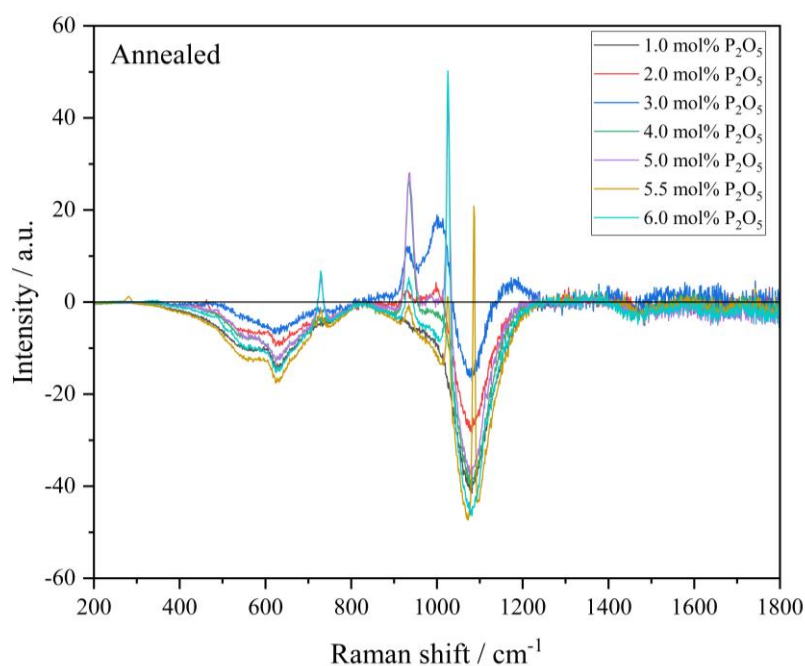


Figure 59 - Raman Difference Spectra (RDS) obtained by subtracting the Raman spectrum for NBSP0.0 (base glass) from the Raman spectra of the other NBSP samples (NBSP1.0 to 6.0)

Raman Intensity, cm^{-1}	Assignment	Reference
729	Symmetric stretching of P-O-P	(Gangadharan et al., 2002; Yadav & Singh, 2015)
937	P-O stretching in PO_4^{3-} Q^0 tetrahedra	(Cheng, 2014; Hayward, 1993; Mysen, 1998; Trimble et al., 2016; Wang & Cheng, 2016; Yadav & Singh, 2015)
1000	P-O stretching in $\text{P}_2\text{O}_7^{4-}$	(Cheng, 2014; Grussaute et al., 2000; Kiran et al., 2017; Muñoz et al., 2006; Mysen, 1998)
1026	P-O symmetric stretching vibration of pyrophosphate Q^1 units	(Gangadharan et al., 2002; Giacomazzi et al., 2017; Marcial et al., 2020; Seshadri et al., 2020)
	Asymmetric stretching modes of Si-O- $\text{NB}\emptyset$	(Raskar et al., 2008; Zielniok et al., 2007)
	Asymmetric stretching of PO_3	(Gangadharan et al., 2002; Yadav & Singh, 2015)
1109	P-O stretching in $\text{P}^{2(1\text{B})}$	(Cheng, 2014; Hayward, 1993; Mysen, 1998; Trimble et al., 2016; Wang & Cheng, 2016; Yadav & Singh, 2015)
1445	BO_3 units with one bridging bond of BO_4 tetrahedra	(Seshadri et al., 2020)

Table 33 - Raman peak maxima with associated referenced assignments

4.1.3.8 MAS NMR

The MAS NMR experiments and associated data were conducted in Canada during Covid, where analysis and discussions were carried out with Professor Josef Zwanziger and Dr Ulrike Werner-Zwanziger through online zoom meetings (Werner-Zwanziger & Werner, 2021b, 2021c, 2021a, 2022a).

4.1.3.8.1 ^{11}B MAS NMR

Figure 60 shows the ^{11}B MAS NMR spectra of the NBSP samples deconvoluted and fitted with a Gaussian line shape using the DmFit software. At 0.0 mol% P_2O_5 there were two distinct peaks, where the broader, smaller peak at approximately 14.7-15.0 ppm was associated with ^{11}B non-ring units (Angeli et al., 2012) and displayed the typical broadening line shape normally observed for quadrupolar boron nuclei. The sharper peak at approximately 0.0 ppm was associated with ^{11}B units (comprising 1B, 3Si) (Angeli et al., 2012). As the P_2O_5 was incrementally increased another peak formed that was superimposed over the ^{11}B peak and was centred at approximately -3.0 ppm. According to literature, this peak is associated with P-O- ^{11}B linkages (Grussaute et al., 2000; Muñoz et al., 2006, 2008; Ohtsuki et al., 2011). As the P_2O_5 content increased the intensity of the P-O- ^{11}B peak also increased, whereas the ^{11}B peak shifted to more negative values, suggesting there may be an increase in the P-O- ^{11}B linkages (Qiu et al., 2008). The ratio of ^{11}B : ^{11}B chemical shift peak intensities stayed the same within uncertainty ($\pm 2\%$) (Table 34). The spectral line shapes displayed by the NBSP5.0, 5.5, and 6.0 (transparent and opaque) samples were very similar, which coincided with the occurrence of crystallisation, where there was the removal of Na^+ , P^{5+} , and O^{2-} from the glassy matrix, as supported by XRD patterns (Figure 40). When the transparent and translucent spectra of the NBSP6.0 were compared, there was a distinct lack of sharp features, suggesting that boron was not significantly involved in the formation of the crystalline phases.

Sample	Atom % $^{11}\text{B} \pm 2$	Atom % $^{11}\text{B} \pm 2$
NBSP0.0	23.3	76.7
NBSP1.0	22.5	77.5
NBSP2.0	21.4	78.6
NBSP3.0	21.6	78.4
NBSP4.0	20.4	79.6
NBSP5.0	22.6	77.4
NBSP5.5	23.7	76.3
NBSP6.0 (opalescence)	23.2	76.8
NBSP6.0 (translucent)	23.9	76.1

Table 34 - NBSP ^{11}B atom peak intensities of ^{11}B and ^{11}B

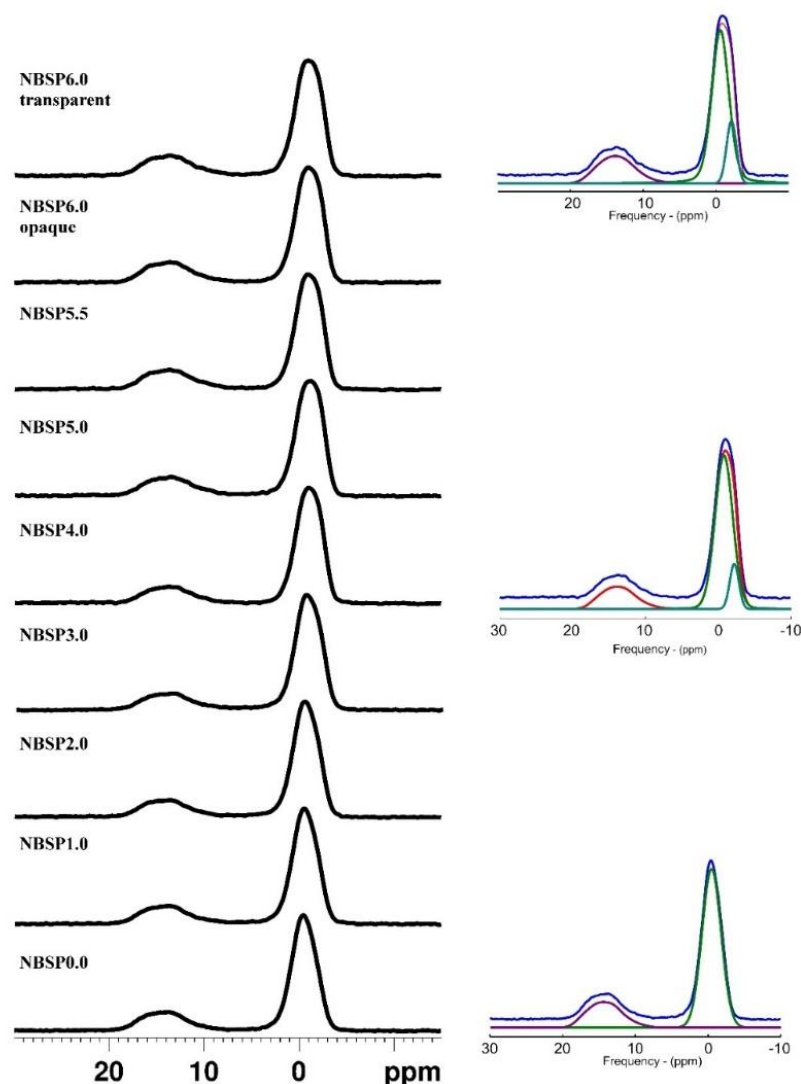


Figure 60 - ^{11}B MAS NMR spectra of NBSP0.0-6.0 samples with fitted Gaussian line shapes

4.1.3.8.2 ^{23}Na MAS NMR

Figure 61 shows the ^{23}Na MAS NMR spectra for the NBSP samples, which provided information on the distribution of Na^+ cations as either a modifier cation in the glass system and/or its involvement as a charge compensator (El-Damrawi, et al., 2017). Between 0.0 to 3.0 mol% P_2O_5 , the spectra were dominated by a broad symmetric peak centred approximately at -10 ppm, which suggested the initial incorporation of the Na in the network was as a glass modifier (El-Damrawi et al., 1992, 2016; El-Damrawi, et al., 2017). The overall spectral lines of the Na peaks were quite broad and lacking definition, which could be attributed to the lack of signal resolution and quadrupolar broadening due to the samples amorphous nature and subsequent structural disorder (Stebbins, 2020), resulting

in the masking of different bonding environments. At 4.0 mol% P_2O_5 the peak broadened further suggesting there may be a second distinct Na environment (Krishnamurthy et al., 2020). At 5.0 mol% P_2O_5 , the line shape started to become asymmetric, with a new peak feature occurring suggesting the accumulation and precipitation of some of the Na^+ cations in the glass phase causing the formation of clusters (El-Damrawi et al., 2017). This formation of clusters implies the beginnings of crystallisation of a Na bearing phase (Krishnamurthy et al., 2020), which can be confirmed by the XRD Rietveld analysis (Figure 41) and Raman spectroscopy (Figure 57) where the presence of Na_3PO_4 and $Na_4P_2O_7$ were identified as the crystal phases. As the P_2O_5 content continued to be increased, the spectral line shapes became increasingly more asymmetric, implying that P atoms were in close vicinity to Na atoms. The ^{31}P MAS NMR data indicated that the samples that contained both glassy and crystalline components were similar, where comparison to ^{23}Na MAS NMR data showed an increase in the intensity of the spectral features associated with the crystalline components. The samples with 0.0-3.0 mol% P_2O_5 displayed similar spectral line shapes, suggesting that Na may not be introduced immediately as the next nearest neighbour to P, where this may be due to the comparatively low concentration ratio of Na to P. On the other hand, the widening of the already broad spectral line of the NBSP4.0 sample may be also correlated to the occurrence of orthophosphates as indicated by ^{31}P MAS NMR spectra, whose charge may attract Na cations. The Na atoms experience a wider distribution in environments due to the addition of Q^0_P sites, leading to a wider range of quadrupole coupling interactions, resulting in wider spectral lines. Krishnamurthy et al. (2020) identified $Na_4P_2O_7$ crystals in similar glass systems using ^{31}P and ^{23}Na MAS NMR results.

Overall, the ^{23}Na MAS NMR results confirm the findings of the ^{31}P MAS NMR data, where the Na environment is being impacted by the introduction of P, suggesting that Na atoms are in close proximity to P atoms upon the formation of orthophosphates and pyrophosphates in samples with ≥ 4.0 mol% P_2O_5 . Although Na atoms are still in abundance in the glassy environments of the samples, and hence is not likely to be the limiting factor that forces phase separation to occur.

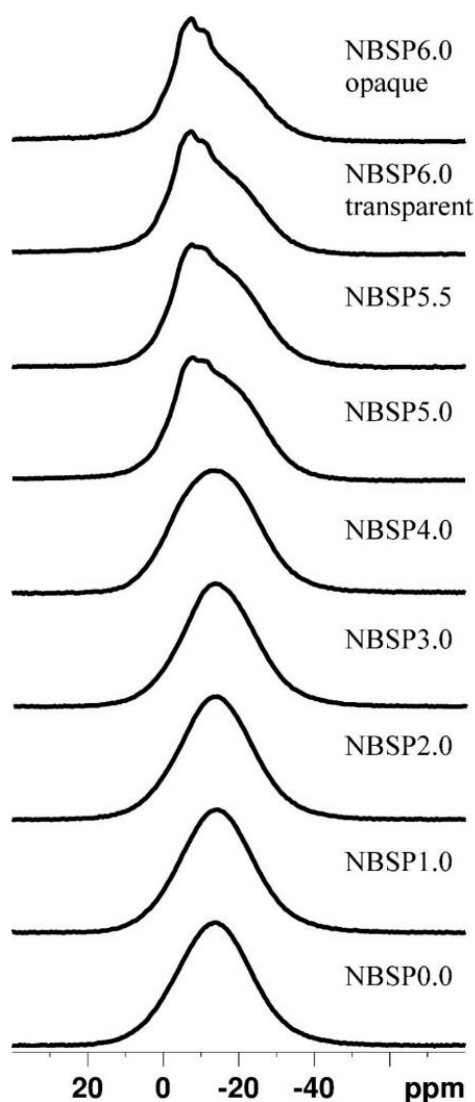


Figure 61 - ^{23}Na MAS NMR spectra

4.1.3.8.3 ^{31}P MAS NMR

Figure 62 presents the ^{31}P MAS NMR spectra for the NBSP samples, where Table 35 records and Figure 63 graphically presents the relative intensities for the ^{31}P identified peaks obtained from spectral fitting. The samples doped with 1.0-3.0 mol% P_2O_5 displayed a prominent broad peak centred at $\sim 3.0 \pm 5$ ppm, a smaller peak at $\sim 15.0\text{-}16.0 \pm 5$ ppm, and possibly another minor peak at ~ -8.0 to 9.0 ± 5 ppm, however it is within the noise level and difficult to distinguish. In the 4.0 mol% P_2O_5 doped sample, the spectral line shape changes, where the peak at 14 ± 5 ppm has transitioned from being a low broad peak to a sharp intense peak, and the peak at 3.0 ± 5 ppm reducing in intensity, forming a broad peak. When the samples were doped with ≥ 5.0 mol% P_2O_5 , the spectra began to exhibit characteristic crystalline signals with a peak position of 2.6 ± 0.1 ppm, where the peak base was slightly asymmetrical due to its maximum intensity not matching

that of the amorphous peak in the same area. The relative intensity of this peak increased with increasing P_2O_5 content, but due to the slow relaxation of the P (Youngman, 2018) it was difficult to determine the precise intensities. There were also differences in the spectra between the transparent and opaque NBSP6.0 sample, which could be due to the presence of the crystalline phases as well as variation in relaxation times, where crystals with a larger size take longer to relax (Youngman, 2018). There was also a small but real shift in the peak positions in the samples NBSP1.0-3.0 at 16 ± 5 ppm and NBSP4.0-6.0 at 14 ± 5 ppm, suggesting that there may have been changes in the next nearest neighbour environments of the P atoms.

According to literature, the peaks at $3.0-3.5 \pm 5$ ppm could be attributed to $P_{1B}^{(1)}$ units (Krishnamurthy et al., 2020; Muñoz et al., 2006), 15.0 ± 5 ppm could be assigned to $P_{0B}^{(0)}$ (Krishnamurthy et al., 2020; Muñoz et al., 2006), -7.0 ± 5 ppm could be ascribed to $P_{2B}^{(2)}$ (Krishnamurthy et al., 2020; Muñoz et al., 2006), and the peak at 2.6 ± 0.1 ppm could be attributed to $P_{1B}^{(0)}$ in $Na_3P_2O_7$ (Krishnamurthy et al., 2020; Lu et al., 2022; Muñoz et al., 2006).

When the ^{31}P and ^{11}B spectra were evaluated, the peak shapes displayed by ^{11}B MAS NMR spectra suggested that there may have been the insertion of P into the B environment, even though the relative intensity of $[^3]B$ and $[^4]B$ stayed constant. When the P_2O_5 content was ≥ 4.0 mol%, $P^{(0)}$ units were formed, as evidenced by the occurrence of the sharp peak at $15.0-16.0 \pm 5$ ppm, there was a small chemical shift to lower ppm values with increasing P_2O_5 content. This chemical shift indicated there may have been a change in the next nearest neighbour environment, especially when the P_2O_5 solubility limit was exceeded leading to the formation of $Na_4P_2O_7$ ($P^{(1)}$) and its precipitation out of the glass system, as confirmed by XRD, Rietveld analysis, and Raman spectroscopy.

Therefore, considering the above comments, it can be understood that when P_2O_5 was initially added to the NBS glass system, it formed an increasing number of P-O- $[^4]B$ linkages which led to the re-polymerisation of the silicate and boron sub-networks. However, as the P_2O_5 content increased, only a small fraction may have been involved with the formation of the P-O- $[^4]B$ linkages, where the remainder were involved in Q^0_P and Q^1_P species, leading to an increasingly more connected silicate sub-network that was partially linked to the borate sub-

network, where Na^+ cations are partially removed to act as charge compensators for the P atoms, leading to the subsequent increase in BØs (Tilocca & Cormack, 2007). The ^{23}Na MAS NMR spectral data should inform further on whether Na^+ cations were being scavenged by P and used as charge compensators.

Similar effects have been reported for disilicate glasses with the additions of small concentrations of P_2O_5 where the ^{31}P MAS NMR spectra showed that modifier cations were scavenged by P, producing orthophosphate and pyrophosphate units, resulting in the reduction of NBØs in the silicate network and the conversion of Q^3 units to Q^4 units (Canevali et al., 2005; Mackenzie & Smith, 2002; Raskar et al., 2008). It was also reported that when 5.0 mol% P_2O_5 was added to the disilicate glass system, the orthophosphate resonance in the ^{31}P MAS NMR spectra at 15.0 ppm was progressively replaced by a resonance at 2.5 ppm, which was attributed to $\text{Na}_4\text{P}_2\text{O}_7$ (Canevali et al., 2005; Mackenzie & Smith, 2002; Raskar et al., 2008). Krishnamurthy et al. (2020) reported on a similar glass system, where ^{23}Na MAS NMR spectra for a $\text{SiO}_2\text{-Na}_2\text{O-B}_2\text{O}_3\text{-Al}_2\text{O}_3\text{P}_2\text{O}_5\text{-Cs}_2\text{O-MoO}_3$ glass system displayed evidence of a Na bearing crystalline phase (poorly crystallized), which was assigned to crystalline $\text{Na}_4\text{P}_2\text{O}_7$.

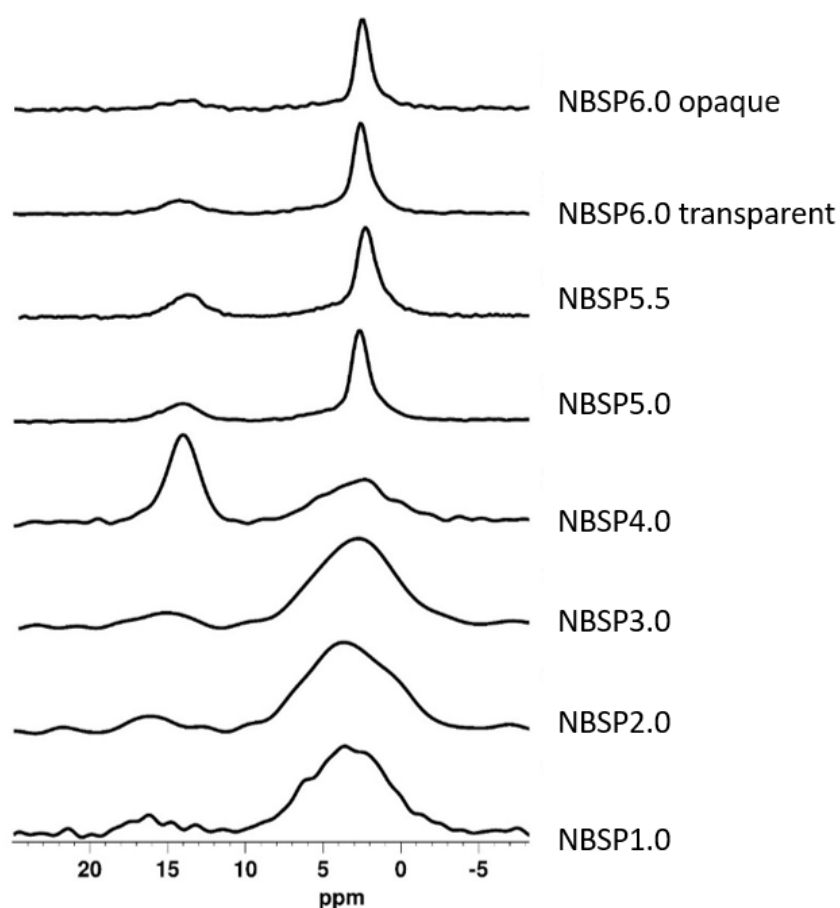


Figure 62 - ^{31}P MAS NMR spectra of NBSP samples

Sample	14.9 $\pm$ 5 ppm	3.1 $\pm$ 5 ppm	2.6 $\pm$ 15 ppm	-6.8 $\pm$ 5 ppm
NBSP0.0	-	-	-	-
NBSP1.0	11	89	-	-
NBSP2.0	7	93	-	-
NBSP3.0	9	85	-	6
NBSP4.0	48	48	-	5
NBSP5.0	20	27	49	4
NBSP5.5	22	21	55	2
NBSP6.0 (opalescence)	17	12	61	-
NBSP6.0 (translucent)	10	30	68	2

Table 35 - Normalised ^{31}P MAS NMR intensities derived from Gaussian line shape fitting (in atom % $\pm$ 5).

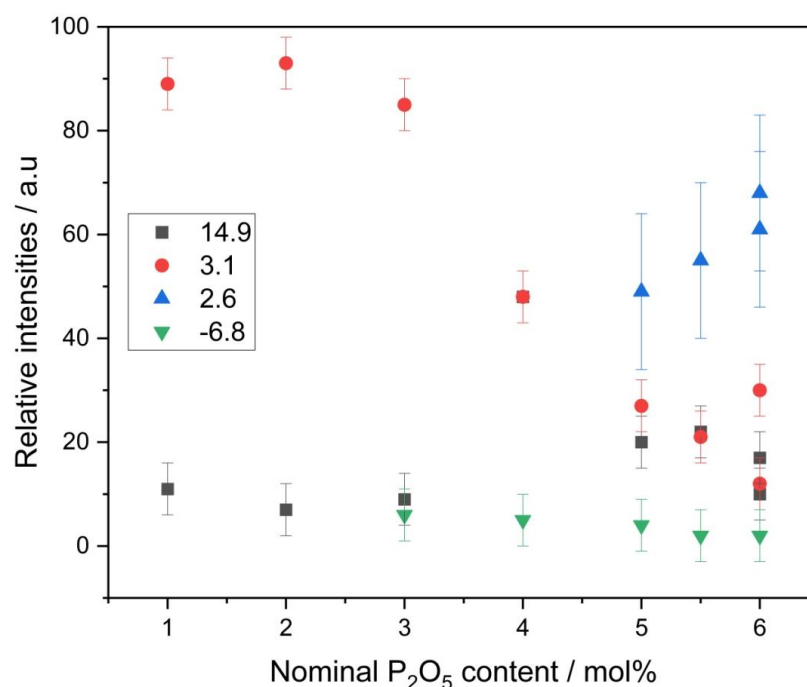


Figure 63 - Relative intensities for ^{31}P peaks obtained from spectral fitting as tabulated in Table 35

4.1.3.8.4 ^{29}Si MAS NMR

Figure 64 depicts the ^{29}Si MAS NMR spectra of the NBSP samples. The spectra were difficult to interpret and were not deconvoluted due to the broad line shapes and overlapping of the different Q^n unit sites, and their low signal resolution. According to literature, the average chemical shifts for Q^n units in an alkali borosilicate glass are ~ -70 , -80 , -90 , and 100 ppm (Krishnamurthy et al., 2020; Lu et al., 2022; Martin et al., 2005; Stone-Weiss et al., 2020).

The samples with 0.0 to 3.0 mol% P_2O_5 had a line shape centred at approximately -90 ppm, which according to Nanmba et al. (2004) can be attributed to not just Q^3 units with one NBØ but also to Q^4 species with $^{[4]}\text{B}$ as the second neighbour, and bridging oxygens (BØs) in $^{[4]}\text{B}\text{-O-Si}$ bridges. The samples displaying evidence of crystalline components (4.0–6.0 mol% P_2O_5) showed an asymmetrical line shape that shifted to more negative frequencies (to the right) as the P_2O_5 content increased, and which could be fitted with two distinct Gaussians pertaining to specific Q^n species i.e., Q^3 and Q^4 . The shift to lower ppm with increasing P_2O_5 indicates a conversion of Q^3 to Q^4 units (Muñoz et al., 2006; Stone-Weiss et al., 2020; Zhao et al., 2021), resulting in the re-polymerisation of the glassy network, as the amount of NBØs reduces. This behaviour agrees with Muñoz et al. (2006) where they reported that the lower

chemical shift of ^{29}Si spectra was an indication that the silicate network was re-polymerising due to the increased proportions of Q^3 and Q^4 units and/or reduction in the average amount of BO_3 and BO_4 units connected to silicates. Stone-Weiss et al. (2020) also suggested that the observed shift trend may also reflect a reduction in Q^3_{Si} units or an increase in the number of Si-O-P linkages, in accordance with the charge balance constraint: $[\text{Si}^{3+}] + [{}^{[4]}\text{B}^{3+}] + [\text{P}^2] = 2[\text{P}^1] = [\text{Na}]$.

Analysis of Figure 64 showed no distinct peaks above the background noise due to poorly resolved line shapes, where such peaks would have indicated the presence of specific Si units. These Si units have been previously identified in literature to be approximately centred at -160 and -220 ppm (Youngman et al., 2006).

In summary, as the P_2O_5 content increased there was the polymerisation of Q^3 to Q^4 units, which was consistent with the removal of Na cations from the glass network to precipitate out as sodium phosphate crystals, where P was in the P^1_{OB} environment. When P_2O_5 was initially added to the glass system, the phosphate was added as P^3 , where NBØs and required charge compensatory cations were provided by the glassy matrix, specifically the Si sub-network, because the ^{11}B MAS NMR data did not show a change in the relative intensity of the ${}^{[3]}\text{B}$ and ${}^{[4]}\text{B}$ peaks but did indicate phosphate incorporation into its surrounding.

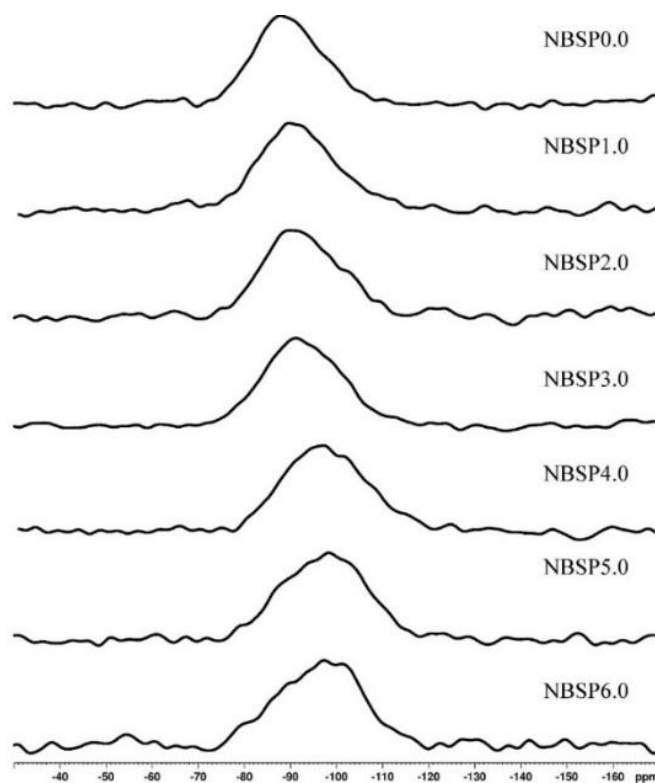


Figure 64 - ^{29}Si MAS NMR spectra

4.1.3.8.5 Oxygen Distribution

Yamashita et al. (1998) reported that with increasing P_2O_5 content, the Si Q^3 unit disappeared with the spectra consisting of only Si Q^4 units.

Due to the poorly resolved line shapes of the ^{29}Si MAS NMR spectra, it is not possible to accurately determine the oxygen distribution of the silica. However, basic compositional analysis based on oxygen bonded to boron [OB] and oxygen bonded to phosphorus [OP] can be used to calculate the estimated amount of oxygen bonded to silicon based on the MAS NMR data.

The mathematical analysis to calculate the oxygen distribution of [OB] and [OP] are located in 8.6 Appendix 8.6 and are based on internal correspondence with Professor Josef Werner and Dr Ulrike Werner-Zwanziger (Werner-Zwanziger & Werner, 2022b).

The average O per Si value can be estimated from the distribution between Q^3_{Si} and Q^4_{Si} species and is plotted in Figure 65. The amount of O available for Si bonding is the amount of O in O-Si bonding, [OSi], that is left over from eqn 44:

$$[\text{OSi}] = [\text{O}] - [\text{OB}] - [\text{OP}] \quad (44)$$

$$[OSi] = [O] - \left[\left([3]B * \frac{3}{2} + [4]B * 4/2 \right) B - [Q^0 * 4 + Q^1 * 3.5 + Q^2 * 3]P \right]$$

Where the average O available per Si is $\text{Average}(O/Si) \equiv [OSi]/[Si]$.

Hence, the uncertainty of $[OSi]$ is calculated in a similar fashion to $\Delta[OB]$ and $\Delta[OP]$, resulting in

$$\Delta([OSi]) = \sqrt{(\Delta([O]))^2 + (\Delta([OB]))^2 + (\Delta([OP]))^2} \quad (45)$$

Where the uncertainty of the average is calculated by:

$$\Delta\left(\text{average}\left(\frac{O}{Si}\right)\right) = \sqrt{\left(\frac{1}{[Si]} \cdot \Delta([OSi])\right)^2 + \left(\frac{[OSi]}{[Si]^2} \cdot \Delta([Si])\right)^2} \quad (46)$$

And consequently, the uncertainty of the Q^n speciation is:

$$\Delta Q^4_{Si} = 2 * \Delta\left(\text{average}\left(\frac{O}{Si}\right)\right) \quad \Delta Q^3_{Si} = \Delta Q^4_{Si}$$

Which results in the following values (Table 36) where the distribution of Q^4_{Si} and Q^3_{Si} are plotted in Figure 65.

Sample	[OSi]	Average (O/Si)	Q^4_{Si}	Q^3_{Si}
NBSP0	127.0 (2.6)	2.28 (0.05)	0.45 (0.10)	0.55 (0.10)
NBSP1	123.5 (2.6)	2.24 (0.05)	0.53 (0.10)	0.47 (0.10)
NBSP2	120.1 (2.6)	2.19 (0.05)	0.61 (0.11)	0.39 (0.11)
NBSP3	116.9 (2.7)	2.16 (0.05)	0.68 (0.11)	0.32 (0.11)
NBSP4	111.8 (3.0)	2.09 (0.06)	0.83 (0.12)	0.17 (0.12)
NBSP5	109.8 (3.6)	2.07 (0.07)	0.86 (0.14)	0.14 (0.14)
NBSP5.5	108.0 (3.8)	2.05 (0.07)	0.90 (0.15)	0.10 (0.15)
NBSP6 (opalescence)	106.8 (4.0)	2.04 (0.08)	0.93 (0.16)	0.07 (0.16)
NBSP6 (translucent)	106.6 (4.0)	2.03(0.08)	0.94 (0.16)	0.06 (0.16)

Table 36 - Analysis and uncertainties of Si as well as average oxygen per silicon value estimated from the distribution of Q^3 and Q^4 species

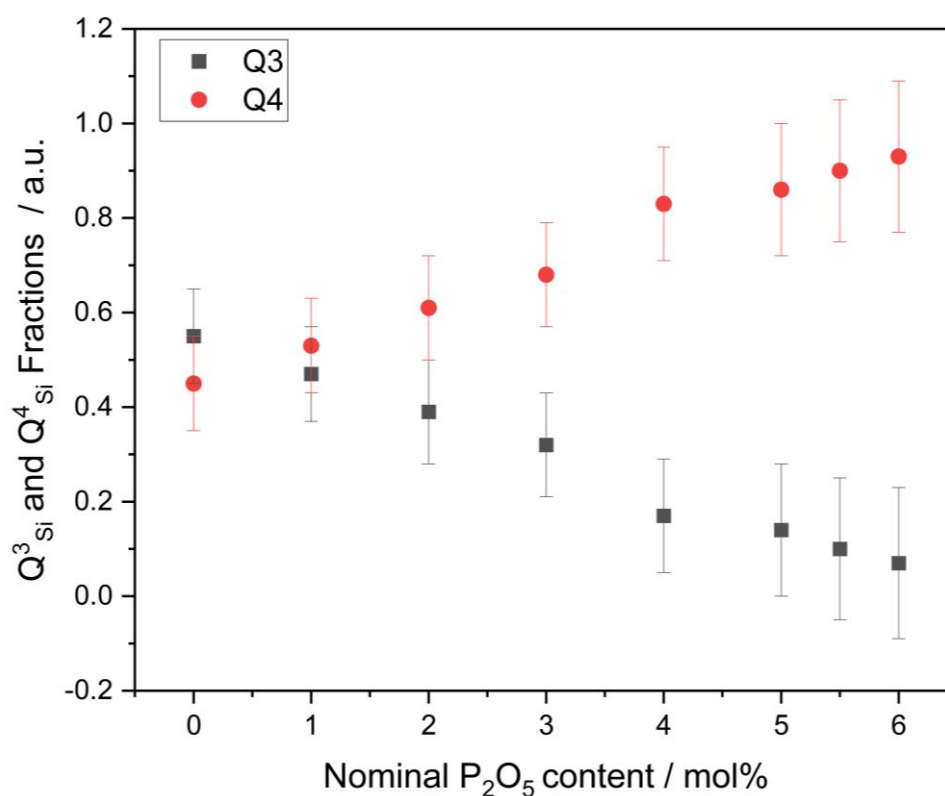


Figure 65 - Distribution of Q³ and Q⁴ Si species as a function of the nominal P₂O₅ content

The distribution of Q₃ and Q₄ Si species in Figure 65 agrees with previous literature where Stone-Weiss et al. (2020) attributed the reduction in Q³_{Si} units to the successful competition of P₂O₅ over SiO₂ in '*attracting network modifiers and/or effective charge sharing between P and B units in P-O-[⁴B linkages*'. Kirkpatrick and Brow (1995) stated that '*phosphorus has the ability to scavenge charge balancing modifier cations from the silicate sub-network, increasing its polymerization*' where this effect can be seen increasing the Q⁴:Q³ ratio with increasing P₂O₅ content. This scenario can be characterised by the reaction '*P-O-P + Si-O-M → P-O-M + Si-O-Si*', where the right-side of the equation is thermodynamically favoured (Kirkpatrick & Brow, 1995). This behaviour exhibited by P has also been reported in similar studies by Cheng (2004) for a phosphate-doped borosilicate glass system, and Zhao et al. (2021) for a P₂O₅-Na₂O-Al₂O₃-SiO₂ glass system.

In summary, the MAS NMR data has shown that P₂O₅ added to the borosilicate glass system enters as Q³_P but changes to Q⁰_P, Q¹_P, and Q²_P, as confirmed by ³¹P MAS NMR spectra. The lack of change in the [³B]:[⁴B] ratio with increasing P₂O₅, suggested that the P preferentially enters the [⁴B] sub-network, but is supplied O from the silicate sub-network, causing NBØs on the Si to transform

into BØs resulting in its re-polymerisation, as evidenced by the decrease in Q^3_{Si} and increase in Q^4_{Si} units (Figure 65). Once the NBØs are unavailable, the P bonds with itself resulting in segregation and formation of Q^0_P and Q^2_P clusters, which eventually form crystalline $Na_4P_2O_7$. The Na MAS NMR confirms this, where it demonstrated that the Na cations cluster and precipitate at 4.0-5.0 mol% P_2O_5 resulting in the crystallisation of an Na-bearing phase.

4.1.4 Summary

This work has demonstrated what happens with phase separation in relevant glasses, and more importantly, the knock-on effects this has on the glass structure, even below the P_2O_5 solubility limit in terms of nano-scale phase separation, which may affect the chemical durability, and re-polymerisation of the silicate sub-network, which will also impact the glass durability and potentially increase melt viscosity. The work also found that the solubility limit has two aspects, where it could be regarded as the point at which crystallisation occurs or the point at which homogeneous materials develop inhomogeneity at a measurable length scale.

This work has also demonstrated the importance and effect of thermal treatment of the sodium borosilicate glass system and how this can affect other properties such as the crystallisation behaviour and viscosity, where the point at which phase separation and crystallisation occur changes depending on whether the glass melt, was air quenched, annealed, or subjected to the HLW and LAW CCC heat treatments.

- XRD showed that between 0.0-3.0 mol% P_2O_5 , the annealed glasses were X-ray amorphous. However, >4.0 mol% P_2O_5 there were identifiable crystalline phases i.e., Na_3PO_4 and $Na_4P_2O_7$. When the samples were quenched, the point at which crystallisation occurred differed, where crystal phases were identified at ≥ 5.0 mol% P_2O_5 .
- The difference in crystallisation behaviour can be attributed to annealing of phase-separated glasses at temperatures above T_g of the second (sodium phosphate) phase, which facilitated crystallisation of this phase at lower P_2O_5 contents. This then affected T_g , which both increased and decreased, showing the dual effect of P_2O_5 evidenced in literature.

- The samples that underwent the HLW and LAW CCC regimes showed an onset of crystallisation earlier than the annealed or quenched samples.
- Increasing the P_2O_5 content had the effect of increasing the T_g onset, which was indicative of the silicate network re-polymerising.
- The viscosity data demonstrated that NBSP0.0 had the lowest viscosity and shear rate at 950°C, whilst NBSP6.0 had the highest with a value of $\text{Log}(\eta / \text{dPas}) = 1.721$.
- The occurrence of non-Newtonian behaviour and increase in viscosity in some of the glass melts may have been a result of phase separation, where the sodium phosphate phases may have been acting as the major viscous phase.
- Raman spectra and MAS NMR spectral data indicated that the silicate sub-network was re-polymerising with increasing P_2O_5 content, as evidenced by the reduction in the intensity of the reedmergnerite- / danburite-like structure peak at 630 cm^{-1} , as well as the calculated distribution of Q^3_{Si} and Q^4_{Si} species.

4.2 NBSI-S and NBSIS-P Glass Series

4.2.1 Introduction

The glasses studied in this chapter are sodium borosilicate glasses doped with SO_3 and P_2O_5 , with the compositions $\text{Na}_2\text{O-B}_2\text{O}_3\text{-SiO}_2\text{-xSO}_3$ and $\text{Na}_2\text{O-B}_2\text{O}_3\text{-SiO}_2\text{-SO}_3\text{-xP}_2\text{O}_5$. Both glass system's undoped base glass had the nominal composition $27.9\text{Na}_2\text{O-16.3B}_2\text{O}_3\text{-55.8SiO}_2$, which lays outside the immiscibility region in the $\text{Na}_2\text{O-B}_2\text{O}_3\text{-SiO}_2$ ternary phase diagram. The study aims to establish the solubility limit of SO_3 and whether P_2O_5 has a positive effect of increasing this limit, and the effects on thermal properties and crystallisation behaviour. This study is important because SO_3 is present in both HLW and LAW waste streams, and there has been little research into increasing its solubility by utilising P_2O_5 . This study should help provide further information on the effects of altering P_2O_5 content and its potential effects on more complex nuclear waste compositions abundant in SO_3 .

4.2.2 Experimental Procedures

Two sets of glasses were prepared for the determination of SO_3 solubility limit and effects of P_2O_5 on the solubility of SO_3 in borosilicate glasses. The borosilicate glass to establish the SO_3 solubility compromised $\text{Na}_2\text{O-B}_2\text{O}_3\text{-SiO}_2\text{-xSO}_3$, where $x = 1.00, 1.50, 1.75, 1.875, 2.00, 2.25$ mol%, whilst the borosilicate glass with a fixed amount of SO_3 but varying P_2O_5 compromised $\text{Na}_2\text{O-B}_2\text{O}_3\text{-SiO}_2\text{-SO}_3\text{-xP}_2\text{O}_5$, where $x = 1.0, 2.0, 3.0, 4.0, 5.0$ mol%. SO_3 was incorporated into the glass systems as Na_2SO_4 , whilst the P_2O_5 was incorporated as $\text{NH}_4\text{H}_2\text{PO}_4$. 50g batches of the NBSi-Sx and 80g batches of the NBSiS-Px glass were prepared using the melt-quench method using the precursors SiO_2 , Na_2CO_3 , B_2O_3 , Na_2SO_4 and $\text{NH}_4\text{H}_2\text{PO}_4$. The precursors were weighed and transferred to a plastic bag before being milled for 10 seconds in a steel mill to thoroughly mix the contents. The batch was then placed in an alumina crucible and heated in an electric furnace at a rate of $5^\circ\text{C}/\text{min}$ to 1150°C , where it was left to dwell for 3 hours before the glass melt was poured into a steel mould and air quenched at room temperature. The NBSiS2.25-Px samples were then crushed and milled in a tungsten carbide mill at 700RPM for 240 seconds, before being mixed with approximately 250 ml of DI water. This mixture was then heated on a stirring hot plate for one hour at 90°C , after which the solution was filtered, and then the slurry was washed further with ethanol and left to dry in an oven at 100°C .

for 2 hours. The dried powder NBSi-Sx samples were analysed using XRD to establish the solubility limit and crystallisation behaviour of the glasses. The bulk NBSiS-Px samples were then analysed using bulk density, whilst the dried powder samples were then analysed using XRF, XRD, DTA, and Raman spectroscopy to characterise the solubility limit of SO₃ and the effects of adding P₂O₅ to the glass systems. Further details of experimental methodology can be read in *Chapter 3: Experimental Methodology*.

4.2.3 Results and Discussion

4.2.3.1 NBSi-Sx

4.2.3.1.1 Visual Observations

Visual inspection of the glasses in Figure 66, revealed optical transparency from 1.00 to 1.75 mol% (1.27 to 2.20 wt%) SO₃. At 1.875 mol% and above SO₃ content, the glasses started to become cloudy where a salt phase separated from the bulk melt and migrated to the surface of the sample. However, whilst the 1.875 mol% sample displayed cloudiness, the XRD pattern did not display any measurable crystalline peaks (Figure 68).

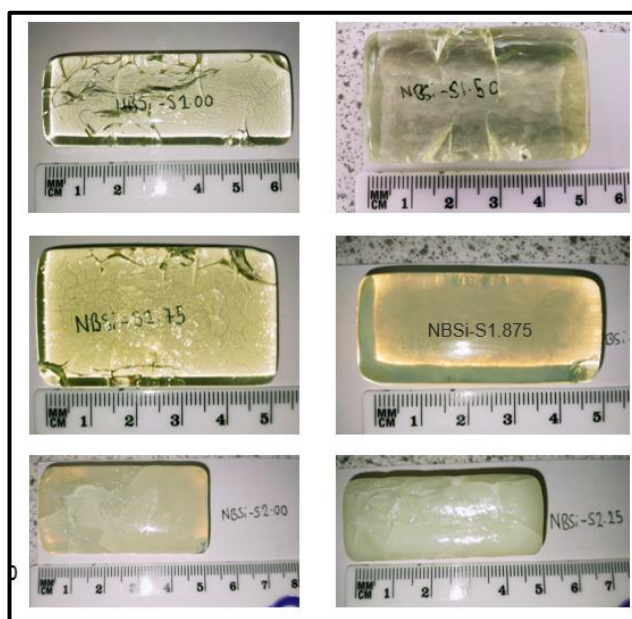


Figure 66 - NBSi-Sx samples

4.2.3.1.2 XRF

Figure 67 shows the graphical XRF abundance results from Table 37. The results showed that as the SO₃ content increased, there was little variation in the SiO₂ and Na₂O content within error, with the SiO₂ content varying between 51.54-57.39

mol% and the Na₂O content varying between 26.34-30.74 mol%. The NBSi-S1.00-2.25 had evidence of Al contamination, which may have come from the alumina crucibles used to melt the glass batches. The base glass did not show Al₂O₃ contamination because its composition was from the same compositional sample as the NBSP0.0 sample, where this was melted in a 90%Pt-10%Rh crucible. The SO₃ content increased linearly within error in accordance with the nominal composition. Further discrepancies in the composition may have been due to the heat treatment of the glass and subsequent melting time (Xu et al., 2021), the volatilisation of the SO₃ during melting, the part of the melt from which the glass sample was taken for analysis, the removal of water-soluble phases during the removal of the salt layer, and any uncertainties associated with the preparation and analysis of XRF.

Sample		Oxide (mol%)					
		SiO ₂	Na ₂ O	Al ₂ O ₃	SO ₃	B ₂ O ₃ *	SUM
NBSi-S0.00	Nominal	55.81	27.91	-	0.00	16.28	100
	Pro'ratd	57.39 ±	26.34 ±	-	0.00	16.27	100
	Analysed	0.01	0.01				
NBSi-S1.00	Nominal	55.26	27.63	-	1.00	16.12	100
	Pro'ratd	51.54	30.04	1.22	1.10	16.11	100
	Analysed	±0.01	±0.01	±0.03	±0.02		
NBSi-S1.50	Nominal	54.98	27.49	-	1.50	16.03	100
	Pro'ratd	52.42 ±	28.78	1.25	1.60	15.94	100
	Analysed	0.01	±0.01	±0.02	±0.02		
NBSi-S1.75	Nominal	54.84	27.42	-	1.75	15.99	100
	Pro'ratd	52.05 ±	28.79	1.49	1.78	15.88	100
	Analysed	0.01	±0.01	±0.02	±0.02		
NBSi-S1.875	Nominal	54.77	27.38	-	1.875	15.97	100
	Pro'ratd	51.41 ±	29.43	1.32	2.00 ±	15.83	100
	Analysed	0.01	±0.01	±0.02	0.02		

NBSi-S2.00	Nominal	54.7	27.35	-	2	15.95	100
	Pro'ratd Analysed	52.36	28.99	1.27	1.62	15.76	100
NBSi-S2.25	Nominal	54.56	27.28	-	2.25	15.91	100
	Pro'ratd	49.38 ±	30.74	1.58	2.54 ±	15.76	100
	Analysed	0.01	±0.01	±0.02	0.01		

Table 37 - XRF analysis of NBSi-Sx samples

*B₂O₃ used the nominal composition, where it cannot be measured using XRF.

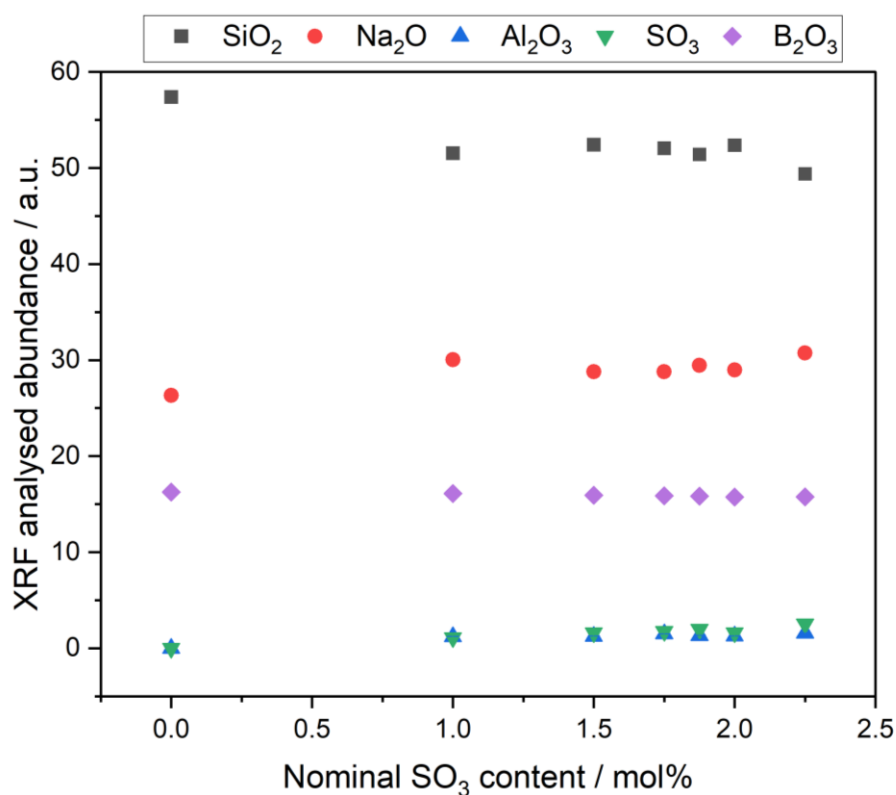


Figure 67 - XRF results in mol% of the NBSi-Sx glasses

4.2.3.1.3 X-ray Powder Diffraction

Figure 68 shows the XRD patterns for NBSi-Sx glasses, which were used to establish the solubility limit of SO₃ in the glasses and the crystalline phases which occurred if this was exceeded. The XRD patterns showed that as the S content increased, the samples became increasingly more crystalline, where the crystalline phase identified was sodium sulphate (Na₂SO₄, PDF#: 04-010-4832 and 00-024-1132, (Swanson et al., 1974)), which had an orthorhombic crystal structure (Appendix 8.8, (Figure 154) (Table 84)). The Na₂SO₄ was identified in

the 2.00 and 2.25 mol% SO_3 samples (Figure 69 and Figure 70), however, there was evidence of a low intensity unidentifiable peak at $\sim 27^\circ 2\theta$ in the NBSi-S1.00, 1.50, 1.75, and 1.875 samples. In these two samples, the solubility limit had been exceeded, forming a sulphate-rich salt layer on the top of the samples, which precipitated out during cooling of the melt, where this has been identified to be the phase separated layer called '*gall*' (Krishnamurthy & Kroeker, 2022) (Figure 66). This gall layer is detrimental for radioactive waste glasses because it is a water soluble phase, which could negatively impact the chemical durability of the glass, and it also sequesters radioactive isotopes e.g., Cs which could then leach out of the glass matrix (Jantzen, 1999; Krishnamurthy & Kroeker, 2022). The XRD patterns suggested that the solubility limit of S was between 1.875 and 2.00 mol% (2.34 and 2.51 wt%). Na_2SO_4 is an inorganic salt that is soluble in water (161-190 g/l at 20°C and 430 g/l at 100°C) with a melting point of 884°C , and density of 2.7 g/cm^3 (Lide et al., 2005).

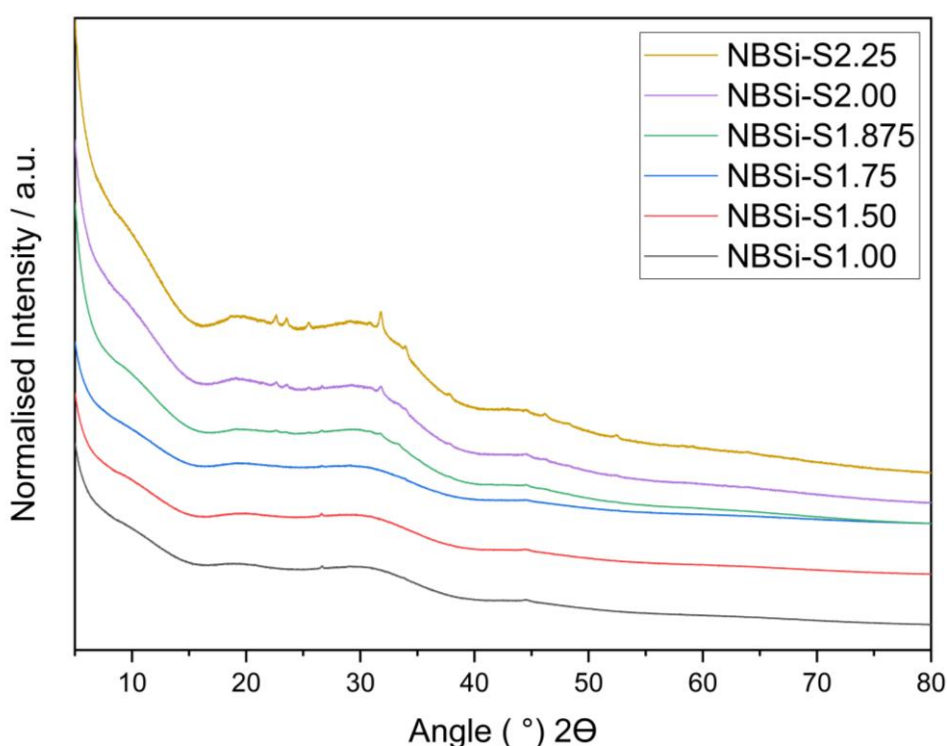


Figure 68 - XRD patterns of NBSi-Sx samples

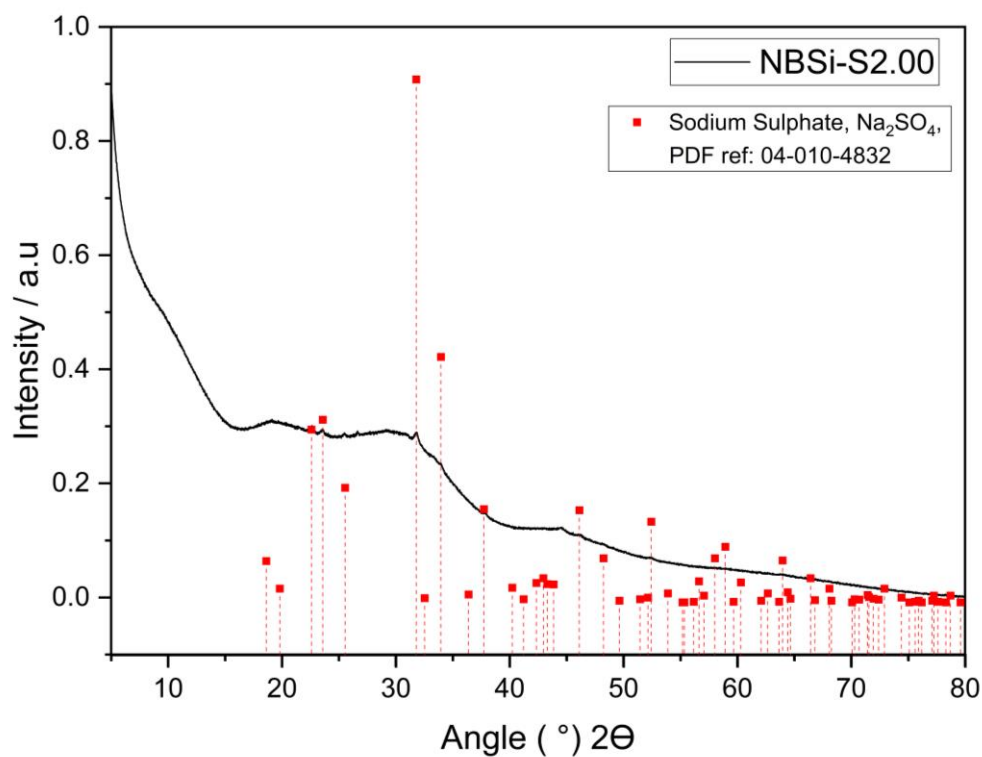


Figure 69 - XRD pattern with identified crystal phase of NBSi-S2.00

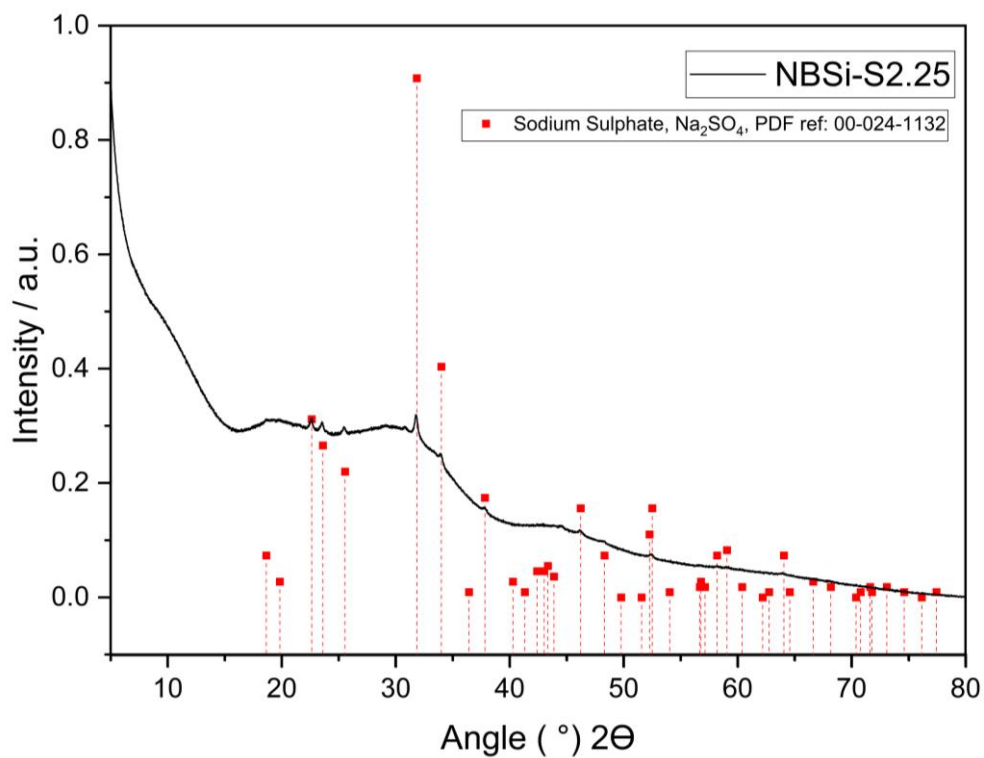


Figure 70 - XRD pattern with identified crystal phase of NBSi-S2.25

4.2.3.2 NBSiS-Px

4.2.3.2.1 Visual Observations

Visual assessment of the NBSiS-Px samples (Figure 71) showed that the base glass (NBSiS-P0.0) was cloudy, and the P_2O_5 doped samples were all opaque, indicating the presence of phase separation and crystallisation.

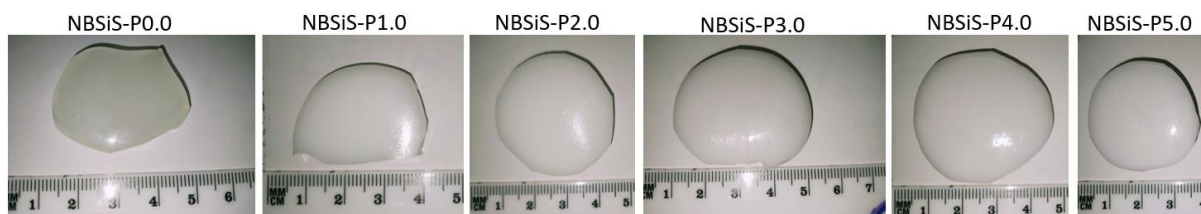


Figure 71 - Images of NBSiS-Px samples

4.2.3.2.2 XRF and ICP-OES

Figure 72 shows the graphical XRF abundance results from Table 38. The results show that as the P_2O_5 content increased, there was little variation in the SiO_2 and Na_2O content within error, with the SiO_2 content varying between 50.54-53.62 mol% and the Na_2O content varying between 27.14-28.20 mol%. The SO_3 results showed that as the P_2O_5 content increased the SO_3 contents reduced within error, where the SO_3 content was 2.27 mol% in the base glass and 2.12 mol% at 5.0 mol% P_2O_5 (Figure 73). The decrease in the SO_3 content may have been due to its supersaturation in the melt, leading to the crystallisation of excess SO_4^{2-} as Na_2SO_4 (Xu et al., 2020). The discrepancies in the composition may have been due to the heat treatment of the glass and subsequent melting time (Xu et al., 2021), the volatilisation of the SO_3 during melting, the part of the melt from which the glass sample analysed was taken, the removal of water-soluble phases during the removal of the salt layer, and any uncertainties associated with the preparation and analysis of XRF.

The results shown in Figure 73 do not mirror what has been previously reported in literature (Krishnamurthy & Kroeker, 2022; Vienna et al., 2014) where additions of P_2O_5 have seen notable increases in the solubility of SO_3 . It should be noted, that differences in how the glass was saturated with SO_3 has resulted in different results, e.g., the introduction of SO_2 gas in the melt in the form of a gas mixture comprising of N_2 , SO_2 , and O_2 (Vienna et al., 2014; Xu et al., 2021). The experimental work described in this chapter supersaturated the glasses by

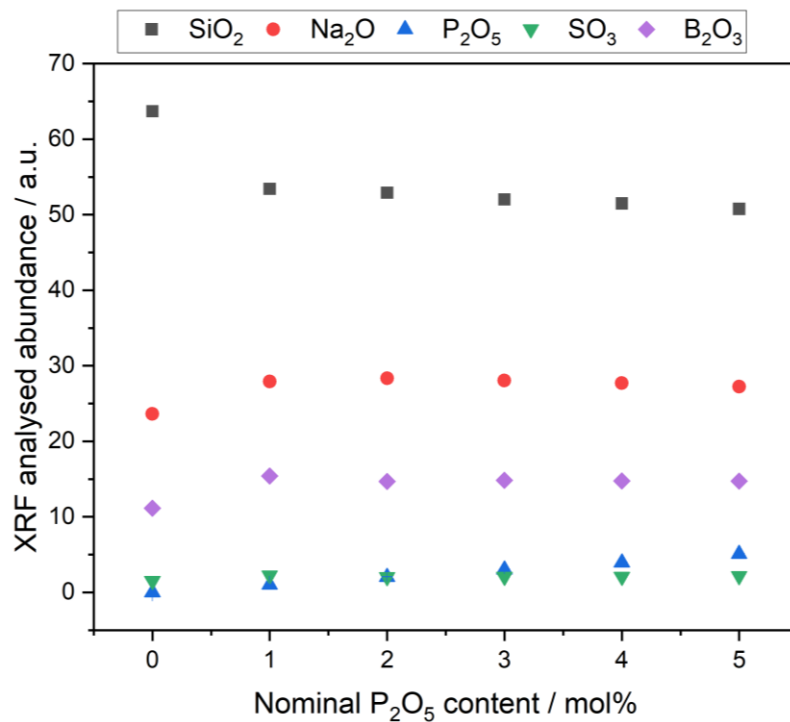
adding Na₂SO₄ as a raw material to the rest of the batch materials (Vienna et al., 2014), by adding 2.25 mol% (2.81 wt%), which had been determined to be above the solubility limit, as identified by XRD (Figure 68). The solubility of SO₃ in glass melts is largely governed by the glass composition and redox conditions, where Na₂O content is one of the main influences on the SO₃ solubility (Bingham et al., 2017; Manara et al., 2007; Vienna et al., 2014; Xu et al., 2021). The Na⁺ cations preferentially charge compensate the SO₄²⁻ anions in the glass over other ionic species e.g., Li⁺ and Ca²⁺ (Bingham et al., 2017; Xu et al., 2020, 2021). The presence of P⁵⁺ will be competing for Na⁺ cations because of its high cation field strength (2.13 Å⁻²), and may result in O²⁻ sharing rather than clustering and crystallisation (Bingham et al., 2017; Krishnamurthy & Kroeker, 2022). Additions of P₂O₅ have seen an increase in the solubility of SO₃ (≤ 3.0 mol%) where higher concentrations have seen this trend reverse (Vienna et al., 2014). However, the XRF and ICP-OES data did not seem to agree with the above statement, where the SO₃ solubility saw no notable change within error after the addition of P₂O₅. The XRF and ICP-OES results were the same within error at 0.0, 1.0, 4.0, and 5.0 mol% P₂O₅. At 2.0 and 3.0 mol% P₂O₅, the results were not the same within error, where the XRF values were higher than the ICP-OES. The XRF had values of 2.17 ± 0.02 and 2.14 ± 0.02 mol% SO₃ for 2.0 and 3.0 mol% P₂O₅, respectively, whereas the ICP-OES values were 2.05 ± 0.15 and 2.09 ± 0.15 mol% P₂O₅, respectively. The overall XRF results were the same within error when P₂O₅ was added to the composition, except between 3.0 and 4.0, and 4.0 and 5.0 mol% P₂O₅ and the overall ICP-OES results upon the addition of P₂O₅ were all the same within error.

Sample		Oxide (mol%)				
		SiO ₂	Na ₂ O	P ₂ O ₅	SO ₃	B ₂ O ₃
NBSiS2.25-P0.00	Nominal	54.56	27.28	0.00	2.25	15.92
	Analysed	63.64 ±	23.61 ±	0.00	1.63 ±	11.12
	and pro-rat'd	0.01	0.01		0.02	±0.15*
	Analysed and pro-rat'd	63.70 ±	23.64 ±	0.00	1.54	11.13
		0.01	0.01		±0.15*	±0.15*
NBSiS2.25-P1.00	Nominal	54.00	27.00	1.00	2.25	15.75

	Analysed	53.47 ±	27.94 ±	1.01 ±	2.16 ±	15.42
	and pro-rat'd	0.01	0.01	0.02	0.02	±0.15*
	Analysed	53.42 ±	27.91 ±	1.01 ±	2.26	15.41
	and pro-rat'd	0.01	0.01	0.02	±0.15*	±0.15*
NBSiS2.25- P2.00	Nominal	53.44	26.72	2.00	2.25	15.59
	Analysed	52.84 ±	28.29 ±	2.05 ±	2.17 ±	14.65
	and pro-rat'd	0.01	0.01	0.02	0.02	±0.15*
	Analysed	52.90 ±	28.32 ±	2.05 ±	2.05	14.67
	and pro-rat'd	0.01	0.01	0.02	±0.15*	±0.15*
NBSiS2.25- P3.00	Nominal	52.88	26.44	3.00	2.25	15.43
	Analysed	51.99 ±	28.01 ±	3.03 ±	2.14 ±	14.84
	and pro-rat'd	0.01	0.01	0.02	0.02	±0.15*
	Analysed	52.01 ±	28.02 ±	3.03 ±	2.09	14.84
	and pro-rat'd	0.01	0.01	0.02	±0.15*	±0.15*
NBSiS2.25- P4.00	Nominal	52.33	26.16	4.00	2.25	15.25
	Analysed	51.49 ±	27.72 ±	3.97 ±	2.06	14.77
	and pro-rat'd	0.01	0.01	0.02	0.02	±0.15*
	Analysed	51.48 ±	27.71 ±	3.97 ±	2.07	14.76
	and pro-rat'd	0.01	0.01	0.02	±0.15*	±0.15*
NBSiS2.25- P5.00	Nominal	51.77	25.88	5.00	2.25	15.11
	Analysed	50.77 ±	27.26 ±	5.10 ±	2.14 ±	14.73
	and pro-rat'd	0.01	0.01	0.02	0.02	±0.15*
	Analysed	50.76 ±	27.26	5.10 ±	2.15	14.73
	and pro-rat'd	0.01	0.01	0.02	±0.15*	±0.15*

* Indicates value obtained by ICP-OES

Table 38 - XRF (mol%) and nominal composition of NBSiS-Px samples, with ICP-OES values for SO₃ and B₂O₃, as indicated by *



**Error bars are too small to be plotted*

Figure 72 - Graphical representation of XRF and ICP-OES analysis of NBSiS-Px samples, where SO_3 and B_2O_3 have been measured by ICP-OES

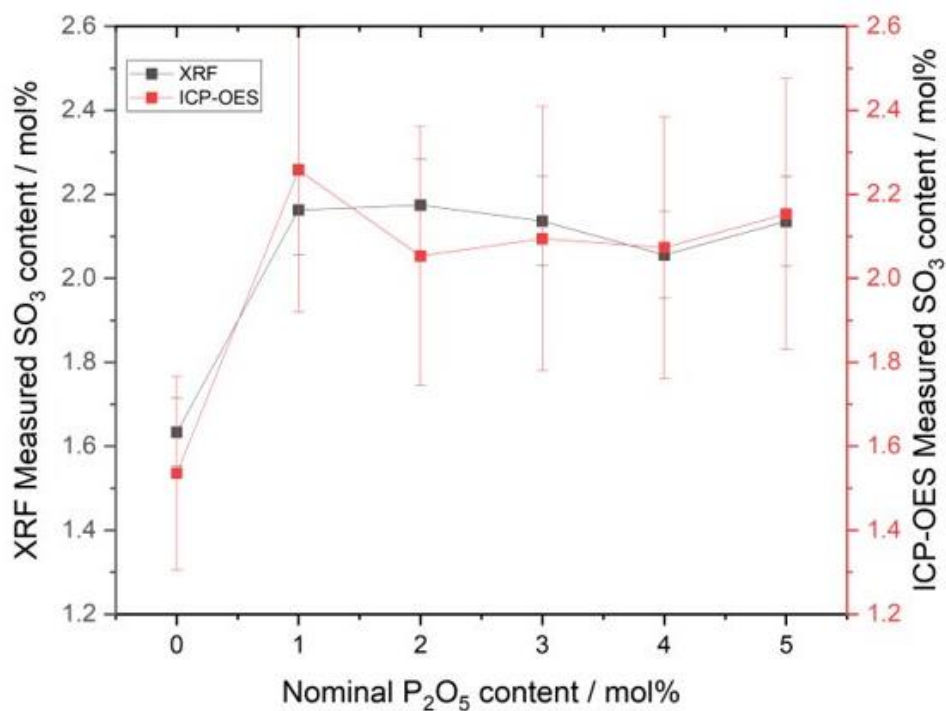


Figure 73 – Comparison of Analysed residual SO_4^{2-} content as a function of the nominal P_2O_5 content by XRF and ICP-OES

4.2.3.2.3 Bulk Density and Molar Volume

Figure 74 depicts the variation in the bulk density and molar volume of the samples as a function of their nominal P₂O₅ contents, where the bulk density varies in the range of 2.504 ± 0.003 to 2.522 ± 0.010 g.cm⁻³ and the molar volume between 33.536 and 36.708 cm³/mol. The densities of the samples decreased linearly within error with increasing P₂O₅ content, whilst the molar volume increased. When P₂O₅ enters the glass structure, it exists as an isolated tetrahedra, occupying free space in the glass structure without necessarily connecting to the glass network (Xu et al., 2020). The change in the molar volume behaviour is caused by the changes in the short-range structure with increasing P₂O₅ content, where P₂O₅ increases the molar volume resulting in a more open and less compact glass structure, contributing to the decrease in the density. This less compact glass structure is beneficial for increased cation mobility (Sułowska et al., 2021). The decrease in density but increase in molar volume with the introduction of P₂O₅, demonstrates the mixed glass former effect (MGFE) (Chanshetti et al., 2011). The density is often dominated by the short range atomic packing of constituent atoms and ions in the glass, but the lack of strong MGFE in the molar volume may suggest that the short range order (the first co-ordination sphere around each atom/ion) is not strongly affected by it (Chanshetti et al., 2011).

Sample	Bulk Density (g.cm ⁻³)					Molar mass of glass (M)	V _{mol} (cm ³ /mol)
	1	2	3	Average	STDEV (1σ)		
0	2.511	2.530	2.524	2.522	0.010	84.568	33.536
1	2.512	2.513	2.514	2.513	0.001	86.036	34.240
2	2.509	2.509	2.519	2.512	0.006	87.504	34.831
3	2.508	2.508	2.509	2.508	0.001	88.972	35.473
4	2.504	2.507	2.512	2.507	0.004	90.441	36.073
5	2.500	2.506	2.506	2.504	0.003	91.909	36.708

Table 39 - Bulk density, Molar volume and V_m of the NBSiS-Px samples

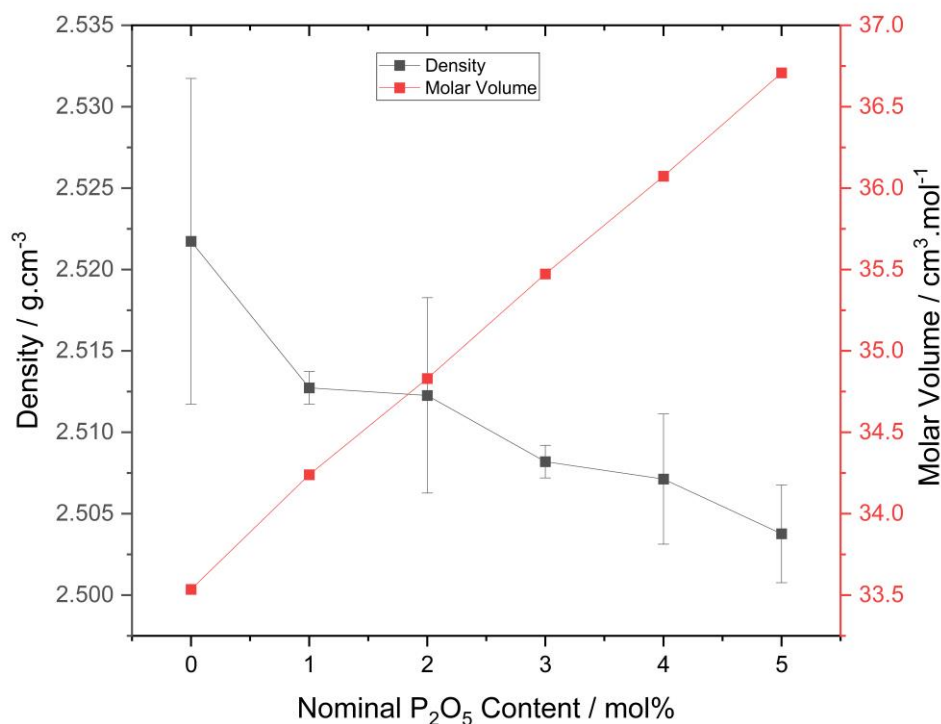


Figure 74 - Bulk density of NBSiS-Px samples as a function of their nominal P₂O₅ content

4.2.3.2.4 X-ray Powder Diffraction

Figure 75 shows that only the base glass was mostly X-ray amorphous, except for an unidentifiable peak at $\sim 5^\circ 2\theta$ which may potentially be caused by X-ray scattering of a weakly present phase, where its concentration is too low for XRD to measure. When 1.0 mol% P₂O₅ was added to the base glass, the XRD pattern showed crystalline peaks that were identified to be sodium phosphate (Na₃PO₄, PDF#: 04-009-5232 (Newsam et al., 1980)), which had a cubic crystal structure (Appendix 8.8 (Figure 155 and Table 85)). When 2.0 and 3.0 mol% P₂O₅ were added to the glass, the peaks identified in NBSiS-P1.0 increased in relative intensity, with the crystalline phase also being identified as sodium phosphate (Na₃PO₄, PDF#: 04-009-5232 (Newsam et al., 1980)) (Figure 77 and Figure 78). When 4.0 mol% P₂O₅ was added, instead of there just being one crystalline phase present, there were now two, identified to be sodium phosphate (Na₃PO₄, PDF#: 04-009-5232 (Appendix 8.8 (Figure 155 and Table 85)) (Newsam et al., 1980) and Na₄P₂O₇, PDF#: 04-018-4331 (Appendix 8.8 (Figure 156 and Table 85) (Leung & Calvo, 1972)) (Figure 79). The Na₄P₂O₇ had an orthorhombic crystal structure (Appendix 8.8 (Figure 155 and Table 85)). At 5.0 mol% P₂O₅ the intensity of the peaks at $\sim 20^\circ 2\theta$ and $34^\circ 2\theta$ reduced in intensity (Figure 80), with

an increase in the relative intensity of $\text{Na}_4\text{P}_2\text{O}_7$ specific peaks. There was a distinct lack of sulphate specific crystal phase peaks, even though the Raman spectra (Figure 83) indicated the presence of sulphate crystalline specific intensities. The absence of these peaks may be due to the majority of the Na_2SO_4 crystal phase dissolving in the washing process, where the samples were crushed and dissolved in DI water at 90°C . The phase separation in the glass may have been induced by either the SO_3 , P_2O_5 , or both depending on whether they had exceeded their solubility and were in excess (Li et al., 1995). However, the occurrence of sodium phosphate in all glasses except the base glass, suggests that phosphates may be instigating the phase separation.

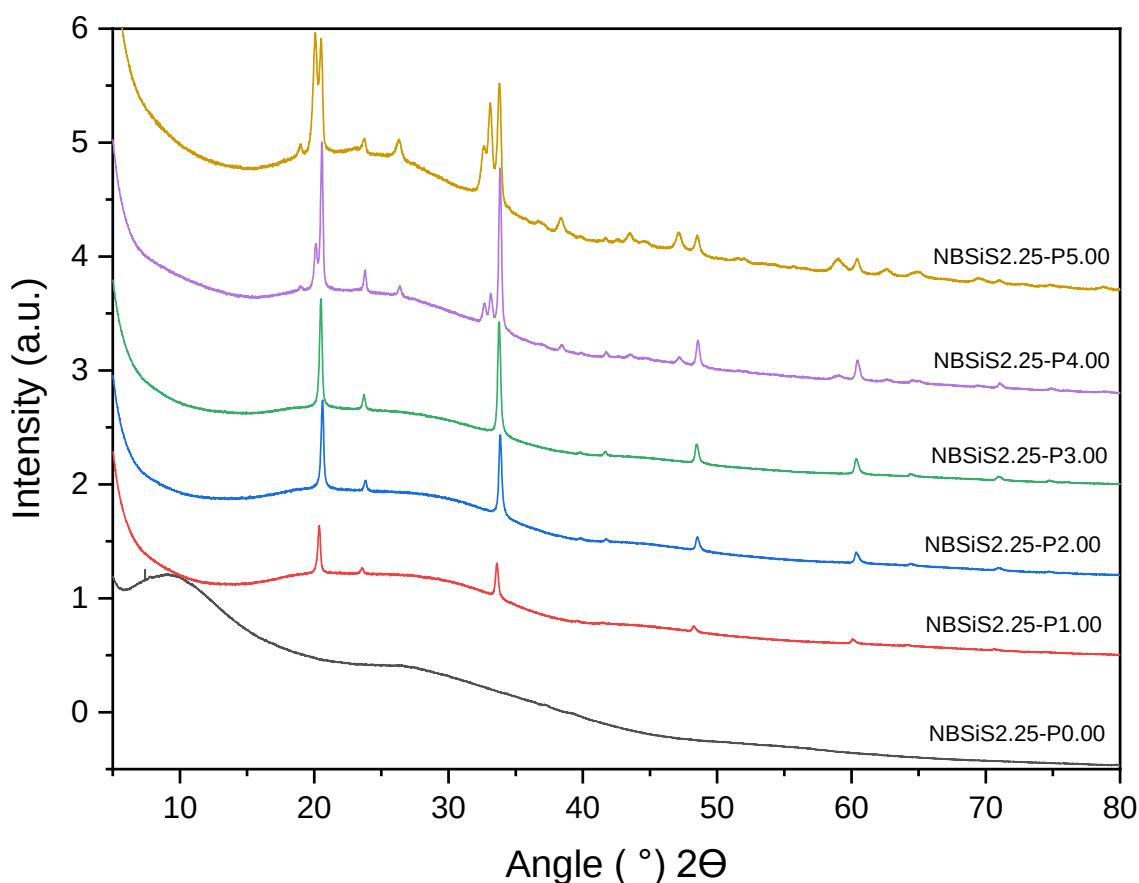


Figure 75 - NBSiS-Px XRD Patterns

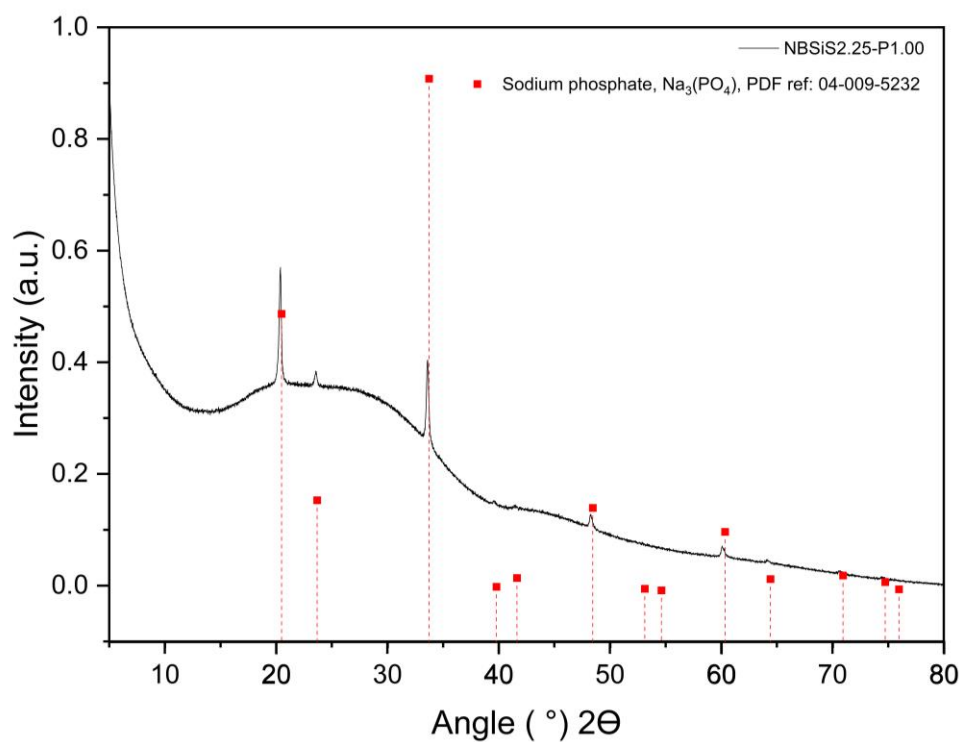


Figure 76 - XRD pattern with identified crystal phases of NBSiS-P1.00

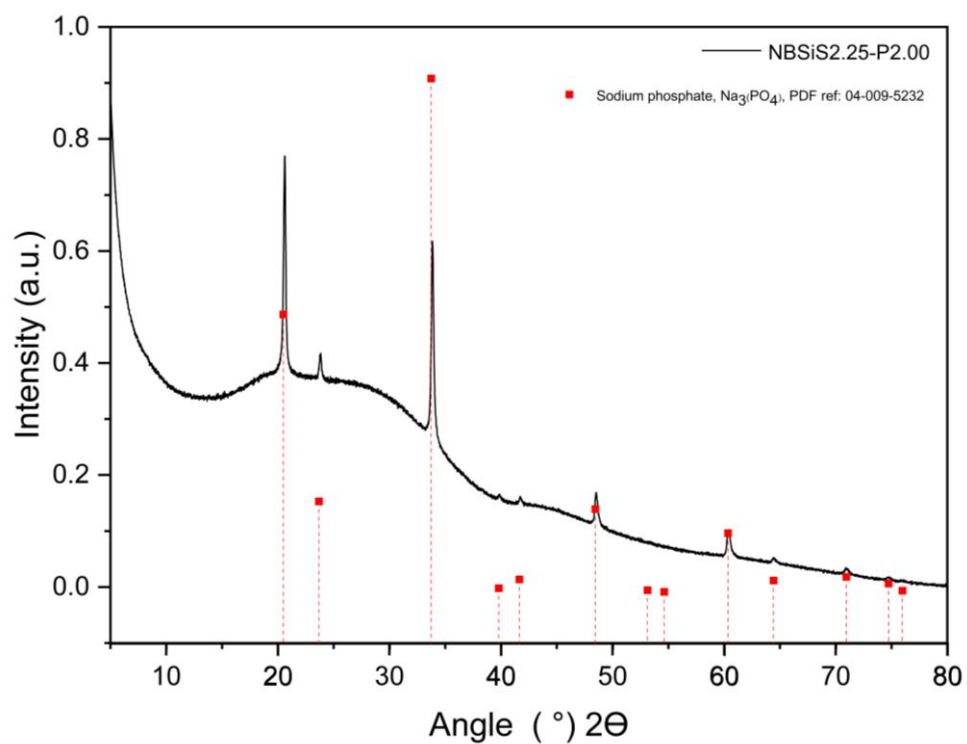


Figure 77 - XRD pattern with identified crystal phases of NBSiS-P2.00

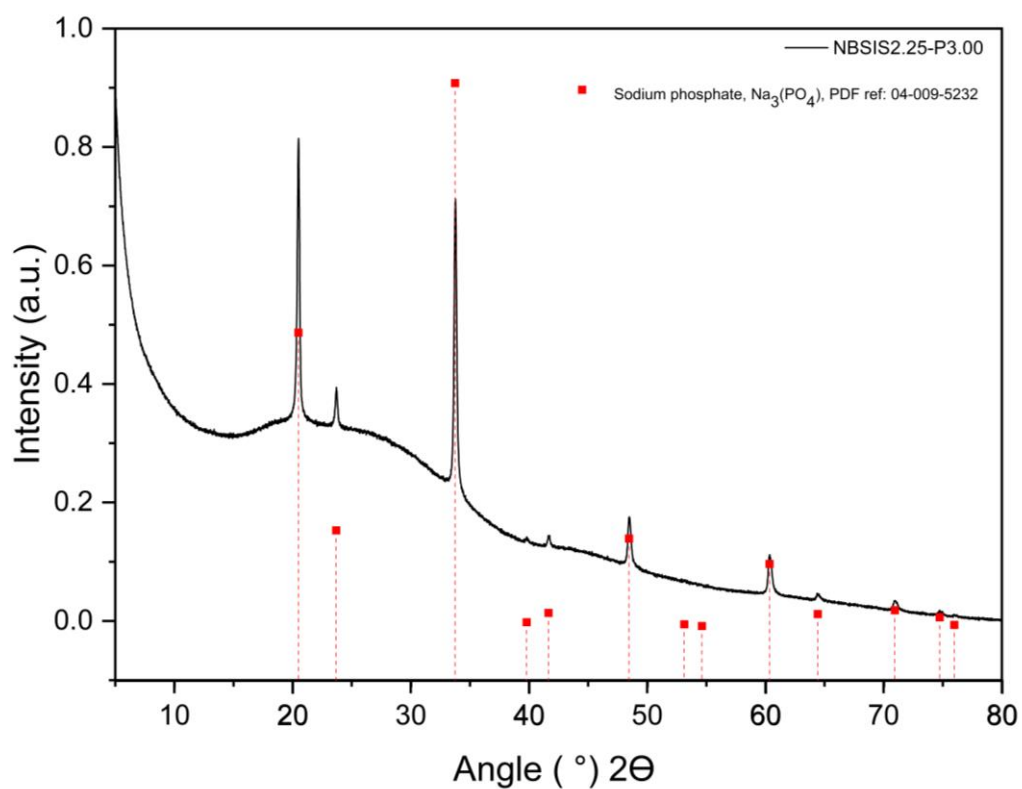


Figure 78 - XRD pattern with identified crystal phases of NBSiS-P3.00

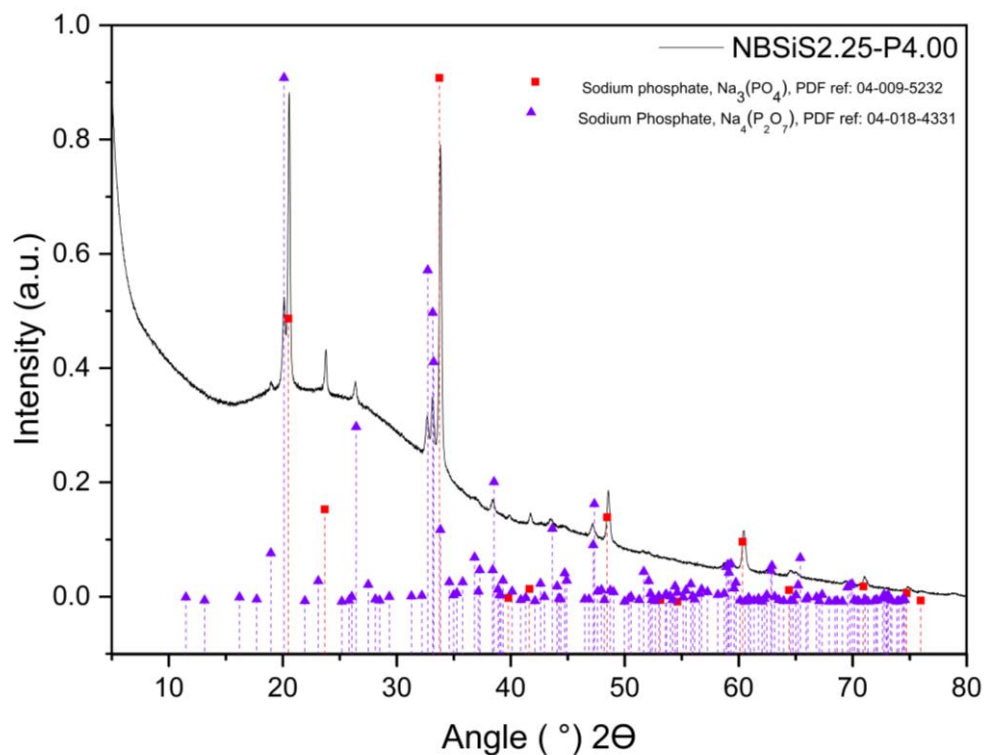


Figure 79 - XRD pattern with identified crystal phases of NBSiS-P4.00

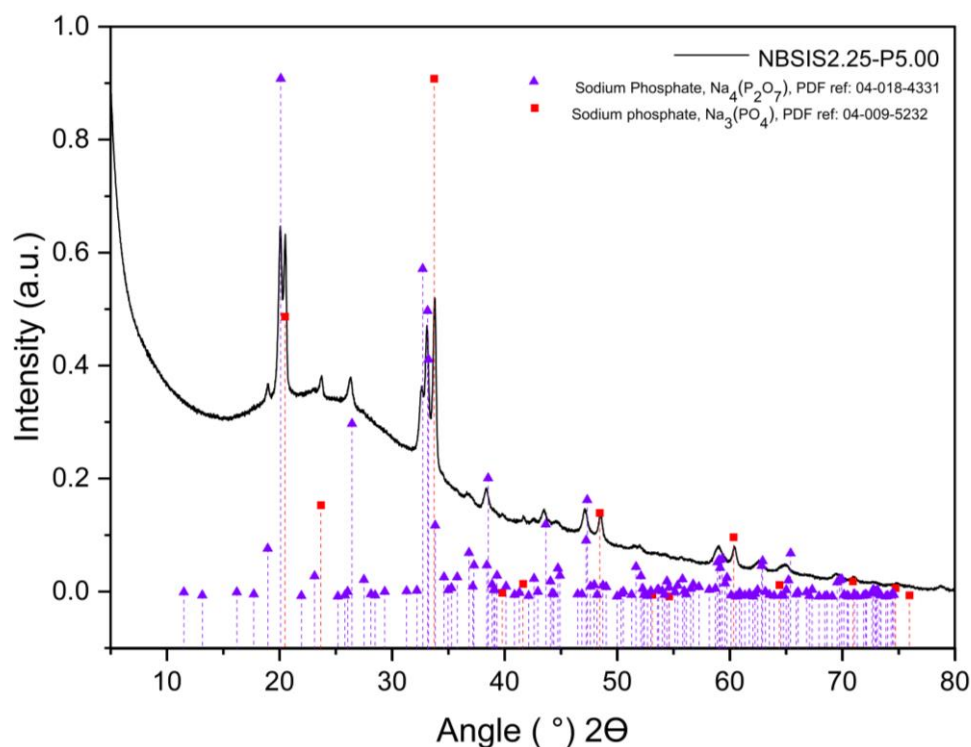


Figure 80 - XRD pattern with identified crystal phases of NBSiS-P5.00

4.2.3.2.5 DTA

Figure 81 illustrates the DTA curves for the NBSIS-Px samples at a heating rate of 10°C/min. It was observed that the T_g shifted to higher temperatures with increasing P_2O_5 content.

The T_g onset and T_g midpoint of the NBSiS-Px samples increased with increasing P_2O_5 content, however, the T_x (onset of crystallisation temperature), T_c (maximum crystallisation temperature), and T_m (melting temperature) decreased. For the 5.0 mol% P_2O_5 sample, there were two distinct T_c and T_m temperatures, T_{c1} , T_{c2} , T_{m1} , and T_{m2} , indicating a crystal form transformation or the simultaneous precipitation of different crystals in the sodium borosilicate base glass (Wang et al., 2019). These crystallisation events may have been caused by Na_3SO_4 and/or Na_3PO_4 and $Na_4P_2O_7$, as identified by XRD patterns. Banach and Makara (2011) reported that the T_c of $Na_4P_2O_7$ was 200-250°C. “*Na₂SO₄ has five different polymorphs depending on the temperature ranging from room temperature to 240°C*” (Correcher et al., 2004). Na_2SO_4 crystals are present in phase 5 (thernadite) which has an orthorhombic structure between 50-180°C, three stable phases (III, II, and I) which are detected between 180°C to the melting point, 884°C, where they have the orthorhombic (III) and hexagonal (II) crystal structures (Correcher et al., 2004). There has been no evidence in literature of the identification of

phase IV (Correcher et al., 2004). The T_c temperatures recorded in Table 40 are much higher than those reported in literature, however, they were only for the minerals and not for the crystalline phases present in a glass system.

The T_g of the base glass was lower than what has been previously reported by Lonergan et al. (2020), however, this may have been due to the SO_3 content being 3.0 mol% and the addition of $CaCO_3$ to their glass composition. The increase in the T_g may have been due to removal of NBØs in the glass network that led to increased cross-linking, resulting in stronger bonding that would have required more energy to break the bonds (Lonergan et al., 2020). The glass stability (GS) parameters are used to best predict the glass forming ability (GFA) and accounts for a glass' resistance towards devitrification upon re-heating (Avramov et al., 2005). The GS parameters are based on T_g , T_x , and T_m . The GFA parameters calculated were the Weinburg parameter ($K_w = (T_c - T_g)/T_m$), the Hruby parameter ($K_H = (T_x - T_g)/(T_m - T_x)$), and the ratio of reduced glass transition temperature ($T_{rg} = T_g/T_m$) (Avramov et al., 2005; Jiusti, Cassar, et al., 2020; Thombre, 2016). The higher the K_H value for a certain glass, the higher the stability against crystallisation upon heating, and the higher the glass ability to vitrify upon cooling (Nascimento et al., 2005). The T_{rg} values ranged between 0.45 (0.0 mol% P_2O_5) to 0.63 (4.0 mol% P_2O_5), where the change in T_{rg} was not linear. The K_H parameter displayed a decrease with increasing P_2O_5 content, ranging from 0.34 to 0.19. The K_w parameter also initially decreased when 1.0 mol% P_2O_5 was added to the base glass, from 1.61 to 0.74, after which there was little fluctuation until 3.0 mol% P_2O_5 , where the K_w value decreased to 0.44, before increasing to 0.70 at 4.0 mol% P_2O_5 . Sakka and Mackenzie (1971) reported that $T_{rg} = 2/3$, also known as the two thirds rule, where a T_{rg} value equal to or more than this value means the glass system should easily form a glass due to low nucleation rates (Dri et al., 2007). If this is the case, this suggests that none of the NBSiS-P glasses displayed a good glass forming ability. The decrease in the K_H and K_w parameter in the 1.0 mol% P_2O_5 doped sample, suggested that there was a decrease in the glass stability upon heating. The continued decrease in the K_H parameter between 1.0-3.0 mol% P_2O_5 may have been due to the decrease in Na^+ acting as a network modifier, and instead acting as a charge compensator (Rodrigues et al., 2018). The DTA traces (Figure 81) did not display obvious evidence of two T_g 's, which is indicative of a phase separated glass system.

Sample	T_g – onset $\pm 2^\circ\text{C}$	T_g midpoint $\pm 2^\circ\text{C}$	T_x $\pm 2^\circ\text{C}$	T_c $\pm 2^\circ\text{C}$		T_m $\pm 2^\circ\text{C}$		T_{rg}	K_H^*	K_w^*
				1	2	1	2			
NBSiS- P0.0	510	522	788	888	-	1124	-	0.45	1.61	0.34
NBSiS- P1.0	525	536	738	836	-	1026	-	0.51	0.74	0.30
NBSiS- P2.0	543	553	668	696	-	851	-	0.64	0.68	0.18
NBSiS- P3.0	544	559	655	709	-	906	-	0.60	0.44	0.18
NBSiS- P4.0	559	572	697	733	-	893	-	0.63	0.70	0.19
NBSiS- P5.0	567	578	-	728	842	812	888	0.51	0.74	0.30

Table 40 - DTA thermal parameters and theoretical glass stability parameters

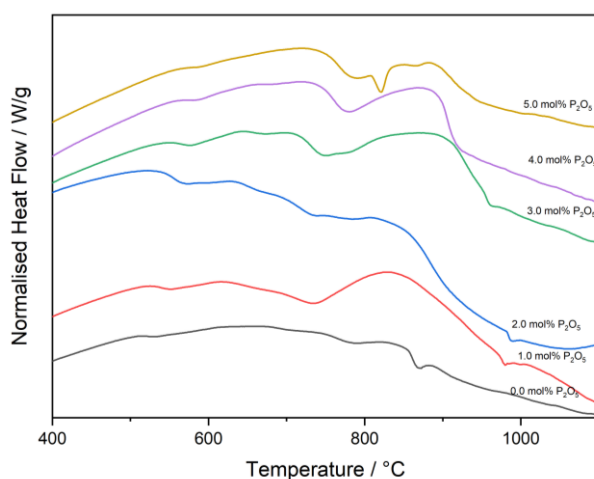


Figure 81 - DTA curves of the NBSiS-Px samples

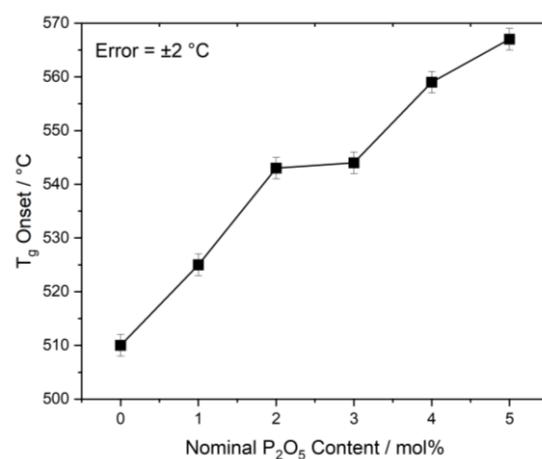


Figure 82 - T_g onset as a function of P_2O_5 content

4.2.3.2.6 Raman Spectroscopy

The Raman spectra of the sodium borosilicate glass doped with SO_3 and P_2O_5 (Figure 83) contained three broad regions, 300–800, 800–1200 and 1200–1600 cm^{-1} . The low frequency region between 300–800 cm^{-1} has contributions from the mixed stretching and bending modes of Si-O-Si units and ring breathing modes

e.g., metaborate rings (Koroleva et al., 2011). The vibrations in the region 800–1200 cm^{-1} are attributed to the stretching vibrations of terminal groups of Si-O species in $\text{SiO}_4 \text{Q}^n$ tetrahedrons, where n is the number of NBØs per atom (Angeli et al., 2010; Fabian et al., 2020; Koroleva et al., 2011). The high frequency region between 1200-1600 cm^{-1} , can be assigned to B-O⁻ stretching in chain-type metaborate groups (Koroleva et al., 2011; Manara et al., 2009). The RDS highlights the sulphate and phosphate specific intensities present in the samples, indicating if there is a change in the relative intensities (Figure 84).

The 300–800 cm^{-1} Region

In this region, the Raman spectra displayed some low-level intensity peaks, with two identifiable bands at ~630 and 772 cm^{-1} . The band at 630 cm^{-1} may be attributed to a mixture of assignments i.e., the breathing mode of B-O-Si(B) in reedmergnerite- and / or danburite-like rings with Na^+ ions instead of a Ca^{2+} ions acting as charge compensators for $^{[4]}\text{B}$ units (Angeli et al., 2010b, 2012a; Manara et al., 2009), or by metaborate vibrations of the ring-type (Koroleva et al., 2011), and/or the Raman-active modes associated with S^{6+} in sulphate tetrahedra (SO_4^{2-}) observed in sulphate crystals (Lenoir et al., 2009; McKeown et al., 2001). The band at ~732 cm^{-1} can be attributed to the symmetric stretching of P-O-P (Yadav & Singh, 2015). The relative intensity of the band at 630 cm^{-1} does not exhibit notable change with increasing P_2O_5 content, however, the relative intensity of the band at 732 cm^{-1} only becomes apparent from 4.00 mol% P_2O_5 , after which the intensity does not increase at 5.00 mol% P_2O_5 . The peak at 732 cm^{-1} was matched to the same peak exhibited by the $\text{Na}_4\text{P}_2\text{O}_7$ crystalline standard.

The 800–1200 cm^{-1} Region

This region contains contributions from bands at 938, 992, 1028, 1077, 1100, 1115, 1131, and 1152 cm^{-1} . The bands associated with P are at 938, 1028, 1077, and 1115 cm^{-1} , where 938 cm^{-1} can be assigned to PO_4^{3-} (Q^2) symmetric stretching (Manghnani et al., 2011; Mysen, 1998; Yadav & Singh, 2015; Yamashita et al., 1998), 1028 cm^{-1} may be attributed to P-O symmetric stretching vibrations of the pyrophosphate Q^1 unit (Gangadharan et al., 2002; Giacomazzi et al., 2019; Rinke & Eckert, 2011), 1077 and 1115 cm^{-1} can be attributed to the asymmetric stretch of PO_3 (Bhongale et al., 2001) which can be matched to a

peak in the $\text{Na}_4\text{P}_2\text{O}_7$ standard. The band at 1000 cm^{-1} may have been caused by multiple different contributions from the following: (i) P-O stretching in $\text{P}^{2(1\text{B})}$ (Raskar et al., 2008), (ii) PO_2 vibrations of P^2 units connected to two B atoms ($\text{P}^{2(2\text{B})}$) (Zielniok et al., 2007), (iii) PO_3 vibrations of P^1 species (Zielniok et al., 2007), (iv) and the and Si-O stretching in the Q^3 unit (Manara et al., 2009).

The bands associated with SO_3 are seen at 992 cm^{-1} which could be due to S-O symmetric stretching modes (ν_1)¹ within the sulphate tetrahedra (Brendebach et al., 2009; Lenoir et al., 2010; Lonergan et al., 2020; Saini et al., 2022), which matches the intense peak in the thenardite standard. The bands at 1100, 1131, and 1152 cm^{-1} could be attributed to U_3 (vibrational mode) in (SO_4^{2-}) (Prieto-Taboada et al., 2019; Saini et al., 2022). The other vibrational modes associated with S containing glasses were not visible i.e., 469 cm^{-1} attributed to asymmetric S-O bending modes (ν_2), and 620 cm^{-1} associated with asymmetric O-S-O bending modes (ν_4). These particular vibrational modes are difficult to identify due to them overlapping with vibrational mode bands associated with the borosilicate network (Lenoir, Grandjean, & Neuville, 2008; Saini et al., 2022). It was inferred that S was present as S^{6+} , due to the distinct lack of the characteristic bands related to S-S bonds in polysulphide chains or rings in the region of $300\text{--}460\text{ cm}^{-1}$, or bands in the $950\text{--}970$ and $970\text{--}990\text{ cm}^{-1}$ region attributed to SO_3^{2-} (sulphite) groups (Xu et al., 2020).

The band at 938 cm^{-1} was not present in the base glass, but occurred upon additions of 1.00 mol% P_2O_5 , increasing in relative intensity with increasing P_2O_5 content, where its presence suggests that the glass has some level of heterogeneity (Li et al., 1995). The band at 992 cm^{-1} was present in all samples but decreased in relative intensity with 5.00 mol% P_2O_5 additions. The lack of increase and subsequent decrease in the $[\text{SO}_4]^{2-}$ band suggests that there is a lack of interaction between the S and P in the glass (Li et al., 1995). The frequency shift seen between the sulphate crystal standard and sulphate bearing glass indicates the effect of charge compensating Na^+ ions in the glass (Lenoir, Grandjean, & Neuville, 2008). The broad peak centred at $\sim 1100\text{ cm}^{-1}$ became increasingly broader with a reduction in the relative intensity of the peak with increasing P_2O_5 content, until a small sharp peak occurred at 5.00 mol% P_2O_5 centred at 1115 cm^{-1} , accompanied by the small peak at 732 cm^{-1} . Hence the P

¹ Vibrational mode

and S interaction depends on the extent of saturation of both species in the glass, where their interactions may promote phase separation in the glass (Li et al., 1995).

The 1200–1600 cm^{-1} Region

The high-frequency region represents the ‘*stretching vibrations of B^3 and asymmetric three-coordinated boron species linked to two $B\emptyset$ and one $NB\emptyset$ atoms, B^2 , linked together to form a chain*’ (Saini et al., 2022). The Raman difference spectra (Figure 84) highlights that with increasing P_2O_5 content, the relative intensity and area of the broad band centred around 1467 cm^{-1} decreases, accompanied by an decrease then increase in the broad band centred about 1400 cm^{-1} ($^{[4]}\text{B-O-}^{[4]}\text{B}$ linkages), reflecting the tendency of the anionic formation of $^{[4]}\text{B}$ rather than $^{[3]}\text{B}$ linked to two $B\emptyset$ s and one $NB\emptyset$ units in the glasses (Saini et al., 2022), suggesting that the borate network is re-polymerising. Without using MAS NMR, it is not possible to accurately establish the effects of P_2O_5 on the structure of these glasses, and why the threshold of SO_3 reduces upon the increase of P_2O_5 . Table 41 summarises the Raman shift peaks and their referenced attributions.

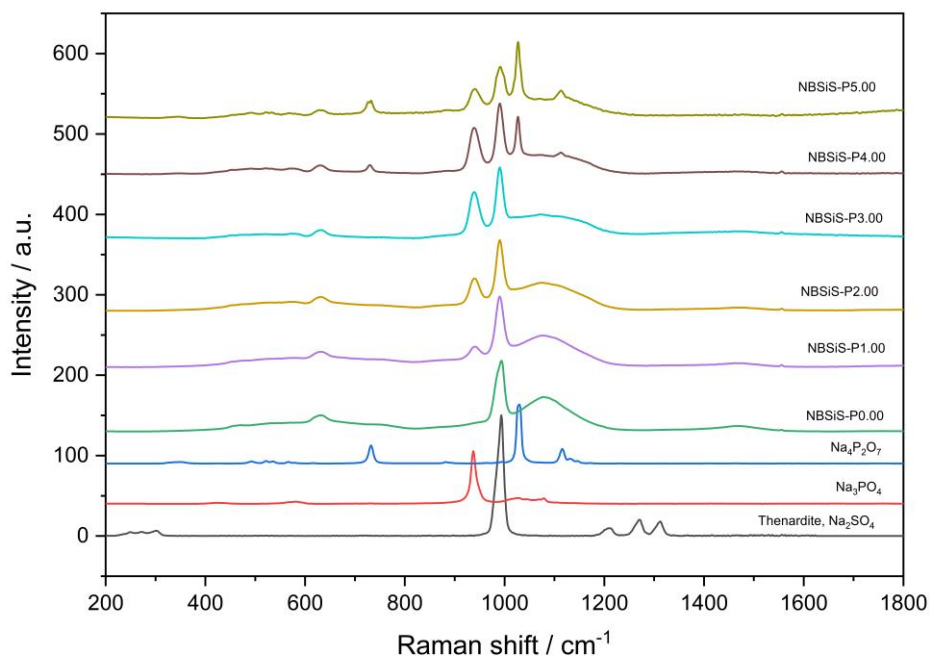


Figure 83 - Raman spectra of NBSiS-Px samples, Na_2SO_4 , Na_3PO_4 , and $\text{Na}_4\text{P}_2\text{O}_7$ standards

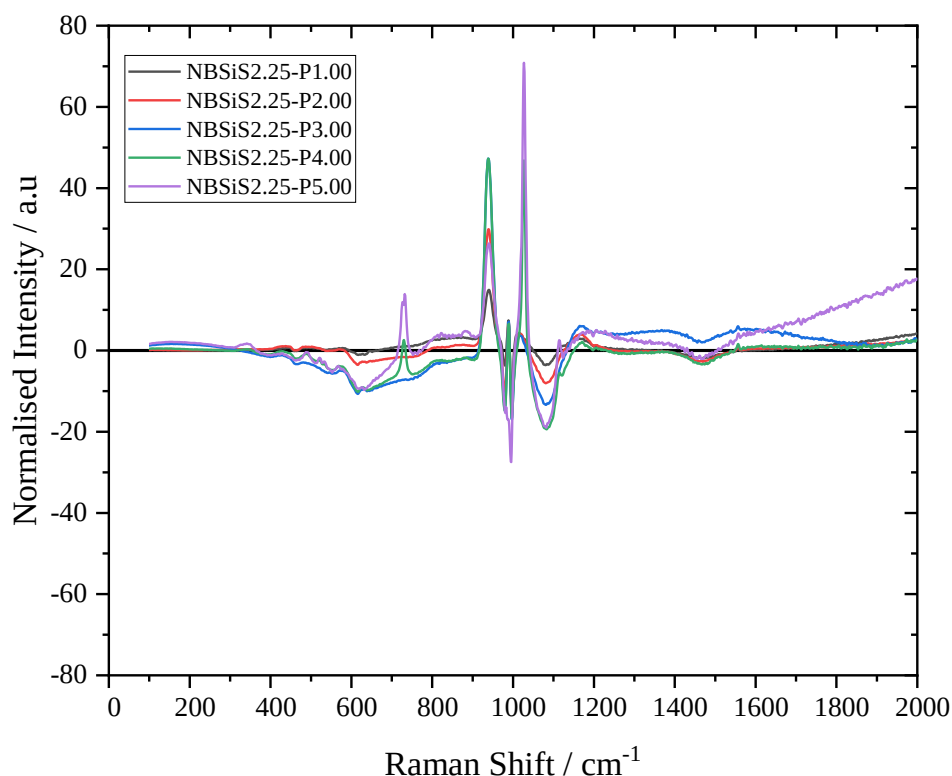


Figure 84 - Raman difference spectra of NBSiS-Px samples

Raman shift (cm ⁻¹)	Association
630 (Angeli et al., 2010b, 2012a; Koroleva et al., 2011; Manara et al., 2009) (Lenoir et al., 2009; McKeown et al., 2001)	Breathing mode of B-O-Si(B) in reedmergnerite- and / or danburite- like rings with Na ₂ O instead of CaO as a charge compensator for ^[4] B units, Asymmetric O-S-O bend modes
732 (Yadav & Singh, 2015)	Symmetric stretching of P-O-P
938 (Manghnani et al., 2011; Mysen, 1998; Yadav & Singh, 2015; Yamashita et al., 1998)	PO ₄ ³⁻ symmetric stretch
992 (Brendebach et al., 2009; Lenoir et al., 2010; Lonergan et al., 2020; Saini et al., 2022)	S-O symmetric stretching modes within the sulphate tetrahedra
1028	P ₂ O ₇ ⁴⁻ symmetric stretch

(Cheng, 2004).	
1077 (Bhongale et al., 2001)	Asymmetric stretch of PO_3
1100 (Lenoir, Grandjean, & Neuville, 2008; Saini et al., 2022) (Zielniok et al., 2007) (Raskar et al., 2008) (Manara et al., 2009)	Asymmetric O-S-O stretching modes, $\text{U}_3(\text{SO}_4^{2-})$ P-O stretching vibration of the $\text{P}(\text{Q}_1)$ Chain P-O stretching in $\text{P}^2_{(1\text{B})}$ Si-O ⁻ stretching in the Q^3 unit
1115 (Bhongale et al., 2001)	Asymmetric stretch of PO_3
1131 (Lenoir, Grandjean, & Neuville, 2008; Saini et al., 2022)	$\text{U}_3(\text{SO}_4^{2-})$
1152 (Lenoir, Grandjean, & Neuville, 2008; Saini et al., 2022)	$\text{U}_3(\text{SO}_4^{2-})$

Table 41 - Summary table of sulphate and phosphate specific intensities with referenced associations

4.2.4 Summary

- Increasing the P_2O_5 content in the NBSiS-Px glasses had a negligible effect on the sulphur solubility, as evidenced by the XRF results.
- Na_3SO_4 crystal phase was present in the NBSiS-Px base glass as evidenced by the XRD pattern.
- Na_3PO_4 and $\text{Na}_4\text{P}_2\text{O}_7$ crystal phases were present from 1.0 mol% P_2O_5 as evidenced by XRD patterns.
- Increasing the P_2O_5 content, caused a linear decrease in the bulk density and increase in the molar volume, suggesting that the glass network was becoming less compact.
- Increasing P_2O_5 content led to a linear increase in the T_g onset, leading to a removal of NBØs and the subsequent re-polymerisation of the glass network.
- Raman spectra evidenced sulphur existing as sulphate (S^{6+}) from the “fingerprint” like Raman intensity at $\sim 992\text{ cm}^{-1}$.

- Raman spectra of the NBSiS-Px samples, evidenced key phosphate specific intensities located at ~732, 938, 1028, 1077, 1100, and 1115 cm^{-1} .
- Additions of phosphorus to the NBSiS-Px glasses, resulted in the re-polymerisation of the glass network as evidenced by the Raman spectra, in particular the Q^n region and boron specific region.

4.3 HLW Glass Series

4.3.1 Introduction

The glass system studied in this chapter is a simplified, alkali rich aluminoborosilicate-based glass system comprising oxides from the HLW compositions PNNL and ORP, where some compositions were taken from the IHLW report 24590-HLW-RPT-05-001 (Vienna & Kim, 2008). While this composition is a simplification of Hanford HLW compositions, it is still deemed a complex glass system to analyse because it comprises of 8-components based on $\text{SiO}_2\text{-B}_2\text{O}_3\text{-Fe}_2\text{O}_3\text{-Al}_2\text{O}_3\text{-Na}_2\text{O-CaO-Li}_2\text{O-xP}_2\text{O}_5$. The undoped base glass had a nominal composition of $12.9\text{Na}_2\text{O-7.9Al}_2\text{O}_3\text{-46.64SiO}_2\text{-5.66CaO-5.86Fe}_2\text{O}_3\text{-12.31B}_2\text{O}_3\text{-8.71Li}_2\text{O}$ (mol%). If the main sodium borosilicate glass composition components, $12.9\text{Na}_2\text{O-43.6SiO}_2\text{-12.3B}_2\text{O}_3$, is plotted on the ternary phase diagram, the composition is not located in the immiscibility region.

The study of this simplified glass system is important because P_2O_5 incorporation in nuclear borosilicate glasses has not been widely studied due to its low abundance in HLW streams. However, this study should aid in the better understanding of the potential effects of altering the P_2O_5 content and its potential subsequent effects on more complex nuclear waste compositions.

4.3.2 Experimental Procedures

The HLW glasses were based on the $\text{Na}_2\text{O-Li}_2\text{O-CaO-Fe}_2\text{O}_3\text{-Al}_2\text{O}_3\text{-B}_2\text{O}_3\text{-SiO}_2\text{-xP}_2\text{O}_5$ glass system, where $x = 0.00, 0.3125, 0.625$, and 1.25 mol%. Batches of 130 grammes were prepared utilising the melt-anneal method using the precursors Na_2CO_3 , Li_2CO_3 , CaCO_3 , Fe_2O_3 , $2(\text{Al}(\text{OH})_3)$, H_3BO_3 , SiO_2 , and $\text{NH}_4\text{H}_2\text{PO}_4$. The precursors were weighed and transferred to a plastic bag before being milled for 10 seconds in a steel mill to thoroughly mix the contents. The batch was then placed in an alumina crucible and heated in an electric furnace at a rate of 5°C/min to 1150°C , where it was left to dwell for 3 hours before the glass melt was poured into a steel mould and annealed at 500°C for 2 hours, before cooling at a rate of 1°C/min to 25°C . The bulk samples were then analysed by Raman spectroscopy, prepped, and mounted in epoxy resin for SEM/EDS analysis, then milled into powders for XRD, XRF, ICP-OES, XAS, and Mössbauer spectroscopy. Further details of experimental methodology can be read in *Chapter 3: Experimental Methodology*.

4.3.3 Results and Discussion

4.3.3.1 Annealed Samples

4.3.3.1.1 Visual Observations

Figure 85 shows the top view images of the HLW samples. All the samples were all very dark in colour and did not show any visible signs of crystallinity or phase separation on the top surface. However, the residual melt in the crucibles (Appendix 8.9 Figure 157) suggested the presence of either unmelted or crystallised material, which accumulated at the bottom of the crucibles. Upon closer inspection, the colour of the unmelted material was a dark red, resembling Fe_2O_3 . However, XRD and/or SEM/EDX would need to be used to confirm the material in the crucible. The viscosity of the glass melts was fluid, but upon increasing additions of P_2O_5 , they became somewhat more viscous.

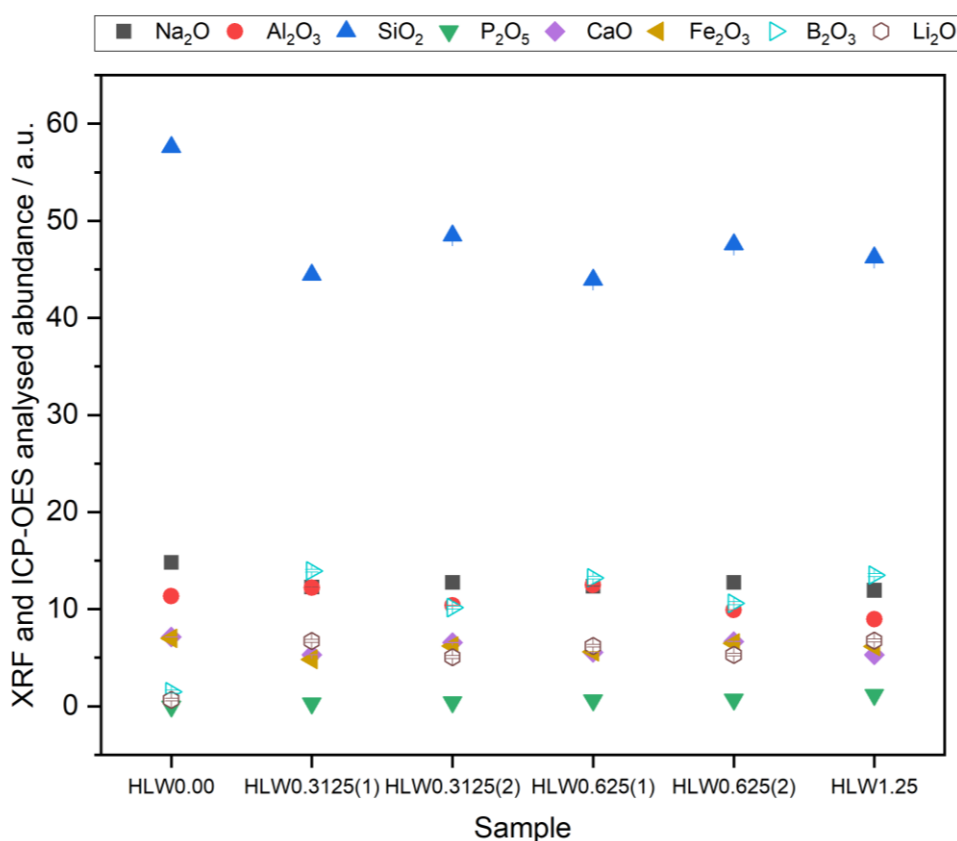


Figure 85 - Image of HLW samples (HLW0.00 (left), HLW0.3125, HLW0.625, and HLW1.25 (right))

4.3.3.1.2 XRF and ICP-OES

Table 42 presents the XRF and ICP-OES results for the HLW samples and Figure 86 graphically represents the data from said table. The HLW0.00 sample displayed slightly elevated SiO_2 content and dramatically decreased B_2O_3 and Li_2O contents when compared to the nominal composition and subsequent samples. The elevated SiO_2 content in the HLW0.00 sample may have been due to SiO_2 contamination from the milling process produced from cleaning the mill. HLW0.3125 and HLW0.625 were re-analysed due to the elevated Al_2O_3 contents in the original compositions and were likely caused by the use of Al_2O_3 as the batch material rather than $2\text{Al}(\text{OH})_3$. Hence, there are two analyses for these samples representing the original sample (1) and re-batched sample (2) using $2\text{Al}(\text{OH})_3$ as the source of Al. The analysis of HLW0.3125(2) showed slight

discrepancy when compared to the nominal composition for Na₂O, Al₂O₃, SiO₂, CaO, Fe₂O₃, and B₂O₃. However, there was an elevation in the P₂O₅ content by 0.0975 mol%, and then a decrease in the Li₂O content of 3.62 mol%. The HLW0.625(2) sample also displayed slight discrepancies in the composition for Na₂O, Al₂O₃, SiO₂, CaO, Fe₂O₃, and B₂O₃, but an increase in P₂O₅ by 0.065 mol% and decrease in Li₂O by 3.34 mol%. The HLW1.25 sample exhibited a reduction in the P₂O₅ content by 0.06 mol% and Li₂O content by 1.84 mol%, whilst the other oxides present displayed slight discrepancies from the nominal composition. Further discrepancies in the composition may have been due to the heat treatment of the glass and subsequent melting time (Xu et al., 2021), the volatilisation of Li₂O and B₂O₃ (Kapoor, et al., 2021) during melting which would account for their lower values, the part of the melt from which the glass sample analysed was taken, and any uncertainties associated with the preparation (milling) and analysis of the sample by XRF and ICP-OES.



***Hollow markers = analysed by ICP-OES**

Figure 86 - XRF and ICP-OES analysed composition of HLW samples with associated error. Error bars that are not shown have errors that are too small to plot.

Table 42 - Nominal and analysed composition via XRF and ICP-OES of HLW samples in mol%

		Oxide (mol%)							
Sample		Na ₂ O	Al ₂ O ₃	SiO ₂	P ₂ O ₅	CaO	Fe ₂ O ₃	B ₂ O ₃ *	Li ₂ O*
HLW0	Nominal	12.94	7.87	46.64	0.00	5.66	5.86	12.31	8.71
	Analysed pro-rat'd	14.82 ± 0.02	11.34 ± 0.01	57.59 ± 0.01	0.00	7.12 ± 0.01	6.98 ± 0.01	1.48 ± 0.15	0.67 ± 0.15
HLW0.3125 (1) (SHU)	Nominal	12.90	7.85	46.49	0.3125	5.65	5.84	12.27	8.68
	Analysed pro-rat'd	12.27 ± 0.00	12.20 ± 0.01	44.43 ± 0.02	0.29 ± 0.00	5.31 ± 0.00	4.83 ± 0.00	13.95 ± 0.15	6.73 ± 0.15
HLW0.3125 (2)	Nominal	12.90	7.85	46.49	0.3125	5.65	5.84	12.27	8.68
	Analysed pro-rat'd	12.75 ± 0.02	10.40 ± 0.01	48.49 ± 0.01	0.41 ± 0.05	6.55 ± 0.01	6.19 ± 0.01	10.15 ± 0.15	5.06 ± 0.15
HLW0.625 (1) (SHU)	Nominal	12.86	7.82	46.35	0.625	5.63	5.82	12.24	8.65
	Analysed pro-rat'd	12.35 ± 0.00	12.48 ± 0.01	43.94 ± 0.01	0.61 ± 0.00	5.56 ± 0.00	5.61 ± 0.00	13.23 ± 0.15	6.22 ± 0.15
HLW0.625 (2)	Nominal	12.86	7.82	46.35	0.625	5.63	5.82	12.24	8.65
	Analysed pro-rat'd	12.76 ± 0.02	9.92 ± 0.01	47.56 ± 0.01	0.69 ± 0.03	6.66 ± 0.01	6.50 ± 0.01	10.60 ± 0.15	5.31 ± 0.15
HLW1.25	Nominal	12.78	7.77	46.06	1.25	5.59	5.79	12.16	8.6
	Analysed pro-rat'd	11.95 ± 0.00	8.94 ± 0.00	46.21 ± 0.00	1.19 ± 0.00	5.30 ± 0.00	6.15 ± 0.00	13.5 ± 0.15	6.76 ± 0.15

*ICP-OES analysis

4.3.3.1.3 X-ray Powder Diffraction

Figure 87 shows the XRD patterns for the HLW samples, where there are two patterns for HLW0.3125 and 0.625 due to the batching error with the Al_2O_3 source resulting in significant elevated concentrations when analysed by XRF. The glasses were re-batched with the correct Al_2O_3 source and re-analysed by XRD and XRF to ensure that the crystallisation behaviour was the same, which it was.

The HLW0.00 XRD pattern was X-ray amorphous within the machine's capability, after which crystalline peaks occur in the 0.3125, 0.625 and 1.25 mol% P_2O_5 samples. The 0.1325 and 0.625 mol% P_2O_5 samples contained hematite (Fe_2O_3 , PDF#: 98-018-284, 98-008-8417 (Hanawalt et al., 1938)), which has a fully occupied trigonal crystal structure (Appendix 8.9 Figure 158). The 1.25 mol% P_2O_5 sample contained predominantly sodium calcium phosphate ($\text{NaCa}(\text{PO}_4)$, PDF#: 04-017-4455, (Celotti & Landi, 2003)) and a small contribution from hematite. The $\text{NaCa}(\text{PO}_4)$, (Appendix 8.9 Figure 159) crystal has an orthorhombic structure and is fully occupied. The presence of $\text{NaCa}(\text{PO}_4)$, at 1.25 mol% P_2O_5 but not in the 0.625 mol% P_2O_5 sample, implies the solubility limit of P_2O_5 lies between the two. The formation of the $\text{NaCa}(\text{PO}_4)$ crystal phase leads to the removal of one mole Na and one mole Ca to charge compensate the P, causing the reduction in NBØs leading to the glass network re-polymerising. The presence of Fe_2O_3 suggests that this was either unmelted material, as the Fe was not present as magnetite (Fe_3O_4), which is the crystallised form of Fe, or that the hematite may be a secondary phase formed as a result of being exposed to an oxidising atmosphere during melting at high temperatures (Ahmadzadeh et al., 2017).

The $\text{NaCa}(\text{PO}_4)$ phase at 1.25 mol% P_2O_5 had a calculated nominal composition of 33.33 Na_2O -33.33 CaO -33.33 P_2O_5 mol%, where the T_g was reported to be $\sim 395^\circ\text{C}$ (Mandlule et al., 2014). The annealing of the glasses was at 480°C which was above the T_g of the $\text{NaCa}(\text{PO}_4)$, phase. Heating above this temperature may have allowed for the nuclei present in the melt/matrix to agglomerate and grow until they had reached their critical size where they precipitated out as crystals (Liu et al., 2011; Ong et al., 2018).

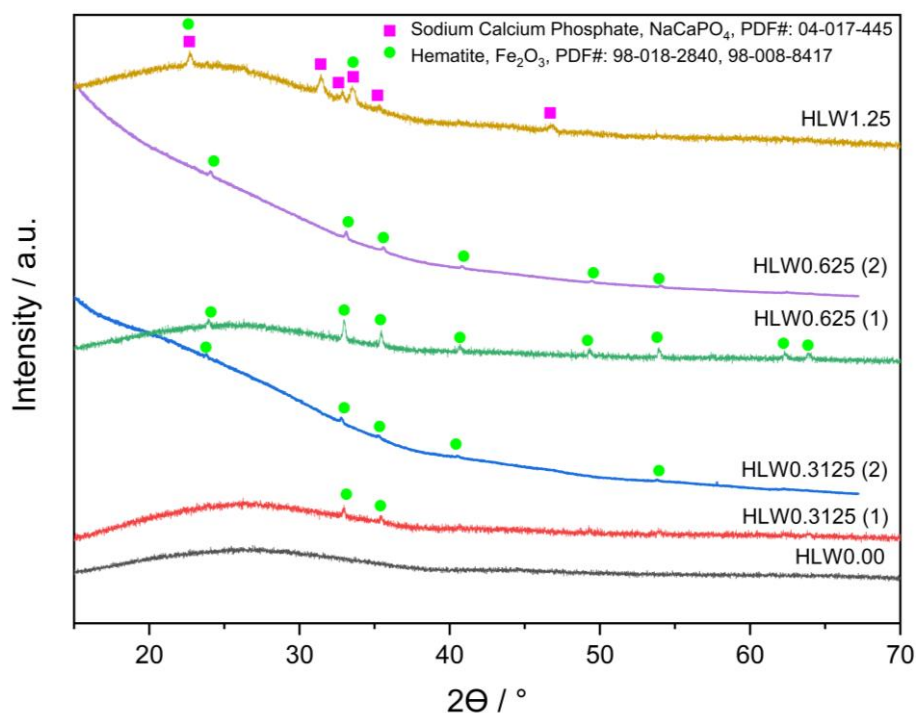


Figure 87 - XRD patterns with identified crystal phases for the HLW samples

4.3.3.1.4 Bulk Density and Molar Volume

Table 42 and Figure 88 show the bulk density and molar volume (V_{mol}) of the HLW samples (HLW0.00, HLW0.3125 (2), HLW0.625 (2), and HLW1.25) as a function of the P_2O_5 content. The bulk density of the samples ranged between 2.619 ± 0.000 to $2.645 \pm 0.026 \text{ g/cm}^3$, while the molar volume values ranged between 34.291 – $35.294 \text{ cm}^3/\text{mol}$, where the density decreased linearly, and the molar volume increased linearly as the P_2O_5 content increased. The un-doped base glass had the highest density value and lowest V_{mol} , whilst the 1.25 mol% doped sample had the lowest density but highest V_{mol} . The un-doped base glass also had a larger error than the other samples and may be due to the error in the retrieval of the first measurement that had a value of 2.676, which was much higher than the other values. The change in the molar volume behaviour is caused by the changes in the short-range structure with increasing P_2O_5 content, where P_2O_5 increases the molar volume resulting in a more open and less compact glass structure, contributing to the decrease in the density. This less compact glass structure is beneficial for increased cation mobility (Sułowska et al., 2021). The increase in the V_{m} indicates that the glass structure is expanding to accommodate the larger coordinated atoms (Shelby, 2005), where ions are re-

organised into more closely packed arrangements; this can be seen affecting the CTE (Figure 91), where there is a positive linear change in the volume.

Sample	Bulk Density (g.cm^{-3})					Molar mass of glass (M)	V_{mol} (cm^3/mol)
	1	2	3	Average	STDEV (1σ)		
0.00	2.676	2.628	2.632	2.645	0.026	90.710	34.291
0.3125	2.645	2.642	2.642	2.643	0.001	91.152	34.488
0.625	2.630	2.637	2.633	2.633	0.003	91.577	34.775
1.25	2.619	2.62	2.619	2.619	0.000	92.451	35.294

Table 43 - Bulk density and molar volume as a function of nominal P_2O_5 content (mol%)

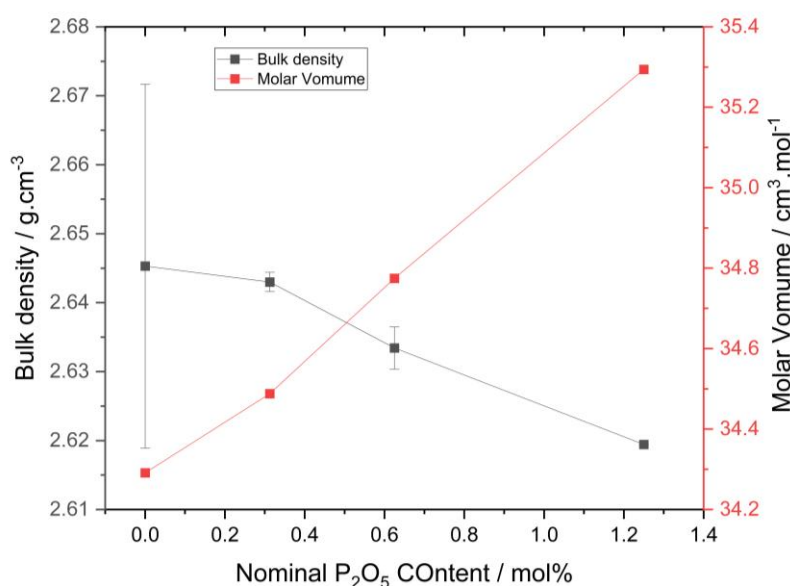


Figure 88 - Graph showing bulk density and molar volume as a function of nominal P_2O_5 content (mol%)

4.3.3.1.5 DTA

Table 44 refers to the experimental and theoretical DTA thermal parameters for the HLW samples obtained from analysis of the DTA traces (Figure 89). As the P_2O_5 content increased, the T_g onset, T_g midpoint, and T_c decreased between 0.00-0.625 mol% P_2O_5 , but then decreased at 0.625 mol% P_2O_5 . The T_x decreased upon the addition of 1.00 mol% P_2O_5 , but then increased between 0.625-1.25 mol% P_2O_5 . The T_g onset ranged between $472\text{-}478 \pm 2^\circ\text{C}$, the T_g

midpoint ranged between $470-483 \pm 02^\circ\text{C}$, T_x ranged between $605-733 \pm 2^\circ\text{C}$, and T_m ranged between $864-988 \pm 2^\circ\text{C}$. The T_{rg} ranged between 0.48-0.55, the K_H ranged between 0.51-1.00, and the K_W ranged between 0.23-0.36.

The glass system being studied was a multi-oxide glass, susceptible to the effects of the mixed glass former (MGF) and mixed alkali effect (MAE), which in turn affects the physical, thermal, and chemical properties non-linearly (Hyun et al., 2022).

Due to the sheer complexity of the glass system, it is difficult to establish the effect that other components have without establishing their role in the glass structure. To illustrate this complexity where it is not clear what role a component has, consider the situation for Al^{3+} which could be acting as either a glass former or modifier depending on whether the surrounding environment is more acidic or basic (Baek et al., 2018). If the surroundings are more acidic, then Al^{3+} would act as a network former in the form of AlO_4 , where it is charge compensated by alkaline-earth cations including Ca^{2+} and Na^+ (Baek et al., 2018). If the surrounding environment is more basic, Al^{3+} would act as a network modifier either as AlO_5 or AlO_6 , de-polymerising the glassy network (Baek et al., 2018). The only way to establish the structural role of Al^{3+} in such a complex glass system would be to determine its oxidation state via XANES or electron energy loss spectroscopy (EELS). Neither technique was implemented in this study to analyse the oxides, Fe_2O_3 , B_2O_3 , P_2O_5 , SiO_2 , Na_2O , CaO , and Li_2O . However, XANES was used to examine the Fe oxidation state via the Fe K-edge, where it was determined in conjunction with Mössbauer spectroscopy that Fe was acting mostly as a glass former.

The T_g onset (Figure 90) exhibited a sharp linear decrease between 0.00-0.625 mol% P_2O_5 , followed by an increase at 1.25 mol% P_2O_5 . The decrease in the T_g onset agrees with Lu et al. (2021) where they reported that the increasing P_2O_5 content changed and increased the $\text{Na}(\text{Na} + \text{Al})$ ratio in a P-containing sodium aluminoborosilicate glass, resulting in the replacement of the high-strength Si-O-Al linkages for low-strength B-O-P and Al-O-P linkages, and the formation of de-polymerised PO_4^{3-} and $\text{P}_2\text{O}_7^{4-}$ units, as established by ^{27}Al , ^{29}Si , ^{31}P , and ^{11}B MAS NMR. The combination of these structural aspects decreased the viscosity of the glasses and subsequently the T_g (Lu, et al., 2021). To confirm if this was the case, future work investigating the rheology and structure of these glasses

would need to be conducted. The increase in the T_g onset at 1.25 mol% P_2O_5 corresponds with the formation of the $NaCa(PO_4)$ crystal phase as identified by XRD. The increase in T_g and formation of $NaCa(PO_4)$ may be due to the removal of network modifiers acting as charge compensators for P, which in turn re-polymerises the glassy network, reducing the number of NBØs (Cheng, 2004).

The glass criteria T_{rg} , K_W and K_H are of a particular importance for vitrified products, as they provide an indication of the thermal stability of the glass, i.e., its resistance to crystallisation (Fouad et al., 2021). The T_{rg} provides information on the forming ability of a glass, where values are almost constant for most inorganic materials, reflecting the two-thirds rule, where Fouad et al. (2021) cited Turnbull (1969) stating that values of $T_{rg} > 0.66$ reflect the suppression of homogeneous crystal nucleation due to slow crystallisation kinetics. Zanotto (1987) reported that glasses that have $T_{rg} > \sim 0.58-0.60$ exhibited mostly heterogeneous crystallisation, whilst glasses displaying homogeneous nucleation had $T_{rg} < 0.58-0.60$. The T_{rg} values for the HLW samples suggested that all the samples formed glasses, but that the increase in the T_{rg} value with increasing P_2O_5 content implied that the glasses had a decreasing resistance to crystallisation but exhibited homogeneous nucleation.

The K_H is a stability factor (Fouad et al., 2021) and takes into account the ease of melting (Kozmidis-Petrovic & Šesták, 2012). The variation in T_{rg} and K_H are dependent on the composition of the glass, and hence any variations in these parameters are due to variations in its thermal properties (N'Dri et al., 2007). A glass system with $K_H \geq 0.4$ displays good thermal stability (Farid et al., 2016), and therefore, all the HLW samples exhibited good thermal stability. However, the drastic initial decrease in the K_H parameter with the addition of 0.3125 mol% P_2O_5 from 1.00 to 0.51 a.u. suggests that the thermal stability of the glasses decreased. The K_W parameter is also a glass forming ability parameter used alongside or instead of K_H , where the trend displayed mirrored the K_H parameter, where the value decreased drastically upon the addition of 0.3125 mol% P_2O_5 before increasing at 0.625 mol% P_2O_5 . Therefore, the base glass (HLW0.00) was the most thermally stable glass system.

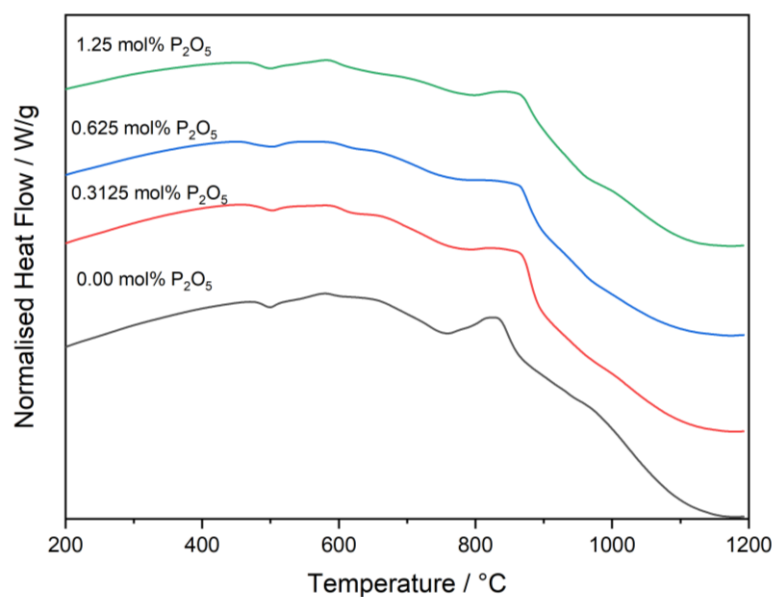


Figure 89 - DTA traces of HLW samples

Sample	T_g onset ± 2 (°C)	T_g midpoint ± 2 (°C)	$T_x \pm 2$ (°C)	$T_c \pm 2$ (°C)	$T_m \pm 2$ (°C)	T_{rg}	K_H	K_W
0	478	483	733	833	988	0.48	1.00	0.36
0.3125	472	481	605	671	868	0.54	0.51	0.23
0.625	454	470	609	668	864	0.53	0.60	0.25
1.25	473	481	610	698	865	0.55	0.54	0.26

Table 44 - DTA thermal parameters for HLW samples

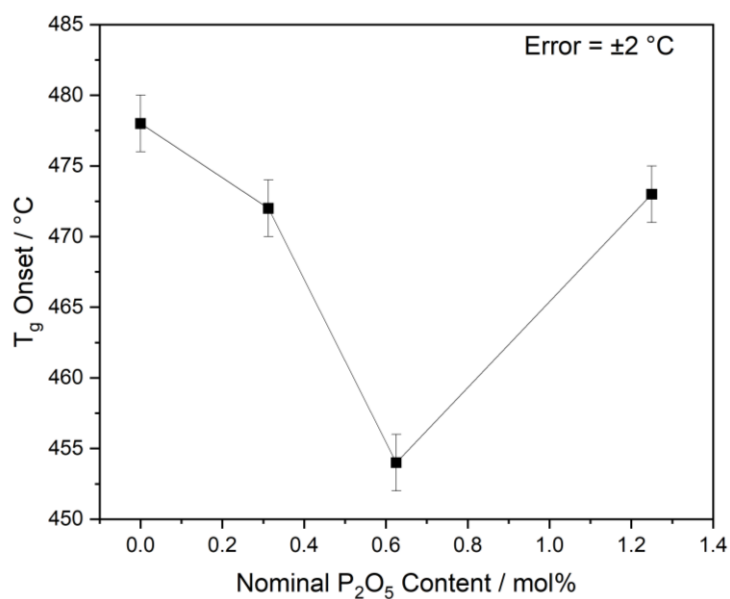


Figure 90 - T_g onset of HLW samples

4.3.3.1.6 Dilatometry

Figure 91 depicts the thermal parameters produced by dilatometry as reported in Table 45 for the HLW samples (HLW0.00, HLW0.3125 (2), HLW0.625 (2), and HLW1.25) (Figure 91). The T_g onset ranged between 448-455 $\pm 5^\circ\text{C}$, the T_g midpoint ranged between 470-487 $\pm 5^\circ\text{C}$, the T_d ranged between 496-506 $\pm 5^\circ\text{C}$, and the CTE ranged between 10.8874-11.6043 $\times 10^{-6} \text{ K}^{-1}$. The T_g onset and midpoint, and T_d values were the same within error, where a horizontal line can be drawn through the points, suggesting that increasing P_2O_5 in these samples had little effect on the polymerisation behaviour of the glass network. However, the CTE increased linearly with increasing P_2O_5 content, where the highest CTE value corresponded to the highest T_g onset value (HLW0.625), suggesting there was no increase in the asymmetrical units in the glass system, e.g., Al-O-P and P-O-B linkages, which would have de-polymerised the glass structure. The increase in the CTE implies that the free volume has been reduced with the introduction and increase in the P_2O_5 content (Shelby, 2005).

Sample	T_g Onset $\pm 5^\circ\text{C}$	T_g midpoint $\pm 5^\circ\text{C}$	$T_d \pm 5^\circ\text{C}$	CTE $\pm 2 \times 10^{-7} (\text{K}^{-1})$
HLW0.00	455	476	496	11.1232×10^{-6}
HLW0.3125 (2)	455	487	506	11.6043×10^{-6}
HLW0.625 (2)	448	484	506	11.4746×10^{-6}
HLW1.25	449	470	496	10.8874×10^{-6}

Table 45 - Thermal parameters of HLW samples collected by dilatometry

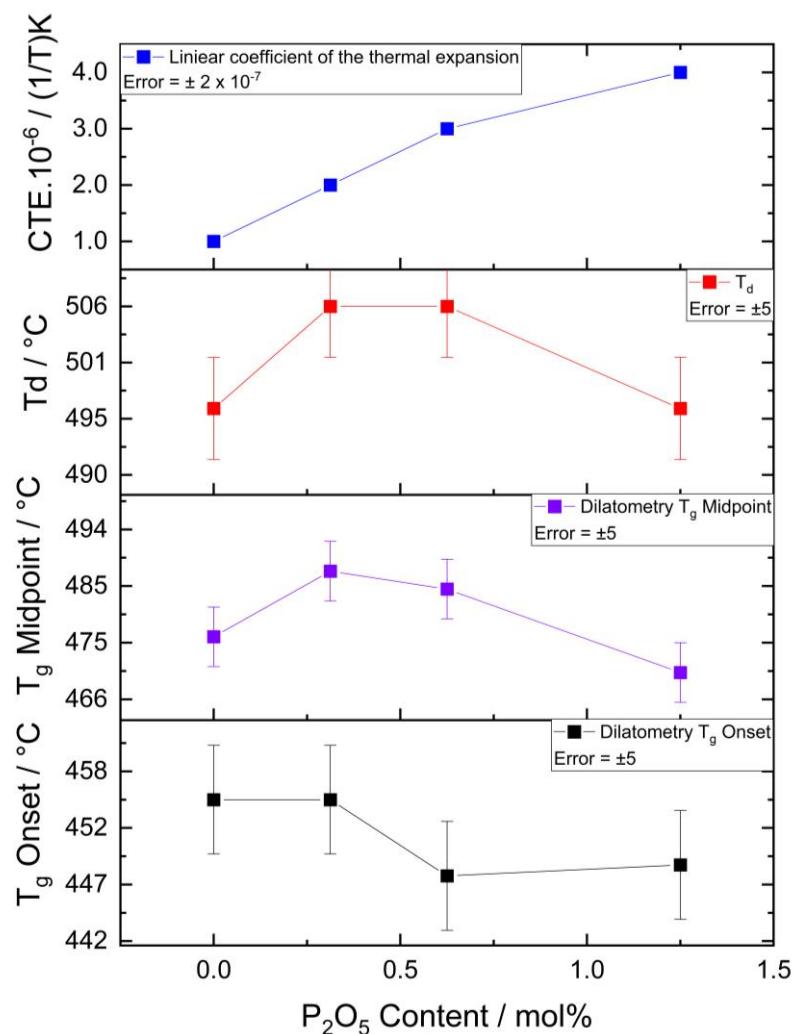


Figure 91 - Graph showing the effects increasing the P₂O₅ content has on the CTE, T_g onset and mid-point, and T_d

4.3.3.1.7 Raman Spectroscopy

Figure 92 shows the Raman spectra of the HLW samples (HLW0.00, HLW0.3125 (1), HLW0.625 (1), and HLW1.25). The base glass exhibited low intensity peaks at ~496, 574, and 756 cm⁻¹, an intense region between 800-1200 cm⁻¹, with peaks identified at ~952 and 1037 cm⁻¹, a broader low intensity region between 1200-1500 cm⁻¹, with peaks identified at ~1263 and 1375 cm⁻¹. When 0.3125 mol% P₂O₅ was added to the base glass composition, the peak at 496 cm⁻¹ increased, whilst the shoulder at ~574 stayed the same, and the peaks at 756, 957, 1037, 1263, and 1375 cm⁻¹ decreased in relative intensity. When the P₂O₅ content was increased to 0.625 mol% P₂O₅, the peaks at ~496, 574, 952, 1037, 1263, and 1375 cm⁻¹ decreased in relative intensity, and the peak at 756 cm⁻¹ stayed the same. At 1.25 mol% P₂O₅ all the peaks decreased in relative intensity, with a shoulder forming at ~1037 cm⁻¹.

The peaks at 496 and 574 cm^{-1} can be associated with symmetrical stretching and partial deformation vibrations of Si-O-Si bridges (Koroleva et al., 2011; McKeown et al., 2000), and the symmetric stretching in Si-O-Al bonds (Lu et al., 2021) or symmetric stretching of Al-O-Al bonds from $[\text{AlO}_4]$ (Hyun et al., 2022). Whilst the peak at 756 cm^{-1} may be attributed to a mixture of four-coordinated boron in six-membered diborate and boroxol rings (Fabian et al., 2020; Möncke et al., 2015), as well as Al-O $^-$ in the $[\text{AlO}_4]$ (Hyun et al., 2022). Between 0.00-0.625 mol% P_2O_5 , the peak at 952 cm^{-1} could be attributed to Q^2 Si-O stretching in structural units with two NBØs per Si or other Q^2 units (Brentrop et al., 2009a, 2009b; Solonenko et al., 2017a, 2017b). When 1.25 mol% was added to the glass system the peak at 952 cm^{-1} became more intense and may be attributed to V_1PO_4 in the $\text{NaCa}(\text{PO}_4)$ crystal phase, as previously identified by XRD (Figure 87). The 1032 cm^{-1} peak is located in the Q^n units region, where it may be attributed to the stretching of Q^3 units (Brentrop et al., 2009a, 2009b; Solonenko et al., 2017a, 2017b), as well as contain contributions from P-O stretching vibrations in pyrophosphate units (Bih et al., 2013; Litasov & Podgornykh, 2017; Mysen, 1998; Trimble et al., 2016). Baert et al. (2011) reported that the presence of Fe contributes to the Q^2 and Q^3 regions, with contributions from Fe^{3+} - SiO_4 tetrahedra at $\sim 980 \text{ cm}^{-1}$, and Fe^{2+} at $\sim 1090 \text{ cm}^{-1}$, respectively. The peaks at 1263 and 1375 cm^{-1} are in the region associated with B-O $^-$ stretching in metaborate rings and chains (Möncke et al., 2015; Yadav & Singh, 2015). Hematite is present in all the samples according to XRD patterns and is an antiferromagnetic material with a collective spin that can be excited in a magnon (a quasiparticle that is a collective excitation of the electrons' spin structure on a crystal lattice), where an intense characteristic feature at approximately 1320 cm^{-1} occurs and is assigned to a two-magnon scattering, which arises from the interaction of two magnons created on antiparallel close spin states (de Faria et al., 1997). However, the concentration of hematite in the samples is so low that it did not form this concentrated peak in the Raman spectra or produce a sextet in the Mössbauer spectra (Figure 95 and Figure 96).

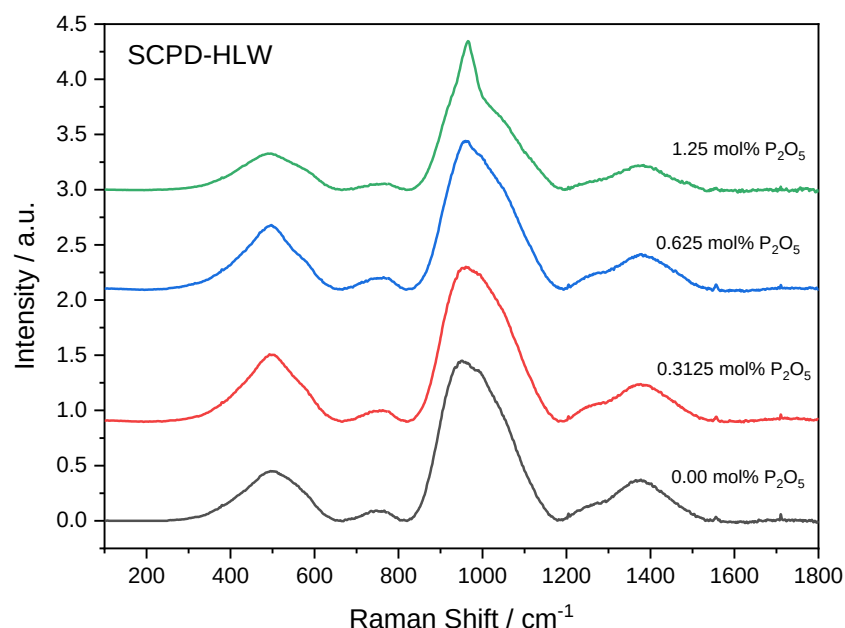


Figure 92 - Raman spectra of HLW samples

4.3.3.1.7.1 Fitting Q^n Speciation Region

Fitting of the HLW Raman spectra using Gaussian line shapes implemented through the OriginPro software package, has allowed the qualitative and semi-quantitative analysis of the Q^n speciation in the samples (Appendix 8.12, Figure 161). This approach does not consider the area overlaps, meaning that the values produced for each Q^n speciation is subject to error. It should be noted that future work should implement other structural techniques for the accurate analysis of the Q^n speciation in these glasses. Figure 94 shows a graphical representation of the polymerisation behaviour of the glass network as a function of the nominal P_2O_5 content, where the decrease in the ratio suggests the de-polymerisation of the network, and increase suggests its re-polymerisation (Manara et al., 2009). The Gaussian line fits for each sample are available in the Appendix (8.12). Interestingly, the graphical shape presented in the DTA T_g onset graph (Figure 90) mirrors what is presented in Figure 94, where a decrease/increase in the Q^n speciation ratio sees it mirrored in the T_g .

From evaluating Table 46 and Figure 93, the base glass contained a mixture of Q^n species, but predominantly Q^4 units. Upon the addition of 0.3125 mol% P_2O_5 the glass network de-polymerised as evidenced by the decrease in Q^4 units from 66.33% to 1.82% and increase in Q^3 and Q^2 units from 1.18 to 61.85% and 26.50 to 30.97%, respectively. When 0.625 mol% P_2O_5 was added, the Q^3 units reduced by 49.73%, whilst the Q^2 and Q^4 units increased by 8.25% and 38.92%,

respectively. When 1.25 mol% P_2O_5 was added the Q^4 and Q^2 units decreased by 38.62 and 27.03%, respectively, whilst the Q^1 and Q^3 units increased by 54.65 and 11.00%, respectively. From evaluating Figure 94, it suggests that as the P_2O_5 content increased the glass network did not change within relative error, where a straight line can be drawn. However, the associated statistical error with this methodology is quite high, where they were calculated using error propagation. The-repolymerisation of the glassy network, as suggested by Figure 93, may be due to the formation of the $NaCa(PO_4)$ crystal phase, where Na^+ and Ca^{2+} cations are removed from the glass network to charge compensates the P, leading to a reduction in NBØ's and the glass network's subsequent re-polymerisation.

Nominal									
P_2O_5	Q^1	Relative	Q^2	Relative	Q^3	Relative	Q^4	Relative	
content	(%)	error	(%)	error	(%)	error	(%)	error	
(mol%)									
0	5.98	23.71	26.50	6.69	1.18	6.06	66.33	0.48	
0.3125 (1)	5.37	6.28	30.97	1.52	61.85	0.67	1.82	4.38	
0.625 (1)	7.92	14.32	39.22	7.07	12.12	17.51	40.74	1.46	
1.25	18.92	0.46	12.19	0.39	66.77	0.10	2.12	1.11	

Table 46 - Calculated relative Q^n speciation percentage abundancies

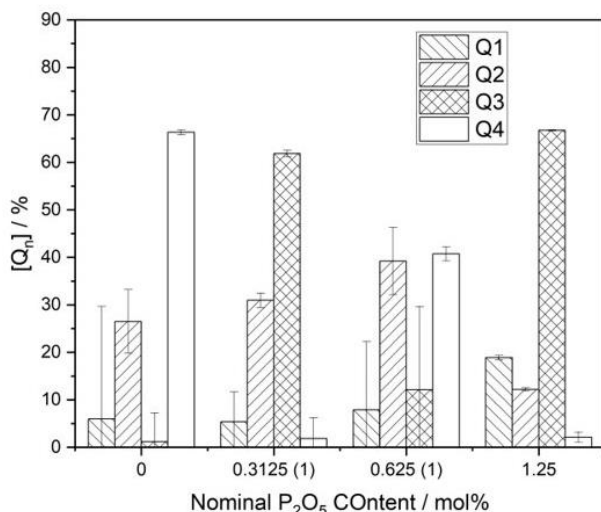


Figure 93 - Graphical representation of relative abundancies with relative errors of Q^n species in HLW samples

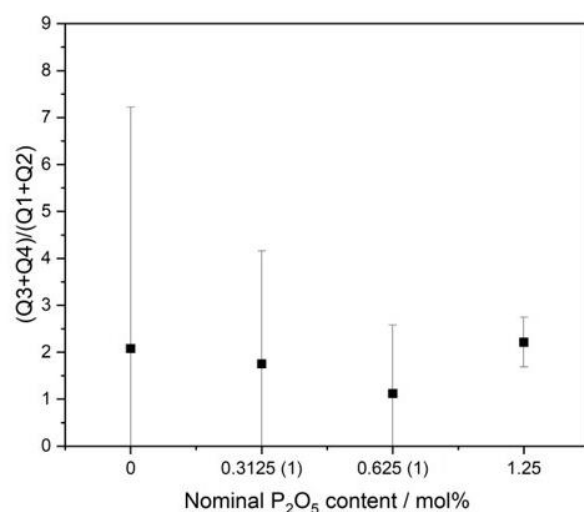


Figure 94 - Ratio $(Q_3 + Q_4) / (Q_1 + Q_2)$ with relative error, which is indicative of the silica network polymerisation

4.3.3.1.8 Mössbauer Spectroscopy

4.3.3.1.8.1 Lorentzian Site Analysis

^{57}Fe Mossbauer spectroscopy was used to investigate the potential changes in the oxidation state of Fe in the samples when the P_2O_5 content was increased. Figure 97 illustrates the Mössbauer spectra fitted with Gaussian line shapes using Lorentzian fitting parameters for the annealed HLW samples (HLW0.00, HLW0.3125 (1), HLW0.625 (1), and HLW1.25) with increasing P_2O_5 content, using the Recoil software package (Rancourt & Lagarec, 1998).

The HLW samples nominally contain between 5.79-5.86 mol% Fe_2O_3 . The fitted hyperfine parameters analysed for these samples showed the presence of Fe^{2+} and Fe^{3+} components, especially as the spectra displayed some asymmetry indicating a distribution of the Fe^{2+} environment (Rossano et al., 2008). In Figure 95, doublet D1 represents octahedrally-coordinated Fe^{3+} ions, doublet D2 represents tetrahedrally-coordinated Fe^{3+} ions, and doublet D3 represents octahedrally-coordinated Fe^{2+} ions (Bingham et al., 2007; Dyar & Burns, 1981; Stoch & Stoch, 2015). The quadrupole splitting reveals the asymmetry in the charge-density distribution, whilst the centre shift reflects the amount of charge-density of the probed nucleus, which depends on the degree of localised and de-localised charge (El-Denglawey et al., 2021). Higher centre shift values are associated with five or six coordinated Fe atoms, whilst higher quadrupole splitting values are indications of low coordination symmetry of Fe atoms in tetrahedral sites (El-Denglawey et al., 2021). The centre shift values for Fe^{3+} ranged from 0.27-0.30 mm/s (Table 47), which is typical of atoms in a tetrahedral coordination (Cochain et al., 2012; Li et al., 2002; Zawada, 2020). The centre shift value for the Fe^{2+} atoms ranged between 0.92-1.00 mm/s, which is at the lower end of the octahedral coordination range (Cochain et al., 2012; Li et al., 2002; Zawada, 2020). As the P_2O_5 content increased between 0.00-0.625 mol%, the mean centre shift value for Fe^{2+} decreased but not substantially, implying little influence of P_2O_5 on its coordination. However, the Fe^{3+} was present mainly in the tetrahedral coordination (61%) in the undoped base glass (HLW0.00), with some sites present in the octahedral coordination (31%). When the P_2O_5 content was increased to 0.625 mol%, the site population of Fe^{3+} in the octahedral coordination increased to 68%, whilst the tetrahedral coordinated Fe^{3+} decreased to 29%. Upon further additions of P_2O_5 , the Fe^{3+} octahedral sites decreased

marginally, and the tetrahedral sites increased slightly. Overall, the initial addition of 0.625 mol% P_2O_5 saw an increase in the Fe^{3+} network modifier content and reduction in the network former content. However, upon further additions of P_2O_5 the network former content increased again.

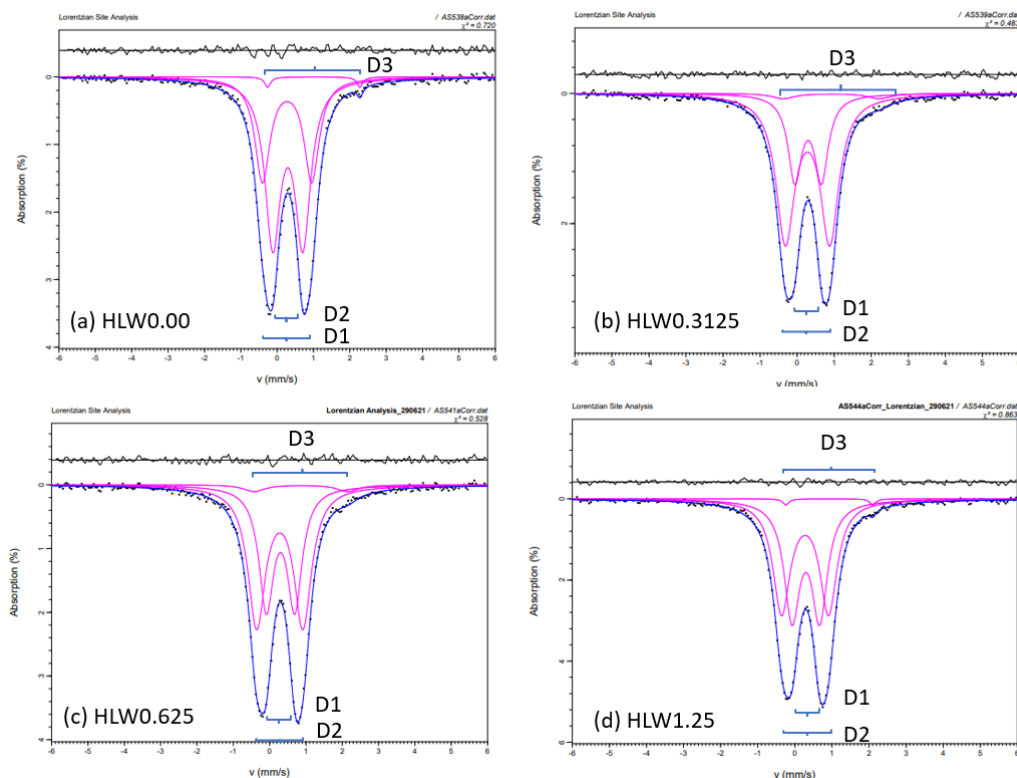


Figure 95 - Gaussian line shapes using Lorentzian fitting parameters of Mossbauer spectra of HLW samples

Sample	Dou blet Site	CS (mm/ s)	QS (mm/ s)	Line width (mm/ s)	Site popu lation s (%)	Redu ced χ^2	Expected Reduced χ^2	Fe coordination
HLW0.00	1	0.27	1.35	0.25	37	0.720	1.0 $\pm$ 0.181444	Fe_{Oct}^{3+}
	2	0.29	0.83	0.26	61			Fe_{Tet}^{3+}
	3	1	2.54	0.25	2			Fe_{Oct}^{2+}
HLW0.3125	1	0.28	1.2	0.3	68	0.483	1.0 $\pm$ 0.181071	Fe_{Oct}^{3+}
	2	0.3	0.72	0.2	29			Fe_{Tet}^{3+}
	3	0.92	2.59	0.36	3			Fe_{Oct}^{2+}
HLW0.625	1	0.28	1.27	0.29	56	0.528	1.0 $\pm$ 0.180702	Fe_{Oct}^{3+}
	2	0.3	0.78	0.25	41			Fe_{Tet}^{3+}
	3	0.86	2.57	0.35	3			Fe_{Oct}^{2+}
HLW1.25	1	0.28	1.27	0.26	51	0.863	1.0 $\pm$ 0.181444	Fe_{Oct}^{3+}
	2	0.3	0.74	0.28	48			Fe_{Tet}^{3+}
	3	0.93	2.34	0.16	1			Fe_{Oct}^{2+}

Table 47 - Fitted Mössbauer parameters for HLW samples calculated from Gaussian line shapes using Lorentzian fitting parameters

4.3.3.1.8.2 xVBF Site Analysis

The Mössbauer spectra of the HLW samples were deconvoluted using the Voight-based hyperfine distribution (x-VBF) method developed by Rancourt and Ping (1991) (Figure 96), where the hyperfine parameters are recorded in Table 48. This methodology was employed because Rancourt et al. (1998; 1991) identified the shortcomings of Lorentzian peaks in fitting Mössbauer spectra, where a number of generalised Fe species were assumed to have their own “*continuous distribution of quadrupole splitting or hyperfine magnetic field consisting of Gaussian components*” (Kukkadapu et al., 2003). The distinct lack of a sextuplet in the samples is due to the dilute nature of the glasses, indicating an absence of magnetic phases (Costa et al., 2014). The Fe^{3+} doublet is paramagnetic and occurs due to the lack of or decreased spin-spin interaction between the Fe^{3+} sites at lower Fe concentrations (Kukkadapu et al., 2003). The spectra of the HLW samples showed a doublet spectrum with little asymmetry, however, there was a slight underfitting of the HLW0.3125(1) sample spectrum, indicating the presence

of Fe^{2+} . The hyperfine parameters suggested that the majority of the Fe^{3+} present was in the tetrahedral coordination in the base glass, before being present as the octahedral coordination in the P_2O_5 doped samples. The HLW0.3125 sample also showed evidence of having octahedrally coordinated Fe^{2+} present.

The Lorentzian and xVBF methodologies both suggest that Fe is present predominantly as $\text{Fe}_{\text{Oct}}^{3+}$ and $\text{Fe}_{\text{Tet}}^{3+}$, however, the xVBF method did not fit contributions from the Fe^{2+} environment, other than in the HLW0.3125 sample. However, the Lorentzian methodology did fit for the Fe^{2+} environment, suggesting that it was present as $\text{Fe}_{\text{Oct}}^{2+}$.

The Mössbauer analysis has shown that the Fe in the samples is predominantly present as both a network former and modifier, but that doping the HLW samples with P_2O_5 does change the Fe^{3+} environment, where there is an increase in the network forming content, suggesting the de-polymerisation of the glass network. Cizman et al. (2017) reported that additions of Fe_2O_3 to borosilicate glass systems as a network former or modifier, resulted in the conversion of BO_4 tetrahedra to triangular BO_3 units, leading to the decrease in polymerisation of the $[\text{SiO}_{4/2}]$ tetrahedral group, and that $\text{Fe}_{\text{Oct}}^{2+}$ occupy interstitial sites near triangular BO_3 units, whilst $\text{Fe}_{\text{Tet}}^{3+}$ substitute with Si.

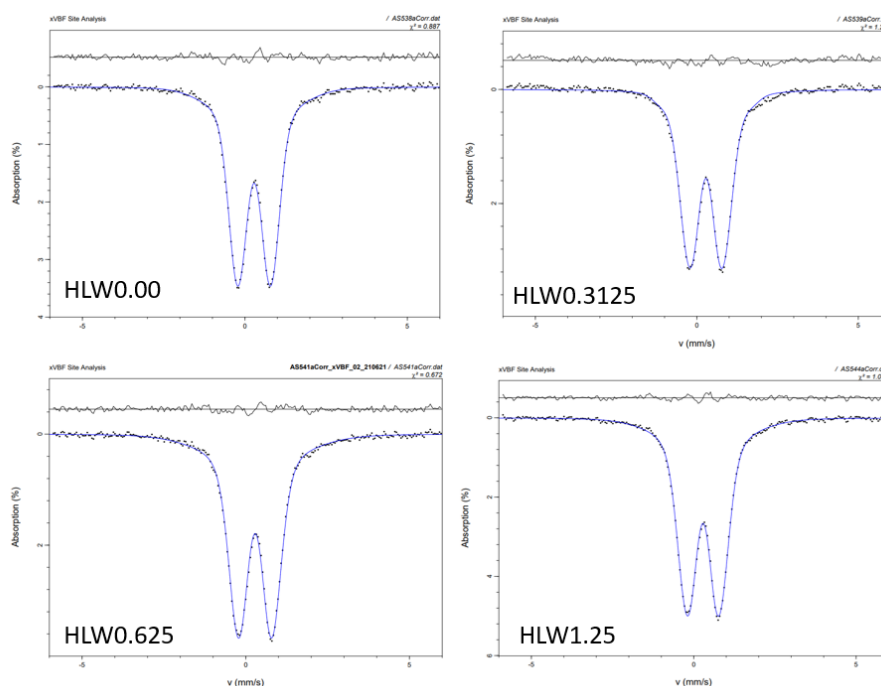


Figure 96 – xVBF line fits of Mössbauer spectra of HLW samples

Sample	CS Component	CS (mm/s)	QS (mm/s)	Site populations (%)	STDEV	Reduced χ^2	Fe redox & coordination
HLW0.00	1	0.29	2.1	15	0.66186	0.887	Fe_{Oct}^{3+}
			1.0	85			Fe_{Tet}^{3+}
HLW0.3125	1	0.28	1.08	82	0.50176	1.208	Fe_{Oct}^{3+}
			0.75	14			Fe_{Tet}^{3+}
	2	0.9	2.81	4			Fe_{Oct}^{2+}
HLW0.625	1	0.27	0.9	24	0.35676	0.678	Fe_{Tet}^{3+}
	2	0.29	1.2	76			Fe_{Oct}^{3+}
HLW1.25	1	0.31	1.07	22	0.42445	1.047	Fe_{Oct}^{3+}
	2	0.29	0.74	78			Fe_{Tet}^{3+}

Table 48 - Fitted Mossbauer parameters for HLW samples calculated from xVBF fitting

4.3.3.2 Fe K-edge XANES

As previously stated, the HLW0.3125 and 0.625 samples analysed by XANES were conducted on the samples with elevated Al_2O_3 content, however, due to the samples displaying similar crystallisation behaviour, there should be a minimal effect on the XANES data produced.

XANES spectra were corrected and normalised using the ATHENA work package (Ravel & Newville, 2005). Figure 97 presents the Fe K-edge XANES data for the HLW series samples. Figure 98 shows the spectra with three labelled features labelled A, B, and C. Feature 'A' is the pre-edge and is the $1s \rightarrow 3d$ configuration where the lowest energy transitions occur at approximately 7112 eV (Westre et al., 1997). Feature 'B' is the shoulder of the spectra where the $1s \rightarrow 4s$ transition occurs, and feature 'C' is the edge crest where the $1s \rightarrow 4p$ transition occurs at approximately 7125 eV (Berry et al., 2003; Westre et al., 1997). Table 49 records the Gaussian peak energies and associated intensities, and integrated intensities and centroid position values for the HLW samples.

Feature 'A' is of particular interest for XANES analysis as it is the pre-edge peak and can be deconvoluted using Gaussian line shapes to establish the Fe oxidation state and coordination number, using the calculated intensity, integrated intensity, and average centroid position, and then comparing them with known Fe

references from literature, such as those published by Wilke et al. (2001). In minerals where there is no mixing of Fe^{2+} and Fe^{3+} , the Fe^{2+} coordination is tetrahedral where two pre-edge features will be exhibited at approximately 7111 eV and 7113 eV (Henderson et al., 2014). When Fe^{2+} has three components fitted then it is present in the octahedral coordination, but the third component may be quite weak in comparison to the others due to site distortion (Henderson et al., 2014). There is also the 5-fold coordination where two peaks are observed, and the 8-fold coordination, where two maxima are observed (Henderson et al., 2014). Fe^{3+} can be present in a 4-fold coordination and exhibits one pre-edge peak with a centroid position of 7113.5 eV. The 5-fold coordinated Fe^{3+} exhibits a single peak when it is in a trigonal bipyramidal configuration and two peaks when it is in a square configuration (Henderson et al., 2014). 6-coordinated Fe^{3+} ($[\text{Fe}^{3+}]$) exhibits two peaks whose centroid positions are at 7112.8 eV and 7114.3 eV (Henderson et al., 2014).

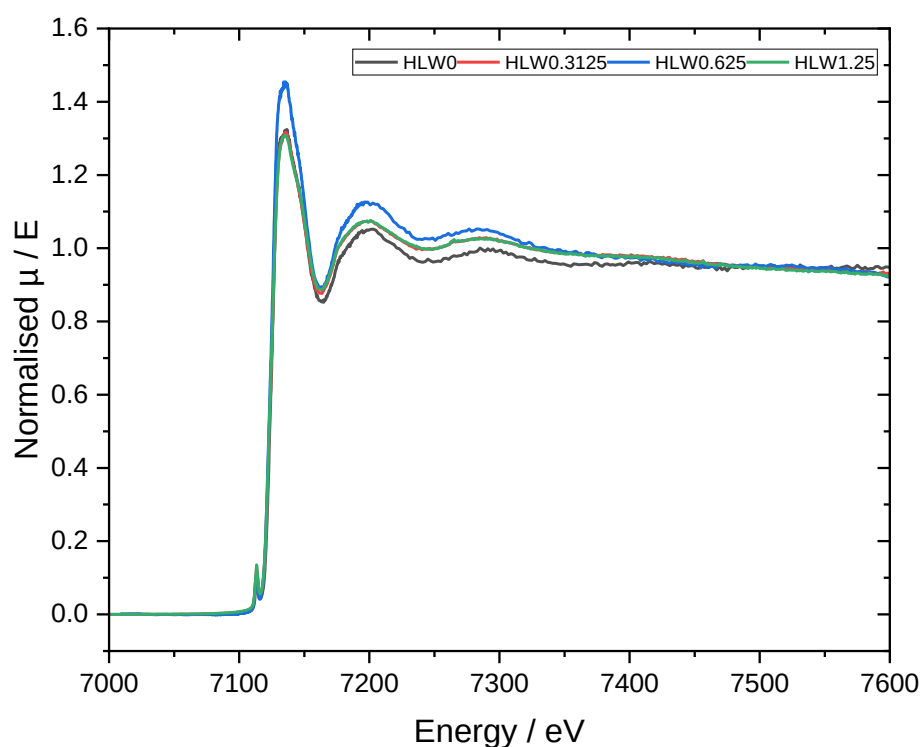


Figure 97 - Fe K-edge XANES spectra of HLW0 and HLW0.625 (1) (collected at B18) and HLW0.3125 (1) and HLW1.25 (collected at BM-28)

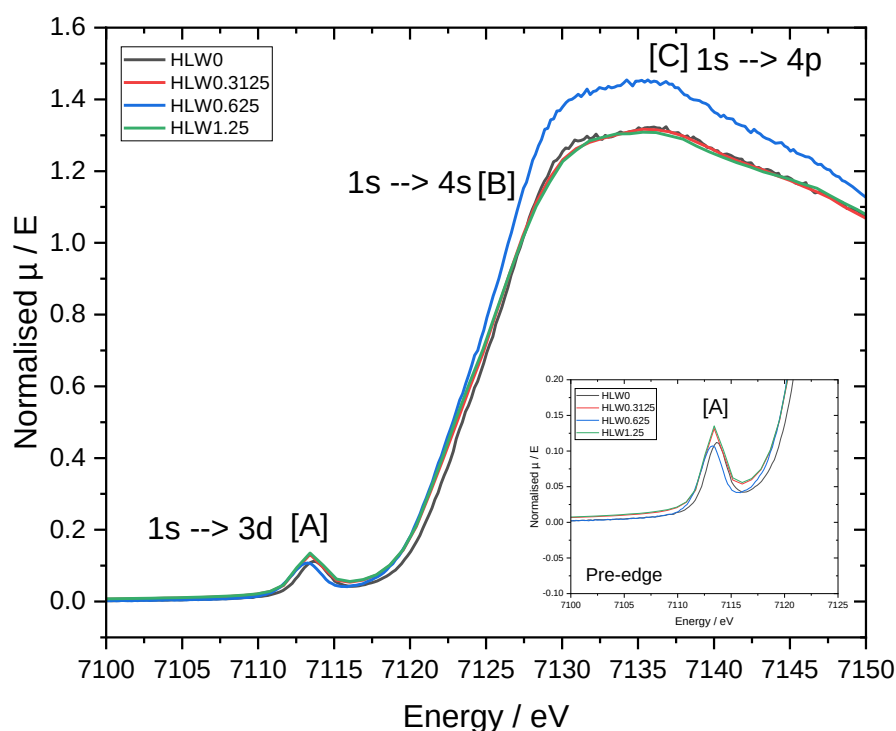


Figure 98 - Fe K-edge XANES spectra of HLW samples with annotated orbital transitions and an inserted graph showing a close-up of the pre-edge region. In this study, the Fe oxidation state was estimated from the energy of the absorption edge (E_0) and interpolating it between the energies measured for a set of reference samples. The intensity and position of the pre-edge region provides information on the Fe oxidation state and coordination environment, where the area under the pre-edge is dependent on the site symmetry (Joseph et al., 2017). The fitting of the pre-edge feature and reference compounds were performed in the energy range 7107-7120 eV, in accordance with the methodology proposed by Wilke et al. (2001), (*the pre-edge fitting line shapes are available in the Appendix 8.15*). Gaussian components were fitted to the pre-edge feature using a least squares minimalization routine in Excel, where the total area under the pre-edge feature was obtained by summing the integrated intensity under each pre-edge feature (Joseph et al., 2017). These values were then plotted in a variogram (Figure 99) and compared to data reported by Wilke et al. (2001). According to Table 49, the Fe in the samples existed as both Fe^{2+} and Fe^{3+} in the glass network, where the centroid positions in Figure 99 suggested that the oxidation state of the Fe was Fe^{3+} and the coordination was either tetrahedral and/or octahedral due to the fact that the pre-centroid energies were located in-between both sets of standards provided by Wilke et al. (2001). Evaluating Table 49 suggests that Fe in the HLW0.00 sample was present as Fe^{3+}

with tetrahedral and/or octahedral coordination and that HLW0.3125, 0.625, and 1.25 had Fe present as Fe²⁺, where the coordination was unknown, and Fe³⁺ where the coordination was tetrahedral and/or octahedral.

These results were compared to the room temperature Mössbauer spectra (Figure 95 and Figure 96) to validate the Fe oxidation state and coordination number, where it confirmed that the Fe was present as both Fe²⁺ and Fe³⁺ in the glass network, but that Fe²⁺ contributions were marginal. According to Lorentzian fitted Mössbauer spectra of the HLW samples, the Fe²⁺ had a sixfold coordination in all samples, occupying one site, and acting as a network modifier. The Fe³⁺ occupied two sites having a coordination of tetrahedral and octahedral, confirming that Fe was acting as both network former and modifier in the glass.

Sample	Gaussian energy (eV)	Intensity (a.u.)	Integrated intensity (a.u.)	Centroid position (eV)	Margin of error
HLW0.00	7113.6	0.211	0.22	7113.9	4.39829 x 10 ⁻⁶
	7115.1	0.012			
HLW0.3125	7113.4	0.213	0.24	7113.5	2.19 x 10 ⁻³
	7113.2	0.032			
HLW0.625	7113.1	-	0.22	7113.5	8.05104 x 10 ⁻⁶
HLW1.25	7113.5	0.223	0.26	7113.5	2.22 x 10 ⁻³
	7113.2	0.033			

Table 49 - Gaussian peak energies and associated intensities and integrated intensities and centroid position values for the HLW samples based on Gaussian line shapes

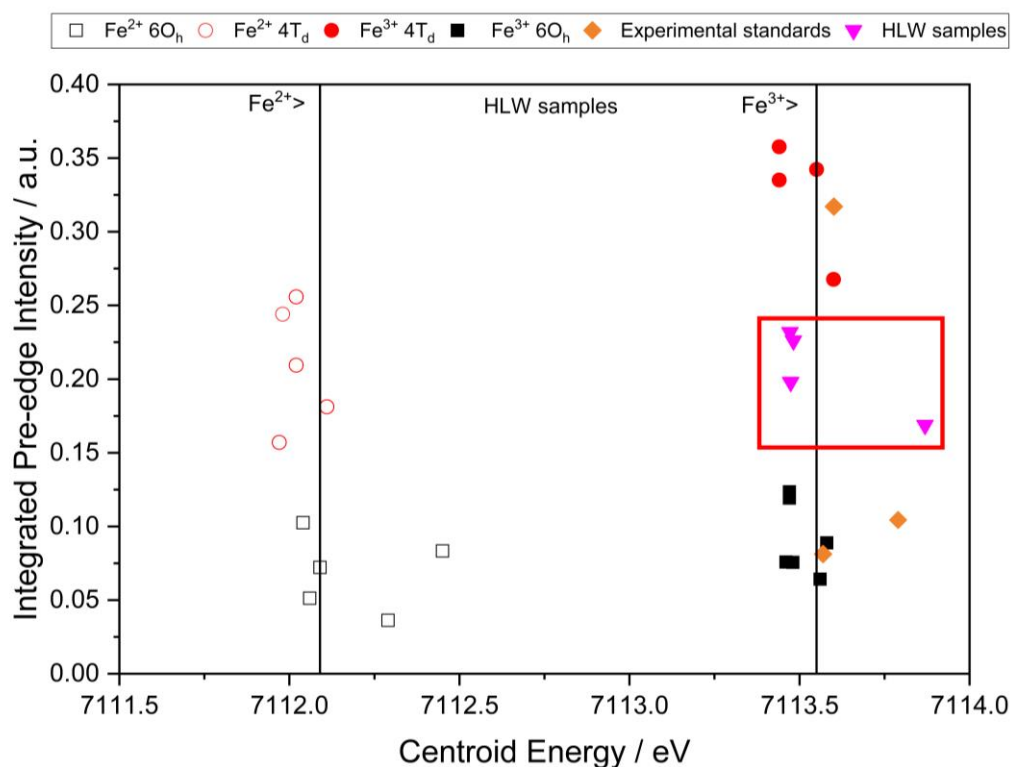


Figure 99 - A variogram plotting the average centroid value plotted with experimental standards and samples from Wilke et al. (2001)

4.3.3.3 SEM/EDS

Figure 100 shows the backscattered SEM images at a magnification of 2000x and associated EDS maps for the HLW samples. It should be noted that there was an operational issue with the SEM at the time the experiment was conducted. Hence, the HLW0.3125 image is the scanning electron (SE) image instead of backscattered electron image (BSE), and some of the maps were not fully developed for certain elements, i.e., P, Fe, and Ca in the HLW0.3125 and 0.625 samples. However, point scans at 10000x were conducted to confirm the oxides present (Figure 162 and Figure 163 in the Appendix 8.13 and 8.14). From evaluating the EDS maps, they suggested that the crystal phase present in the samples were predominantly formed of Fe and O, which could be associated with the formation of hematite, as previously identified by XRD patterns (Figure 87). However, there was no evidence in the HLW1.25 sample of the NaCa(PO₄) crystal phase, but this may have been due to the sample section used to form the SEM sample. The NaCa(PO₄) phase may have been present in a different part of the bulk glass not used to form the SEM sample. There are further EDS point scans at 10000x magnification in the *Appendix 8.13* for samples HLW0.3125 and

1.25. The morphology of some the crystals looked to be from the trigonal system, where others seemed to have a prism shape. Figure 101 and Figure 102 showed the LAW1.25 sample at 30000x and 100000x, where there seemed to be evidence of small grey and black droplets scattered in a matrix of grey. These droplets seemed similar to those previously seen in the NBSP samples with 4.0-6.0 mol% P₂O₅ (Figure 53 to Figure 56), where these were indicative of phase separation.

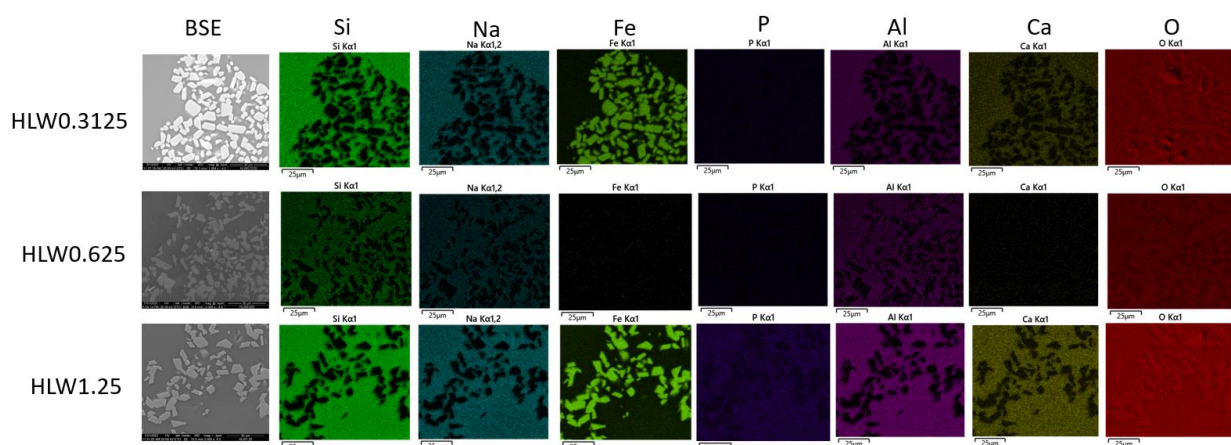


Figure 100 - Backscattered SEM images and associated EDS maps for HLW0.3125, 0.625, and 1.25 samples

Sample	Element (oxide wt%)													
	Si	σ	Na	σ	Fe	σ	P	σ	Al	σ	Ca	σ	O	σ
HLW0.3125	11.9	0	7.6	0.0	34.7	0.0	0.2	0.0	8.1	0.0	2.4	0.0	34.7	0.0
HLW0.625	3.9	0.2	6.8	0.4	0.1	0.0	-	-	3.6	0.2	-	-	62.1	2.7
HLW1.25	11.1	0.2	6.6	0.1	22.7	0.4	0.7	0.0	5.6	0.1	2.3	0.0	43.9	1.0

Table 50 – EDS mapping spectra for HLW samples



Figure 101 – Backscattered SEM image of HLW1.25 at x30k using a JOEL JSM-7001F field emission SEM

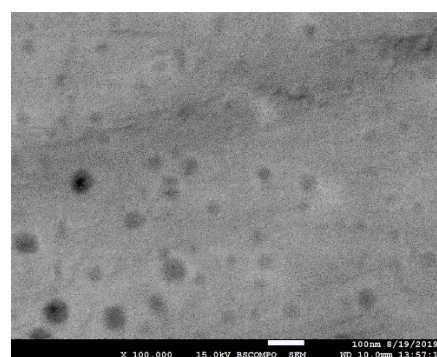


Figure 102 – Backscattered SEM image of HLW1.25 at x100k using a JOEL JSM-7001F field emission SEM

4.3.4 CCC Heat Treated HLW Samples

4.3.4.1 Visual Observations

Figure 103 shows the optical images of centreline canister cooled (CCC) HLW0.00 and 1.25 samples at varying magnifications using optical microscopy. Both samples were deep red in colour, where particle size was seen to influence the colour of hematite due to the reflectance of the red section of the spectrum decreasing with increasing particle size (Jiang et al., 2022). Particles or aggregates with sizes 1.5-5 μm , 0.1-0.5 μm , and <0.1 μm range in colour from purple to red to orange, respectively (Jiang et al., 2022). The thin needle-like channels observed in both HLW samples, may be attributed to hematite crystals orientated with their c-axes perpendicular to the observation of the sample (Wisniewski et al., 2011). The grain shape also has an influence, where needle-like morphology is more yellow in colour than cube-like particles (Wisniewski et al., 2011). Coarsely crystalline hematite particles with crystal sizes >5 μm can be grey in colour or even darker as to appear black (Wisniewski et al., 2011). Red coloured fine grained hematite is evidence of an oxidising environment (Wisniewski et al., 2011) and has been previously reported to be present in heat treated samples from the Hanford Site AZ-101 composition (Matyas et al., 2010).

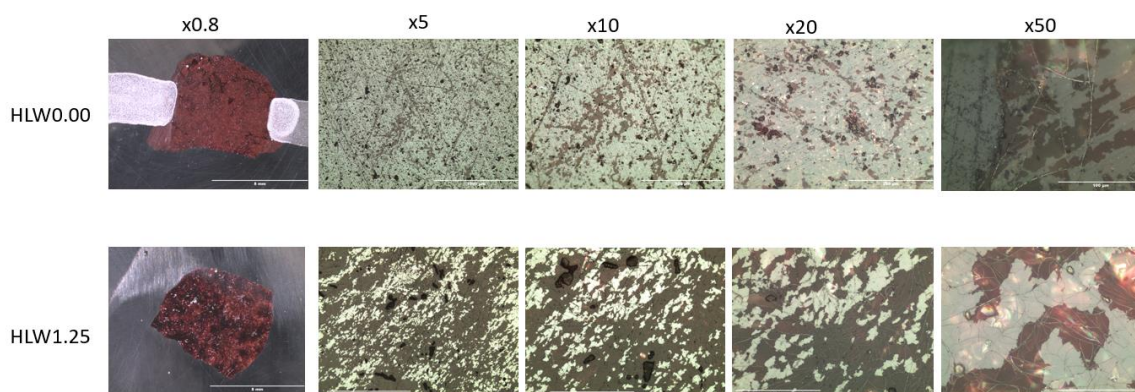


Figure 103 – Optical images of the CCC HLW0.00 and 1.25 samples at x0.8, 5, 10, 20, and 50 magnification

4.3.4.2 X-ray Powder Diffraction

Figure 104 shows the XRD patterns for the CCC heat treated HLW0.00 and 1.25 samples. The base glass and 1.25 mol% P_2O_5 sample showed that the crystal phases present were hematite (Fe_2O_3 , PDF#: 01-89-8103, 01-76-4579, crystal group: rhombohedral, space group: R-3c (Taylor, 1984)) (Appendix 8.16 Figure 168 and Table 89) and nepheline ($\text{NaAlSi}_3\text{O}_8$, PDF#: 04-016-1739, 01-079-0994,

crystal system: hexagonal, space group: P63 (Dimitrijevic et al., 2004)) (Appendix 8.16 Figure 169 and Table 89). However, the HLW1.25 sample had evidence of an amorphous hump present. There was also the distinct lack of NaCa(PO₄) present, which was previously identified in the annealed samples. However, there continued to be the presence of Fe₂O₃ in the 1.25 mol% doped sample and its development in the 0.00 mol% sample, indicating that the base glass may have had small Fe₂O₃ nuclei present, which when undergoing heat treatment clustered together and grew in size, before nucleating and forming the final crystalline phase (Erdemir et al., 2009). The formation of NaAlSiO₄ indicated that the glass melt had a high Na₂O and Al₂O₃ content, where the residual glass phase would have a lower chemical durability (Marcial et al., 2016; Riley et al., 2002). The Fe₂O₃ and NaAlSiO₄ acted as nucleation sites, which increased the number of crystals present (Matyas et al., 2010).

The formation of NaAlSiO₄ removes one mole Al and two moles Si from the glass network, which then require charge compensating by Na⁺ cations, changing the residual glass composition and negatively affecting the chemical durability of the final waste form (Deshkar et al., 2022). The amount of Fe that enters the NaAlSiO₄ structure is dependent on the melt composition and how much of the Fe-containing spinel forms upon cooling, where a certain proportion of Fe is consumed prior to NaAlSiO₄ formation (Marcial et al., 2016). However, there was no evidence of a spinel crystal phase. Lu et al. (2021) reported that the partial substitution of Al₂O₃ for P₂O₅ (≤5.0 mol%) resulted in two impacts on the phase evolution: (i) the suppression of carnegite resulting in the crystallisation of NaAlSiO₄ only, and (ii) the reduction in the intensity of XRD reflections via the retardation of the crystallisation kinetics, where P₂O₅ additions resulted in the suppression of crystallisation after heat treatment. Similar behaviours can be seen occurring in the 0.00 and 1.25 mol% P₂O₅ doped samples, thus agreeing with observations made by Lu et al. (2021). The suppression of NaAlSiO₄ formation caused by the additions of P₂O₅ may be due to the formation of Al-O-P linkages, where Al is taken from the aluminosilicate network, which in turn promotes the formation of Si-O-Si linkages over Si-O-Al (Deshkar et al., 2022; Lu et al., 2021). However, to assess whether this is the case, ²⁷Al, ³¹P, ²⁹Si, ²³Na, and ⁴³Ca MAS NMR would need to be conducted to characterise the speciation and bonding in the glass networks. The increased formation of Al-O-P linkages may be a contributing factor as to why NaCa(PO₄) is no longer present in the 1.25

mol% P_2O_5 doped sample, where the P^{5+} atoms are instead being charge compensated not only by Na^+ but by Al^{3+} as well, forming $AlPO_4$ units, leaving a proportion of Na^+ cations available to charge compensate AlO_4^- units. Deshkar et al. (2022) reported that the presence of Li_2O is known to “*reduce the Si/B mixing in the glass network and increase the coordination of Na^+* ”, affect the ratio of ring-to-non-ring BO_3 units, and cause the formation of five-coordinated Al in the glass structure. Dubinsky (2006) commented that the abundance of Al-O-Al and Si-O-Si bridging oxygen linkages increases with increasing fictive temperature, where the reaction $2Al-O-Si \leftrightarrow Al-O-Al + Si-O-Si$ shifts to the right with increasing temperature. Hence, the presence of Si-O-Al linkages in the glass structure are pertinent for the crystallisation of $NaAlSiO_4$ (Deshkar et al., 2022).

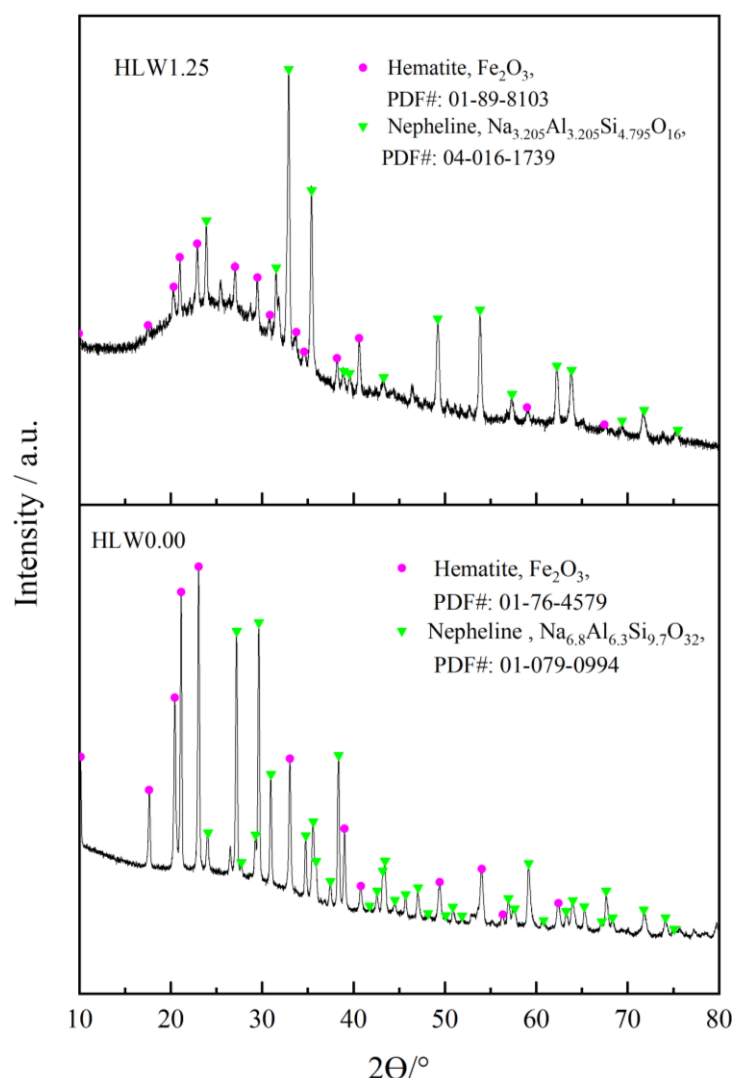


Figure 104 – CCC heat treated HLW0.00 and HLW1.25 XRD patterns with identified crystal phases

4.3.4.3 Raman Spectroscopy

Figure 105 shows the CCC heat treated HLW0.00 and 1.25 Raman spectra and Table 51 lists the Raman shifts and referenced associations. The base glass exhibited peaks in the low frequency region at 225, 245, 294, 412, 502, 612, 662 cm^{-1} , low intensity, broad peaks at 826, 1048, and 1108 cm^{-1} in the mid-frequency region, and a very intensive peak at 1323 cm^{-1} and a small low intensity peak at 1557 cm^{-1} in the high frequency region. When 1.25 mol% was added, the same peaks were present that were in the spectrum for the base glass, apart from the occurrence of a small sharp peak at 962 cm^{-1} . The peaks associated with the occurrence of Fe_2O_3 (Figure 170) are 225, 245, 294, 412, 502, 612, 662, and 1320 cm^{-1} , where 225 and 502 cm^{-1} are attributed to A_{1g} modes, 245, 294, 412, 612 cm^{-1} were attributed to E_g modes, 662 cm^{-1} was attributed to 1LO (longitudinal optical), and 1323 cm^{-1} was attributed to 2LO (Marshall et al., 2020). A_{1g} and E_g are associated with Γ point phonon modes that occur below $\sim 620 \text{ cm}^{-1}$, where the phonons are classified further into five internal modes ($2A_{1g} + 3E_g$), which involve motions within a single $\text{Fe}(\text{O})_6$ octahedral unit, where E_g modes are external phonon modes which involve the rotation and translations of entire Fe_2O_3 units (Marshall et al., 2020; Massey et al., 1990; Porto & Krishnan, 1967). The 1LO mode has been attributed to “*disorder-induced breaking of symmetry properties for the scattering LO phonon*” (Marshall et al., 2020; McCarty, 1988). The band at 1323 cm^{-1} was associated with the 2LO mode which has been attributed to a “*two-phonon scattering process, which is an overtone of the LO mode at $\sim 660 \text{ cm}^{-1}$* ” (Lopez et al., 2009; Marshall et al., 2020; Marshall & Olcott Marshall, 2013; Shim & Duffy, 2002). McCloy et al. (2015) reported that the band at $\sim 962 \text{ cm}^{-1}$ was attributed to polarised boroxol ring vibrations. There is a distinct lack of characteristic peaks associated with NaAlSiO_4 in the Raman spectra for the HLW samples (Figure 171), however, these may be overshadowed by the intense peaks produced by Fe_2O_3 .

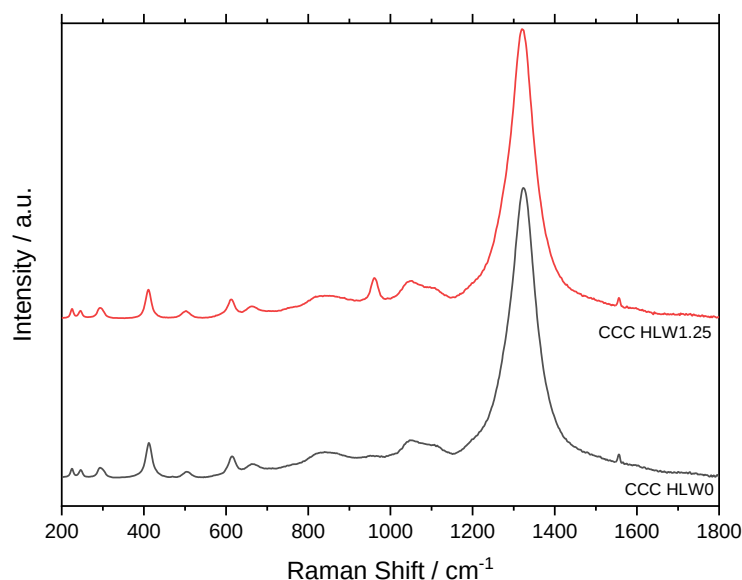


Figure 105 – Raman spectra of CCC heat treated HLW0.00 and 1.25

Raman shift / cm ⁻¹	Association	Reference
225	A _{1g} modes in Fe ₂ O ₃	(Marshall et al., 2020; Massey et al., 1990; Porto & Krishnan, 1967)
245	E _g modes in Fe ₂ O ₃	(Marshall et al., 2020; Massey et al., 1990; Porto & Krishnan, 1967)
294	E _g modes in Fe ₂ O ₃	(Marshall et al., 2020; Massey et al., 1990; Porto & Krishnan, 1967)
412	E _g modes in Fe ₂ O ₃	(Marshall et al., 2020; Massey et al., 1990; Porto & Krishnan, 1967)
502	A _{1g} modes in Fe ₂ O ₃	(Marshall et al., 2020; Massey et al., 1990; Porto & Krishnan, 1967)
612	E _g modes in Fe ₂ O ₃	(Marshall et al., 2020; Massey et al., 1990; Porto & Krishnan, 1967)
662	1LO in Fe ₂ O ₃	(Lopez et al., 2009; Marshall et al., 2020; Marshall & Olcott Marshall, 2013; Shim & Duffy, 2002)
826	-	-
926	polarised boroxol ring vibrations	(McCloy et al., 2015)
1048	-	-

1108	Fe ₂ O ₃ characteristic peak	(Marshall et al., 2020; Massey et al., 1990; Porto & Krishnan, 1967) (Lopez et al., 2009; Marshall et al., 2020; Marshall & Olcott Marshall, 2013; Shim & Duffy, 2002)
1323	2LO Fe ₂ O ₃	

Table 51 -Raman shifts and references attributions

4.3.5 Summary

- XRD confirmed the presence of Fe₂O₃ and NaCa(PO₄) in the HLW samples, were SEM/EDS identified Fe₂O₃ crystals in the P₂O₅ doped samples. The solubility limit of P₂O₅ lay between 0.625 and 1.25 mol% P₂O₅. There was a distinct lack of NaCa(PO₄) crystal morphologies present in the HLW1.25 sample. However, there was evidence of a droplet like morphology often associated with nucleation-type phase separation.
- The bulk density of the annealed samples ranged between 2.619-2.645 g/cm³, while the molar volume values ranged between 34.291-35.294 cm³/mol, where the density decreased linearly, and the molar volume increased linearly as the P₂O₅ content increased. The increase in the molar volume indicated that the structure may have been expanding to accommodate P₂O₅, which was seen affecting the CTE.
- The T_g onset for DTA ranged between 454.4-477.9 ±0.5°C and the dilatometric T_g ranged between 448-455 ±5°C. The T_d ranged between 496-506 ±5°C and the CTE ranged between 10.8874-11.6043 x 10⁻⁶ K. The DTA T_g values suggested that the glass network was de-polymerising between 0.00-0.625 mol% P₂O₅, but then re-polymerised at 1.25 mol% P₂O₅ upon the formation of NaCa(PO₄). The dilatometric T_g and T_d could be fitted with a horizontal line within error, suggesting increased P₂O₅ content had little effect on these parameters. The CTE increased linearly with increasing P₂O₅ content, implying that the free volume was reducing, and that the glass network was not de-polymerising.
- Raman spectroscopy of the annealed samples displayed broad peaks, where the 1.25 mol% doped sample displayed a peak characteristic of NaCa(PO₄) at ~952 cm⁻¹. There was a distinct lack of sharp characteristic peaks associated with hematite in these samples, but they may have been overlapped with other peaks. Fitting of the Qⁿ speciation region suggested

that between 0.00-0.625 mol% P_2O_5 the glass de-polymerised, whilst at 1.25 mol% P_2O_5 the glass re-polymerised.

- A combination of Mössbauer spectroscopy and Fe K-edge XANES confirmed that iron in the base glass was present as predominantly Fe_{Tet}^{3+} and Fe_{Oct}^{3+} with a marginal contribution of Fe_{Oct}^{2+} . Increased additions of P_2O_5 did see a change in the iron coordination where there was a decrease in Fe_{Tet}^{3+} and increase in Fe_{Oct}^{3+} , suggesting an increase in the modifier content of the glass resulting in its de-polymerisation.
- The CCC heat treated samples were identified to have both Fe_2O_3 and $NaAlSiO_4$ present, where visually the XRD pattern of the 1.25 mol% P_2O_5 doped sample evidenced an amorphous hump where the base glass did not. Literature has suggested that P_2O_5 may have an effect of suppressing the occurrence of nepheline due to the formation of Al-O-P linkages which promotes the formation of Si-O-Si over Al-O-Si.
- Raman spectra of the samples were very similar evidencing the presence of Fe_2O_3 . However, the 1.25 mol% P_2O_5 doped sample exhibited a sharp peak at $\sim 962\text{ cm}^{-1}$, which according to literature is attributed to boroxol ring vibrations. There was no evidence of the intense, sharp characteristic peaks associated with nepheline, however, the smaller peaks may have been overshadowed by the hematite peaks.

4.4 LAW Glass Series

4.4.1 Introduction

The glass system studied in this chapter is a simplified, alkali rich aluminoborosilicate-based glass system comprising oxides from the WTP-LAW and ORP-LAW compositions provided by PNNL. While this composition is a simplification of Hanford LAW compositions, it is still deemed a complex glass system to analyse because comprises 8-components based on SiO_2 - B_2O_3 - Fe_2O_3 - Al_2O_3 - Na_2O - CaO - Li_2O - $x\text{P}_2\text{O}_5$. The undoped base glass had a nominal composition of $20.02\text{Na}_2\text{O}$ - $4.93\text{Li}_2\text{O}$ - 12.72CaO - $1.69\text{Fe}_2\text{O}_3$ - $5.29\text{Al}_2\text{O}_3$ - $9.27\text{B}_2\text{O}_3$ - 46.09SiO_2 (mol%). The nominal composition of the main sodium borosilicate glass components in the undoped glass was $20.0\text{Na}_2\text{O}$ - $9.3\text{B}_2\text{O}_3$ - 46.1SiO_2 , which when plotted on the Na_2O - B_2O_3 - SiO_2 ternary phase diagram is not located in the immiscibility region. The study of this simplified glass system is important because P_2O_5 incorporation in nuclear borosilicate glasses has not been widely studied due to its low abundance in LAW waste. However, this study should aid in the better understanding of the potential effects of altering the P_2O_5 content and its potential subsequent effects on more complex nuclear waste compositions.

4.4.2 Experimental Procedures

The LAW glasses were based on the Na_2O - Li_2O - CaO - Fe_2O_3 - Al_2O_3 - B_2O_3 - SiO_2 - $x\text{P}_2\text{O}_5$, where $x = 0.00, 0.625, 1.25, 1.875, 1.94, 2.00, 2.25$, and 2.50 mol%. Batches of 130 grammes were prepared utilising the melt-anneal method using the precursors Na_2CO_3 , Li_2CO_3 , CaCO_3 , Fe_2O_3 , $2(\text{Al}(\text{OH})_3)$, H_3BO_3 , SiO_2 $\text{NH}_4\text{H}_2\text{PO}_4$. The precursors were weighed and transferred to a plastic bag before being milled for 10 seconds in a steel mill to thoroughly mix the contents. The batch was then placed in an alumina crucible and heated in an electric furnace at a rate of $5^\circ\text{C}/\text{min}$ to 1150°C , where it was left to dwell for 3 hours before the glass melt was poured into a steel mould and annealed at 500°C for 2 hours, before cooling at a rate of $1^\circ\text{C}/\text{min}$ to 25°C . The bulk samples were then analysed by Raman spectroscopy, prepped, and mounted in epoxy resin for SEM/EDS analysis, then milled into powders for XRD, XRF, ICP-OES, XANES, and chemical durability testing. Further details of experimental methodology can be read in *Chapter 3: Experimental Methodology*.

4.4.3 Results and Discussion

Note regarding nomenclature: in this chapter concentrations were described in either mol% or wt%. In these results and subsequent discussion, the concentrations will use the nomenclature 'LAW' where the following number represents the P_2O_5 content in mol% e.g., LAW1.25 = 1.25 mol% P_2O_5 . The 'LAW' initials are derived from the name used in PNNL reports, where LAW means 'Low-Level Activity Waste'.

4.4.3.1 Annealed LAW Samples

4.4.3.1.1 Visual observations

Visual observations of the LAW glass samples (Figure 106) showed that between LAW0.00-1.94 the samples took on a dark amber colour, however, the LAW1.94 sample started to present small white blotches on the surface of the sample. When the P_2O_5 content was increased to 2.00 mol% P_2O_5 the sample took on a darker hue of amber where the blotches were replaced by streaks of a creamy green colour upon the surface of the samples. The LAW2.50 sample showed obvious creamy white blotches on the surface of the sample. The blotches and streaks suggested that the samples have exceeded their P_2O_5 solubility limit, resulting in amorphous-crystalline phase separation. Figure 172 in Appendix 8.18 shows the top view images of the crucibles with remnants of the LAW glass melts, with associated comments to describe the pouring conditions.

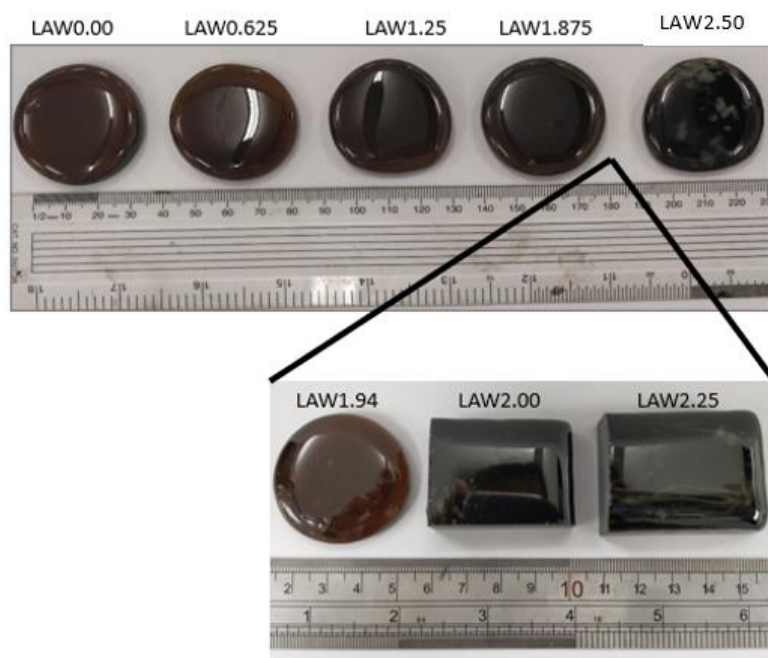


Figure 106 – Top view images of LAW samples (0.00-2.50 mol% P_2O_5)

4.4.3.1.2 XRF and ICP-OES Compositional Analysis

Table 52 and Figure 107 show the LAW samples analysed by both XRF and ICP-OES, where the LAW0.625, 1.875, and 2.50 samples were analysed at Sheffield Hallam University and the other samples were analysed at GTS, hence the difference in associated errors. Figure 107 visually showed that there were depleted levels of Li_2O when compared to the nominal composition. The low Li_2O content may have been due to the fact that it was added to the glass melt as lithium carbonate (Li_2CO_3), which has a low melting point ($722^\circ C$) (Merck, 2021) and is quite volatile (Lu et al., 2021), resulting in the loss of some of the Li_2O during melting. The other components in the glass are either slightly elevated or depleted when compared to the nominal composition, however, this may have been due to a number of reasons e.g., contaminations from the crucible material resulting in elevated Al_2O_3 , heat treatment of the glass, what part of the melt was poured and analysed to form the cooled glass i.e., the beginning, middle or end of the melt, and also any uncertainties associated with preparation and analysis by XRF and ICP-OES. ICP-OES analysis of B and Li was not conducted on the LAW2.50 sample because there was no more sample available at the time analysis was conducted.

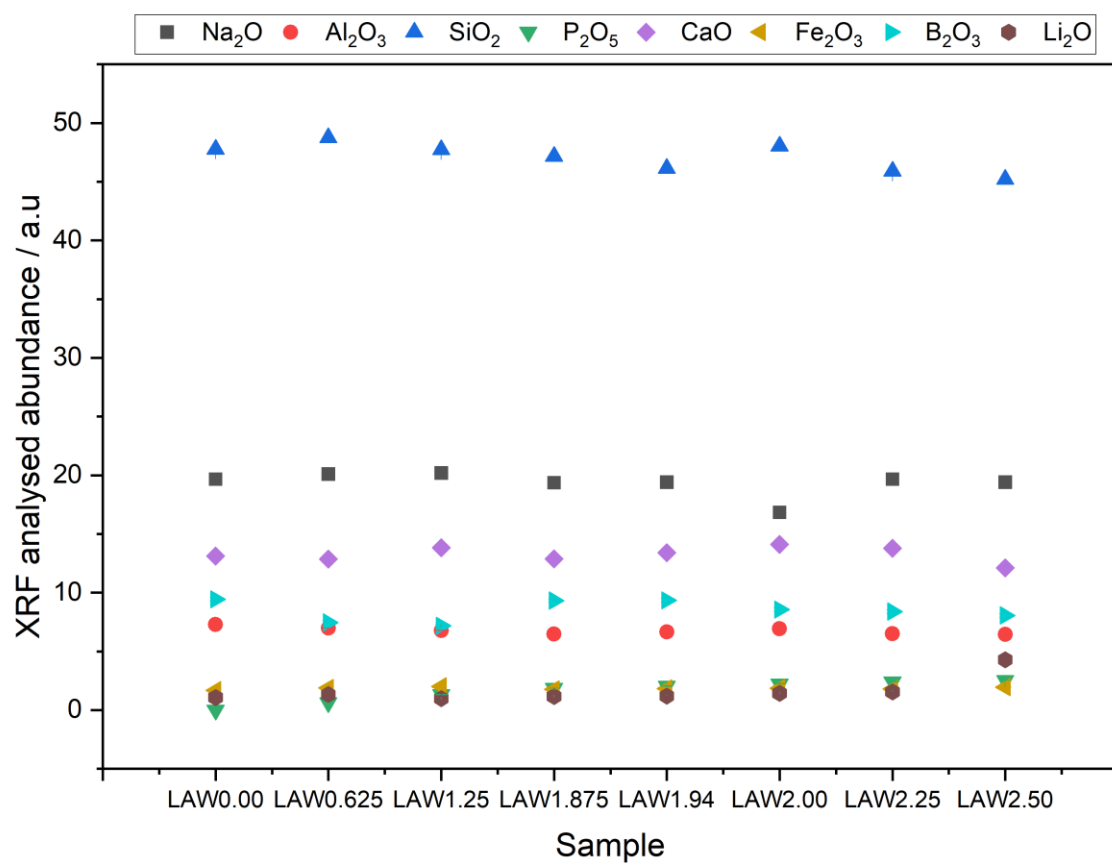


Figure 107 – XRF and ICP-OES analysed composition of LAW samples with associated error. Error bars that are not shown have errors that are too small to plot.

Table 52 – XRF and ICP pro-rat'd analysis of LAW samples

Sample		Normalised Oxide (mol%)							
		Na ₂ O	Al ₂ O ₃	SiO ₂	P ₂ O ₅	CaO	Fe ₂ O ₃	B ₂ O ₃ *	Li ₂ O*
LAW0	Nominal	20.02	5.29	46.09	0.00	12.72	1.69	9.27	4.93
	Analysed and	19.67 ±	7.27 ±	47.76 ±	0.00	13.11 ±	1.69 ±	9.43 ±	1.07 ±
	Pro-rat'd	0.01	0.01	0.01		0.00	0.00	0.15	0.15
LAW0.625	Nominal	19.89	5.25	45.81	0.625	12.64	1.68	9.21	4.9
	Analysed and	20.11 ±	6.98 ±	48.75 ±	0.64 ±	12.86±	1.88 ±	7.46 ±	1.32 ±
	Pro-rat'd (SHU)	0.00	0.00	0.00	0.00	0.00	0.00	0.15	0.15
LAW1.25	Nominal	19.77	5.22	45.52	1.25	12.56	1.67	9.16	4.86
	Analysed and	20.19 ±	6.77 ±	47.72 ±	1.31 ±	13.83 ±	2.02 ±	7.18 ±	0.98 ±
	Pro-rat'd	0.01	0.01	0.01	0.02	0.00	0.00	0.15	0.15
LAW1.875	Nominal	19.64	5.17	45.23	1.875	12.48	1.66	9.07	4.83
	Analysed and	19.37 ±	6.48 ±	47.16 ±	1.86 ±	12.87 ±	1.77 ±	9.33 ±	1.17 ±
	Pro-rat'd (SHU)	0.00	0.01	0.02	0.00	0.00	0.00	0.15	0.15
LAW1.94	Nominal	19.63	5.18	45.2	1.94	12.47	1.65	9.09	4.83
	Analysed and	19.41 ±	6.65 ±	46.13 ±	2.04 ±	13.39 ±	1.83 ±	9.35 ±	1.2 ± 0.15
	Pro-rat'd	0.01	0.01	0.01	0.02	0.00	0.00	0.15	
LAW2.00	Nominal	19.62	5.18	45.17	2.00	12.46	1.65	9.09	4.83
	Analysed and	16.83 ±	6.94 ±	48.02 ±	2.23 ±	14.12 ±	1.86 ±	8.56 ±	1.44 ±
	Pro-rat'd	0.01	0.01	0.01	0.02	0.00	0.00	0.15	0.15
LAW2.25	Nominal	19.57	5.17	45.06	2.25	12.43	1.65	9.06	4.82
	Analysed and	19.66 ±	6.52 ±	45.89 ±	2.40 ±	13.78 ±	1.81 ±	8.39 ±	1.55 ±
	Pro-rat'd	0.02	0.01	0.01	0.02	0.00	0.00	0.15	0.15

LAW2.50	Nominal	19.52	5.15	44.94	2.25	12.4	1.65	9.04	4.8
	Analysed and	19.41 ±	6.44 ±	45.22 ±	2.53 ±	12.10 ±	1.95 ±	8.06	4.28
	Pro-rat'd (SHU)	0.01	0.01	0.02	0.00	0.00	0.00		

Bold italics is for nominal composition, * is for ICP-OES analysis

4.4.3.1.3 X-ray Powder Diffraction

Figure 108 shows the XRD patterns for the LAW samples with varying P_2O_5 content. Between 0.00 to 1.875 mol% P_2O_5 the samples were X-ray amorphous, but at 1.94 mol% P_2O_5 there was a slight visible peak at $\sim 32^\circ 2\theta$. However, this peak was too weak to be associated with a particular crystal phase. As the P_2O_5 content continued to increase, the samples become progressively more crystalline, with the identifiable phase being sodium calcium phosphate (Figure 173 and Table 90 in Appendix 8.19) ($NaCa(PO_4)$, PDF#: 00-029-1193 (Morris et al., 1978)) at 2.00, 2.25, and 2.50 mol% P_2O_5 (Figure 109). This crystal phase has a density of 3.21 g/cm^3 (Olsen et al., 1977) with a solubility of $1 \times 10^3 \text{ mg/l}$ in H_2O at pH 7 (Jalota et al., 2007). The formation of the $NaCa(PO_4)$ crystal phase suggests that the P_2O_5 solubility limit lies between 1.875 and 1.94 mol% P_2O_5 . When Na and Ca are added to silicate glass systems with low concentrations of P, they generally favour the coordination of phosphates over silicates, leading to the removal of both cations from the silicate network (Tilocca & Cormack, 2007). However, at higher P_2O_5 concentrations, Ca^{2+} has a stronger affinity than Na^+ for phosphates, which leads to the clustering of calcium phosphate-rich regions (Tilocca & Cormack, 2007). This glass-in-glass separation is the pre-requisite for crystallisation (Tilocca & Cormack, 2007). The removal of the Na^+ and Ca^{2+} ions from the glass network to charge compensate the PO_4^{3-} in $NaCa(PO_4)$, leads to the increase in $B\ddot{O}$ s and the subsequent re-polymerisation of the glass network. The formation of this crystal phase may affect the chemical durability of the glass, where removal of Ca and Na cations may affect the mechanisms of glass alteration. It is not known whether the Na^+ and Ca^{2+} ions are taken from the B or Si sub-networks to charge compensate the P and would need to be established using structural techniques e.g., P K- and L_{II, III}-edge XANES.

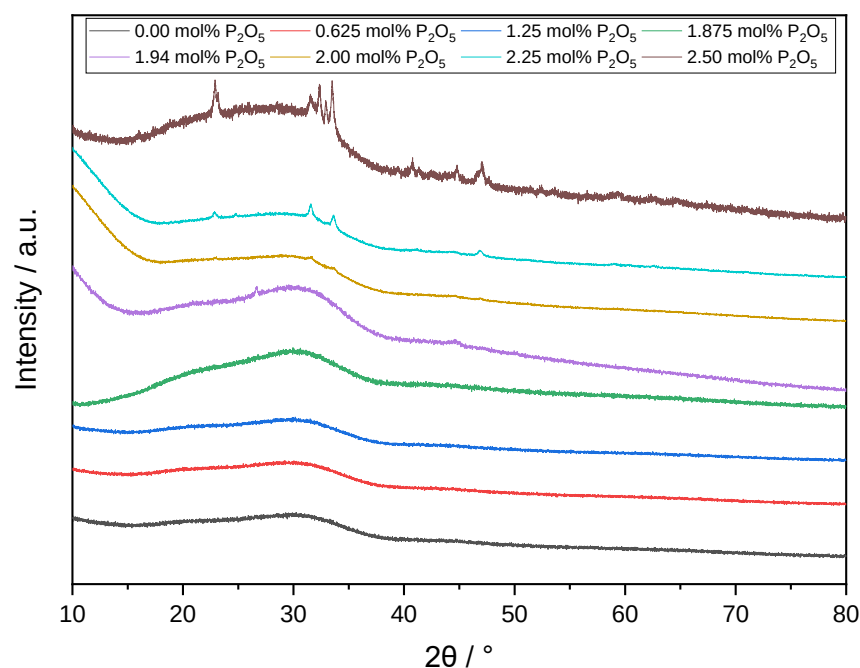


Figure 108 - XRD patterns for LAW glasses

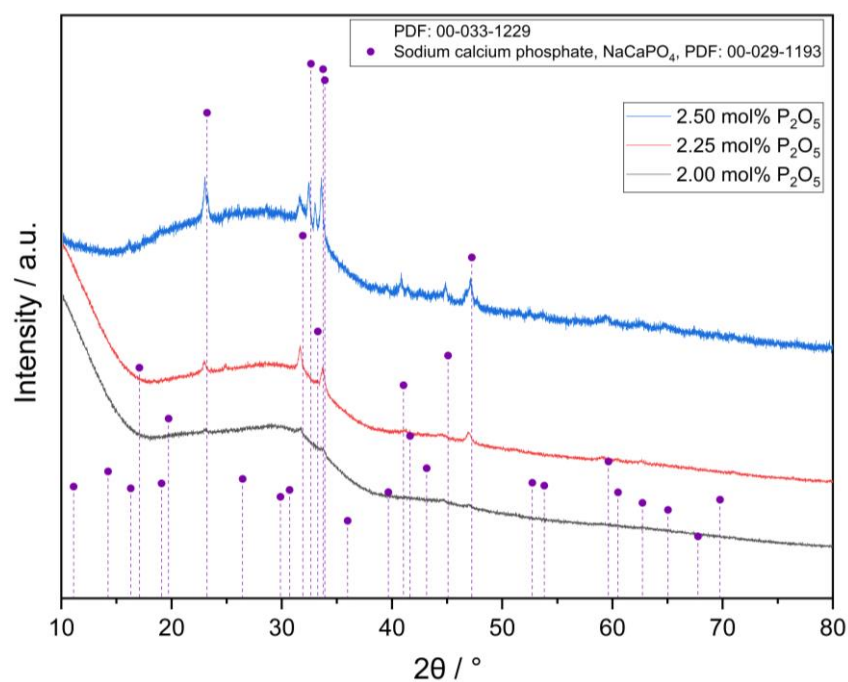


Figure 109 - XRD patterns with identified crystal phases for glasses with 2.00, 2.25, and 2.50 mol% P_2O_5

4.4.3.1.4 DTA

The DTA traces of the LAW samples are presented in Figure 110, where the measured and calculated thermal parameters are recorded in Table 53. As the P_2O_5 content increased, the T_g onset, T_g midpoint, T_c , and T_m all exhibited non-linear behaviour. The T_g onset ranged between 473-482°C, where its value

decreased upon the initial addition of 0.625 mol% P_2O_5 , before increasing at 1.25 mol% P_2O_5 , followed by a decrease again at 1.875 mol% P_2O_5 , then an increase at 1.94 mol% P_2O_5 , before decreasing again at 2.00 mol% P_2O_5 . The T_g midpoint ranged between $479-491 \pm 2^\circ\text{C}$, where its values followed a similar behavioural trend to the T_g onset. The increase and decrease in T_g shows the dual effect of P_2O_5 which has been observed by other researchers e.g., Cheng (2014). T_x ranged between $553-645 \pm 2^\circ\text{C}$ where the initial value increased between 0.00-1.25 mol% P_2O_5 before decreasing until 1.94 mol% P_2O_5 , after which it increased until 2.25 mol% P_2O_5 . T_c followed a similar behaviour to T_x and ranged between $580-693 \pm 2^\circ\text{C}$, however, instead of the value increasing between 1.94 and 2.25 mol% P_2O_5 , it decreased. T_m ranged between $709-860 \pm 2^\circ\text{C}$, where the initial value increased upon the addition of 0.625 mol% P_2O_5 , then continued to decrease until 1.875 mol% P_2O_5 , followed by a sharp decrease at 1.94 mol% P_2O_5 , this was then followed by an increase at 2.00 mol% P_2O_5 which continued when 2.25 mol% P_2O_5 mol% was added to the glass system. The glass formability parameters, T_{rg} ranged between 0.55-0.68 a.u., K_H ranged between 0.32-0.91 a.u., and K_W ranged between 0.12-0.24 a.u.

Similarly to the HLW glass system investigated in chapter 4.3, the LAW glass system is a multi-oxide glass, susceptible to the effects of the mixed glass former (MGF) and mixed alkali effect (MAE), which in turn effects the physical, thermal, and chemical properties non-linearly (Hyun et al., 2022). The sheer complexity of the glass system makes it difficult to establish and correlate the effects of a single component in the glass based on its role in the glass system, especially if it is a glass intermediate where it can act as a glass former and/or modifier, e.g., Al^{3+} and Fe^{3+} . An example of the effects of Al_2O_3 acting as either a glass former or modifier is described in chapter 4.3 (HLW). However, obvious variations will try to be linked to changes in the P_2O_5 content and overall crystallisation behaviour.

The decrease in the T_g may be due to the replacement of Si-O-Al linkages for low-strength B-O-P and Al-O-P linkages, and formation of de-polymerised PO_4^{3-} and $P_2O_7^{4-}$ units (Lu et al., 2021). The increase in T_g at 1.94 mol% P_2O_5 may be due to the formation of $NaCa(PO_4)$ crystals, where Na^+ and Ca^{2+} are removed from the glassy network to charge compensate P units, resulting in a reduction in NBØs and subsequently the re-polymerisation of the glassy network (Cheng, 2004). Achigar et al. (2021) had studied a similar glass system to the one in this

study ($\text{SiO}_2\text{-B}_2\text{O}_3\text{-Al}_2\text{O}_3\text{-Fe}_2\text{O}_3\text{-Na}_2\text{O-Li}_2\text{O-CaO-xP}_2\text{O}_5$) where they reported that increasing P_2O_5 from 0.0 to 4.7 mol% significantly increased the T_g . They linked this to previous literature where they reported that in borosilicate glass systems, the change in T_g had been due to the high $\text{Na}_2\text{O/B}_2\text{O}_3$ ratio >1 where the removal of alkali or alkaline earth ions are used to charge compensate PO_4^{3-} and $\text{P}_2\text{O}_7^{4-}$ units when P_2O_5 is added to the glass, re-polymerising the glass network (Achigar et al., 2021). O'Donnell et al. (2008) reported that when increasing additions of P_2O_5 were added to a bioactive glass, the T_g did not increase as expected, but instead decreased, contradicting the theory. They also commented that P additions need to be charge compensated by modifier cations e.g., Ca and Na, which are taken from the silicate network, resulting in its re-polymerisation.

The T_{rg} values ranged between 0.55-0.68 a.u., where increases in P_2O_5 content saw this value increase and decrease non-linearly. The values suggested that all the LAW samples except LAW1.94 and 2.00 exhibited homogenous nucleation with a resistance to crystallisation (Zanotto, 1987). LAW2.25 had the lowest value of 0.58 a.u., even though it exhibited crystallisation, where the value produced may have been for the amorphous part of the material. The K_H parameter is dependent on the composition of the glass where variations in the K_H value are due to variations in the glass's thermal properties (Kozmidis-Petrovic & Šesták, 2012). A glass system with $K_H \geq 0.4$ displays good thermal stability (Farid et al., 2016), and therefore, LAW0.00-1.94 exhibited good thermal stability. However, LAW2.00 and 2.25 did not, where they had values of 0.35 a.u. and 0.32 a.u., respectively. The K_W parameter ranges stayed the same between 0.00-1.25 mol% P_2O_5 with a value of 0.25, but then continued to decrease upon further additions of P_2O_5 between 1.875-2.25 mol% P_2O_5 . The reduction in the K_W parameter at >1.875 mol% P_2O_5 coincides with evidence of crystallinity, as shown by XRD patterns (Figure 108). Therefore, the LAW0.00-1.25 samples are the most thermally stable, according to the K_W parameter (Ravagli et al., 2017).

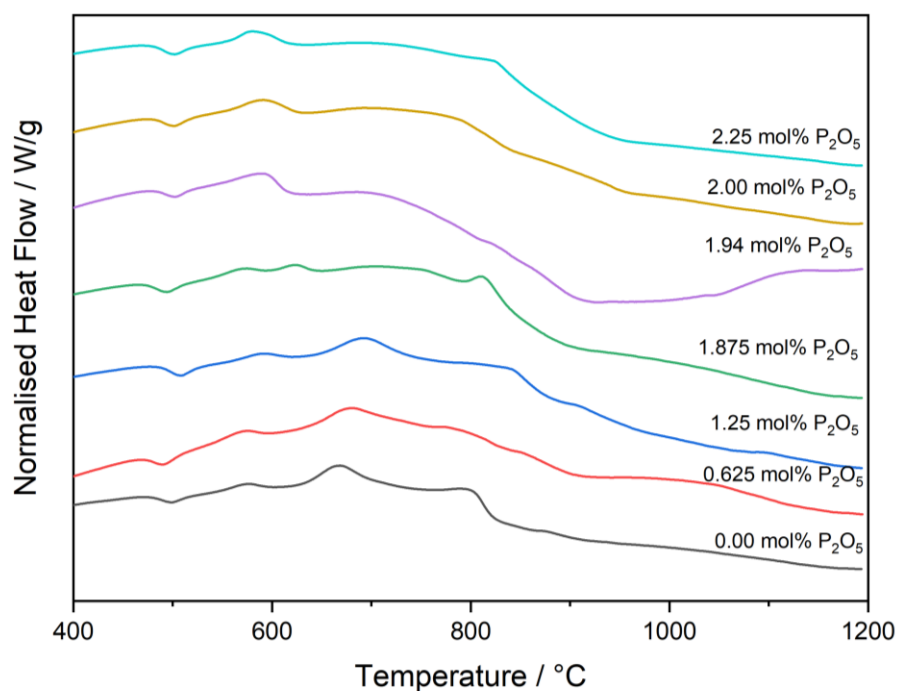


Figure 110 - DTA traces of LAW samples

Sample	T _g onset ±2 (°C)	T _g midpoint ±2 (°C)	T _x ±2 (°C)	T _c ±2 (°C)	T _m ±2 (°C)	T _{rg}	K _H	K _W
0.00	478	487	631	668	799	0.60	0.91	0.24
0.625	472	479	645	679	860	0.55	0.80	0.24
1.25	488	491	653	693	843	0.58	0.87	0.24
1.875	473	479	606	624	812	0.58	0.65	0.19
1.94	482	485	553	591	709	0.68	0.46	0.15
2.00	479	481	560	591	789	0.61	0.35	0.14
2.25	479	483	563	580	825	0.58	0.32	0.12

Table 53 - DTA thermal parameters for LAW samples

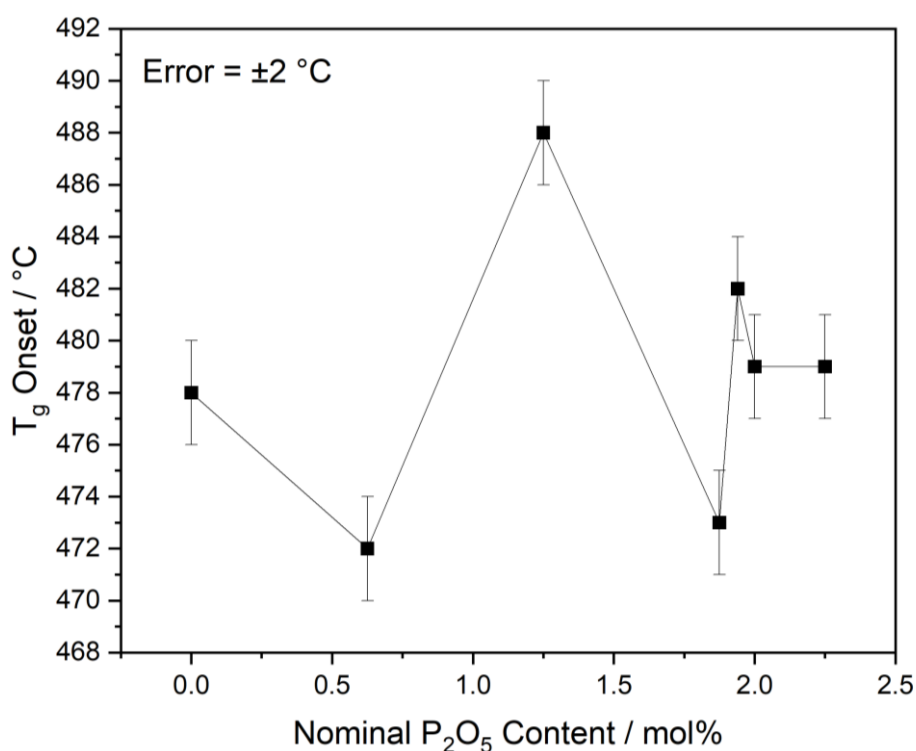


Figure 111 - DTA T_g onset of LAW samples (0.00-2.25 mol% P₂O₅)

4.4.3.1.5 Bulk Density, Molar Volume and Thermal Parameters acquired by Dilatometry

From evaluating Table 54, the value of the bulk density ranged between 2.616 ± 0.003 to 2.630 ± 0.025 g/cm³, where the density of the P₂O₅-free glass had a higher density than the majority of the subsequent glasses with nominally the same content for the composition. The density varied, increasing, and decreasing with the gradual increase in P₂O₅ in the glass composition. The molar volume (V_{mol}) increased linearly within error with increasing P₂O₅ content. As P₂O₅ was introduced as a network former to the glass system, BØs appeared to form because Na, Ca, and Li were likely being removed from the glass network to charge compensate the P. Additionally, as P₂O₅ was added, ^[4]B tetrahedral transforms to ^[3]B trigonal units, pentaborate linkages (P-O-B) were created, and NBØs were formed (Klyuev, 2005). This increase in NBØs may decrease the volume of the network structure and may be the reason for the increase in the density at 2.00 and 2.25 mol% P₂O₅ (Chanshetti et al., 2011). Additionally, density increase could be explained by the re-organisation of the ions into more closely packed arrangements, causing structural changes that resulted in the formation of the crystal phases (Sułowska et al., 2021). The decrease in the density with

the introduction of P₂O₅ suggests the glass structure may be more open and less compact, which is beneficial for increased cation mobility (Sułowska et al., 2021).

Sample	Average Bulk Density (g/cm ³)	STDEV, σ	V _m (cm ³ /mol)	T _g Onset $\pm 5^{\circ}\text{C}$	T _g midpoint $\pm 5^{\circ}\text{C}$	T _d $\pm 5^{\circ}\text{C}$	CTE $\pm 2 \times 10^{-7}$ (K ⁻¹)
LAW0.00	2.630	0.001	33.34	446	474	492	13.1825 x 10 ⁻⁶
LAW0.625	2.627	0.001	33.68	446	470	492	13.0916 x 10 ⁻⁶
LAW1.25	2.621	0.002	34.13	465	486	508	12.5260 x 10 ⁻⁶
LAW1.875	2.630	0.025	34.36	453	472	495	13.3395 x 10 ⁻⁶
LAW1.94	2.626	0.003	34.61	461	469	506	12.9005 x 10 ⁻⁶
LAW2.00	2.616	0.003	34.65	463	494	508	13.2481 x 10 ⁻⁶
LAW2.25	2.623	0.006	34.70	458	482	500	13.4852 x 10 ⁻⁶
LAW2.50	2.630	0.001	33.34	446	474	492	13.7859 x 10 ⁻⁶

Table 54 - LAW bulk density, molar volume, and thermal parameters acquired by dilatometry

Figure 112 depicts the thermal parameters produced by dilatometry as reported in Table 54. The T_g onset is the same within error between 0.00 and 0.625 mol% P₂O₅, but then increased at 1.25 mol% P₂O₅ from 446-465 $\pm 5^{\circ}\text{C}$. Subsequently, T_g decreased at 1.875 mol% P₂O₅ to 453°C, before increasing within error until 2.00 mol% P₂O₅, then decreasing again within error down to 446°C. The T_g midpoint and T_d displayed a similar graphical trend to the T_g onset. The increase in the T_g onset suggested that there was a decrease in the NBØs in the glass network resulting in its re-polymerisation, whilst the decrease indicated that the glass network was instead becoming de-polymerised due to the increase in NBØs. The increase in NBØs and subsequent decrease in the T_g was mirrored in the density, where the value increased at 2.25 and 2.50 mol% P₂O₅. The increasing and decreasing behaviour exhibited by the T_g displayed the dual effect that P₂O₅ can have on borosilicate glass systems, even one as complex as this. The CTE graph showed that as the P₂O₅ content increased the CTE increased, where the highest CTE value corresponded to the lowest T_g onset value,

suggesting there was an increase in asymmetrical units in the glass structure, suggesting the network is de-polymerising, meaning there should be an increase in NBØs in the glass structure (Klyuev, 2005). CTE can also be affected by changes in the free volume, where a high free volume value suggests that bonds are able to rotate and flex instead of stretch with increasing temperature, resulting in a low CTE value (Shelby, 2005). Filling the free volume eliminates this mechanism, which in turn increases the CTE (Shelby, 2005). Hence, the occurrence of NaCa(PO₄) at higher P₂O₅ contents may be affecting the glass structure, which in turn affects the physical and thermal properties of the glass, where re-polymerisation is caused by the decrease in NBØs by the removal of network modifiers used as charge compensators for P. The re-polymerisation of the glass network results in the increase in density, reduction in the V_{mol} , and increase in the CTE. It should be noted that whilst there was evidence of a phosphate rich crystalline phase in LAW2.00-2.50, the dilatometric traces did not show any evidence of two T_g 's, which would be indicative of phase separation.

Achigar et al. (2021) reported on the incorporation of P₂O₅, MoO₃, and ZrO₂ in an alkali rich glass matrix belonging to the SiO₂-B₂O₃-Al₂O₃-Fe₂O₃-Na₂O-Li₂O-CaO glass system. Increasing P₂O₅ content from 0.0 to 4.7 mol% led to an increase of 13°C and 39°C in T_g , respectively, for the compositions of series S10 and S20. Series S10 and S20 comprised of SiO₂-B₂O₃-Na₂O-CaO-Li₂O-Al₂O₃-Fe₂O₃-ZrO₂-P₂O₅-MoO₃-Cs₂O with additions of 10 wt% and 20 wt% waste, respectively. The increase in the T_g can be explained by the withdrawal of alkali and alkaline earth cations from the glassy network to charge compensate the isolated PO₄³⁻ and P₂O₇²⁻ units, which resulted in the network becoming more polymerised. The incorporation of P₂O₅ saw the crystallisation of NaCa(PO₄), NaLi₂(PO₄), and Li₃(PO₄) phases, where the P was present as non-connected PO₄³⁻ units. The absence of Na₃PO₄ suggested that the Ca, Li, Na, and P separate the glassy network, and can be explained by the following: (i) in alkali and alkaline earth silicate glasses, P is incorporated into the glass structure as isolated orthophosphate units surrounded by alkali and alkaline earth cations to charge compensate it in de-polymerised regions. (ii) Li⁺ and Ca²⁺ cations have higher field strengths compared to Na⁺ and have a higher tendency to separate from the silicate network, leading to separation or crystallisation. (iii) In borosilicate glasses Na⁺ ions preferentially react with B atoms to charge compensate the BO₄⁻ units compared to Li⁺ and Ca²⁺ cations. Hence, these considerations suggest that Ca

and Li have a higher affinity than Na for joining phosphate species in depolymerised regions, eventually forming crystalline phases. At higher Na₂O content, a fraction of the Na⁺ ions mix with the Ca²⁺ and Li⁺ ions with orthophosphate units, eventually forming NaCa(PO₄) and NaLi₂(PO₄) crystals.

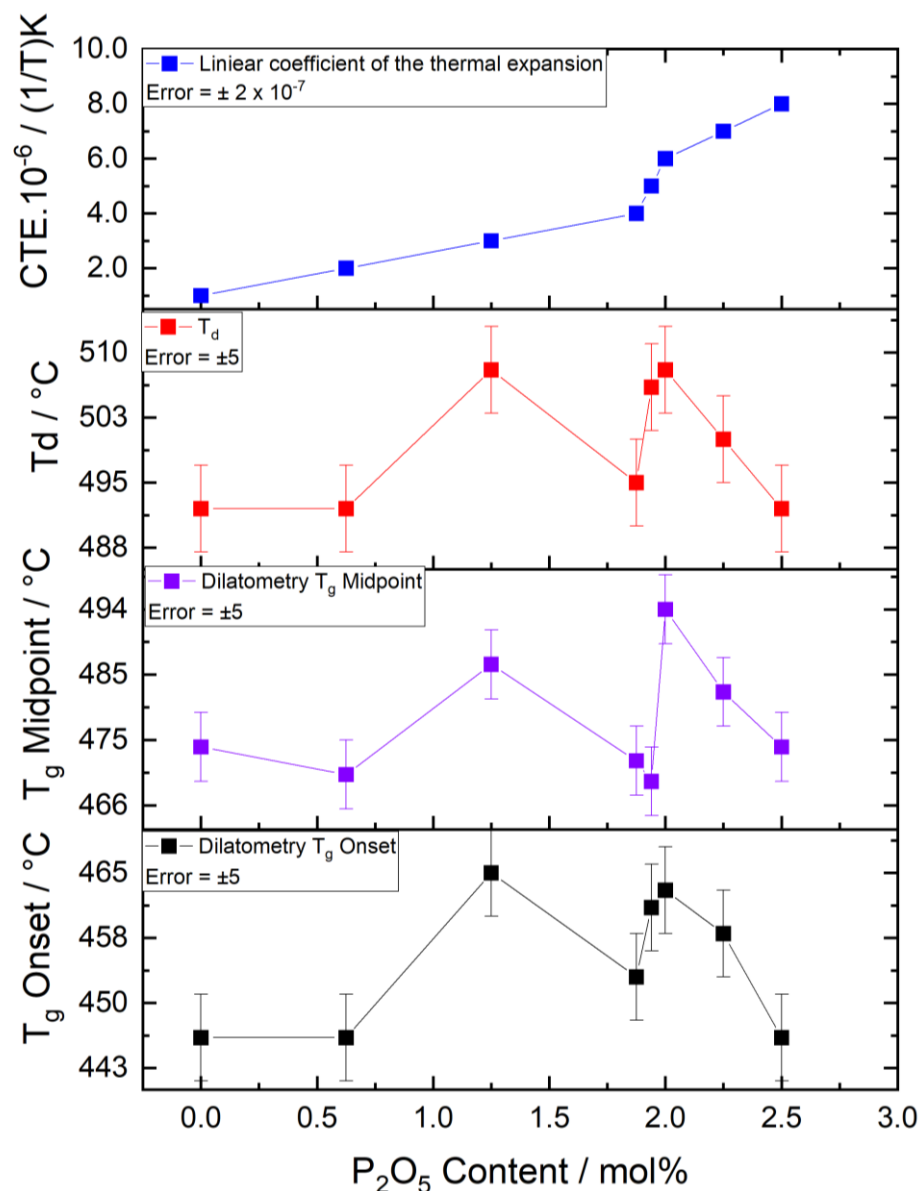


Figure 112 - Graphical representation of thermal parameters for the LAW samples

4.4.3.1.6 Raman Spectroscopy

Figure 113 shows the Raman spectra of the LAW samples. The base glass exhibited low intensity peaks at ~498, 574, and 630 cm⁻¹, an intense region between 800-1200 cm⁻¹ with peaks identified at 966 and 1042 cm⁻¹, and a broader low intensity region between 1200-1500 cm⁻¹, with a peak identified at ~1427 cm⁻¹.

¹. When increasing amounts of P₂O₅ were added to the glass system a prominent peak began to form at 966 cm⁻¹, where its intensity increased, and its position shifted to a lower wavelength of ~951 cm⁻¹. Accompanying this peak was the change in intensity of the peak located at ~1032 cm⁻¹, where it decreased in intensity between 0.625-1.875 mol% P₂O₅, then increased at 1.94 and 2.00 mol% P₂O₅, before decreasing again at 2.25 and 2.50 mol% P₂O₅. The peak located at ~498 cm⁻¹ decreased at 0.625 mol% P₂O₅, increased at 1.25 mol% P₂O₅, decreased again at 1.875 mol% P₂O₅, before increasing again at 1.94 mol% P₂O₅, before continuing to decrease at between 2.00-2.50 mol% P₂O₅. The low intensity region between 1200-1500 cm⁻¹ with a maximum peak at ~1427 cm⁻¹ decreased in its relative intensity between 0.625-1.875 mol% P₂O₅, before increasing at 1.94 mol% P₂O₅, then decreasing again at 2.00-2.50 mol% P₂O₅.

The peaks at ~498, 574, and 630 cm⁻¹ are located in the low intensity region of the spectra (300-800 cm⁻¹), where intensities at 498 and 574 cm⁻¹ can be attributed to symmetrical stretching and partial deformation vibrations of Si-O-Si bridges (Koroleva et al., 2011; McKeown et al., 2000). The intensity at ~630 cm⁻¹ can be attributed to the breathing mode of B-O-Si(B) bonds from reedmergnerite- and danburite-like rings that consist of [SiO₂] and [BO₄] tetrahedra in a mixed borosilicate phase or the bending of ring-type metaborate groups, composed mainly from B triangles (Hayward, 1993; Wang & Cheng, 2016; Yadav & Singh, 2015). The peaks at ~966, 1032 and 1042 cm⁻¹ are in the mid-frequency region associated with Qⁿ speciation (800-1200 cm⁻¹). The peak at 966 cm⁻¹ is the main characteristic peak associated with NaCa(PO₄) (buchwaldite), as identified by XRD and SEM/EDS mapping (Bersani et al., 2021; Comesaña et al., 2015; Čukanov & Vígassina, 2020). Figure 114 shows the Raman spectra for the 'white' splotches identified on the surface of LAW1.94, 2.00, and 2.25 (there was not enough sample for LAW2.50 at the time). They all exhibited the strong characteristic peak at 966 cm⁻¹, as well as peaks at ~584 and 1021 cm⁻¹ associated with NaCa(PO₄). Comesaña et al. (2015) identified other characteristic peaks for β- NaCa(PO₄), where there were peaks at 218 and 247 cm⁻¹ which were attributed to the Ca-PO₄ lattice; 428 and 450 cm⁻¹ which were attributed to V₂ PO₄; 567, 586, and 598 cm⁻¹ which were attributed to V₄ PO₄; 966 cm⁻¹ which was attributed to V₁ PO₄; and 1013, 1024, and 1046 cm⁻¹ which were attributed to V₃ PO₄. The peak at 1042 cm⁻¹ can be attributed to the stretching of Q³ units, however, it cannot be determined by which species, as this glass system

contains not only silicates but P, Al, and Fe species that can contribute to the Q^n speciation region. The intensity at 1427 cm^{-1} is located in the high frequency region which contains contributions from B-O stretching vibrations linked to $^{[3]}\text{B}$ units (Möncke et al., 2015a), where deconvolution of the peaks, according to literature, provides Gaussian components at $\sim 1320\text{ cm}^{-1}$ for loose $^{[3]}\text{B}$ units, 1410 cm^{-1} for $^{[3]}\text{B}$ units linked to $^{[4]}\text{B}$ units, 1480 cm^{-1} for $^{[3]}\text{B}$ units linked to $^{[3]}\text{B}$ units, and 1515 cm^{-1} for $^{[3]}\text{B}$ units linked to boroxol rings (Bisbrouck et al., 2021; Möncke et al., 2015a; Seshadri et al., 2020b). Therefore, the intensity at 1427 cm^{-1} could be attributed to $^{[3]}\text{B}$ units linked to $^{[4]}\text{B}$ units. The overall effect of adding and increasing the amount of P_2O_5 leads to an increase in the Q_p^0 units, decrease in the Q^3 units, and varying quantity of $^{[3]}\text{B}$ and $^{[4]}\text{B}$ units based on the changes in the relative intensity of the low and high frequency regions. The presence of $\text{NaCa}(\text{PO}_4)$ indicates that there has been the removal of network modifiers from the silicate and borate sub-networks to act as charge compensators for the P, however, it cannot be determined which network these have been taken from. The removal of network modifiers results in the re-polymerisation of the glass network, where there is a reduction in NBO_3 s, and the conversion of BO_4 units to BO_3 units (Ghanem & Mohamed, 2021). Table 55 lists the main Raman shifts identified and their associations based on literature.

Cheng (2014) investigated the effects of P_2O_5 in aluminoborosilicate glasses on the structure, where glasses were prepared in the compositional range $x\text{P}_2\text{O}_5\text{-}y\text{Al}_2\text{O}_3\text{-(}100\text{-}x\text{-}y\text{)(Na}_2\text{O. B}_2\text{O}_3\text{. SiO}_2\text{)}$, where $y = 0, 3, 6, 12$. The Raman spectra of the Al_2O_3 -bearing, phosphate-free glass (NBS- $y\text{Al}$, $y = 0, 6, 12$) exhibited a band at 630 cm^{-1} that decreased with increasing Al_2O_3 content, where it disappeared from the spectrum of the NBS-12Al sample. The 630 cm^{-1} band was assigned to $^{[4]}\text{B}$ tetrahedra bonded to silicate species, similar to the danburite ($\text{CaB}_2\text{Si}_2\text{O}_8$) structure where Si_2O_7 and B_2O_7 pairs are interconnected in four-membered rings. This assignment was further supported by the ^{11}B resonance at -0.8 ppm , which was in agreement with what had been reported for $^{[4]}\text{B}$ sites in danburite. The Raman spectra of the P_2O_5 doped samples, NBS-3Al- $x\text{P}$ ($x = 0, 1, 1.5, 3, 3.5$, where the NBS-6Al-1.5P and -6P samples presented a band at 980 cm^{-1} , which was attributed to the PO_4^{3-} units.

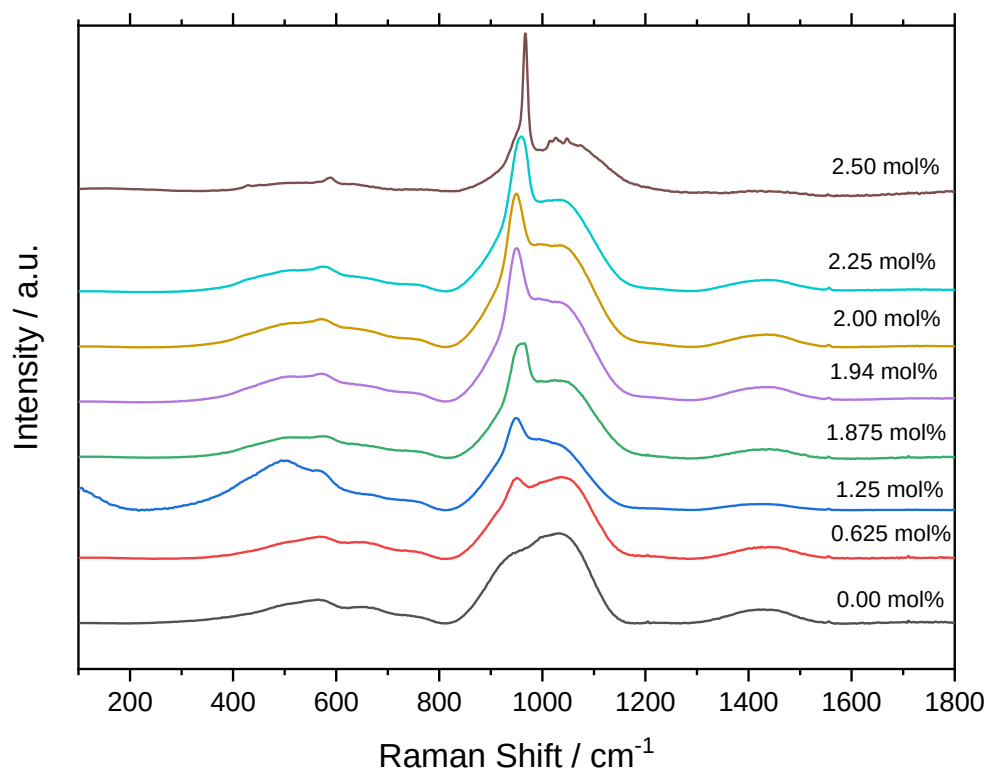


Figure 113 - Raman spectra of LAW samples

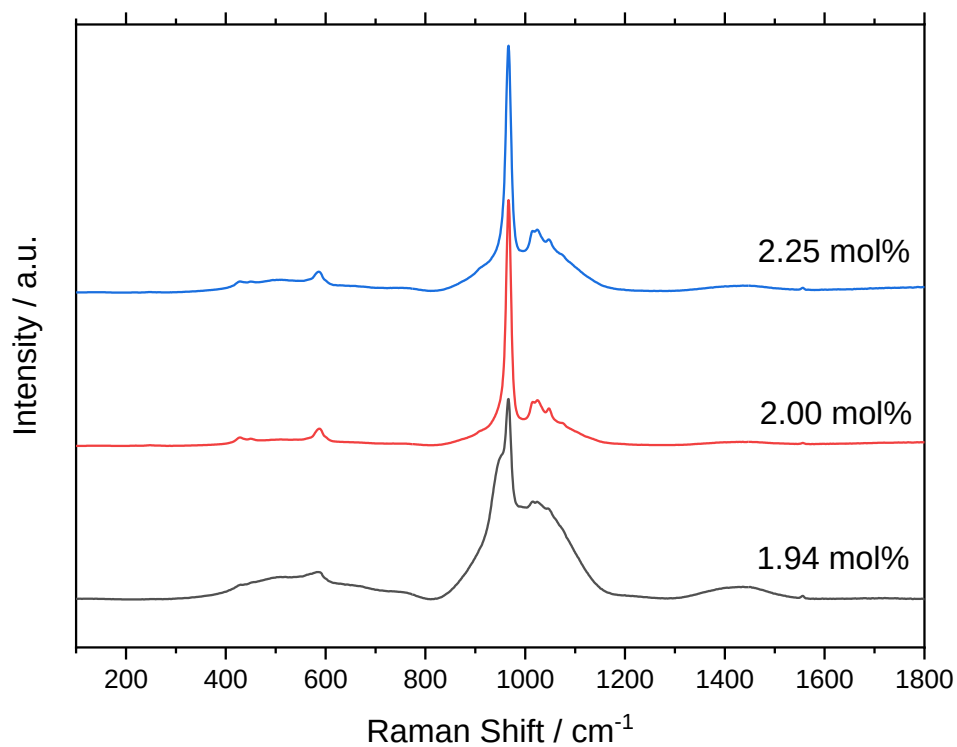


Figure 114 - Raman spectra of crystallised 'white splotches' on the surface
LAW1.94, 2.00 and 2.25 samples

Raman Shift (cm ⁻¹)	Attribution	Reference
498	Reedmergnerite [Bsi ₃ O ₈] ⁻ and danburite [B ₂ Si ₂ O ₈] ²⁻	(Yadav & Singh, 2015)
574-630	Ring breathing modes	(Yadav & Singh, 2015)
	Reedmergnerite [Bsi ₃ O ₈] ⁻ and danburite [B ₂ Si ₂ O ₈] ²⁻	(Yadav & Singh, 2015)
951/966	Si-O stretching in structural units with two NBØs per silicon or other Q ² units	(Brentrup et al., 2009a, 2009b; Solonenko et al., 2017a, 2017b)
	Orthoborate groups	(Yadav & Singh, 2015)
	Stretching vibrations of Si-O bond due to the presence of BO ₄ units	(Yadav & Singh, 2015)
	B-O-Si stretching vibration in alumino-borosilicate glass	(Yadav & Singh, 2015)
	V ₁ PO ₄	(Comesaña et al., 2015)
1042	stretching of Q ³ units	(Brentrup et al., 2009a, 2009b; Solonenko et al., 2017a, 2017b)
1427	B-O ⁻ stretching in metaborate rings and chains	(Yadav & Singh, 2015)

Table 55 – Key Raman intensities with association according to literature

4.4.3.1.6.1 Fitting the Qⁿ Speciation Region

Fitting of the LAW Raman spectra using Gaussian line shapes implemented through the OriginPro software package, has allowed the qualitative and semi-quantitative analysis of the Qⁿ speciation in the samples (Figure 175 and Figure 176 in Appendix 8.21 and 8.22). This approach does not take into account the area overlaps, meaning that the values produced for each Qⁿ speciation is subject to error. It should be noted that future work should implement other structural techniques for the accurate analysis of the Qⁿ speciation in these glasses. Figure 116 shows a graphical representation of the polymerisation behaviour of the glass network as a function of the P₂O₅ content, where the decrease in the ratio suggests the de-polymerisation of the network and increase in the ratio suggests re-polymerisation (Manara et al., 2009).

From evaluating Table 56 and Figure 115, the base glass contained a mixture of Q¹, Q², Q³, and Q⁴ species, where additions of 0.625 and 1.25 mol% P₂O₅ saw the percentage of these units fluctuate. Upon the addition of 1.875 and 1.94 mol% P₂O₅, the level of Q¹, Q², Q³, and Q⁴ species were similar, where Q¹ ranged between 8.9-13.5%, Q² between 12.6-15.2%, Q³ between 37.3-38.1%, and Q⁴ between 34.0-40.4%. However, when 2.00 mol% P₂O₅ was added the level of Q⁴ species increased from 40.4% to 47.4% at the expense of the Q¹, Q² and Q³ species, suggesting that the glass network was re-polymerising. This idea that the glass network is re-polymerising is further supported by the presence of NaCaPO₄ which removes one mole each of Na⁺ and Ca²⁺ cations from the glass network to charge compensate the P₂O₅. Upon additions of 2.25 mol% P₂O₅, the amount of Q³ species increased instead to 49.2%, at the expense of the Q¹, Q², and Q⁴ species. At 2.50 mol% P₂O₅, there was no longer the presence of Q¹ units and the presence of Q² and Q³ units had values of 11.3 and 9.5%, respectively, whilst the Q⁴ unit had a value of 79.2%. This increase and decrease in Q³ and Q⁴ units demonstrated that further additions of P₂O₅ has re-polymerised the glass network, which is further supported by Figure 116.

Nominal P ₂ O ₅ content (mol%)	Q ¹ (%)	RE	Q ² (%)	RE	Q ³ (%)	RE	Q ⁴ (%)	RE
0.00	3.5	2.22	22.4	1.96	52.7	1.82	21.4	2.21
0.625	11.6	0.09	8.2	0.84	46.1	11.49	34.1	1.07
1.25	12.6	1.61	12.7	1.06	50.6	1.56	24.2	1.82
1.875	13.5	1.44	15.2	0.60	37.3	1.87	34.0	1.71
1.94	8.9	1.29	12.6	0.51	38.1	0.99	40.4	0.72
2.00	8.3	1.64	10.8	0.55	33.5	1.11	47.4	0.61
2.25	16.3	2.22	17.5	0.41	49.2	1.43	17.0	1.09
2.50	0.0	0.00	11.3	0.26	9.5	0.19	79.2	0.13

Table 56 – Calculated relative Q_n speciation percentage abundancies with relative error (RE)

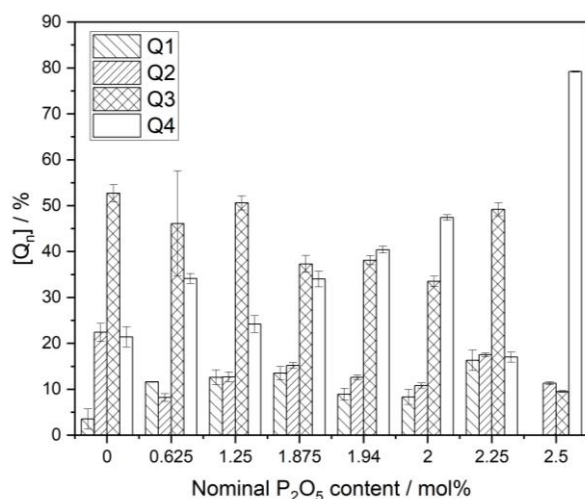


Figure 115 – Graphical representation of relative abundances of Qⁿ species in LAW samples

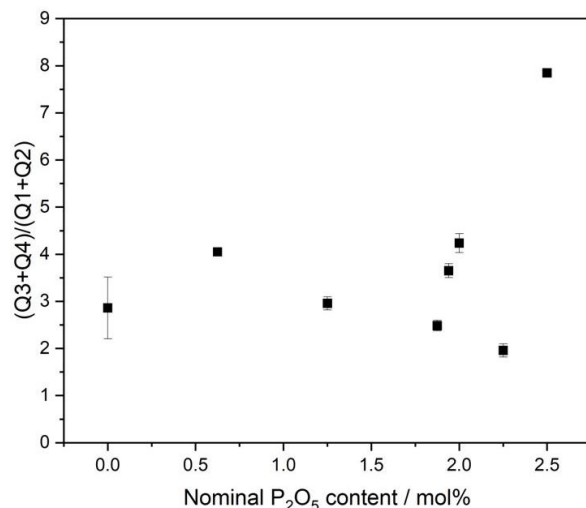


Figure 116 – Ratio (Q3 + Q4) / (Q1 + Q2) with relative error, which is indicative of the silicate sub-network polymerisation

4.4.3.1.7 Fe K-edge XANES

Due to limitations in the number of samples allowed to be ran by XAS, only four samples were selected i.e., the base glass with no P₂O₅, and at the time, where the solubility limit may have been in the absence of the LAW1.94 sample, and samples that exceeded said solubility limit i.e., LAW1.875, 2.00, and 2.25.

XANES spectra were corrected and normalised using the ATHENA work package (Ravel & Newville, 2005). Figure 117 shows the Fe K-edge XNAES data for the LAW0.00, 1.875, 2.00 and 2.25 glass samples. The Fe oxidation state was estimated from the energy of the absorption edge (E_0) and interpolating between the energies measured for a set of reference samples. The intensity and position of the pre-edge region provides information on the Fe oxidation state and coordination environment, where the area under the pre-edge is dependent on the site symmetry (Joseph et al., 2017). The fitting of the pre-edge feature and reference compounds were performed in the energy range 7107-7120 eV, in accordance to the methodology proposed by Wilke et al. (2001). Gaussian components were fitted to the pre-edge feature using a least squares minimalization routine in Excel, where the total area under the pre-edge feature was obtained from the summing of the integrated intensity under each pre-edge feature (Table 57) (Joseph et al., 2017). These values were then plotted in a variogram (Figure 118) and compared to data reported by Wilke et al. (2001). The centroid positions suggested that the oxidation state of the Fe in the LAW

samples was Fe^{3+} . The area under the pre-edge indicated that the Fe had an average coordination number between four- and six-fold. The data could not be compared to Mössbauer spectroscopy to help validate these results, because the Fe content was too low to conduct room temperature Mössbauer spectroscopy, and low temperature Mössbauer spectroscopy was not available at the time. The Fe K-edge XANES data suggested that increasing the P_2O_5 content had little effect on the Fe oxidation and coordination, where Fe in the glasses had the role of a glass network former, Fe^{3+} . The pre-edge fitting line shapes are available in the Appendix (8.22) of this chapter.

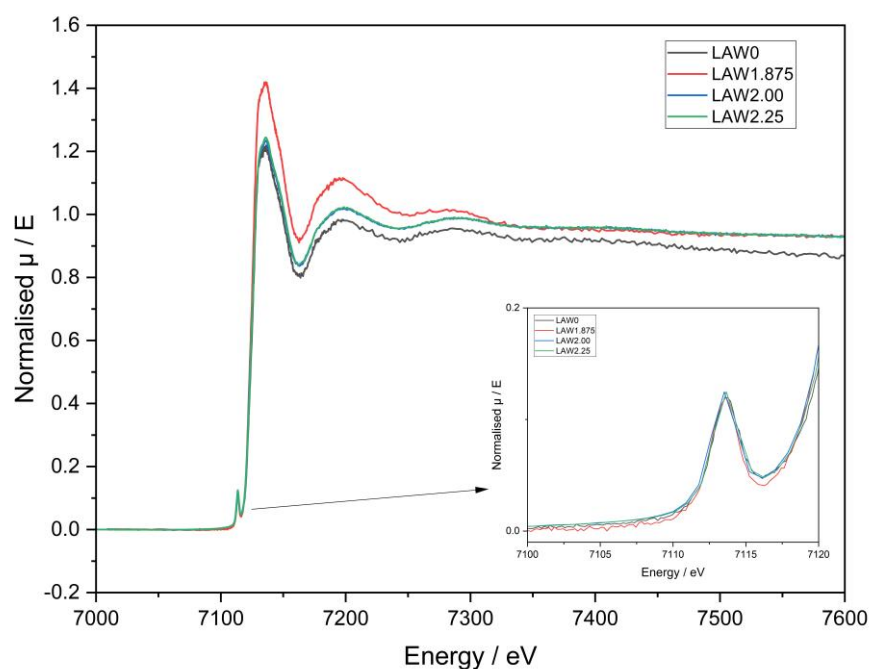


Figure 117 – Fe K-edge XANES of LAW0.00, 1.875, 2.00 and 2.25 samples

Sample	Components (eV)	Intensity (a.u.)	Integrated intensity (a.u.)	Centroid position (eV)	Margin of error
LAW0	7113.59	0.223	0.22	7113.6	4.84×10^{-4}
LAW1.875	7113.48	0.234	0.23	7113.5	5.70×10^{-4}
LAW2.00	7113.47	0.215	0.22	7113.5	0.0025
LAW2.25	7113.59	0.222	0.22	7113.6	0.0025

Table 57 – Pre-edge parameters for LAW samples obtained from Fe K-edge XANES

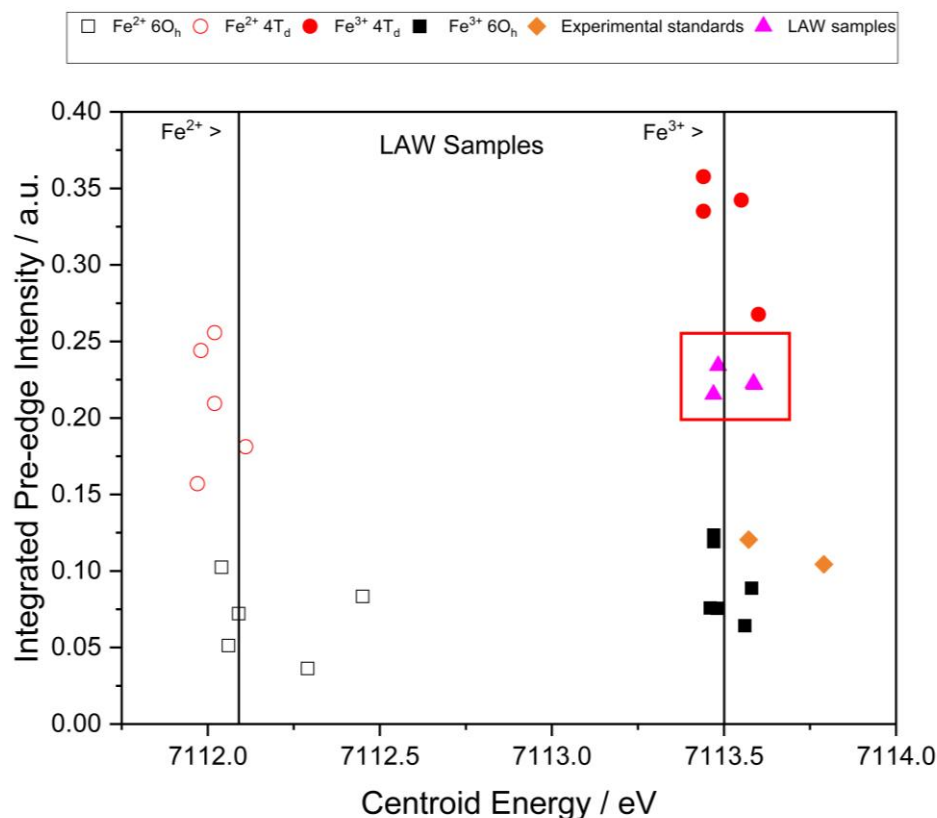


Figure 118 – Variogram showing LAW samples and experimental standards with Wilke et al. (2001) Fe reference data

4.4.3.1.8 SEM/EDS

Figure 119 shows the back scattered SEM images and associated EDS maps of LAW1.875 – 2.50 at a magnification of x2000. Table 58 contains the EDS mapping spectra for the LAW samples. LAW1.875 and 1.94 displayed EDS maps associated with amorphous samples, where no evidence of crystalline material was present. LAW2.00 – 2.50 exhibited phase separated dispersed globular morphological features which corresponded to NaCa(PO₄) because of its high concentration of Na⁺, Ca²⁺, PO₄³⁻ and O²⁻, where the morphology suggested it may have been formed via the nucleation and growth mechanism. Figure 120 - Figure 122 show the globular morphology at magnifications 1000x, 5000x, and 10000x.

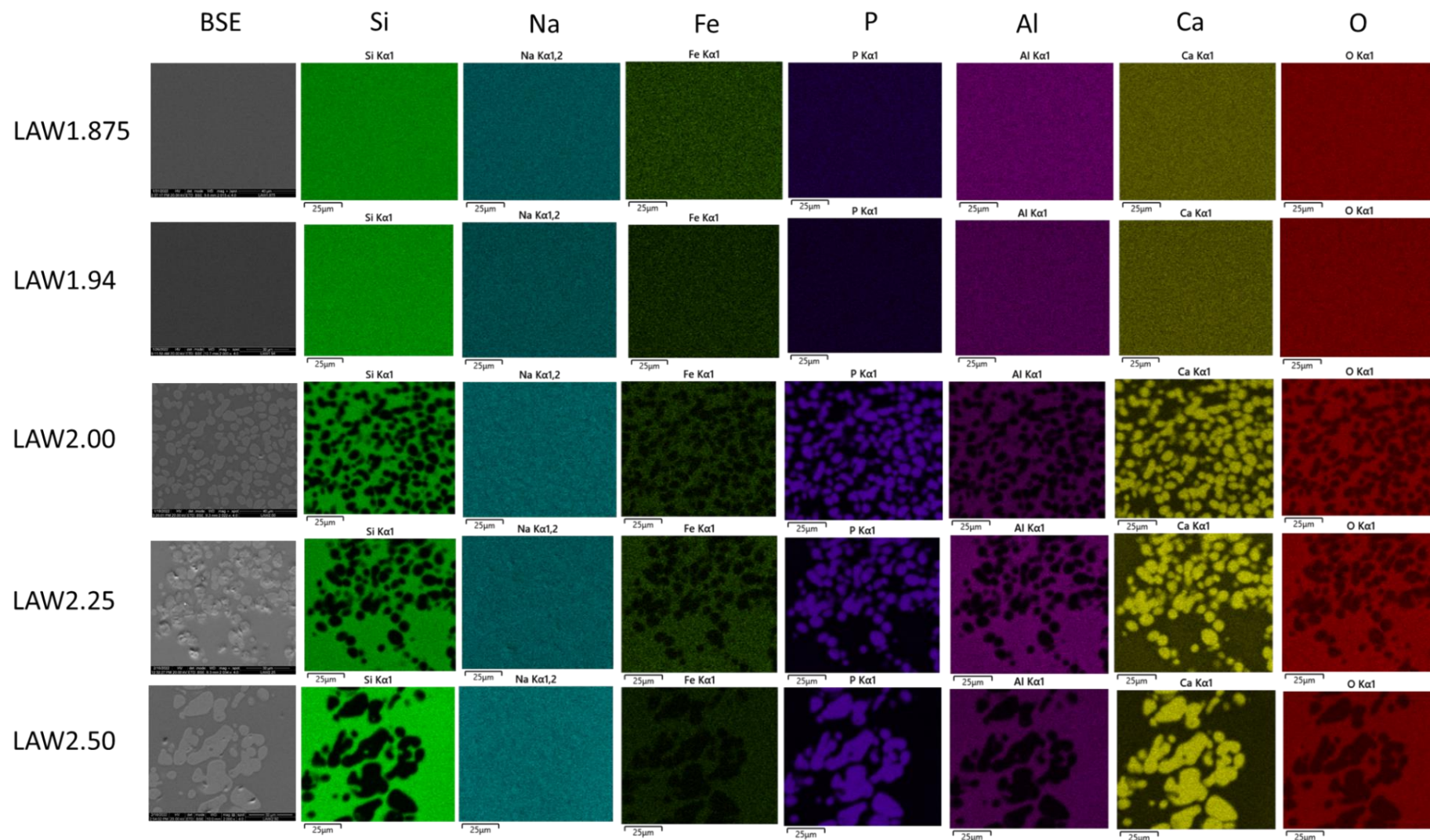


Figure 119 - EDS mapping of LAW1.9875, 1.94, 20.00, 2.25 and 2.50

Sample	Element (oxide wt%)													
	Si	σ	Na	σ	Fe	σ	P	σ	Al	σ	Ca	σ	O	σ
LAW1.875	16.2	0.3	11.4	0.2	2.7	0.0	1.6	0.0	4.2	0.1	6.8	0.1	49.3	0.9
LAW1.94	17.38	0.37	12.16	0.26	2.67	0.06	1.61	0.04	4.86	0.1	7.03	0.15	48.0	1.1
LAW2.00	22.3	0.4	15.1	0.3	1.7	0.0	20.6	0.4	4.6	0.1	19.0	0.3	-	-
LAW2.25	20.2	0.0	14.3	0.0	3.5	0.0	2.4	0.0	8.3	0.0	8.4	0.0	42.8	0.0
LAW2.50	11.5	0.2	10.1	0.2	1.2	0.0	6.4	0.1	2.6	0.0	9.8	0.2	50.0	0.8

Table 58 - EDS mapping spectra for the LAW samples

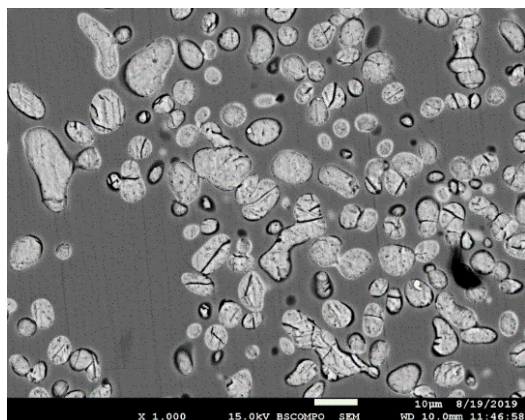


Figure 120 - Backscattered SEM image of LAW2.50 at x1k using a JOEL JSM-7001F field emission SEM

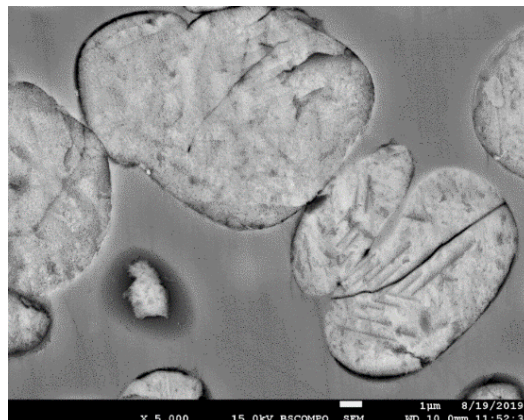


Figure 121 - Backscattered SEM image of LAW2.50 at x5k using a JOEL JSM-7001F field emission SEM

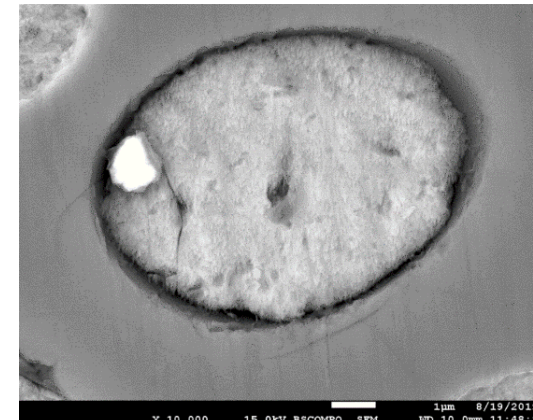


Figure 122 - Backscattered SEM image of LAW2.50 at x10k using a JOEL JSM-7001F field emission SEM

4.4.3.1.9 Chemical Durability

The study of the dissolution kinetics of amorphous materials is of particular importance for vitrified waste stored in subsurface depositories, because if the glass comes into contact with groundwater, processes of interdiffusion, ion exchange, reaction diffusion, and hydrolysis will occur (Ma et al., 2017; Thorpe et al., 2021). Understanding these mechanisms provides an insight into the glass dissolution behaviour, especially as there is uncertainty in the prediction of the long-term release rate of radionuclides, resulting in the adoption of an approach that utilises the most rapid dissolution rate, known as the forward rate (Thorpe et al., 2021). The dissolution kinetics of an alkali borosilicate glass system is a function of composition, pH, temperature, and solution chemistry (Thorpe et al., 2021), where the mechanisms that occur regardless of composition, comprise of two processes of chemical attack: (i) *“the leaching of mobile ions from the glass network driven by H^+/H_3O^+ and (ii) the breakdown of the glass network driven by OH^- ”* (Thorpe et al., 2021). In summary, the initial rate regime is characterised by interdiffusion, ion-exchange, and network hydrolysis (Thorpe et al., 2021). For a glass to be considered chemically durable, its predicted durability response must be more durable by ≥ 2 standard deviations of the benchmark waste glass identified in the DWPF environmental Assessment (EA) based on ASTM C1285 (Jantzen & Brown, 2004). The current PCT specification for Hanford LAW glasses for the normalised release rate of Na, B, and Si should be $< 2 \text{ g/m}^2$ using the 7-day PCT test at 90°C (Kim et al., 2003), where statistical analysis of durability measurements of the DWPF glass is presented in Table 59 (Jantzen et al., 1993).

Leachate Concentration				
	B (g/L)	Li (g/L)	Na (g/L)	Si (g/L)
Mean	16.695	9.565	13.346	3.922
STDEV	1.222	0.735	0.902	0.376

Table 59 - statistical analysis of PCT durability measurements of the DWPF glass taken from (Jantzen et al., 1993)

The glasses in this series, underwent a 7-day PCT-B test to evaluate the effects of increasing P_2O_5 content on the initial dissolution behaviour, where analysed results can be used to inform the first stage (interdiffusion), and potentially the second stage (initial rate) of glass corrosion. However, results were only collected at one time point i.e., the 7th day, meaning that only a minimum initial rate can be

postulated, where some of the samples may have already experienced the rate drop, and that a true initial rate cannot be calculated from one value.

The normalised mass loss of Na is shown in Table 60 and Figure 123. The data does not follow any trends of the NL(B), NL(Si), or NL(P) data. The NL(Na) data showed a gradual decrease in the mass loss rate after 7 days with increasing P₂O₅ content, where values showed that LAW0.00 had the highest value of 1.064 ± 0.061 g/m² followed by LAW0.625, 1.875, 1.94, 2.00, 2.25, and 1.25. However, it should be mentioned that the NL(Na) mass loss data of the LAW1.25 sample may be an anomalous result. The NL(Na) suggested that LAW0.00 dissolved the quickest, and that increased additions of P₂O₅ reduced this value. In most durability studies of borosilicate glasses, B is selected as the glass alteration tracer because it is highly soluble and not incorporated in the alteration products (Piovesan et al., 2018). The NL(B) data (Table 60 and Figure 123) showed that LAW1.875 had the highest total mass loss value of 0.558 ± 0.368 g/m², followed by LAW2.00, LAW0.625, LAW2.25, LAW.00, LAW1.94, and LAW1.25. The durability of the LAW samples except the LAW1.25 sample, are all the same within error, as a horizontal line can be drawn through these results. However, the LAW1.25 sample was less durable than LAW0.00 and 0.625 but was the same within error of the LAW1.875 sample. Therefore, the NL(B) data suggested that LAW1.25 was the most durable. The normalised mass loss data for NL(Si) (Table 60 and Figure 123) showed that LAW2.25 had the highest value of 0.232 ± 0.023 g/m², followed by LAW1.94, LAW1.25, LAW2.00, LAW0.625, LAW1.875, and LAW0.00. The NL(P) data (Table 60 and Figure 123) showed that LAW1.94 had the highest value of 0.839 ± 0.045 g/m², followed by LAW2.00, 2.25, 1.25, 1.875, and 0.625. The NL(P) data (Table 60 and Figure 123) showed that upon the initial addition of 0.625 mol% the mass loss value was 0.000 ± 0.034 g/m², after which it increased to 0.091 ± 0.008 g/m² at 1.25 mol% P₂O₅. At 1.875 mol% P₂O₅, the value increased to its highest value of 0.839 ± 0.045 g/m². The NL(P) mass loss data then decreased with 1.94 mol% P₂O₅ and continued to do so when 2.00 and 2.25 mol% P₂O₅ was added. The NL(P) mass loss data showed that LAW1.875 had the highest value, followed by LAW1.94, LAW2.00, LAW2.25, LAW1.25, and LAW0.625.

The observed pH values for the LAW samples (Table 60) showed that all leachate solutions were very basic, and can be attributed to the release of Li⁺ and Na⁺ ions

into the solution during the course of the dissolution test. However, there will also be contributions from other species in the glass i.e., Fe and Al (Appendix 8.23). The pH gradually decreased between LAW0.00 and LAW1.94, where the values were 11.54 ± 0.13 and 10.85 ± 0.09 , respectively. This decrease in basicity was accompanied by the gradual decrease in the dissolved Na concentration. The pH then increased in LAW2.00 and 2.25, resulting in a more basic leachate solution, and is due to the formation of strong alkali hydroxides, that offset weak boric acid in the leachate solution as the glasses dissolve (Bengisu et al., 2006).

The higher normalised mass loss data of Na in comparison to Si suggested that it was being preferentially released. This preferential release of Na is the result of the ion-exchange reaction mechanism where hydronium ions are dissolving in the glass structure (Stone-Weiss et al., 2018). The increase in pH in samples LAW2.00 and 2.25 may be due to the presence of $\text{NaCa}(\text{PO}_4)$ crystals, identified by XRD, however, there were no increases in the normalised mass loss data or minimum normalised release rate (Table 60). The $\text{NaCa}(\text{PO}_4)$ crystal phase may decrease durability of the glasses due to the microstructural changes to the discontinuous structure (Arbab et al., 2007). The presence of $\text{NaCa}(\text{PO}_4)$ removes Na and Ca from the glassy matrix, resulting in its re-polymerisation, reducing the number of NBØs, which in turn reduces the amount of free volume available for water to attack and for soluble species to escape from (Aboutaleb et al., 2012). This reduction in NBØs and increase in BØs with the addition of P_2O_5 also results in the increased fraction of BO_4 units at the expense of BO_3 units (Bengisu et al., 2006).

The replacement of the more reactive BO_3 units for the more chemically stable BO_4 units is consistent with the lowered corrosion rates exhibited by the LAW samples. Raman spectroscopy data of the LAW glasses suggested that there was an increase in the BØs in the samples as the P_2O_5 content increased (Figure 113). Abotaleb et al. (2012) reported that Ca accelerated the rate of deterioration of the glass, increasing the Si saturation. Carroll et al. (1994) cited Bunker et al. (1986, 1998) where they stated that glass durability is controlled by polymerisation reactions at the glass-solution interface, and that the greater the number of non-bridging silanol bonds, the less durable the glass.

The presence of phase separation and formation of crystal phases can affect the chemical durability of the glass. Phase separation complicates the modelling of

the chemical durability of glass due to knowing the overall composition of the glass but not the separated phases, hence the overall performance of the glass is unpredictable (Jantzen & Brown, 2004). If type A (spinodal decomposition) or type B (nucleation and growth, where the more durable phase is dispersed in a continuous matrix of a less durable phase) phase separation occurs, the chemical durability deteriorates, but if type C occurs (nucleation and growth where the less durable phase is dispersed in a matrix of the durable phase) the chemical durability is barely affected (Taylor et al., 1987). The occurrence of phase separation weakens the glass structure, resulting in making ion exchange easier between the glass components and those of the attacking mediums (Taylor et al., 1987). The formation of NBØs in the silicate network de-polymerises the glass structure generating cavities that are favourable for invasion by H₂O resulting in the exit of soluble species (Aboutaleb et al., 2012). Maghouli and Yekta (2018) reported that the presence of liquid-liquid phase separation, where there is a Si-rich and P-rich phases, results in the P-rich region dissolving more easily, decreasing the chemical durability.

The formation of crystal phases can affect the chemical durability of the glass. When the crystalline material is in contact with water, it experiences chemical reactions i.e., *“hydration, hydrolysis, and ion-exchange or redox reactions”* (Frankel et al., 2018). Chemical bonds in the crystalline material exposed to such environments can be broken by aqueous attack leading to crystal dissolution (Frankel et al., 2018). For the dissolution of crystals in a static experiment, the system will start at far from equilibrium conditions, where the crystal dissolution rate can be treated as constant and independent of undersaturation (Frankel et al., 2018). The 3D lattice structure of the crystal, and surface and morphological defects have a notable impact on the dissolution rate of crystals, where crystal size has been reported to effect the dissolution behaviour i.e., the increased dissolution rates of smaller particles is determined by the increased interfacial area (Frankel et al., 2018). Grain boundaries have also been reported to effect the dissolution rate, where the breaking and/or detachment of bonds may occur more easily due to the weaker chemical bonds in grain boundaries, or where they may also be enriched with soluble elements or form intergranular glassy phases, leading to an increased initial dissolution rate (Frankel et al., 2018).

Sample	Normalised Mass Loss, NL_i (g m ⁻²)								pH	15
	NL_{Si}	15	NL_B	15	NL_{Na}	15	NL_P	15		
LAW0.00	0.155	0.010	0.296	0.020	1.064	0.061	-	-	11.54	0.13
LAW0.625	0.215	0.012	0.309	0.012	0.961	0.032	0.000	0.034	11.56	0.10
LAW1.25	0.180	0.002	0.252	0.006	0.493	0.016	0.091	0.008	10.97	0.01
LAW1.875	0.232	0.023	0.558	0.368	0.861	0.103	0.839	0.045	10.85	0.09
LAW1.94	0.131	0.201	0.289	0.039	0.708	0.106	0.420	0.131	10.85	0.09
LAW2.00	0.231	0.028	0.316	0.042	0.690	0.092	0.382	0.050	11.33	0.04
LAW2.25	0.220	0.003	0.308	0.022	0.634	0.009	0.325	0.012	11.32	0.08

Table 60 - Average Normalised elemental release rate (g.m⁻²) & pH where the calculated error is one standard deviation

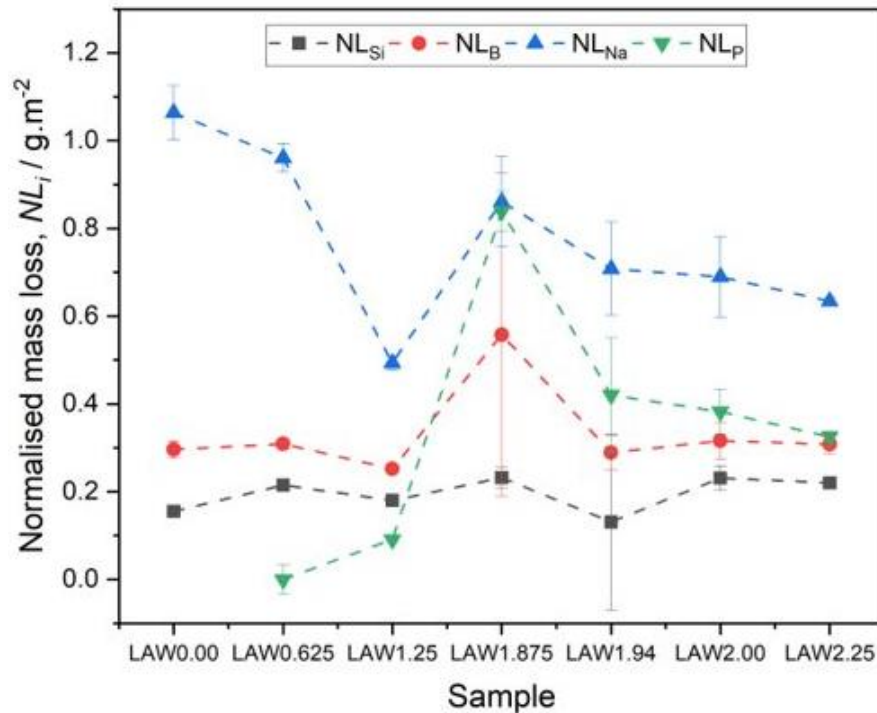


Figure 123 - Normalised mass loss (g.m⁻²) for structural elements and modifiers for a 7-day test leaching in pure water at 90°C

Sample	Minimum normalised release rate, R_i (g m ⁻² d ⁻¹)			
	NL _{Si}	NL _B	NL _{Na}	NL _P
LAW0.00	0.022	0.042	0.152	-
LAW0.625	0.031	0.044	0.137	0.000
LAW1.25	0.026	0.036	0.070	0.013
LAW1.875	0.033	0.080	0.123	0.120
LAW1.94	0.019	0.041	0.101	0.060
LAW2.00	0.033	0.045	0.099	0.055
LAW2.25	0.031	0.044	0.091	0.046

Table 61 - Normalised release rate (g.m⁻².d⁻¹) for structural elements and modifiers for a 7-day test leaching in pure water at 90°C

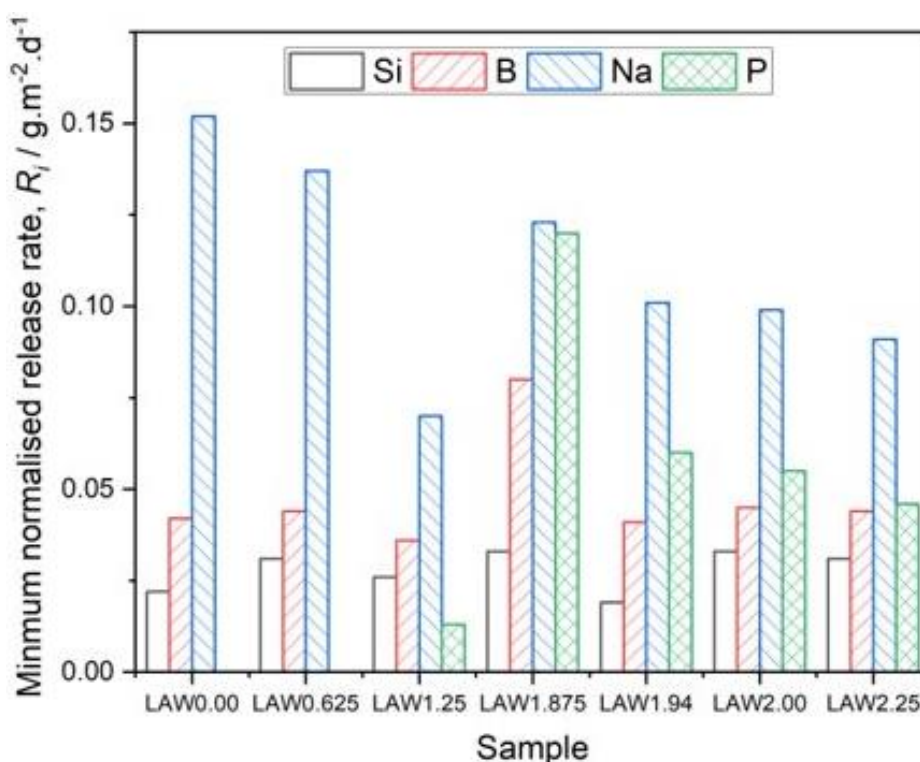


Figure 124 - Normalised release rate (g.m⁻².d⁻¹) for structural elements and modifiers for a 7-day test leaching in pure water at 90°C

When the LAW samples normalised mass loss data was compared to the LAW literature values reported by Smith et al. (2000) (Table 62) the NL_{Si} result were comparable, but the NL_B and NL_{Na} values were much lower, where this study's NL(Si), and NL(Na) values ranged between 0.252-0.558 g/m², 0.131-0.232 g/m², and 0.493-1.84 g/m², respectively. When the LAW samples normalised mass loss data was compared to Thorpe et al. (2017) (Table 62) for LAW A44, ORP LB2,

and LAW A23, the NL_{Si} , NL_B , and NL_{Na} were all much lower, suggesting the samples were more chemically durable. The large differences in the mass loss data can be related to the compositional differences (components and concentration).

Composition	Normalized mass loss (g/m ²)			pH	Reference
	NL_B	NL_{Si}	NL_{Na}		
LAW A88 (simulant AW-101)	0.569	0.196	0.589	9.08 – 9.17	(Smith et al., 2000)
LAWC15 (simulant AN-107)	0.329	0.161	0.335	9.00 – 9.04	(Smith et al., 2000)
LAW A44	0.398 ± 0.005	0.213 ± 0.009	0.814 ± 0.032	11-11.5 ± 0.2	(Thorpe et al., 2017)
ORP LB2	0.987 ± 0.047	0.389 ± 0.034	1.778 ± 0.017	13.2 ± 0.02	(Thorpe et al., 2017)
LAW A23	0.417 ± 0.017	0.311 ± 0.012	1.728 ± 0.015	13.3 ± 0.2	(Thorpe et al., 2017)

Table 62 – relevant literature comparison table of normalised mass loss and pH

The effects of P_2O_5 on the chemical durability of these simplified LAW glasses cannot be fully concluded due to the lack of sufficient data points before and after the 7-day mark used in order to calculate the initial rate. There are also the unaccounted-for effects of the potential presence of liquid-liquid phase separation and crystalline phase separation in the P_2O_5 -doped samples before the occurrence of amorphous-crystalline phase separation, which has not yet been determined by SEM. However, this study has provided an introduction into the effects of increasing P_2O_5 in a far more complex glass system than what has been previously reported, where the minimum normalised release rate can be postulated from the single values collected from the 7-day PCT-B test, where increasing levels of P_2O_5 saw a decrease in the normalised elemental release rate of Na. The presence of crystal phases can affect the chemical durability; however, it is dependent on whether that phase is water soluble and whether it acts as a barrier from aqueous attack. Further work would include prolonged PCT tests where aliquots of solution were taken at 1, 3, 5, 7, 14, 21 and 28 days, with

XRD and SEM analysis of potential alteration layers, and PCT tests of full simulant waste loaded waste glasses with varying P_2O_5 content.

4.4.3.2 CCC Heat Treated LAW Samples

4.4.3.2.1 Visual and Optical Observations

Visual (Figure 125) and optical (Figure 126) observations of the CCC heat treated samples show that between LAW0.00-1.25 the samples have a mixture of glassy material with crystal clusters on the surface. These crystal clusters become more densely packed on the surface as the P_2O_5 content increased. Between LAW1.875-2.50 the samples no longer presented the amber glassy material, and instead presented surfaces that were an opaque brown with varying sizes of macroscale crystals. Samples LAW0.00-1.875 at a magnification of 10x showed crystals with hexagonal and rectangular morphologies, where the hexagonal crystals may have been nepheline. Samples LAW1.94-2.50 exhibited larger hexagonal crystals that seemed to have increased in size with increasing as the P_2O_5 content. It is difficult to determine which crystal phases the structures belong to without the use of SEM/EDS. Due to restrictions in time and equipment, it was decided that optical microscopy would be sufficient when paired with XRD.

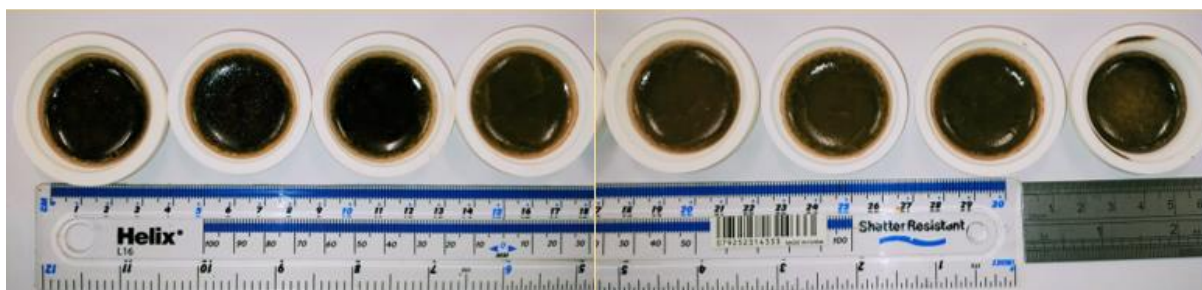


Figure 125 - Top view of CCC LAW samples. LAW0.00 (far left), 0.625, 1.25, 1.875, 1.94, 2.00, 2.25, and 2.50.

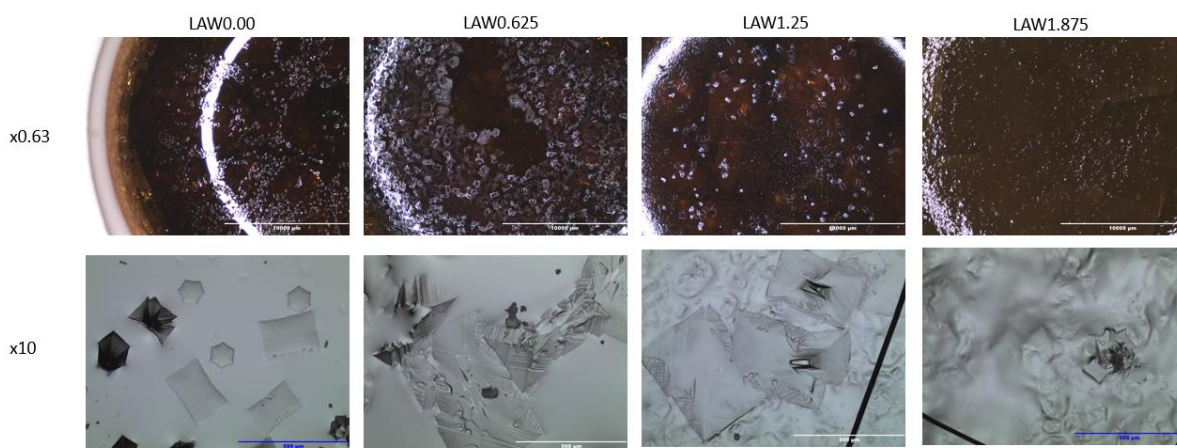


Figure 126 - LAW0.00-1.875 optical assessment of the surface of the samples at a magnification of 0.63x and 10x

4.4.3.2.2 X-ray Powder Diffraction and Rietveld Analysis

Figure 127 shows the XRD patterns for the CCC heat treated LAW samples, where all samples exhibited multiple crystalline peaks. Table 63 and Figure 128 show the results of the Rietveld analysis, where Si was used as the known reference standard. From evaluating these figures, as the P_2O_5 content increased, the degree of crystallinity increased. The base glass had 1.48 wt% of sodium aluminium silicate ($NaAlSiO_4$, PDF#: 01-086-5804, hexagonal, space group: P63 (Xu et al., 2017)) (Figure 183 and Table 93 in Appendix 8.24) and 0.64 wt% quartz (SiO_2 , PDF#: 03-065-0466, hexagonal, space group: P3221 (Lager et al., 1982)) (Figure 186 and Table 93 in Appendix 8.24). The 0.625 mol% sample also had $NaAlSiO_4$ present but with no evidence of quartz. When 1.25 mol% P_2O_5 was added, the $NaAlSiO_4$ content increased from 4.19 to 16.04 wt%, and sodium calcium phosphate crystal phase ($NaCa(PO_4)$, PDF#: 04-016-6900, orthorhombic, space group: Pnam (Ben Amara et al., 1983)) (Figure 185 and Table 93 in Appendix 8.24) was identified with a content of 7.50 wt%. When 1.875 mol% P_2O_5 was added, both the $NaAlSiO_4$ and $NaCa(PO_4)$ content decreased by 3.59 and 3.38 wt%, respectively. There was also the presence of 2.74 wt% calcium aluminium silicate ($Ca_2Al_2SiO_7$, PDF#: 04-015-7928, tetragonal, space group: P-421m (Merlini et al., 2008)) (Figure 184 and Table 93 in Appendix 8.24). At 1.94 mol% P_2O_5 , the $NaAlSiO_4$ continued to decrease to 8.79 wt%, whilst the $NaCa(PO_4)$ and $Ca_2Al_2SiO_7$ contents increased by 5.63 and 1.16 wt%, respectively. Upon further additions of 2.00 mol% P_2O_5 , $NaAlSiO_4$ content decreased to 8.35 wt%, the $NaCa(PO_4)$ contents increased to 13.23 wt%, and the $Ca_2Al_2SiO_7$ contents increased by 30.37 wt% to a value of 34.27 wt%. At 2.25

mol% P_2O_5 , the $NaAlSiO_4$ content increased by 45.76 wt%, whilst the $NaCa(PO_4)$ content increased by 19.28 wt%, and the $Ca_2Al_2SiO_7$ contents decreased by 12.17 wt%. Overall, the amorphous content of these samples decreased between 97.88 and 0.64 wt%, and the crystallinity content increased between 2.12 and 99.36 wt%. This crystallisation behaviour implies that as the P_2O_5 content increased, susceptibility for the samples to crystallise increased with the CCC heating regime, to the point where additions of 2.25 mol% P_2O_5 resulted in an almost fully crystalline sample.

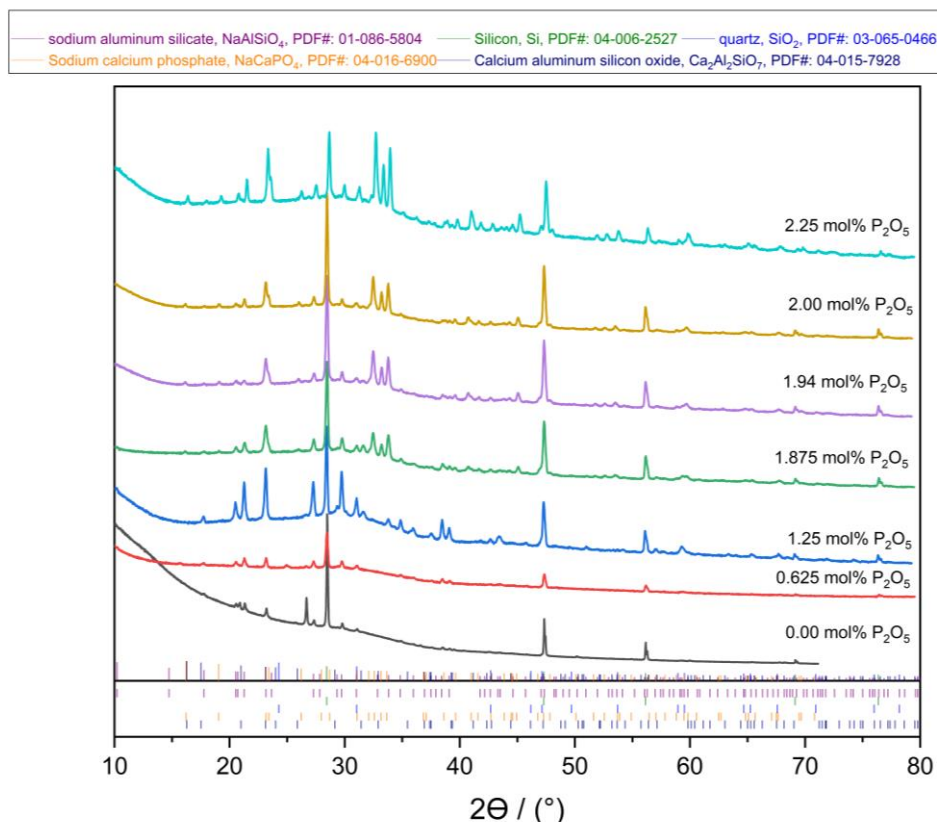


Figure 127 - XRD patterns of the CCC heat treated LAW glasses

Sample	$NaAlSiO_4$ (wt%)	SiO_2 (wt%)	$NaCa(PO_4)$ (wt%)	$Ca_2Al_2SiO_7$ (wt%)	Crystalline (wt%)	Amorphous (wt%)	Sum
LAW0.00	1.48	0.64	0.00	0.00	2.12	97.88	100.00
LAW0.625	4.19	0.00	0.00	0.00	4.19	95.81	100.00
LAW1.25	16.04	0.00	7.50	0.00	23.54	76.46	100.00
LAW1.875	12.45	0.00	7.17	2.74	22.36	77.64	100.00
LAW1.94	8.79	0.00	12.80	3.90	25.49	74.51	100.00
LAW2.00	8.35	0.00	13.23	34.27	55.86	44.14	100.00
LAW2.25	54.11	0.00	33.08	12.17	99.36	0.64	100.00

Table 63 - Rietveld analysis results of the LAW glasses

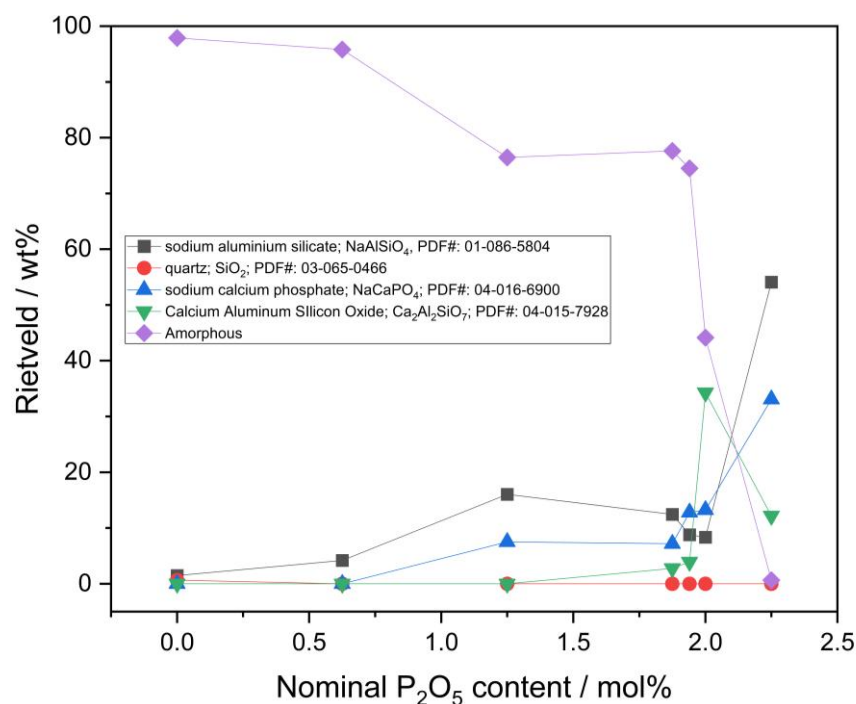


Figure 128 - Graphical representation of Rietveld analysis of LAW glasses
Previous PNNL reports have presented crystallisation information as vol%, hence the conversion of wt% to vol% is calculated using Eq 47 (Lonergan, et al.2021) and information from Table 64. Table 65 presents sample total crystal volume.

$$Vol\%_{crystal} = \frac{\rho_{glass}}{(\rho_{crystal} * (100 / wt\%_{crystal}) + \rho_{crystal})} * 100 \quad (47)$$

Crystal phase	Density (g/cm ³)
NaCaPO ₄	3.108
NaAlSiO ₄	2.620
Ca ₂ Al ₂ SiO ₆	3.043
SiO ₂	2.648

Table 64 - Crystal phase density values

Sample	Total crystal volume (%)
LAW0.00	2.09
LAW0.625	4.05
LAW1.25	19.57
LAW1.875	19.25
LAW1.94	20.91
LAW2.00	39.54
LAW2.25	63.67

Table 65 - Total crystal volume percent for the LAW samples based on the total of NaAlSiO₄, NaCa(PO₄), and Ca₂Al₂SiO₇

The presence of these crystal phases have been previously identified in CCC HLW and LAW glasses (Deshkar et al., 2017; Lonergan et al., 2021; Marcial et al., 2016; McCloy et al., 2011; McCloy & Vienna, 2010), where they have been seen to negatively affect the PCT response (Lonergan et al., 2021), depending on whether they have exceeded their limit constraints (Kim et al., 2011; Lonergan et al., 2021) (Table 66). McCloy and Vienna (2010) reported that Nepheline-like aluminosilicates (NLAS) were to be defined as any oxide crystalline phase that includes Al, Si, and at least one alkali or alkaline-earth element. This included all the feldspathoids: (Na,K)AlSiO₄, NaAlSiO₄, KAlSiO₄, LiAlSiO₄, LiAlSi₂O₆, and LiAlSi₄O₁₀ etc. It also included alkali feldspars e.g., KAlSi₂O₆, KAlSi₃O₈, NaAlSi₃O₈, NaAlSi₂O₆.H₂O, and alkali-earth feldspars e.g., CaAl₂Si₂O₈ and (Na, Ca)AlSi₃O₈. There is also the inclusion of Na₈Al₆Si₆O₂₄(SO₄), (Na, Ca)₈(AlSiO₄)₆(SO₄,S,Cl)₂, Na₄Al₃(SiO₄)₃Cl, NaAlSi₂O₆, Ca₂Al₂SiO₇ etc. Feldspathoids and feldspars are classified as tectosilicates (3D network structures). The constraints are tabulated in Table 66.

Constraint	Limit (wt%)
Na-Al silicate	$Al_2O_3 \leq 15.80 - 0.280*(Na_2O + 0.66*K_2O)$
Na-Al silicate alternative	$Al_2O_3 \leq 11.5$
Na-Ca silicate	$CaO \leq 14.36 - 0.272*(Na_2O + 0.66*K_2O)$
Na-Ca silicate alternative	$CaO \leq 20.84 - 0.528*(Na_2O + 0.66*K_2O)$
Nepheline constraint	$N_{Si} = (g_{SiO_2}) / (g_{SiO_2} + g_{Na_2O} + g_{Al_2O_3}) \leq 0.62$ G_i is the mass fraction of the oxide in the glass

Table 66 - Na-Al and Na-Ca silicate constraints

The LAW glasses did not exceed the NaAlSiO₄ constraint, where the compositions were pro'ratd with additions of P₂O₅. An example calculation is presented below for nominal LAW0.625:

$$N_{Si} = (g_{SiO_2}) / (g_{SiO_2} + g_{Na_2O} + g_{Al_2O_3}) \leq 0.62$$

$$N_{Si} = (0.311g_{SiO_2}) / (0.311g_{SiO_2} + 0.238g_{Na_2O} + 0.093g_{Al_2O_3}) = 0.485 \leq 0.62$$

The LAW glasses also did not exceed the Na-Al or the Na-Ca silicate constraints, implying that that these samples should have a lower susceptibility of forming these crystal phases. However, this was not the case where NaAlSiO₄ formed in the CCC base glass (LAW0.00) and subsequent samples. Although, LAW0.00

and 0.625 produced < 10 wt% which is within the constrain proposed by Lonergan et al. (2021). Samples with ≥ 1.25 mol% P_2O_5 exceeded this constraint, suggesting that increased additions of P_2O_5 may have an impact on the crystallisation behaviour, potentially increasing the likelihood of formation of Na-Al/ Na-Ca silicate crystal phases. This behaviour suggests that additions of 0.625 mol% P_2O_5 is the limit which can be added to the LAW glasses without exceeding Na-Al and Na-Ca silicates constraints and the total crystal volume constraint, where the values were 4.19 wt% (Table 63) and 4.05% (Table 65), respectively. The formation of these crystal phases depletes the glassy matrix of network formers (Si and P), intermediates (Al), and modifiers (Na and Ca), where SiO_2 removes one mole of Si, $NaAlSiO_4$ removes one mole of Na, Al and Si, $NaCaPO_4$ removes one mole of Na, Ca, and P, and $Ca_2Al_2SiO_7$ removes two moles of Ca and Al, and one mole of Si. The formation of $NaAlSiO_4$, or similar phases, are known to impact the chemical durability of the vitrified waste form, as it directly removes Ca and Si, which directly impacts the PCT response (Lonergan et al., 2021). Lonergan et al. (2021) reported that the following crystal phases negatively impacted PCT and VHT responses of CCC WTP LAW glasses: nepheline ($NaAlSiO_4$), Nosean ($Na_8Al_6Si_6O_{24}(SO_4)$), combeite, $Na_2Ca_2Si_3O_9$, Hauyne ($Na_3CaAl_3Si_3O_{12}(SO_4)$), and lazurite ($Na_3CaAl_3Si_3O_{12}(SO_4, S, S_2, S_3, Cl, OH)$). Both $NaCa(PO_4)$ and quartz are soluble in water and will have an impact on the dissolution kinetics. Deshkar et al. (2017) also reported that CCC heat treated aluminoborosilicate glasses formed $NaAlSiO_4$ and that the dissolution kinetics were affected by the volume fraction of this crystal phase, where they exhibited higher NL_B values than their quenched counterparts.

4.4.3.2.3 Raman Spectroscopy

Figure 129 shows the Raman spectra for the CCC heat treated LAW samples and Table 67 lists the Raman shifts and referenced associations. The base glass exhibited low intensity peaks at 505, 569, 658, 660 and 735 cm^{-1} , an intense region with peaks at ~ 950 , 996, and 1025 cm^{-1} , and a broader low intensity region between $1200\text{-}1500\text{ cm}^{-1}$, with identified peaks at ~ 1211 and 1428 cm^{-1} . When increasing amounts of P_2O_5 are added to the glass system a prominent peak at 989 cm^{-1} occurs, increasing in intensity, with the development of two smaller but sharper peaks occurring at ~ 579 and 1023 cm^{-1} . Accompanying these changes was the increase in the relative areas of the low-frequency region ($300\text{-}800\text{ cm}^{-1}$)

and high-frequency region (1200-1500), as demonstrated in the RDS spectra (Figure 130), as the P_2O_5 content increased.

The peaks at 505, 569, 658, 660 and 735 cm^{-1} are located in the low frequency region, where intensities are characteristic of inter-tetrahedral (T-O-T) bending motions (Bechgaard et al., 2017; Jolivet et al., 2019). The intensities at 569, 658/660, and 735 cm^{-1} may have contributions from a mixture of units, where intensities at 505 and 569 cm^{-1} may be attributed to the symmetrical stretching and partial deformation vibrations of Si-O-Si bridges (Koroleva et al., 2011; McKeown et al., 2000), as well as contributions from $V_4 PO_4$ from the $NaCa(PO_4)$ crystal phase in samples LAW1.25-2.50 (Comesaña et al., 2015). The intensities at 569, 658, and 745 cm^{-1} in the base glass and LAW0.625 may be attributed to the different B related vibrations based on the work by Manara et al. (2009) and Jolivet et al. (2019), which corresponded to $[^4]B$, $[^4]B$ in diborate rings, and $[^3]B$ in boroxol rings, respectively.

The peaks at 949, 968, 1025, and 1048 cm^{-1} are in the mid-frequency region associated with Q^n speciation ($800\text{-}1200\text{ cm}^{-1}$). The peak at 968 cm^{-1} identified in LAW0.625-2.25 is the main characteristic peak associated with $NaCa(PO_4)$ (buchwaldite), as identified by XRD Rietveld analysis (Figure 127) (Bersani et al., 2021; Comesaña et al., 2015; Čukanov & Vígassina, 2020). The peak at $\sim 1025\text{ cm}^{-1}$ may be attributed to $V_3 PO_4$ from the $NaCa(PO_4)$ crystal phase (Comesaña et al., 2015). The peak at 1048 cm^{-1} can be attributed to the stretching of Q^3 units, however, it cannot be determined which species is contributing to this peak due to the complex nature of this glass system and the tetrahedral forming species in the glass i.e., Si, P, Al, and Fe. The intensity at 1427 cm^{-1} is located in the high frequency region which contains contributions from B-O stretching vibrations linked to $[^3]B$ units (Möncke et al., 2015), where deconvolution of the peaks, according to literature, provides Gaussian components at $\sim 1320\text{ cm}^{-1}$ for loose $[^3]B$ units, 1410 cm^{-1} for $[^3]B$ units linked to $[^4]B$ units, 1480 cm^{-1} for $[^3]B$ units linked to $[^3]B$ units, and 1515 cm^{-1} for $[^3]B$ units linked to boroxol rings (Bisbrouck et al., 2021; Möncke et al., 2015; Seshadri et al., 2020). Therefore, the intensity at 1427 cm^{-1} could be attributed to $[^3]B$ units linked to $[^4]B$ units.

The presence of quartz, $NaCaPO_4$, $Ca_2Al_2SiO_7$, and $NaAlSiO_4$, as identified by XRD Rietveld analysis (Figure 128), may be contributing to the Raman spectra, however, there has not been any characteristic peaks identified for any of the

crystal phases present except $\text{NaCa}(\text{PO}_4)$. However, the characteristic peaks of the other crystal phases may be overshadowed by the relative intensity of NaCaPO_4 . McCloy et al. (2015) investigated NaAlSiO_4 in three HLW CCC glasses by Raman spectroscopy where they reported intensities for each of the samples. The first sample had intensities at 204, 227, 267, 351, 400, 422, 463, 498, 581, 610, 989, 1034 and 1082 cm^{-1} , the second sample had intensities at 203, 226, 264, 353, 393, 418, 460, 496, 578, 610, 923, 993, 1081, and 1082 cm^{-1} , the third sample had intensities at 159, 206, 267, 349, 401, 411, 467, 550, 682, 969, 989, 1037, 1087, and 1099 cm^{-1} . Bouhifd et al. (2002) reported that $\text{Ca}_2\text{Al}_2\text{SiO}_7$ Raman spectra displayed four Raman bands below 270 cm^{-1} that represented lattice modes, bands at $662\text{ (V}_9\text{)}$, $801\text{ (V}_{11}\text{)}$ and $845\text{ (V}_{12}\text{)}\text{ cm}^{-1}$, attributed to the AlO_4 tetrahedra present in $\text{Ca}_2\text{Al}_2\text{SiO}_7$ at a site having a 4 symmetry. Krishnamurthy (1958) reported that the main Raman shifts of α -quartz were identified to be the following: A class (totally symmetric): 206, 356, and 46 cm^{-1} ; B class (anti-symmetric): 145, 509, 780, and 1046 cm^{-1} ; E class (doubly degenerate): 128, 265, 394-404, 452, 696, 795-806, 1063, and 1160 cm^{-1} .

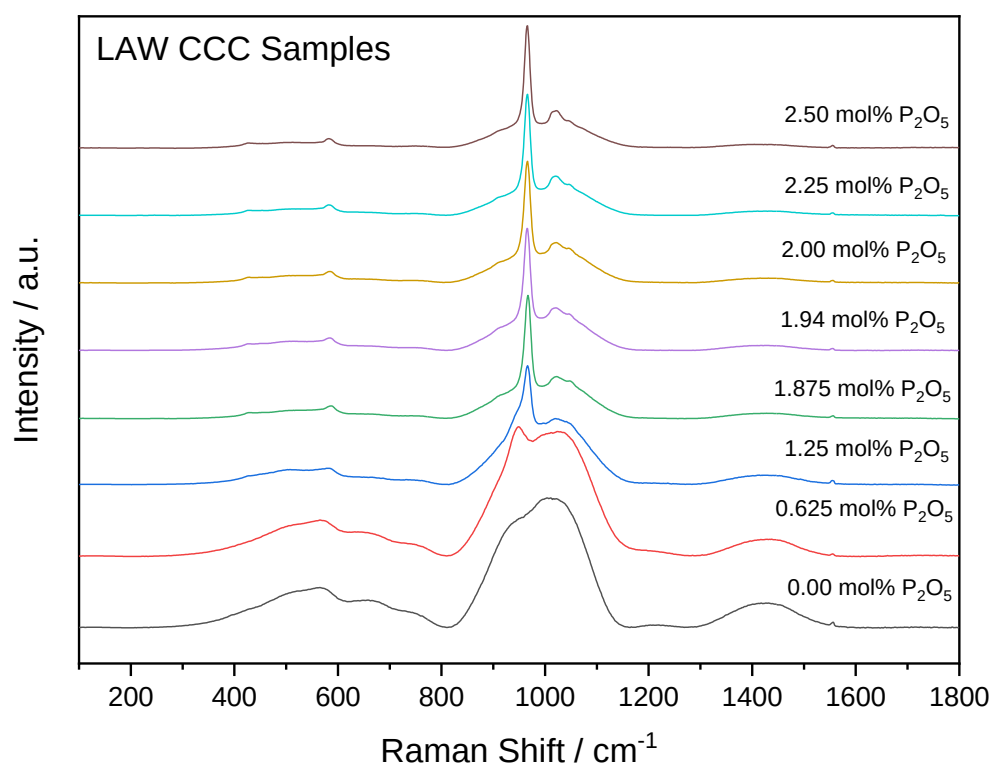


Figure 129 - Raman spectra of CCC heat treated LAW samples

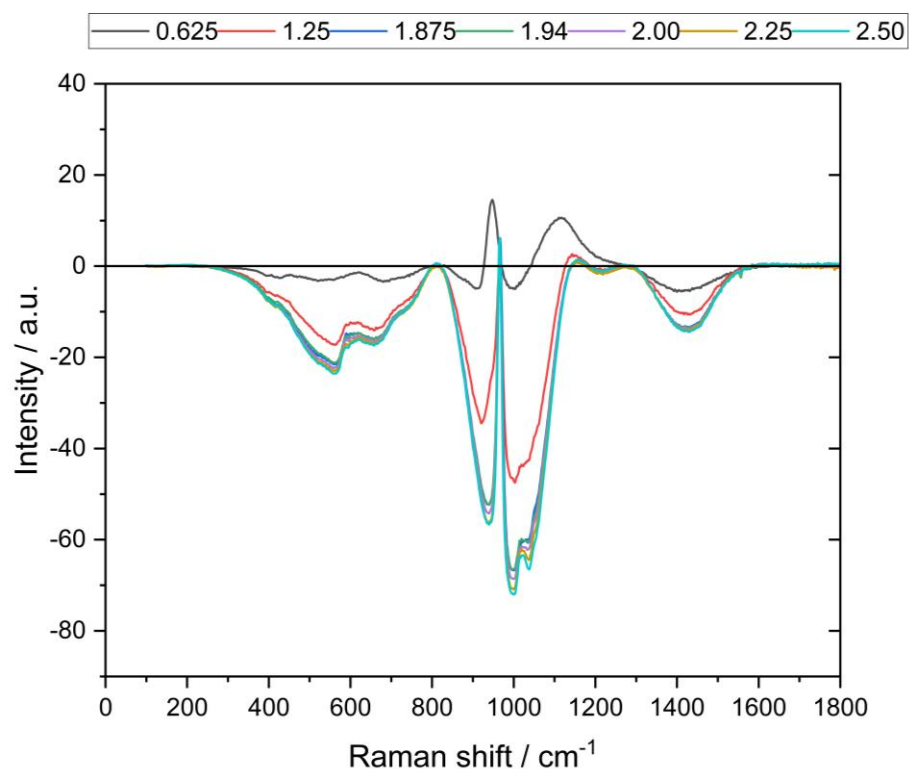


Figure 130 - Raman difference spectra (RDS) of CCC LAW samples

Table 67 - Raman shifts and referenced attributions

Raman shift / cm^{-1}	Association	Reference
505	symmetrical stretching and partial deformation vibrations of Si-O-Si bridges $\text{V}_4 \text{PO}_4$ from the NaCaPO_4	(Koroleva et al., 2011; McKeown et al., 2000)
569	symmetrical stretching and partial deformation vibrations of Si-O-Si bridges $\text{V}_4 \text{PO}_4$ from the NaCaPO_4 $^{[4]}\text{B}$ in diborate rings, and $^{[3]}\text{B}$ in boroxol rings	(Koroleva et al., 2011; McKeown et al., 2000) (Comesaña et al., 2015) (Jolivet et al., 2019)
658	$^{[4]}\text{B}$ in diborate rings, and $^{[3]}\text{B}$ in boroxol rings	(Jolivet et al., 2019)

735	$^{[4]}\text{B}$ in diborate rings, and $^{[3]}\text{B}$ in boroxol rings	(Jolivet et al., 2019)
968	NaCaPO_4 (buchwaldite)	(Bersani et al., 2021; Comesaña et al., 2015; Čukanov & Vigasina, 2020)
1027	V_3PO_4 from the NaCaPO_4 crystal phase	(Bersani et al., 2021; Comesaña et al., 2015; Čukanov & Vigasina, 2020)
1048	Stretching of Q^3 units	(Konijnendijk & Stevels, 1976; McKeown et al., 2000)
1427	$^{[3]}\text{B}$ units linked to $^{[4]}\text{B}$ units	(Bisbrouck et al., 2021; Möncke et al., 2015; Seshadri et al., 2020)

4.4.4 Summary

- XRD and SEM/EDS confirmed the presence of $\text{NaCa}(\text{PO}_4)$ in the annealed samples with ≥ 1.94 mol% P_2O_5 , suggesting that the P_2O_5 solubility limit lies between 1.875 and 1.94 mol%.
- The bulk density of the annealed samples ranged between 2.616 to 2.630 g/cm^3 , where the density of the P_2O_5 -free glass had the highest value. P_2O_5 had a mixed effect on the density, where the value fluctuated, increasing and decreasing as the P_2O_5 content increased. The increase in density may be due to the increase NBØs and re-arrangement of the ions into more closely packed arrangements.
- The increase and decrease behaviour exhibited by the T_g in the annealed samples displayed the dual effect that P_2O_5 can have on borosilicate glass systems. The T_g onset ranged between 473.1-481.6°C for DTA and 445.6-465.2°C for dilatometry.

- The CTE of the annealed samples increased with increasing P_2O_5 content, suggesting there was an increase in the asymmetrical units in the glass structure, indicating the de-polymerisation of said network.
- Raman spectroscopy of the annealed samples evidenced characteristic peaks associated with $NaCa(PO_4)$, as identified by XRD and SEM/EDS. The increase in the P_2O_5 content led to the removal of network forming modifiers to charge compensate $NaCaPO_4$, leading to the reduction in NBO s and subsequent re-polymerisation of the glass network, which could be seen affecting the danburite peak at 630 cm^{-1} and the 1427 cm^{-1} peak located in the BO_3 region, which provided information on the silicate and borate sub-networks.
- The Fe K-edge XANES analysis of the annealed samples suggested that the Fe was present as Fe^{3+} and acting as a network former. The increasing P_2O_5 content in the glasses did not seem to affect the oxidation of the Fe.
- Chemical durability testing of the annealed samples suggested that LAW0.00 had the highest NL_{Na} mass loss value of $1.064 \pm 0.061\text{ g/m}^2$, whilst LAW1.25 had the lowest value of 0.493 ± 0.016 , indicating that LAW0.00 dissolved the quickest. NL_B suggested that LAW1.875 had the highest value $0.558 \pm 0.368\text{ g/m}^2$ and LAW1.25 had the lowest value of $0.252 \pm 0.006\text{ g/m}^2$, indicating that LAW1.875 was the least durable sample whilst LAW1.25 was the most durable. The $NaCa(PO_4)$ phase may have affected the chemical durability of the higher P_2O_5 doped samples.
- XRD Rietveld analysis of the CCC heat treated samples identified $NaAlSiO_4$, SiO_2 , $NaCa(PO_4)$, and $Ca_2Al_2SiO_7$. The samples did not exceed the Hanford nepheline, Na-Al silicate, or Na-Ca silicate constraints, but $NaAlSiO_4$ still formed in the base glass and subsequent samples. LAW0.00 and 0.625 produced $< 10\text{ wt\%}$ in crystal phases but exceeded this with $\geq 1.25\text{ mol\% } P_2O_5$.
- The Raman spectroscopy of the CCC heat treated samples exhibited characteristic peaks associated with $NaCa(PO_4)$, but presence of the other identified crystal phases may have been overshadowed. The samples exhibited similar identifiable peaks as the annealed samples.
- This study has provided a better insight into the effects of P_2O_5 into more complex aluminoborosilicate glasses relevant to Hanford waste glasses, where little has been reported. It has shown that the P_2O_5 threshold is

lower than in the NBSPx samples, where the solubility was between 1.875-1.94 (4.11-4.25 wt%) and 3.0-4.0 mol% P_2O_5 , respectively. However, in the CCC heat treated samples, this solubility limit was reduced to 0.625 mol% (1.39 wt%) P_2O_5 to comply with certain constraints.

4.5 ILAW Glass Series

4.5.1 Introduction

The glass systems studied in this chapter are an average immobilised low activity waste (ILAW) composition comprising of 18 components based on ILAW-Glass 32, 35, and 36. These compositions had high P_2O_5 concentrations ranging between 3.12-3.40 wt%. This glass system is extremely complicated and will rely on previous results of simplified systems from previous chapters to infer the effects of P_2O_5 on the glass system and its properties. The objective of the work described in this chapter is to provide information on P_2O_5 -rich LAW compositions and the potential effects it may have on the structure and subsequent physical, thermal, chemical, and physio-chemical properties, which can then be used to inform current interim databases and models relevant to the Hanford Site.

4.5.2 Experimental Details

The ILAW glasses were based on the SiO_2 - Na_2O - CaO - Al_2O_3 - ZrO_2 - MgO - SO_3 - Fe_2O_3 - SnO_2 - V_2O_5 - Cr_2O_3 - B_2O_3 - Li_2O - $NaCl$ - TiO_2 - NH_4F - K_2O - xP_2O_5 glass system, where $x = 0.00$ and 1.53 mol%. Batches of 130 grammes were prepared utilising the melt-anneal method using the precursors SiO_2 , Na_2CO_3 , $CaCO_3$, $2(Al(OH)_3)$, ZrO_2 , $MgCO_3$, $CaSO_4$, Fe_2O_3 , SnO_2 , V_2O_5 , Cr_2O_3 , $2(H_3BO_3)$, Li_2CO_3 , $NaCl$, TiO_2 , NH_4F , K_2CO_3 , $NH_4H_2PO_4$. The precursors were weighed and transferred to a plastic bag before being milled for 10 seconds in a steel mill to thoroughly mix the contents. The batch was then placed in an alumina crucible and heated in an electric furnace at a rate of $5^\circ C/min$ to $1150^\circ C$, where it was left to dwell for 3 hours before the glass melt was poured into a steel mould and annealed at $500^\circ C$ for 2 hours, before cooling at a rate of $1^\circ C/min$ to $25^\circ C$. The bulk samples were then analysed by Raman spectroscopy, prepped, and mounted in epoxy resin for SEM/EDS analysis, then milled into powders for XRD, XRF, ICP-OES, XAS, and chemical durability testing. Further details on experimental methodology can be read in *Chapter 3: Experimental Methodology*.

4.5.3 Results and Discussion

Note regarding nomenclature: In this chapter concentrations are described in either mol% or wt%. In these results and subsequent discussion, the concentrations will use the nomenclature 'ILAW' where the following number represents the P_2O_5 content in mol% e.g., ILAW1.53 = 1.53 mol% P_2O_5 . The

'ILAW' initials are derived from the name used in PNNL reports, where ILAW means 'Immobilised Low Activity Waste'.

4.5.3.1 Annealed LAW Samples

4.5.3.1.1 Visual observations

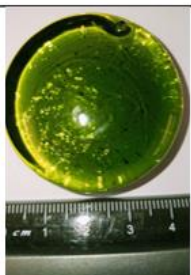
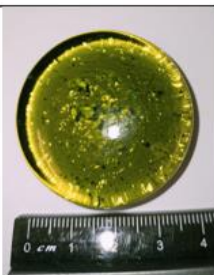
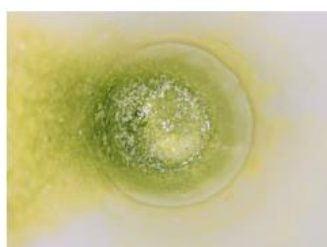
Sample	FS_P0.00	FS_P1.53
Top view of poured glass		
Top view of crucible		
P ₂ O ₅ content (mol%)	0.00	1.53
Comments	The poured glass was very fluid with no evidence of lumps in the sample. However, from inspecting the crucible, there is evidence of white inclusions and some green inclusions left at the bottom of the crucible.	The poured glass was very fluid with evidence of white lumps just under the top surface of the sample. These inclusions poured into the sample when reaching the bottom of the pour. From inspecting the crucible there is evidence of white inclusions and some green inclusions left at the bottom of the crucible and down the side, as previously seen in the ILAW0.00 sample

Figure 131 - Top view images of ILAW0.00 and 1.53 samples

4.5.3.1.2 XRF and ICP-OES

Table 68 and Figure 132 present the ILAW samples analysed by both XRF and ICP-OES. Figure 132 visually shows that there were depleted levels of ZrO₂, SO₃, Fe₂O₃, SnO₂, Li₂O, and P₂O₅ (ILAW1.53) when compared to the nominal compositions. The low ZrO₂ and SnO₂ content may have been due to their presence as unmelted components left in the crucible after pouring, as identified by XRD, as well as the formation of Na₄Zr₂(SiO₄)₃ in the ILAW1.53 sample, which would have also contributed to the reduction in ZrO₂. The low Li₂O content may

have been due to the fact that it was added to the glass melt as lithium carbonate (Li_2CO_3), which has a low melting point (722°C) (Merck, 2021) and is quite volatile (Lu et al., 2021), resulting in the loss of some of the Li_2O during melting. The reduction in SO_3 and P_2O_5 may have been due to their volatilisation during melting (Bell et al., 2020). Further discrepancies in the composition may be attributed to the heat treatment of the glass and subsequent melting time (Xu et al., 2021), the part of the melt from which the glass sample was taken and analysed, and also any uncertainties associated with preparation and analysis by XRF and ICP-OES. The compositions were nominally pro-rat'd for NaCl , TiO_2 , NH_4F , and K_2O , as these could not be measured by the techniques used, meaning that the values of the measured oxides may differ slightly from their nominal values.

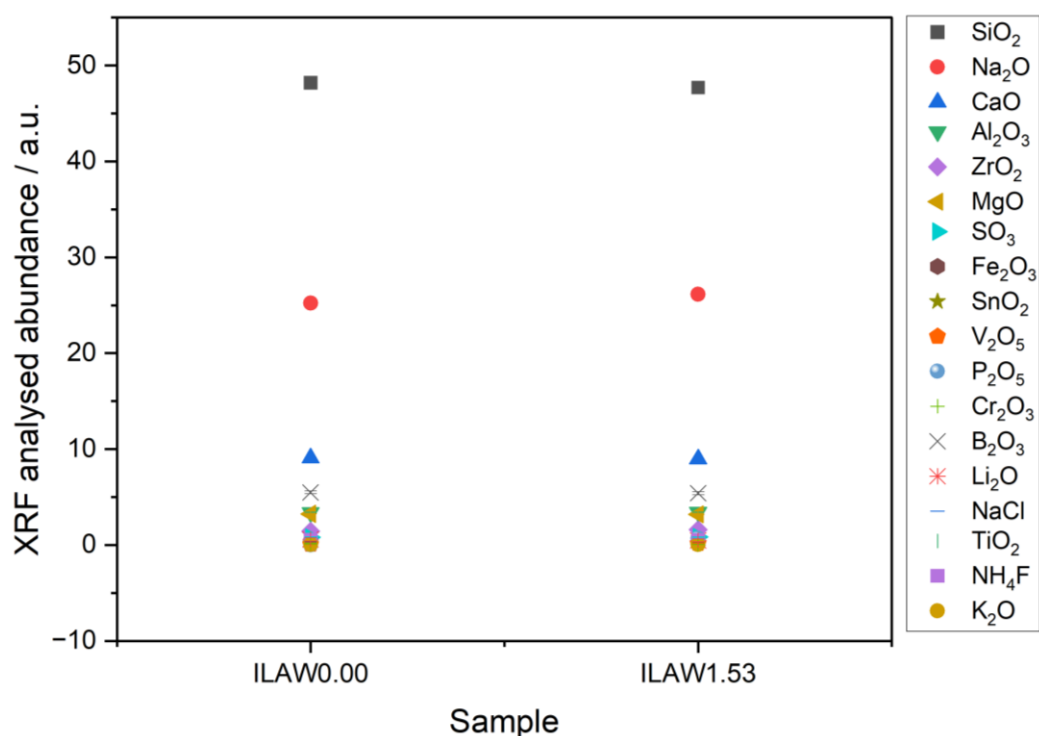


Figure 132 - XRF and ICP-OES analysed composition of ILAW samples with associated error. Error bars that are not shown have errors that are too small to plot

Table 68 - XRF and ICP pro-rat'd analysis of ILAW samples

Sample		Components (mol%)																	
		SiO ₂	Na ₂ O	CaO	Al ₂ O ₃	ZrO ₂	MgO	SO ₃	Fe ₂ O ₃	SnO ₂	V ₂ O ₅	P ₂ O ₅	Cr ₂ O ₃	B₂O₃	Li₂O	NaCl*	TiO ₂ *	NH ₄ F*	K ₂ O*
ILAW0.00	Nominal	45.29	25.48	8.02	4.47	3.72	2.47	1.08	0.61	0.59	0.17	0.00	0.12	5.86	0.89	0.04	0.31	1.10	0.04
		48.19	26.24	9.08	3.40	1.42	3.25	0.80	0.31	0.14	0.06		0.12						
	Analysed	±	±	±	±	±	±	±	±	±	±	0.00	±	5.49	0.57	0.04	0.29	0.54	0.04
		0.01	0.01	0.00	0.01	0.00	0.02	0.03	0.01	0.05	0.04		0.03						
ILAW1.53	Nominal	44.6	25.09	7.9	4.4	3.67	2.43	1.06	0.6	0.58	0.17	1.53	0.12	5.77	0.87	0.04	0.3	1.10	0.04
		47.69	26.14	8.97	3.41	1.61	3.19	0.83	0.29	0.17	0.16	0.71	0.06						
	Analysed	±	±	±	±	±	±	±	±	±	±	±	±	5.39	0.48	0.04	0.29	0.53	0.04
		0.01	0.01	0.00	0.01	0.00	0.02	0.03	0.01	0.04	0.04	0.03	0.03						

Bold italics is for ICP-OES analysed samples, * is for nominal composition, ICP-OES has an error of ±15%

4.5.3.1.3 X-ray Powder Diffraction

4.5.3.1.3.1 Annealed samples

Figure 133 shows the XRD patterns for the ILAW0.00 and 1.53 samples. The samples were both X-ray amorphous with no identifiable Bragg peaks, suggesting that the P_2O_5 solubility had not been exceeded.

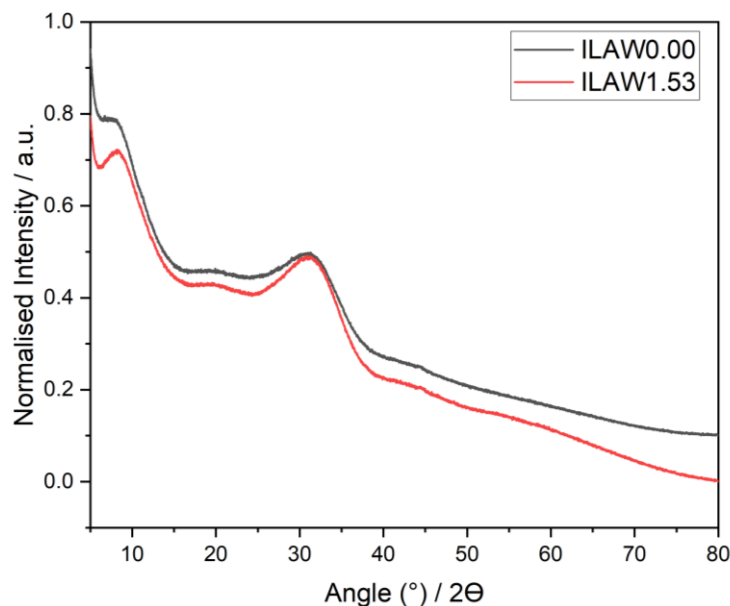


Figure 133 - XRD patterns of ILAW0.00 and 1.53

4.5.3.1.3.1.1 Crucible Material

Figure 134 and Figure 135 show the XRD patterns with identified crystal phases of the settled material at the bottom of the crucibles. The ILAW0.00 crucible melt material was identified to contain alumina (Al_2O_3 , rhombohedral, space group: $R\bar{3}c$, rhombohedral, PDF#: 04-005-4497 (Cherginets et al., 2006)) (Figure 187 and Table 94 in Appendix 8.25), tin oxide (SnO_2 , tetragonal, space group: $P4_2/mnm$, PDF#: 00-041-3855 (Werner, 1956)) (Figure 188 and Table 94 in Appendix 8.25), and zirconia (ZrO_2 , monoclinic, space group: $P2_1/c$, PDF#: 01-086-1451 (Gualtieri et al., 1996)) (Figure 189 and Table 94 in Appendix 8.25). The ILAW1.53 crucible melt material was identified to also contain Al_2O_3 , SnO_2 , ZrO_2 , but also sodium zirconium silicate ($Na_4Zr_2(SiO_4)_3$, rhombohedral, space group: $R\bar{3}cH$, PDF#: 04-010-3835 (Kohler et al., 1983)) (Figure 190 and Table 94 in Appendix 8.25). The presence of Al_2O_3 , SnO_2 , and ZrO_2 suggest that these were unmelted raw materials, whilst the $Na_4Zr_2(SiO_4)_3$ was a precipitated crystal phase. Gervasio et al. (2018) reported that some LAW formulations rich in combined Al_2O_3 , SnO_2 , and ZrO_2 are prone to the precipitation of baddeleyite (ZrO_2) and cassiterite

(SnO_2), which may affect processing and/or reduce melter life. However, the ILAW compositions in this report have Al_2O_3 , P_2O_5 , SnO_2 , ZrO_2 contents that were below or the same as the maximum constraint reported by Gervasio et al. (2018). There was also a distinct reduction in the normalised intensity of the Bragg peaks associated with the crystalline phases identified in ILAW1.53 when compared to ILAW0.00, suggesting that the presence of P_2O_5 may be increasing the solubility of SnO_2 and ZrO_2 in the glass.

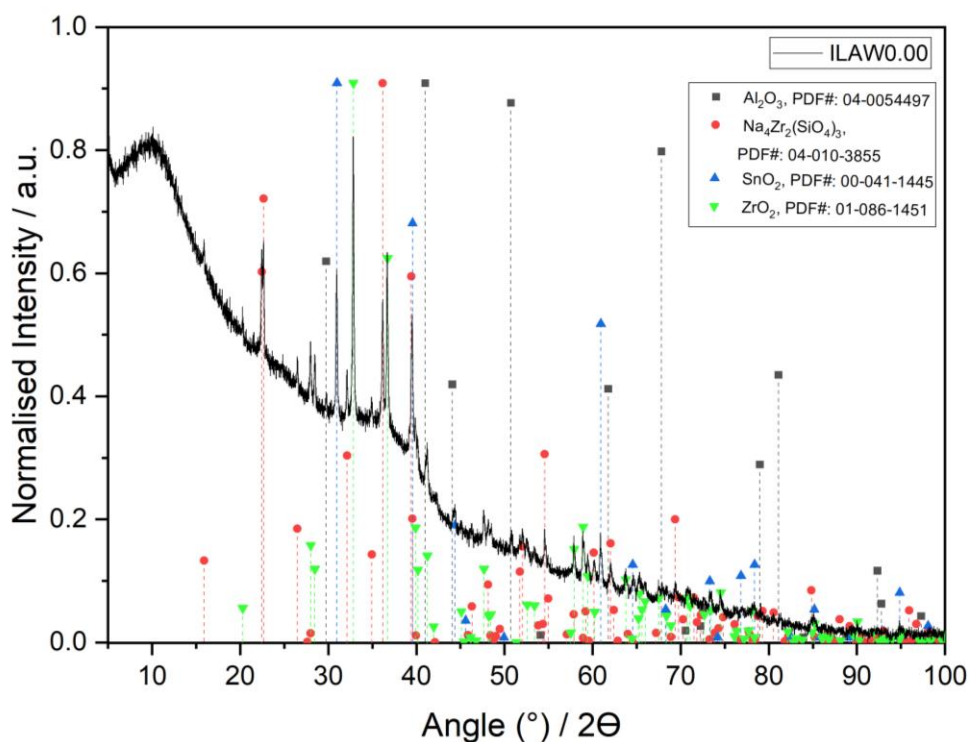


Figure 134 - XRD pattern of settled material in the ILAW0.00 crucible with identified crystal phases

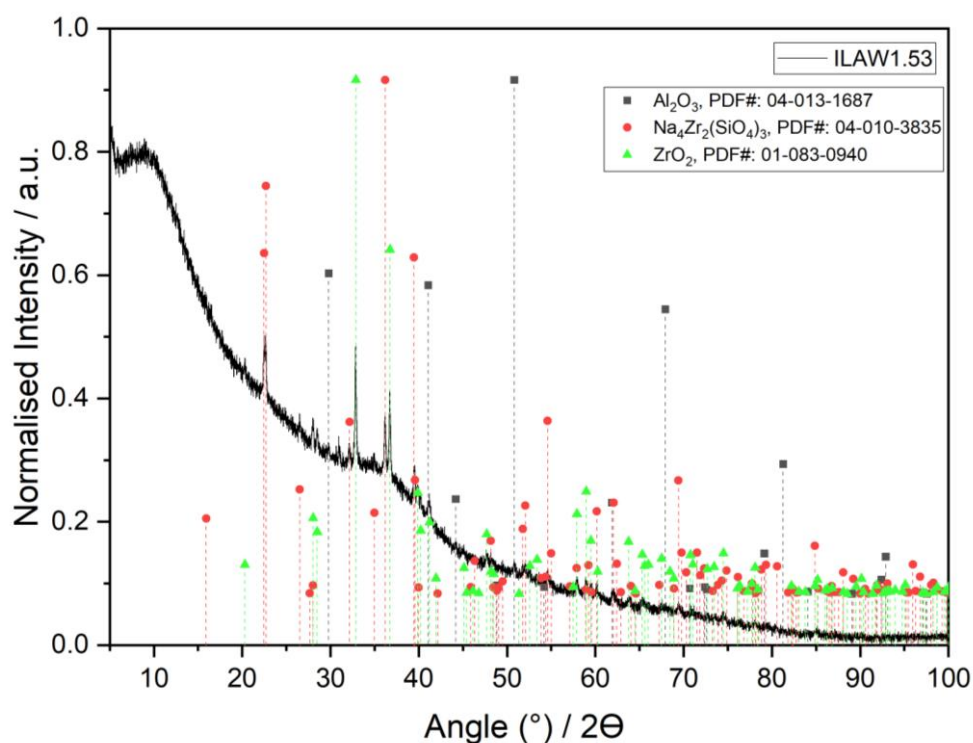


Figure 135 - XRD pattern of settled material in the ILAW1.53 crucible with identified crystal phases

4.5.3.1.4 Bulk Density, Molar Volume and Thermal parameters

4.5.3.1.4.1 Bulk density and Molar volume

The bulk density of the ILAW0.00 sample was 2.676 ± 0.022 g/cm³ and molar volume was 24.494 cm³/mol, whilst ILAW1.53 had a density value of 2.653 ± 0.013 g/cm³ and molar volume 25.157 cm³/mol (Table 69). The decrease in density but increase in molar volume with increasing P₂O₅ content, suggests the glass structure may have become less compact (Sułowska et al., 2021).

4.5.3.1.4.2 Thermal Parameters Measured by Dilatometry

Table 69 states the dilatometric thermal parameters (T_g , T_d , and CTE) for the ILAW0.00 and 1.53 samples. The T_g onset of the 0.00 mol% P₂O₅ sample was 441°C and stayed the same within error upon the introduction of 1.53 mol% P₂O₅. The T_g midpoint and T_d values were also the same within error, where the T_g midpoints were 468 and $469 \pm 5^\circ\text{C}$, respectively, and the T_d values were 490 and $495 \pm 5^\circ\text{C}$, respectively. The CTE increased slightly from 15.5605×10^{-6} to $15.6693 \times 10^{-6} \pm 2 \times 10^{-7}$ K⁻¹. The distinct lack of change in these thermal parameters with the introduction of P₂O₅ suggests that the glass network is neither re-polymerising or de-polymerising, however, the slight increase in CTE

suggests that perhaps there is an increase in asymmetrical units in the glass structure, which may be indicative of the network de-polymerising (Klyuev, 2005).

Sample	Bulk Density (g/cm ³)	STD EV (1 σ)	V _{mol} (cm ³ /mol)	T _g Onset $\pm 5^\circ\text{C}$	T _g midpoint $\pm 5^\circ\text{C}$	T _d $\pm 5^\circ\text{C}$	CTE ± 2 $\times 10^{-7} (\text{K}^{-1})$
ILAW0.00	2.676	0.022	24.494	441	468	490	15.5605 $\times 10^{-6}$
ILAW1.53	2.653	0.013	25.157	443	469	495	15.6693 $\times 10^{-6}$

Table 69 - Bulk density, molar volume, and thermal parameters by dilatometry of ILAW samples

4.5.3.1.4.3 Thermal Parameters Measured by DTA

Figure 136 shows the DTA traces for the ILAW0.00 and 1.53 samples, where the thermal parameters have been recorded in Table 70. The T_g onset and midpoint of the ILAW0.00 sample were $455 \pm 2^\circ\text{C}$ and $464 \pm 2^\circ\text{C}$, respectively, whilst ILAW1.53 had values of $457 \pm 2^\circ\text{C}$ and $462 \pm 2^\circ\text{C}$, respectively. The T_x values for ILAW0.00 and 1.53 were $648 \pm 2^\circ\text{C}$ and $655 \pm 2^\circ\text{C}$, respectively. The T_c and T_m values for ILAW0.00 were $690 \pm 2^\circ\text{C}$ and $855 \pm 2^\circ\text{C}$, whilst the values for ILAW1.53 were $712 \pm 2^\circ\text{C}$ and $850 \pm 2^\circ\text{C}$. There is no notable difference between the T_g onset and midpoint with increasing P₂O₅ content, however, there is an increase in the T_x and T_c but a decrease in the T_m. The increase in the T_x and T_c is expected due to the additions of P₂O₅, where it is a nucleating agent that promotes crystallisation, however its role depends on the glass composition. If P₂O₅ is acting as a glass structure stabiliser due to the formation of P-O-Al complexes, then this “*prevents the formation of heterogeneities and inhibits crystallisation*” (Ariane et al., 2020).

The glass formability parameters i.e., T_{rg} was 0.53 a.u. for ILAW0.00 and 0.54 a.u. for ILAW1.53, K_H was 0.93 a.u. for ILAW0.00 and 1.02 a.u. for ILAW1.53, and K_W was 0.27 a.u. for ILAW0.00 and 0.30 a.u. for ILAW1.53. As mentioned in previous chapters, the T_{rg} provides information on the forming ability of a glass, the K_H is a stability factor (Fouad et al., 2021) and takes into account the ease of melting (Kozmidis-Petrovic & Šesták, 2012), and K_W is a similar parameter to K_H and can be used in conjunction with or used separately. The T_{rg} values for ILAW0.00 and 1.53 were both below 0.66, suggesting that the samples formed

glasses and that they had a degree of resistance to crystallisation and may exhibit homogeneous nucleation due to the $T_{rg} < 0.58-0.60$ (Zanotto, 1987). The K_H value increased by 0.09 with the addition of P_2O_5 , where the values suggested that both samples exhibited good thermal stability because $K_H \geq 0.4$ (Farid et al., 2016). The K_W values mirrored the K_H values where there was a decrease in the value with the addition of P_2O_5 . The P_2O_5 doped glass was the most thermally stable glass according to the K_W and K_H parameters.

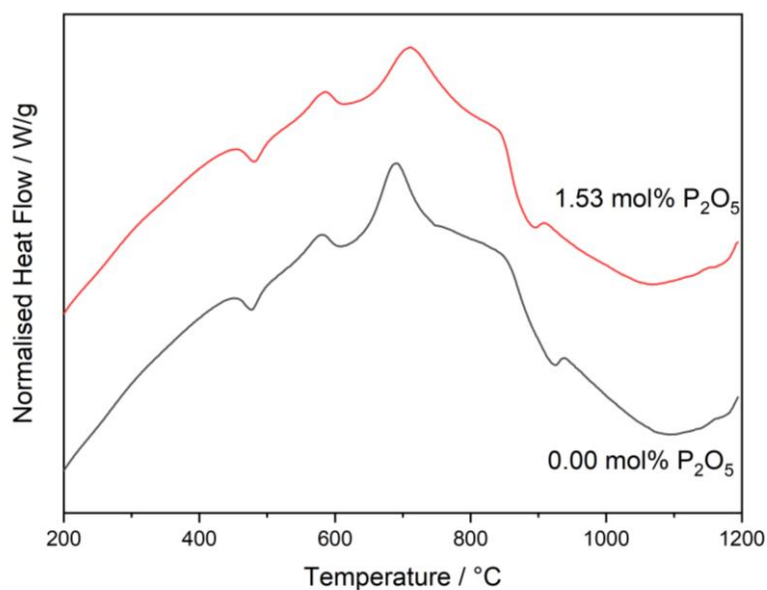


Figure 136-DTA traces of ILAW samples

Sample	T_g onset $\pm 2^\circ\text{C}$	T_g midpoint $\pm 2^\circ\text{C}$	T_x $\pm 2^\circ\text{C}$	T_c $\pm 2^\circ\text{C}$	T_m $\pm 2^\circ\text{C}$	T_{rg}	K_H	K_W
0.00	455	464	648	690	855	0.53	0.93	0.27
1.53	457	462	655	712	850	0.54	1.02	0.30

Table 70 - DTA thermal parameters for ILAW0.00 and 1.53

4.5.3.1.5 Raman Spectroscopy

Figure 137 and Figure 138 show the Raman spectra of ILAW0.00 and 1.53 samples. The spectra cannot be deconvoluted due to the sheer number of components and overlapping contributions from said components. However, it can be qualitatively evaluated where the spectra can be divided into three main regions: low, medium, and high frequency. The low frequency region ranges between $200-800\text{ cm}^{-1}$ where both spectra present peaks centred at ~ 573 and 630 cm^{-1} . In the mid-frequency region ranging between $800-1200\text{ cm}^{-1}$, the

ILAW0.00 displays peaks centred at ~ 855 , 991 , and 1040 cm^{-1} , whilst the ILAW1.53 spectra presents the same peaks with an additional peak centred at $\sim 944\text{ cm}^{-1}$ upon the introduction of $1.53\text{ mol\% P}_2\text{O}_5$. In the high frequency region, both spectra have a broad peak and a narrow sharp peak centred at ~ 1434 and 1556 cm^{-1} , respectively. When $1.53\text{ mol\% P}_2\text{O}_5$ was added to the base glass the relative intensity of the identified peaks reduced. By integrating the area under the spectra between $\sim 1300\text{--}1500\text{ cm}^{-1}$ it can provide an indication of the changes associated with BO_3 tetrahedra, where an increase may suggest the glass network is de-polymerising. The ILAW0.00 sample had an integrated area of $\sim 895\text{ a.u.}$, whilst ILAW1.53 had a value of $\sim 1609\text{ a.u.}$, suggesting that the increase in the relative area with the addition of P_2O_5 is de-polymerising the B sub-network. This change was also accompanied by the formation of a peak at $\sim 944\text{ cm}^{-1}$, which is located in the lower Q^n species region.

The peak at 573 cm^{-1} can be associated with symmetrical stretching and partial deformation vibrations of Si-O-Si bridges (Koroleva et al., 2011; McKeown et al., 2000), the symmetric stretching in Si-O-Al bonds (Lu et al., 2021), or the symmetric stretching of Al-O-Al bonds from $[\text{AlO}_4]$ (Hyun et al., 2022). The peak at 630 cm^{-1} can be attributed to the breathing mode of B-O-Si(B) bonds from reedmergnerite- and danburite-like rings that consist of $[\text{SiO}_2]$ and $[\text{BO}_4]$ tetrahedra in a mixed borosilicate phase or the bending of ring-type metaborate groups, composed mainly from boron triangles (Hayward, 1993; Wang & Cheng, 2016; Yadav & Singh, 2015). The peak at 944 cm^{-1} that is present in the $1.53\text{ mol\% P}_2\text{O}_5$ doped sample may be ascribed to PO_2 symmetric stretching of NBØs, in Q^0 units (Yadav & Singh, 2015). The peak at 991 cm^{-1} can be associated with asymmetric stretching mode of Q^1 units and/or with a small amount of Q^0 species in which P is bonded via O to four Al atoms, AlPO_4 (Logrado et al., 2022), S-O symmetric stretching modes within the sulphate tetrahedra (Brendebach et al., 2009; Lenoir et al., 2010; Lonergan et al., 2020; Saini et al., 2022), as well as PO_4^{3-} units (Cheng, 2014). The band at 1040 cm^{-1} may be ascribed generally to Q^3 tetrahedral units, where the addition of P_2O_5 contributes PO_3 symmetric stretching modes of NBØ on Q^1 tetrahedra (Ma et al., 2014; Zhang & Brow, 2011). The broad band centred at 1434 cm^{-1} contains contributions from B-O stretching vibrations linked to ^{13}B units (Möncke et al., 2015), where deconvolution of the peaks, according to literature, provides Gaussian components at $\sim 1320\text{ cm}^{-1}$ for loose ^{13}B units, 1410 cm^{-1} for ^{13}B units

linked to $^{[4]}\text{B}$ units, 1480 cm^{-1} for $^{[3]}\text{B}$ units linked to $^{[3]}\text{B}$ units, and 1515 cm^{-1} for $^{[3]}\text{B}$ units linked to boroxol rings (Bisbrouck et al., 2021; Möncke et al., 2015; Seshadri et al., 2020). Therefore, the intensity at 1427 cm^{-1} could be attributed to $^{[3]}\text{B}$ units linked to $^{[4]}\text{B}$ units.

Since the P_2O_5 doped sample is below the solubility limit for this glass composition, as evidenced by a lack of measurable crystallinity by XRD, previous studies of simpler glass systems may provide an indication on the structural effects of P_2O_5 . ^{31}P MAS NMR study of the simplified sodium borosilicate glass in chapter 4.1.3.8, suggested that P_2O_5 enters the glass system as Q^3 , but then changes to Q^0 , Q^1 and Q^2 units, where it is initially charge balanced by the silicate network. However, the ILAW glass system has a mixture of glass modifiers that could be acting as charge compensators (Na, Ca, and Li). Although, there is an abundance of Na_2O compared to CaO and Li_2O when reviewing the analysed composition (Table 68).

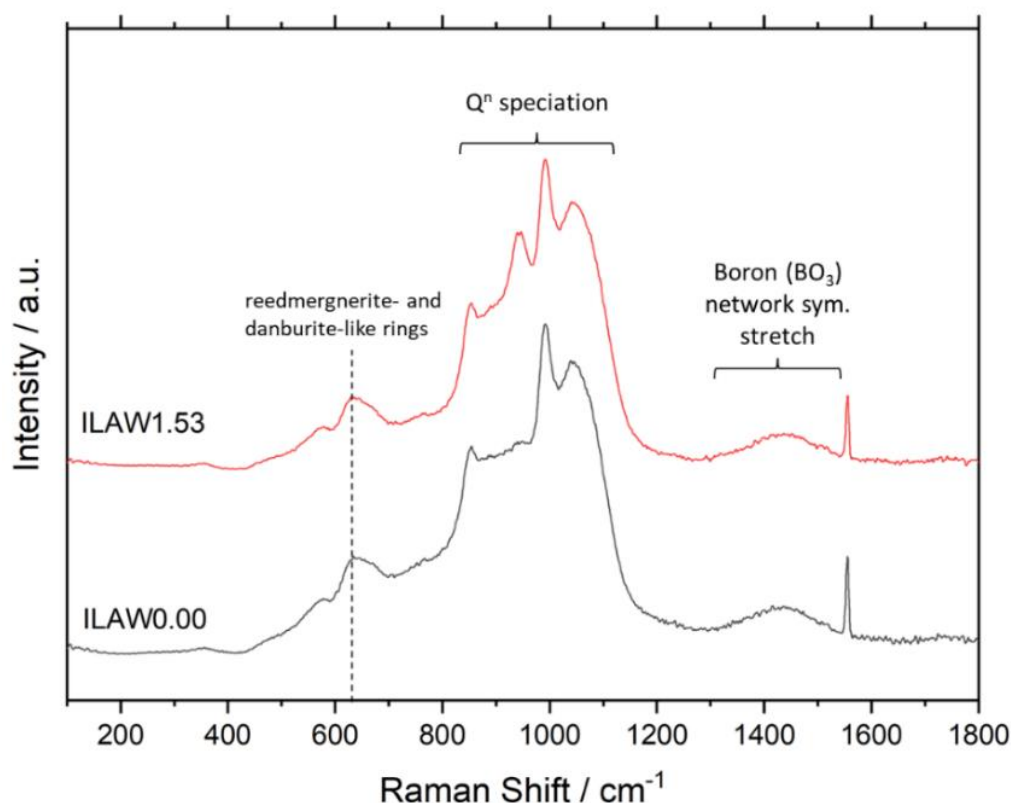


Figure 137 - Raman spectra of ILAW0.00 and 1.53

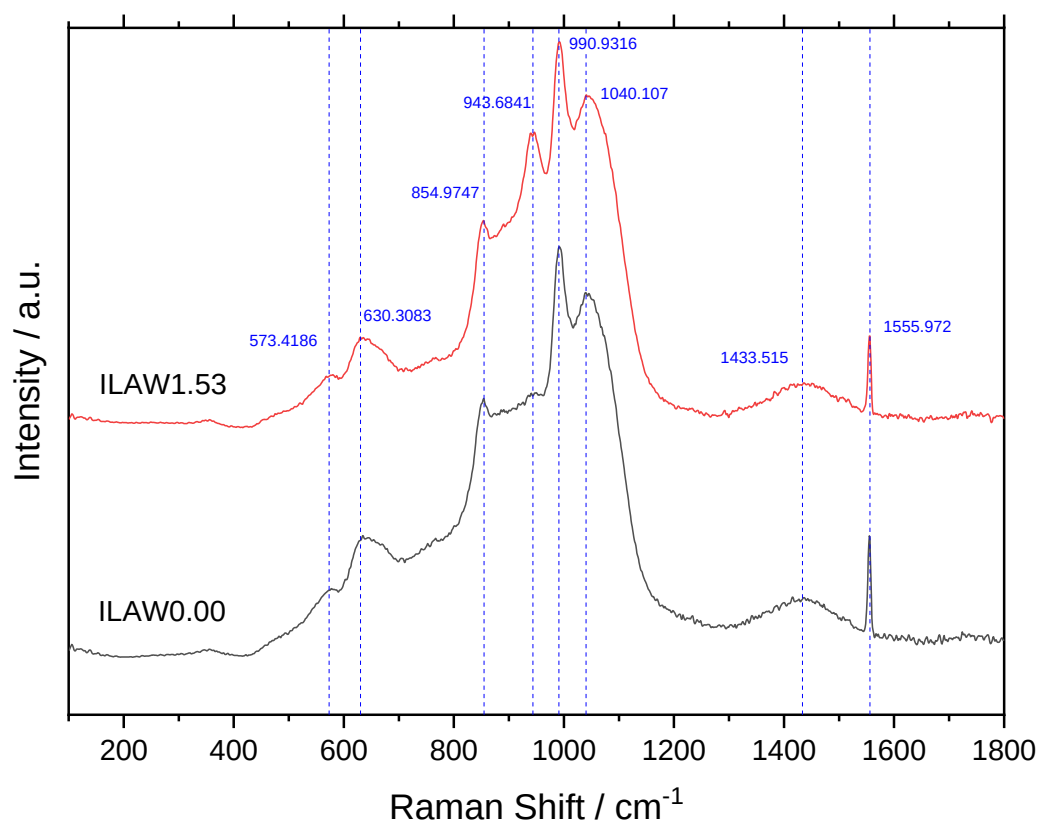


Figure 138 - Raman spectra of ILAW0.00 and 1.53 with assigned peaks

Frequency (cm ⁻¹)	Assignment	Reference
630	Breathing mode of B-O-Si(B) bonds from reedmergnerite- and danburite-like rings that consist of [SiO ₂] and [BO ₄] tetrahedra	(Hayward, 1993; Wang & Cheng, 2016; Yadav & Singh, 2015).
944	PO ₂ symmetric stretching of non-bridging oxygen, in Q ⁰ units	(Yadav & Singh, 2015)
	P-O-P asymmetric stretch	(Ma et al., 2014; Zhang & Brow, 2011)
991	Asymmetric stretching mode of Q ¹ units or a small amount of Q ⁰ species in which P is bonded via oxygen to four aluminium atoms, AlPO ₄	(Logrado et al., 2022)
	S-O symmetric stretching modes within the sulphate tetrahedra	(Brendebach et al., 2009; Lenoir et al., 2010; Lonergan et

	PO ₄ ³⁻ units	al., 2020; Saini et al., 2022) (Cheng, 2014)
1040	Stretching of Q ³ units PO ₃ symmetric stretching modes of NBØ on Q ¹ tetrahedra	(Ma et al., 2014; Zhang & Brow, 2011)
1434	BO ₃ units linked to BO ₄ units	(Bisbrouck et al., 2021; Möncke et al., 2015; Seshadri et al., 2020b).
1556	B–O stretching modes involving with one NBØ of [BO ₃] triangles and molecular oxygen stretching vibration modes	(Yadav & Singh, 2015)

Table 71 - Referenced Raman band assignments for ILAW0.00 and 1.53

4.5.3.2 Fe K-edge XANES

XANES spectra were corrected and normalised using the ATHENA work package (Ravel & Newville, 2005). Figure 139 shows the Fe K-edge XANES data for the ILAW0.00 and 1.53 samples. The Fe oxidation state was estimated from the energy of the absorption edge (E_0) and interpolating between the energies measured for a set of reference samples. The intensity and position of the pre-edge region provides information on the Fe oxidation state and coordination environment, where the area under the pre-edge is dependent on the site symmetry (Joseph et al., 2017). The fitting of the pre-edge feature and reference compounds were performed in the energy range 7107-7120 eV, in accordance to the methodology proposed by Wilke et al. (2001). Gaussian components were fitted to the pre-edge feature using a least squares minimalization routine in Excel, where the total area under the pre-edge feature was obtained from the summing of the integrated intensity under each pre-edge feature (Table 72) (Joseph et al., 2017). These values were then plotted in a variogram (Figure 140) and compared to data reported by Wilke et al. (2001). The centroid positions suggested that the oxidation state of the Fe in the LAW samples was Fe³⁺. The area under the pre-edge indicated that the Fe had an average coordination number between four- and six-fold. The data could not be compared to

Mössbauer spectroscopy to help validate these results, because the Fe content was too low to conduct room temperature Mössbauer, and low temperature Mössbauer was not available at the time. The ILAW0.00 sample had a centroid position value of 7113.70 eV, which is indicative of Fe being Fe³⁺. The ILAW1.53 sample had a centroid position value of 7113.61 eV, which is also indicative of Fe being Fe³⁺, however, its position on the variogram (Figure 140) sees it overlap with a reference material provided by Wilke et al (2001), suggesting that the Fe was Fe³⁺ in tetrahedral coordination. The addition of P₂O₅ to the glass system does not seem to have affected the Fe oxidation and coordination, in accordance with Fe XANES, suggesting that the Fe had the role of a glass former in both samples. The pre-edge fitting line shapes are available in the Appendix (8.27).

Sample	Gaussian energy (eV)	Intensity (a.u.)	Integrated intensity (a.u.)	Centroid position (eV)	Margin of error
ILAW0	7113.30	0.09	0.25	7113.70	5.69 x 10 ⁻⁴
	7113.94	0.159			
ILAW1.53	7113.80	0.241	0.27	7113.61	5.69 x 10 ⁻⁴
	7111.99	0.030			

Table 72 - Pre-edge parameters for ILAW samples obtained from Fe K-edge XANES

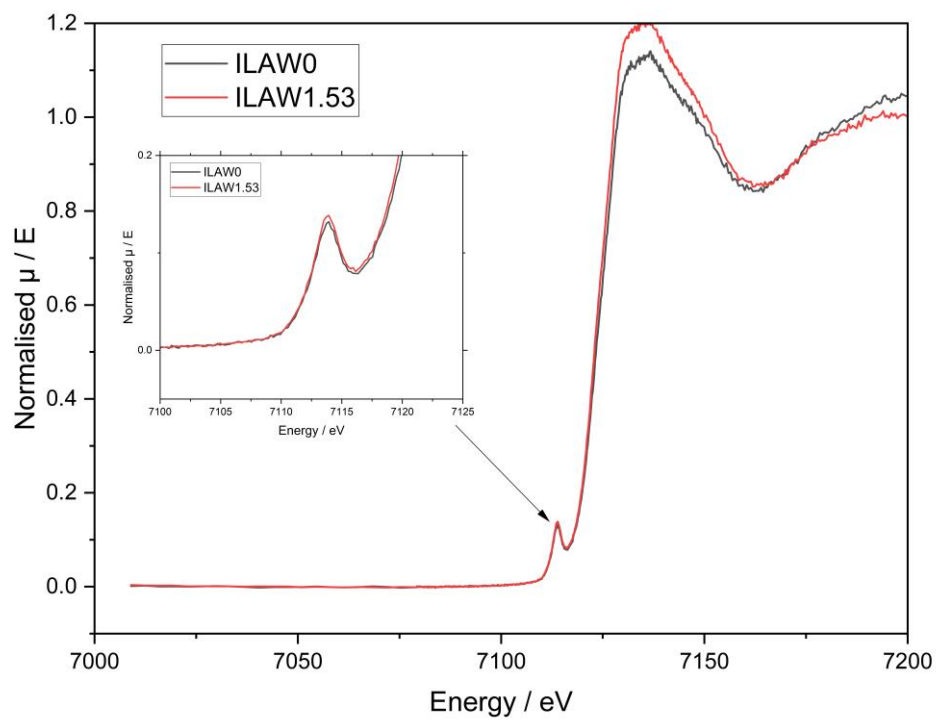


Figure 139 - Fe K-edge XANES of ILAW0.00 and 1.53 samples

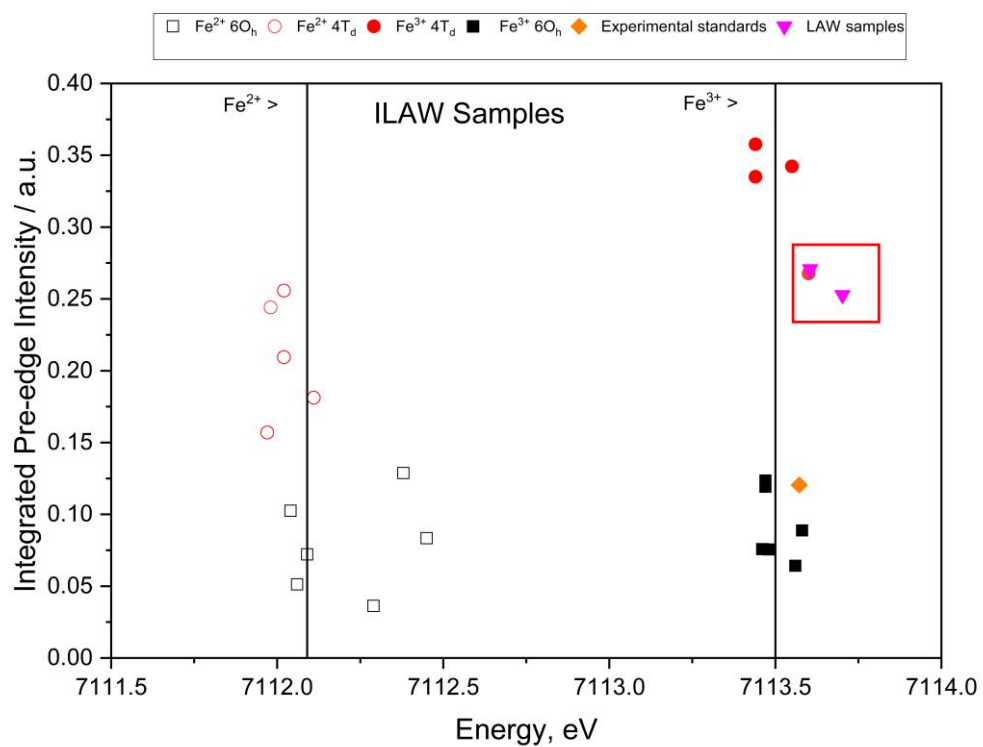


Figure 140 - Variogram showing ILAW samples and experimental standards with Wilke et al. (2001) Fe reference data

4.5.3.3 CCC Heat Treated ILAW Samples

4.5.3.3.1 Visual and Optical Observations

Figure 141 shows the top view of CCC ILAW0.00 and 1.53, where Figure 142 is a closer image of the topological crystalline feature from the ILAW1.53 sample. The heat-treated samples maintain their lime green colour, appearing amorphous, except for the white splotches on the surface of the ILAW1.53 sample, which appear to be crystalline, and were confirmed by XRD. Due to restrictions in time and equipment, SEM analysis was not conducted.

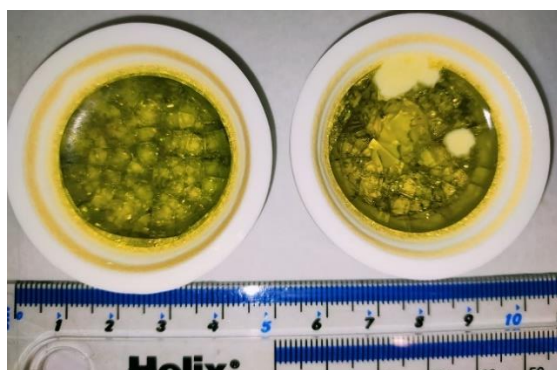


Figure 141 - Top view of CCC heat treated ILAW0.00 (left) and 1.53 (right) samples



Figure 142 - Closer view of crystalline phase in CCC ILAW1.53 sample

4.5.3.3.2 X-ray Powder Diffraction and Rietveld Analysis

Figure 143 depicts the XRD patterns for the CCC heat-treated ILAW0.00 and 1.53 samples. The ILAW0.00 sample showed characteristic Si peaks (used as a reference) and some unidentifiable Bragg peaks between $25-30^{\circ}2\theta$, where Rietveld analysis concluded this sample was 100.00 wt% amorphous. Figure 144 shows the CCC ILAW1.35 XRD pattern with the identified crystalline phases of sodium calcium silicate ($\text{Na}_{5.27}\text{Ca}_3(\text{Si}_6\text{O}_{18})$; PDF#: 01-078-1650, rhombohedral, space group: R-3m, density: 2.8351 g/cm^3 (Fischer & Tillmanns, 1987)) (Figure 194 and Table 95 in Appendix 8.28), and sodium sulphide aluminium silicate sulphate ($\text{Na}_{7.7}((\text{Al}_{5.1}\text{Si}_{6.9})\text{O}_{24})(\text{SO}_4)_{0.88}(\text{S}_3)_{0.76}$; PDF#: 01-076-8976, cubic, space group: P23, density: 2.3203 g/cm^3 (Climent-Pascual et al., 2008)) (Figure 195 and Table 95 in Appendix 8.28). The CCC ILAW1.53 sample was 90.74 wt% amorphous, with 7.28 wt% $\text{Na}_{5.27}\text{Ca}_3(\text{Si}_6\text{O}_{18})$, and 1.98 wt% $\text{Na}_{7.7}((\text{Al}_{5.1}\text{Si}_{6.9})\text{O}_{24})(\text{SO}_4)_{0.88}(\text{S}_3)_{0.76}$. This crystallisation behaviour implies that as the P_2O_5 content increased, susceptibility for the samples to crystallise increased with the CCC heating regime, to the point where additions of 1.53 mol% P_2O_5 resulted in a

partially crystalline sample. The total volume % of crystals in the ILAW1.53 sample was 4.80 vol%. The presence of Na-Ca silicate and Na-Al silicate alternative crystal phases in the ILAW1.53 sample may negatively affect the chemical durability of the residual glass, due to the removal of Si, Al, S, and Na. The constraints for these crystal phases is tabulated in Table 74 (Lonergan et al., 2021; McCloy et al., 2011). The Na-Al silicate alternative constraint was $\text{Al}_2\text{O}_3 = 5.43 > 11.5 \text{ wt\%}$ and the Na-Ca silicate constraint was $\text{CaO} (7.86) \leq 14.36 - 0.272 \cdot (\text{Na}_2\text{O} + 0.66 \cdot \text{K}_2\text{O}) = 7.46$, where both constraints have been fulfilled, suggesting that this composition may be an acceptable waste composition, especially as there is no evidence of a phosphate based crystalline phase, suggesting that the P_2O_5 solubility has not been exceeded.

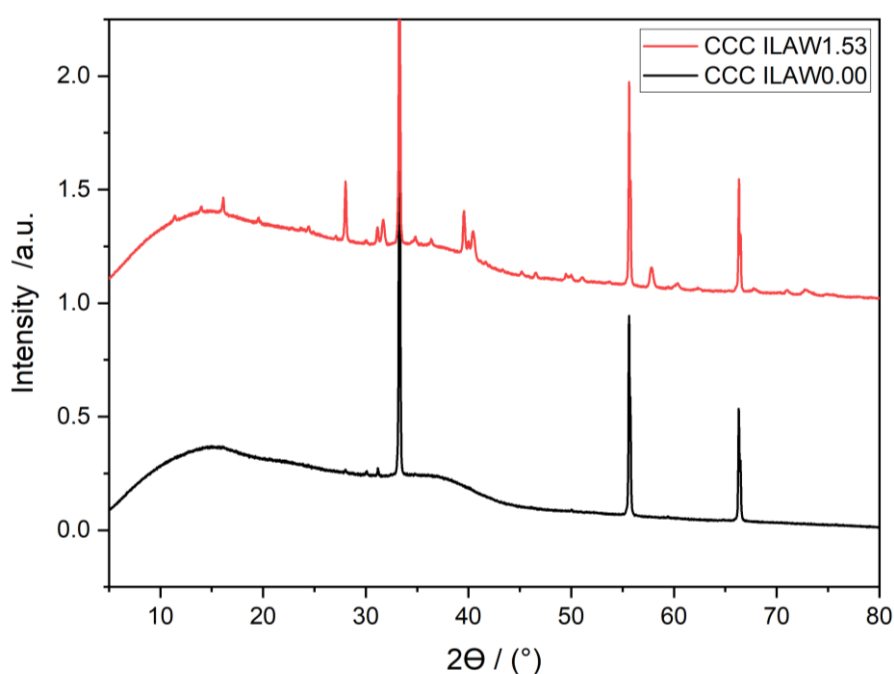


Figure 143 - XRD patterns of CCC ILAW0.00 and ILAW1.53 samples

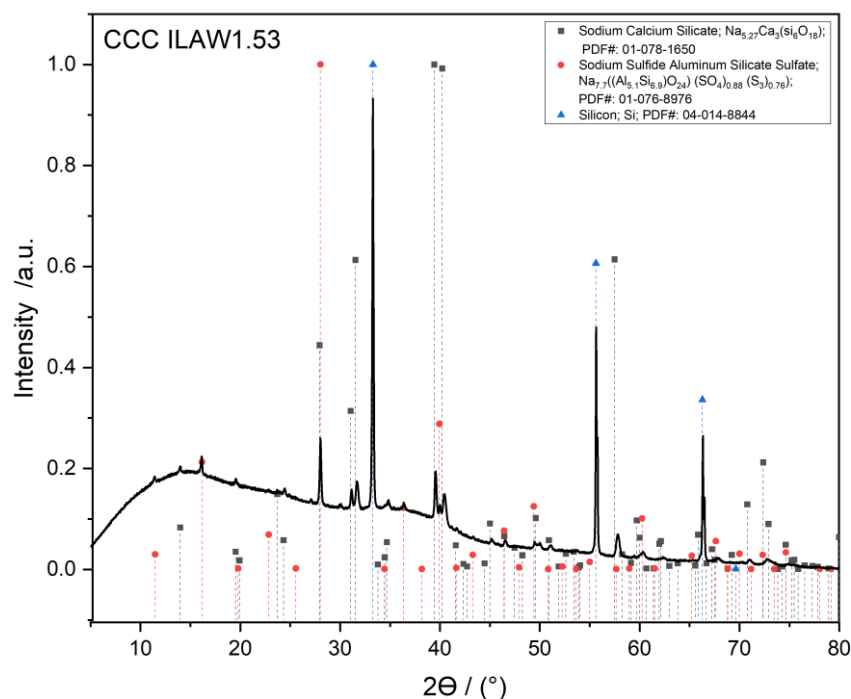


Figure 144 - XRD pattern with identified crystal phases for CCC ILAW1.53

P₂O₅ content	Na_{7.7}((Al_{5.1}Si_{6.9})O₂₄) (SO₄)_{0.88} (S₃)_{0.76}) (wt%)	Na_{5.27}Ca₃(Si₆O₁₈) (wt%)	Amorphous (wt%)	Sum
0.00	0.00	0.00	100.00	100.00
1.53	1.98	7.28	90.74	100.00

Table 73 - Rietveld analysis of CCC ILAW0.00 and 1.53 samples

Constraint	Limit (wt%)
Na-Al silicate	$Al_2O_3 \leq 15.80 - 0.280 \cdot (Na_2O + 0.66 \cdot K_2O)$
Na-Al silicate alternative	$Al_2O_3 \leq 11.5$
Na-Ca silicate	$CaO \leq 14.36 - 0.272 \cdot (Na_2O + 0.66 \cdot K_2O)$
Na-Ca silicate alternative	$CaO \leq 20.84 - 0.528 \cdot (Na_2O + 0.66 \cdot K_2O)$
Nepheline constraint	$N_{Si} = (g_{SiO_2}) / (g_{SiO_2} + g_{Na_2O} + g_{Al_2O_3}) \leq 0.62$ G_i is the mass fraction of the oxide in the glass

Table 74 - Na-Al and Na-Ca silicate constraints

4.5.3.4 Chemical Durability

The glasses in this series, underwent a 7-day PCT-B test at 90°C using ultra high-quality DI water to evaluate the effects of increasing the P₂O₅ content on the initial dissolution behaviour (the degree of leaching), where analysed results can be used to inform the first stage (interdiffusion), and potentially the second stage

(initial rate) of glass corrosion. However, results were only collected on the 7th day due to limited materials and time, meaning only a minimum initial rate could be postulated, where some samples may have already experienced the rate drop, and where an accurate initial rate cannot be calculated from one value.

The normalised mass loss (NL_x) of the pristine ILAW samples and CCC heat treated ILAW samples are recorded in Table 75 and shown in Figure 145. The NL_{Na} of the pristine base glass (ILAW0.00) had a value of $3.686 \pm 0.061 \text{ g/m}^2$, whilst the addition of 1.53 mol% P_2O_5 saw this value increase to $3.825 \pm 0.043 \text{ g/m}^2$. When ILAW0.00 underwent the CCC heat treatment the NL_{Na} reduced to $2.266 \pm 0.003 \text{ g/m}^2$. When ILAW1.53 was heat treated, the NL_{Na} mass loss increased to $4.817 \pm 0.425 \text{ g/m}^2$. The mass loss data suggested that the CCC ILAW1.53 sample experienced the largest mass loss over the 7-day period. In most durability studies of borosilicate glasses, B is selected as the glass alteration tracer because it is highly soluble and not incorporated in the alteration products (Piovesan et al., 2018). The NL_B data (Table 75 and Figure 145) showed that CCC ILAW1.53 had the highest total mass loss with a value of $3.926 \pm 0.349 \text{ g/m}^2$, followed by ILAW1.53, ILAW0.00, and CCC ILAW0.00. Hence, the data suggests that ILAW0.00 was the most chemically durable. The NL_{Si} data showed that ILAW1.53 had the highest value of $1.271 \pm 0.014 \text{ g/m}^2$ followed by CCC ILAW1.53, ILAW0, and CCC ILAW0.00. The NL_P data showed that ILAW1.53 had the highest mass loss of $1.553 \pm 0.071 \text{ g/m}^2$ compared to CCC ILAW1.53 of $0.533 \pm 0.005 \text{ g/m}^2$. The higher normalised mass loss data of Na in comparison to Si, suggested that it was being preferentially released. This preferential release of Na is the result of the ion-exchange reaction mechanism where hydronium ions are dissolving in the glass structure (Stone-Weiss et al., 2018).

The observed pH values (Table 75) indicated that all the leachate solutions were very basic ($> \text{pH } 11$), where this could be attributed to the release of Li, Na, K, and Ca ions into the solution during the course of the dissolution test. However, there were also contributions from other species in the glass i.e., Al, Fe, Ca, Cl, Cr, V, Sn, and S that could affect the pH of the solutions (Appendix 8.29). The pH decreased between the pristine ILAW0.00 and ILAW1.53 samples from 12.35 ± 0.07 to 12.27 ± 0.06 , respectively. When the pristine base glass underwent CCC heat treatment the value decreased to 12.15 ± 0.01 . The pH of the pristine ILAW1.53 sample increased from 12.27 ± 0.06 to 12.36 ± 0.08 . The decrease in

the pH between the pristine and heat treated ILAW0.00 samples was accompanied by a decrease in the normalised mass loss of Na, whereas the increase in pH between the pristine and heat treated P₂O₅ doped samples was instead accompanied by an increase in the normalised release rate of Na. The increase in pH is due to the formation of strong alkali hydroxides that offset weak boric acid in the leachate solution as the glasses dissolve (Bengisu et al., 2006).

The current PCT specification for Hanford LAW glasses for the normalised release rate of Na, B, and Si should be <2 g/m² using the 7-day PCT test at 90°C (Kim et al., 2003; Lu et al., 2021). When the ILAW samples were compared to this parameter, ILAW0.00 and CCC ILAW0.00 were <2 g/m², whereas ILAW1.53 and CCC ILAW1.53 were >2 g/m², meaning that they may not be wholly appropriate to vitrify LAW wastes rich in P₂O₅.

Sample	Normalised Mass Loss (g/m ²)								pH	1σ
	NL _B	1σ	NL _{Si}	1σ	NL _{Na}	1σ	NL _P	1σ		
ILAW0.00	1.809	0.049	0.946	0.024	3.686	0.061	-	-	12.35	0.07
ILAW1.53	2.913	0.016	1.271	0.014	3.825	0.043	1.553	0.071	12.27	0.06
CCC ILAW0.00	1.456	0.014	0.799	0.004	2.266	0.003	-	-	12.15	0.01
CCC ILAW1.53	3.926	0.349	1.109	0.096	4.817	0.425	0.533	0.009	12.36	0.08

Table 75 - Average Normalised elemental mass loss (g/m²) & pH where the calculated error is one standard deviation

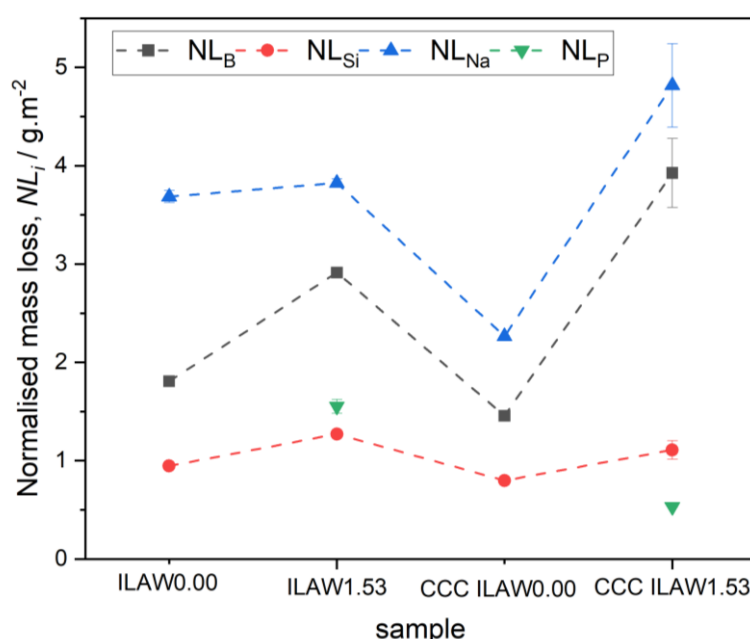


Figure 145 - Normalised mass loss (g/m²) for structural elements and modifiers for a 7-day dissolution test in pure water at 90°C

4.5.3.4.1 Comparison of this study's mass loss data against literature

Smith et al. (2000) studied US Hanford Site LAW pre-treated glasses AW-101 and AN-107, where this study's ILAW PCT parameters and subsequent mass loss data are available in Appendix 8.23. Both the AW-101 and AN-107 simulant glasses normalised Na, Si, and B release rates were $<1 \text{ g/m}^2$, which is considered an indication of a durable glass. The final leachate solution pH range for AW-101 was 9.08-9.17, whilst AN-107 was 9.00-9.04. When compared to the ILAW glasses, the pH values were lower.

Schulz et al. (2002) reported on the chemical durability of LAW glasses, where 55 glasses were tested using the PCT-B method to identify the impact of composition on the long-term corrosion behaviour, in order to develop and improve the acceptable compositional range of Hanford LAW glasses. The PCT normalised mass loss releases at 7 days for HLP-01, HLP-25, HLP-26, and HLP-43 ranged between $\sim 0.68\text{-}0.80 \text{ g/m}^2$ for B, $\sim 0.41\text{-}0.50 \text{ g/m}^2$ for Na, and $\sim 0.15\text{-}0.21 \text{ g/m}^2$ for Si.

The study by Thorpe et al. (2017) has also been previously discussed in Chapter 8.23. Thorpe et al. (2017) reported that LAW A44 > LAW A23 > ORP LB2. When this study's ILAW samples were compared to values reported by Thorpe et al. (2017) the pH values were both basic. Thorpe's values ranged between 0.398 ± 0.005 - 0.987 ± 0.047 (NL_B), 0.213 ± 0.009 - 0.389 ± 0.034 (NL_{Na}), and 0.814 ± 0.032 - 1.778 ± 0.017 (NL_{Si}) g/m^2 .

When the normalised mass loss data of the ILAW samples were compared to those reported by Smith et al. (2000), Schulz et al. (2002), and Thorpe et al. (2017), the NL_B , NL_{Si} , and NL_{Na} values were much higher, where the ILAW samples had values ranging between 1.456 ± 0.049 - 3.926 ± 0.349 (NL_B), 2.266 ± 0.003 - 4.817 ± 0.425 (NL_{Na}), and 0.799 ± 0.004 - 1.271 ± 0.014 (NL_{Si}) g/m^2 , suggesting the samples were less durable.

However, the differences in the values may be due to the different PCT-B parameters used (S/V, container material, test duration) and the glass compositions (components and concentration) of the samples. The values as a result cannot be directly compared but can instead provide an insight into the potential durability behaviour of the glasses.

Table 76 presents the minimum normalised release rate, R_i , of the pristine and CCC heat treated ILAW samples for B, Si, Na, and P. Figure 146 graphically presents the information from Table 76. The NL_B of the pristine base glass is $0.258 \text{ g m}^{-2} \text{ d}^{-1}$, whilst the value for the P_2O_5 doped sample increases to $0.416 \text{ g m}^{-2} \text{ d}^{-1}$. The NL_B values of the CCC heat treated samples for ILAW0.00 was $0.208 \text{ g m}^{-2} \text{ d}^{-1}$ and for ILAW1.53 was $0.561 \text{ g m}^{-2} \text{ d}^{-1}$. When the pristine and heat-treated samples were compared, the CCC ILAW0.00 had a lower value than the pristine sample, whilst the P_2O_5 doped sample had a higher value. The NL_{Si} values of the pristine samples were $0.135 \text{ g m}^{-2} \text{ d}^{-1}$ for ILAW0.00 and $0.182 \text{ g m}^{-2} \text{ d}^{-1}$ for ILAW1.53, whilst the CCC heat treated samples had values of $0.114 \text{ g m}^{-2} \text{ d}^{-1}$ for CCC ILAW0.00 and $0.158 \text{ g m}^{-2} \text{ d}^{-1}$ for CCC ILAW1.53. The NL_{Si} values for the CCC samples were lower than the pristine samples, and the P_2O_5 doped samples had higher values than the undoped glasses. The values for NL_{Na} for the pristine samples were $0.527 \text{ g m}^{-2} \text{ d}^{-1}$ for ILAW0.00 and 0.546 for ILAW1.53, whilst the CCC heat treated samples had values of $0.324 \text{ g m}^{-2} \text{ d}^{-1}$ for CCC ILAW0.00 and $0.688 \text{ g m}^{-2} \text{ d}^{-1}$ for CCC ILAW1.53. The values for NL_{Na} showed a similar trend to the NL_B values, where ILAW0.00 reduced in value when heat treated, whilst ILAW1.53 increased. The NL_P values for the ILAW1.53 and CCC ILAW1.53 were $0.010 \text{ g m}^{-2} \text{ d}^{-1}$ and $0.001 \text{ g m}^{-2} \text{ d}^{-1}$, respectively.

As previously stated, B is used as a tracer for glass dissolution testing, whereas Na provides an indication on the breakdown of the glass structure, but only in solutions with $< \text{pH } 10$ (Walling et al., 2021). The NL_B and NL_{Na} values suggested that the CCC ILAW0.00 was the most durable glass with the lowest dissolution rate, followed by ILAW0.00, ILAW1.53, and CCC ILAW1.53. The solubility of Si should be greater at higher pH (Walling et al., 2021), however, the sample with the highest pH (CCC ILAW1.53) did not have the highest NL_{Si} , rather ILAW1.53 did with a pH of 12.36 as oppose to 12.27. CCC ILAW1.53 had evidence of the crystal phases $\text{Na}_{5.27}\text{Ca}_3(\text{Si}_6\text{O}_{18})$ and $\text{Na}_{7.7}((\text{Al}_{5.1}\text{Si}_{6.9})\text{O}_{24})(\text{SO}_4)_{0.88}(\text{S}_3)_{0.76}$ as confirmed by XRD patterns. The lower NL_{Si} of CCC ILAW1.53, despite the higher pH, may have been due to the incorporation of Ca into the silica gel layer, where it has been reported to lower dissolution rates (Corkhill et al., 2013; Utton et al., 2012; Walling et al., 2021). The formation of the aforementioned crystal phases will reduce the durability of the glass sample, not just due to the Al and Si being consumed and removed from the glass network (Ebert et al., 2005), but because the chemical bonds of the crystalline phases exposed to the aqueous solution will

be attacked, resulting in bond breaking (Frankel et al., 2018). The dissolution rate of the crystals is also affected by their size, where Frankel et al. (2018) reported that the increased dissolution rates of smaller particles were determined by the increased interfacial area. The correlation between the phase compositions and the durability of the samples in relation to NL_B and NL_{Si} were dominated by CCC ILAW1.53, which had the highest content of crystalline phases (9.16 wt%). The presence of the crystalline phases in CCC ILAW1.53 suggested that they developed due to being closer to their high-temperature equilibrium, where the sample was held at a higher temperature for a longer period of time, allowing the for the main phase nucleation sites to grow and crystallise (Simmons et al., 1974). However, the correlation between structure and reactivity is still quite complex to explain, as there are various factors that contribute to the durability behaviour of the glasses, especially as the composition is so complex. For example, where the same element can have opposing effects depending on its concentration in the glass i.e., a multivalent modifier cation where at low concentrations it can limit the hydrolysis of the glass network by mobilising NBØs, and at high concentrations can increase hydrolysis by de-polymerisation of the glass network (Nicoleau et al., 2015). It is unclear by which type of phase separation the crystalline phases arose from i.e., type A (spinodal decomposition), type B (nucleation and growth, where the more durable phase is dispersed in a continuous matrix of a less durable phase), or type C (nucleation and growth where the less durable phase is dispersed in a matrix of the durable phase) (Nicoleau et al., 2015; Taylor et al., 1987; Tomozawa & Doremus, 1979). The type of phase separation that occurs can influence the mobilisation of modifier cations, where polymerisation of the silicate network can increase the surrounding vitreous phase stability (Nicoleau et al., 2015).

Sample	Minimum normalised release rate, R_i (g m ⁻² d ⁻¹)			
	NL _B	NL _{Si}	NL _{Na}	NL _P
ILAW0.00	0.258	0.135	0.527	-
ILAW1.53	0.416	0.182	0.546	0.010
CCC ILAW0.00	0.208	0.114	0.324	-
CCC ILAW1.53	0.561	0.158	0.688	0.001

Table 76 – Sample minimum normalised release rate, R_i (g m⁻² d⁻¹)

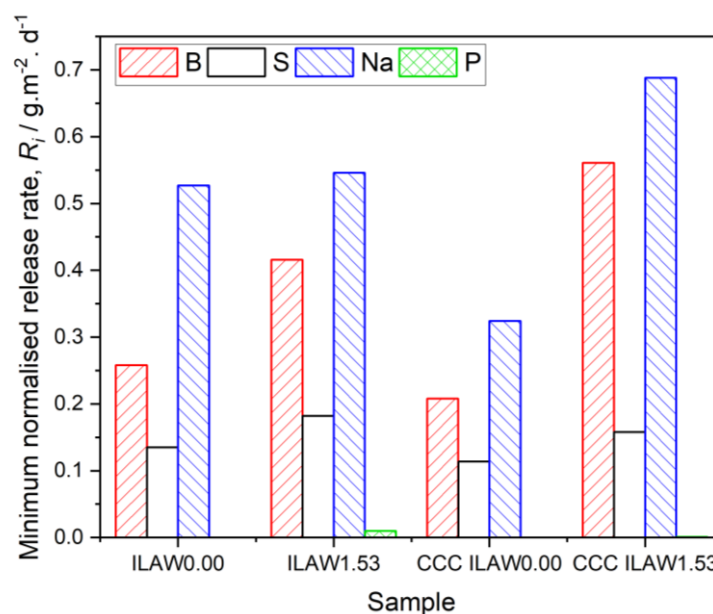


Figure 146 - Normalised release rate ($\text{g.m}^{-2}.\text{d}^{-1}$) for structural elements and modifiers for a 7-day test leaching in pure water Raman Spectroscopy

The effects of P_2O_5 on the chemical durability of these ILAW glasses cannot be fully concluded due to the lack of sufficient data points before and after the 7-day mark used in order to calculate the initial rate. There are also the unaccounted-for effects of the potential presence of liquid-liquid phase separation in the P_2O_5 -doped samples before the occurrence of amorphous-crystalline phase separation in the CCC ILAW1.53 sample, which has not been determined by SEM. However, this study has introduced the effects of increasing P_2O_5 in a far more complex glass system than what has been previously reported, where the minimum normalised release rate can be postulated from the single values collected from the 7-day PCT-B test, where the addition of P_2O_5 saw an increase in the minimum normalised release rate of B, Na, and Si between ILAW0.00 and ILAW1.53, and between ILAW1.53 and CCC ILAW1.53. The presence of crystal phases can also affect the chemical durability of glasses, and is dependent on the morphology, solubility, and whether the phase will act as a barrier against aqueous attack. In order to improve the testing of the chemical durability of these glasses, aliquots of solution would need be taken at 1, 3, 5, 7, 14, 21 and 28 days in order to calculate the normalised release rate, and XRD and SEM/EDS analysis of potential alteration layers and secondary phases.

4.5.3.5 Raman Spectroscopy

Figure 147 shows the Raman spectra of the CCC heat treated ILAW samples, as well for the crystallised 'white splotch' on the surface of the ILAW1.53 sample,

whereas Figure 148 displays the peak centres. The low frequency region ranges between 200-800 cm^{-1} , the mid-frequency region ranging between 800-1200 cm^{-1} , and the high frequency region ranges between 1200-1800 cm^{-1} . The CCC heat treated ILAW0.00 sample exhibits peaks centred at approximately 550, 631, 832, 992, 1043, 1436 cm^{-1} . The ILAW1.53 CCC heat treated sample displayed peaks at $\sim$ 560, 631, 852, 941, 992, 1043, and 1436 cm^{-1} . The addition of P_2O_5 saw the peak at centred at $\sim$ 941 cm^{-1} disappear. The ILAW1.53 crystal phase spectra was dissimilar to the glass samples, exhibiting sharp peaks centred at $\sim$ 282, 337, 440, 550, 592, 852, 897, 984, 1008, and 1072 cm^{-1} .

The peak at 631 cm^{-1} can be attributed to the breathing mode of B-O-Si(B) in reedmergnerite- and/ or danburite- like rings with Ca^{2+} ions acting as charge compensators for ^{14}B units (Angeli et al., 2012; Manara et al., 2009; Möncke et al., 2015; Yadav & Singh, 2015), or by metaborate vibrations of the ring-type (Koroleva et al., 2011). The peak at 941 cm^{-1} may be assigned to PO_2 symmetric stretching of NBØs in Q^0 units (Yadav & Singh, 2015) and/ or P-O-P asymmetric stretch (Ma et al., 2014; Zhang & Brow, 2011). The band at 992 cm^{-1} could have varying contributions due to the different species in the glass, where literature has reported S-O symmetric stretching modes within the sulphate tetrahedra (Brendebach et al., 2009; Klimm & Botcharnikov, 2010; Lenoir et al., 2010; Lonergan et al., 2020; Saini et al., 2022), asymmetric stretching mode of Q^1 units and/or with a small amount of Q^0 species in which P is bonded via O to four Al atoms, AlPO_4 (Logrado et al., 2022), and PO_4^{3-} units (Cheng, 2014). The peak at 1043 cm^{-1} may be attributed to the stretching of Q^3 units (Brentrup et al., 2009a, 2009b; Solonenko et al., 2017a, 2017b), whereas the peak at 1436 cm^{-1} may be assigned to B-O $^-$ stretching in metaborate rings and chains (Yadav & Singh, 2015), and B-O stretch motions within BO_3 triangles (McKeown et al., 2017). The presence of the band at 630 cm^{-1} (reedmergnerite- and/ or danburite-like rings) in both samples suggests some interconnection between the silicate and borate sub-networks. The absence of the peak at 944 cm^{-1} in the CCC ILAW1.53 sample suggests that there are no longer Q^0_{p} species in the glass.

Qualitative analysis of the Raman spectrum of the ‘white’ splotch embedded in glass of the CCC ILAW1.53 sample had identified crystalline phases by XRD to be $\text{Na}_{7.7}((\text{Al}_{5.1}\text{Si}_{6.9})\text{O}_{24})(\text{SO}_4)_{0.88}(\text{S}_3)_{0.76}$ and $\text{Na}_{5.27}\text{Ca}_3(\text{Si}_6\text{O}_{18})$. There is a lack of literature reporting Raman specific peaks for $\text{Na}_{7.7}((\text{Al}_{5.1}\text{Si}_{6.9})\text{O}_{24})$

(SO₄)_{0.88} (S₃)_{0.76}), however, the Raman shifts for combeite (Na_{4.5}Ca_{3.5}Si₆O_{17.5}(OH)_{0.5}), which is a similar crystallite to Na_{5.27}Ca₃(Si₆O₁₈) reported in this study, are located at 279, 346, 423, 453, 532, 588, 620, 903, 986, and 1039 cm⁻¹ (Čukanov & Vigasina, 2020). Hence the peaks at 900 and 982 cm⁻¹ may be assigned to Na_{5.27}Ca₃(Si₆O₁₈). The peaks at 440 and 592 cm⁻¹ may be ascribed to Si Q⁴ and Q² units (Li et al., 2001), respectively. The peak centred at 500 cm⁻¹ may be associated with Al-O⁻ or Al-O-B linkages (Li et al., 2001), whereas the peak at 550 cm⁻¹ may be ascribed to B-O-B stretching in BO₄ units (Li et al., 2001). The other unassigned peaks were difficult to identify without relevant literature available.

When the CCC heat-treated samples were compared to the pristine samples, the spectra were very similar, where peak centres deviated slightly. ILAW0.00 and CCC ILAW0.00 did not have a peak at 944 cm⁻¹, which occurred when 1.53 mol% P₂O₅ was added to the system. When ILAW1.53 was heat treated this peak remained.

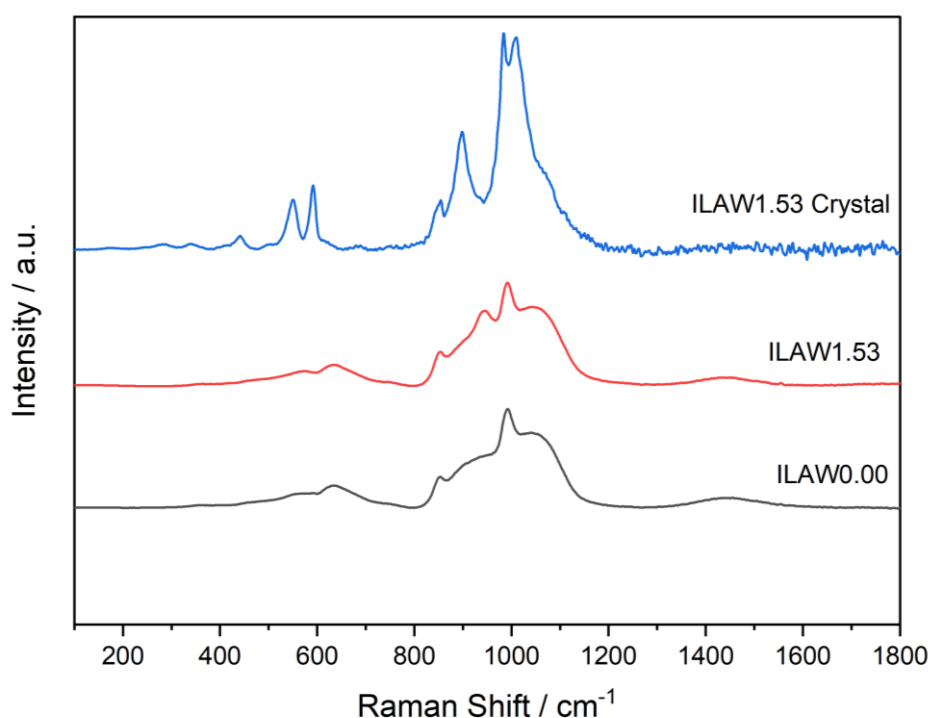


Figure 147 - Raman spectra of CCC ILAW0.00 and 1.53 samples and crystallised 'white blotch' on the surface of the ILAW1.53 sample

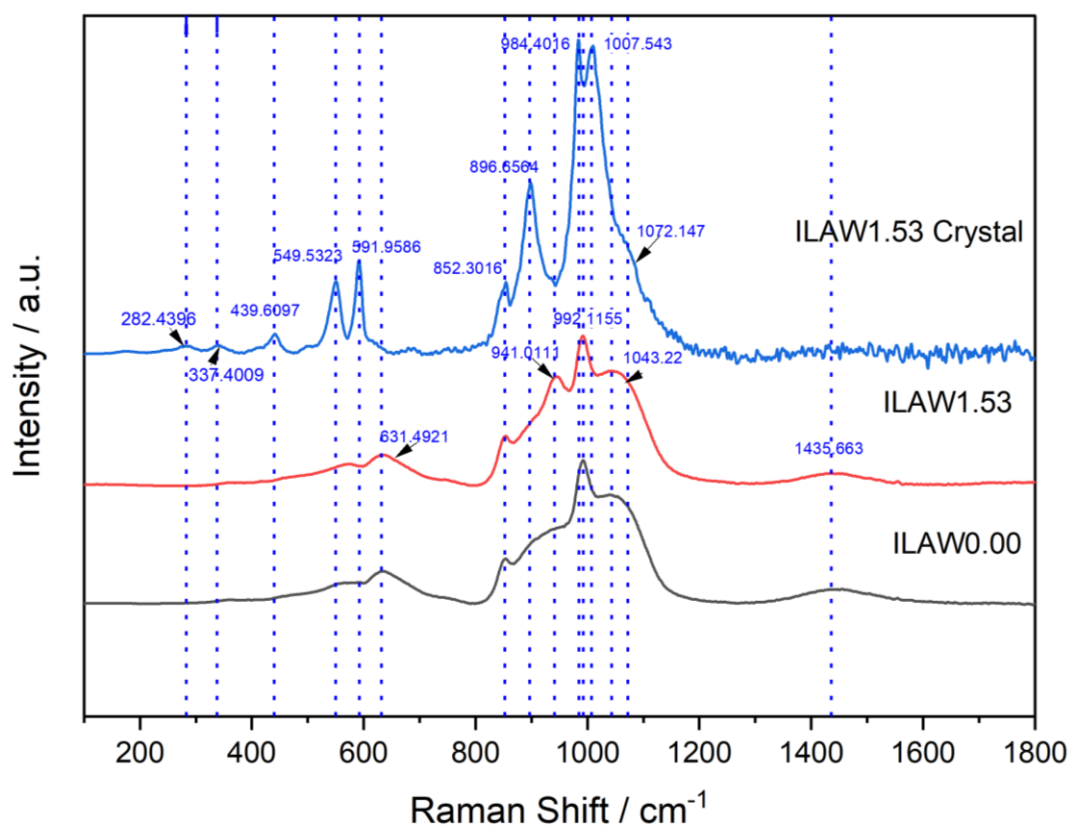


Figure 148 - Raman spectra of CCC ILAW0.00 and 1.53 samples and crystallised 'white blotch' on the surface of the ILAW1.53 sample with peak assignments

4.5.4 Summary

- Pristine ILAW0.00, 1.53, and CCC ILAW0.00 were X-ray amorphous, whilst CCC ILAW1.53 had the identifiable crystalline phases present of $\text{Na}_{7.7}((\text{Al}_{5.1}\text{Si}_{6.9})\text{O}_{24})(\text{SO}_4)_{0.88}(\text{S}_3)_{0.76}$ (1.98 wt%) and $\text{Na}_{5.27}\text{Ca}_3(\text{Si}_6\text{O}_{18})$ (7.28 wt%).
- XRD showed that the P_2O_5 solubility limit had not been exceeded and lies above the average calculated concentration of 1.53 mol%.
- Pristine ILAW0.00 and 1.53 had depleted ZrO_2 and SnO_2 as analysed by XRF, which could be attributed to the unmelted components left in the crucible, as identified by XRD, as well as the formation of $\text{Na}_4\text{Zr}_2(\text{SiO}_4)_3$ in the ILAW1.53 sample, which would have also contributed to the reduction in ZrO_2 .
- The introduction of 1.53 mol% to ILAW0.00 saw a decrease in the density from $2.676 \pm 0.022 \text{ g/cm}^3$ to $2.653 \pm 0.013 \text{ g/cm}^3$, where said decrease implies a reduction in the rigidity of the glass network.

- The dilatometric T_g onset was the same within error and the DTA T_g onset displayed little variance when P_2O_5 was added to the glass system. There was a slight increase in the CTE of $0.1088 \times 10^{-6} K^{-1}$ with additions of P_2O_5 , implying that there may be a slight increase in asymmetrical units suggesting the glass network is de-polymerising.
- The glass forming parameters suggested that the P_2O_5 -doped sample, ILAW1.53, was the most thermally stable glass.
- Raman spectroscopy spectra of the pristine samples presented characteristic peaks associated with reedmergnerite and danburite-like rings, Q^n speciation, and BO_3 symmetric stretching, expected of amorphous materials. However, the 1.53 P_2O_5 doped sample had the addition of a peak at 944 cm^{-1} attributed to PO_2 symmetric stretching of non-bridging oxygen in Q^0 units and / or P-O-P asymmetric stretch. The Raman spectroscopy of the CCC heat treated samples were similar to the pristine samples.
- The Raman spectroscopy of the crystalline material in the CCC ILAW1.53 sample presented characteristic peaks associated with $Na_{5.27}Ca_3(Si_6O_{18})$.
- Fe XANES suggested that Fe in ILAW0.00 and ILAW1.53 was present as Fe^{3+} in a tetrahedral coordination, where additions of P_2O_5 did not affect the Fe. This implied that Fe was acting as a glass former in both glasses.
- Chemical durability testing of the pristine and CCC heat treated glasses showed that the sample with the highest durability, where NL_B was used to assess this, was $CCCILAW0.00 > ILAW0.00 > ILAW1.53 > CCC ILAW1.53$. The sample which dissolved the most with the highest NL_{Na} was $CCCILAW1.53 > ILAW1.53 > ILAW0.00 > CCC ILAW0.00$. The formation of $Na_{7.7}((Al_{5.1}Si_{6.9})O_{24})(SO_4)_{0.88}(S_3)_{0.76}$ and $Na_{5.27}Ca_3(Si_6O_{18})$ may have affected the durability of CCC ILAW1.53.
- In order to establish if the CCC heat treated glasses were durable enough for the purposes of vitrification, the test would need to be done over a longer period of time, with aliquots taken at 1, 3, 5, 7, 14, and 28 days, where the DWPF sample is used as a comparison.
- This study has provided a better insight into the effects of P_2O_5 into more complex LAW glasses relevant to waste glasses, where little has been reported. The samples have a higher P_2O_5 solubility than the simple HLW samples. However, the CCC ILAW1.53 sample produced crystalline

phases that have been previously identified to be problematic if they exceed certain constraints. These crystal phases did not exceed these parameters, suggesting the composition may be acceptable in vitrifying high P_2O_5 containing wastes (≤ 1.53 mol%).

Chapter 5: Discussion

5.1 Introduction

This chapter draws together the information from the preceding five result sub-chapters, to present a coherent image of the effects of P_2O_5 additions on Hanford Waste Site simulant glass compositions, with varying degrees of complexity, focusing on the composition-structure-property relationships and how these relate to the original aims of the project. The structure of this section is based upon the composition-structure-property model of describing glasses.

The aims of the project were the following:

- Understand the effects of varying the amount of P_2O_5 on glass composition, properties, and structure.
- Identify and characterise phase separation in relevant glasses.
- Support increasing waste loading of current high-level activity and low-level activity waste.

5.2 Glass Composition

5.2.1 P_2O_5 Solubility

The glass compositions of all the glass series studied in this project were based on Hanford HLW and LAW borosilicate glass compositions. The base glass was a 4-component glass system, consisting of $Na_2O-B_2O_3-SiO_2-P_2O_5$, where the undoped base glass had a base composition of $27.9Na_2O-16.3B_2O_3-55.8SiO_2$, which lay outside the immiscibility region in the $Na_2O-B_2O_3-SiO_2$ ternary phase diagram. When 3.0-4.0 mol% P_2O_5 was added to the glass system, BS-SEM images indicated there was a nucleation-type morphology, where XRD patterns and ^{31}P and ^{23}Na MAS NMR determined the crystalline phases present to be Na_3PO_4 and $Na_4P_2O_7$. Similar findings have been reported by Stone-Weiss et al. (2020), Krishnamurthy et al. (2020), and Muñoz et al. (2008) where they reported that when >3.0 mol% was exceeded there was evidence of the clustering of Na bearing-phases and their subsequent crystallization. Jantzen et al. (2000) reported that borosilicate glasses containing P_2O_5 could result in crystalline phase separation if the difference in the field strengths (ΔF) between the major glass forming elements ($(SiO_4)^{4-}$, $(BO_4)^{5-}$, $(BO_3)^{3-}$, and $(PO_4)^{3-}$) exceeded 0.3,

where the differences between P and Si, and B and P exceed this limit, but between B and Si did not, as it had a ΔF of 0.06. Hence, the phase separation of crystalline solids insinuates that the NBSP glass system experienced crystalline phase separation (Jantzen, Brown, & Pickett, 2000).

The HLW composition was a simplification of relevant HLW compositions taken from the report 245590-HLW-RPT-05-001 (Vienna & Kim, 2008), and is an 8-component glass system $\text{Na}_2\text{O}-\text{Li}_2\text{O}-\text{CaO}-\text{Fe}_2\text{O}_3-\text{Al}_2\text{O}_3-\text{B}_2\text{O}_3-\text{SiO}_2-x\text{P}_2\text{O}_5$. The undoped base glass had a nominal composition of $12.9\text{Na}_2\text{O}-7.9\text{Al}_2\text{O}_3-46.64\text{SiO}_2-5.66\text{CaO}-5.86\text{Fe}_2\text{O}_3-12.31\text{B}_2\text{O}_3-8.71\text{Li}_2\text{O}$ (mol%). When the values for Na_2O , B_2O_3 , and SiO_2 are taken and plotted on the ternary phase diagram, the glass composition is located in the immiscibility region. However, the addition of the other oxide components would have affected the glass in respect to its immiscibility. When P_2O_5 was added and incrementally increased in the glass, the glass showed evidence of Fe_2O_3 and NaCaPO_4 at higher P_2O_5 , where the P_2O_5 solubility was deemed to be between 0.625-1.25 mol%. The presence of Fe_2O_3 at lower P_2O_5 concentration suggested that it was either unmelted or that the Fe solubility limit had been exceeded.

The LAW compositions were a simplification of relevant LAW compositions based on WTP-LAW taken from the reports VSL-01R3560-2 (Muller et al., 2017) and VSL-03R3460-1 (Muller et al., 2015), and from the Office of River Protection (ORP)-LAW compositions taken from the reports VSL-04R4960-1 (Kruger & Matlack, 2012), VSL-05R5900-1 (Kruger et al., 2013), VSL-06R6900-1 (Kruger, Joseph, et al., 2013), VSL-07R1130-1 (Kruger et al., 2013), VSL-09R1510-2 (Kruger et al., 2013), VSL-10R1790-1 (Kruger et al., 2010). The LAW glass series was an 8-component glass system $\text{Na}_2\text{O}-\text{Li}_2\text{O}-\text{CaO}-\text{Fe}_2\text{O}_3-\text{Al}_2\text{O}_3-\text{B}_2\text{O}_3-\text{SiO}_2-x\text{P}_2\text{O}_5$, where the undoped base glass had a nominal composition of $20.02\text{Na}_2\text{O}-4.93\text{Li}_2\text{O}-12.72\text{CaO}-1.69\text{Fe}_2\text{O}_3-5.29\text{Al}_2\text{O}_3-9.27\text{B}_2\text{O}_3-46.09\text{SiO}_2$ (mol%). When the values for Na_2O , B_2O_3 , and SiO_2 are taken and plotted on the ternary phase diagram, the glass composition was not located in the immiscibility region. However, similarly to the HLW base composition, the addition of further oxide components would have affected the glass in respect to its immiscibility. When P_2O_5 was added and incrementally increased in the glass, the glass showed evidence of NaCaPO_4 at higher P_2O_5 , where the P_2O_5 solubility was deemed to be between 1.875-1.94 mol%.

The P_2O_5 solubility limit of the HLW and LAW glass series are much lower than the simple glass series and can be attributed to the addition of other oxides, where the differences in the solubility limit between HLW and LAW series are due to the concentration and ratios of each oxide. The HLW and LAW series both contain Al_2O_3 , Fe_2O_3 , Li_2O , and CaO which the simple NBSP series did not.

Al_2O_3 is a homogeniser that prevents the amorphous phase separation, where it has been found to inhibit crystallisation of sodium phosphate (Chen et al., 2022). The inhibiting of phase separation in sodium borosilicate glasses has been reported to be due to the formation of B-O-Al-O-Si linkages, which increase the connectivity between the B and Si sub-networks (Du et al., 2000). Al_2O_3 also causes the transfer of Na^+ cations from the B-O network to AlO_4 tetrahedra, changing its coordination from $[^4]B$ to $[^3]B$ (Du et al., 2000). The $-[^3]B-O-Al-$ linkages are far more difficult to break than $[^4]B-O-Si$ linkages, reducing the aggregation of $[B\emptyset]$ groups (Du et al., 2000). Al_2O_3 has been found to strengthen the melt structure via the formation of $[^4]Al-O-Si$ linkages, where the $[^4]Al$ can also be substituted for Si^{4+} , thereby forming $[AlO_{4/2}]^-$ anions that are charge compensated by Na^+ cations in an sodium borosilicate glass (Dantas et al., 2011). Therefore, the Al_2O_3 may be inhibiting crystallisation of sodium phosphate crystal phases from occurring until a higher P_2O_5 content in the LAW glasses compared to the HLW glasses.

The presence of Fe_2O_3 in a SiO_2 - Na_2O_3 - Al_2O_3 - B_2O_3 glass system resulted in the incorporation of Fe^{3+} ions into the glass system, and may potentially have been substituted with Si sites (Cizman et al., 2017; Dantas et al., 2011), where its electrical charge was compensated for by Na^+ cations, resulting in the changing nature of the Si tetrahedra bonds containing O^{2-} ions. (Cizman et al., 2017; Dantas et al., 2011). It has also been reported that when Fe_2O_3 is added as either a network former or modifier, it is involved in the conversion of $[BO_{4/2}]$ tetrahedral groups to trigonal BO_3 groups, resulting in the decrease in the degree of polymerisation of the $[SiO_{4/2}]$ tetrahedral group i.e., de-polymerisation (Cizman et al., 2017). If Fe_2O_3 is present as a glass former than it simultaneously forms $[FeO_{4/2}]^-Na^+$ units, where the Na^+ cation attraction is stronger than those in $[BO_{4/2}]^-Na^+$ units (Cizman et al., 2017). The formation of the $[FeO_{4/2}]^-$ units requires more modifiers to be withdrawn from both the B and Si sub-networks, resulting in the reduction of $[SiO_{4/2}]^-$ units (El-Damrawi, Hassan, & El-Jadal,

2017). Both the HLW and LAW glasses contain Fe_2O_3 , B_2O_3 , SiO_2 , and modifier cations, where such behaviours may be occurring and subsequently effecting the glass structure and properties.

Mazurin (1984) cited by Schuller et al. (2017) reported that the extent of the immiscibility gap can be correlated to the field strength of cations in borosilicate glasses (Lv et al., 2022; Schuller et al., 2017), where the tendency for phase separation increased with increasing cation field strength of alkali and alkaline earths (Schuller et al., 2017). Previous studies have focused on borosilicate glasses in the Na_2O - B_2O_3 - SiO_2 ternary diagram, with additions of alkali or alkaline-earth metal cations, such as Li^+ (Boekenhauer et al., 1994; He et al., 2013; Neyret et al., 2015), K^+ (Boekenhauer et al., 1994; Neyret et al., 2015), and Ca^{2+} (Ceniceros-Orozco et al., 2022; Lai et al., 2016). There have also been studies of mixed-modifier borosilicate systems that have incorporated Na^+/Li^+ (Hattori et al., 2012; He et al., 2013), $\text{Li}^+/\text{Ca}^{2+}$ (Shih & Jean, 2017, 2018), and $\text{Ca}^{2+}/\text{Na}^+$ (Bowes, 1943). However, there has been little literature on systems with a mixture of three alkali and alkaline-earth cations, such as in this study, in particular $\text{Li}^+/\text{Na}^+/\text{Ca}^{2+}$. When these electropositive cations are added to B_2O_3 -bearing glass melts, they induce the conversion of $^{[3]}\text{B}$ to $^{[4]}\text{B}$, leading to an increase in network connectivity (Brow & Tallant, 1997; Lv et al., 2022; Tuheen et al., 2022; Yun & Bray, 1978). However, this behaviour contrasts with what has been seen in phosphate and silicate glasses, where the addition of electropositive cations induces the formation of NBØs (Lv et al., 2022). Lv et al. (2022) reported that the smallest cations, Li^+ and Mg^{2+} , being present as LiO_4 and MgO_4 tetrahedra, may contribute to the glass network as opposed to acting as glass modifiers, where some circumstantial evidence has been reported for MgO - Na_2O - B_2O_3 (Kim & Bray, 1974; Lv et al., 2022), aluminosilicate (Logrado et al., 2021; Lv et al., 2022), and silicate (Lv et al., 2022; Watts et al., 2010) systems, where the $\text{Li}^+ \text{-O}$ and $\text{Mg}^{2+} \text{-O}$ linkages are weaker than the B/Si-O (Lv et al., 2022). The exact roles of the network modifying cations cannot be explained in depth due to the complex nature of the HLW and LAW glasses, inhibiting the use of MAS NMR and XANES, however, their roles can instead be inferred by the involvement of Na^+ and Ca^{2+} cations in the phosphate-bearing crystalline phases formed in the samples when the P_2O_5 solubility is exceeded, based on the above explanations from literature.

Therefore, based on the literature and results presented in this thesis, the effects of compositional differences of the HLW and LAW samples on the P₂O₅ solubility can be inferred. The HLW samples may have had the lowest solubility limit and onset of crystallisation due to (i) its lower modifier content, (ii) elevated Fe₂O₃ and Al₂O₃ content when compared with the LAW series, and (iii) the subsequent roles of the glass structure as a result. The Fe in the HLW and LAW was analysed by Mössbauer spectroscopy and XANES, where it was identified to predominantly be present as a glass former with a marginal contribution as a glass modifier, with increasing P₂O₅ content. Therefore, the presence of [FeO_{4/2}]⁻ may be initially charge compensated by either Na⁺ or Li⁺ cations, which may be taken from either the B or Si sub-network, resulting in the conversion of ^[4]B → ^[3]B and reduction in the [SiO_{4/2}]⁻ units by breaking Si-BØ-Si bridges which are replaced by Si-NBØ - M units, where NBØ = non-bridging oxygen and M = modifier cation (Tilocca et al., 2007). The redox ratio of Fe has been reported to strongly influence the B coordination (Tuheen et al., 2022). The addition of modifiers (Li⁺, Na⁺, and Ca²⁺) results in the conversion of ^[3]B → ^[4]B increasing the connectivity of the glass network, until the formation of ^[4]B reaches its maximum after which it begins to revert back to ^[3]B generating NBØ s first on B and then Si (Bray, 1985; Dell et al., 1983; Tuheen et al., 2022). These changes are a function of the B to Si ratio (K) as described by the Dell, Bray, and Xiao model (Dell et al., 1983) based on ¹¹B MAS NMR Studies (Tuheen et al., 2022). Tuheen et al. (2022) reported that for 4-coordinated 3+ charged cations they will have a negative electrical charge on [MO₄]⁻, where M = Al³⁺, B³⁺, and Fe³⁺. The preference of the modifier cations in the HLW and LAW glasses by Al³⁺, B³⁺, and Fe³⁺ is unknown, however, it could be calculated in future work using the ratio denoted as R, if the exact coordination numbers and number density of a cell is known, where the expression is $R_b^a = \frac{CN_{a-b}}{CN_{a-c}} \times \frac{N_c}{N_b}$, where *a* represents the glass modifiers Na⁺ or Fe²⁺, and *b* and *c* represent the glass modifiers Al³⁺, B³⁺, and Fe³⁺ (Tilocca et al., 2007; Tuheen et al., 2022). Doweidar et al. (2001) reported that for a series of sodium boroaluminosilicate glasses, Na⁺ cations preferentially charge compensated [AlO₄]⁻ to [BO₄]⁻ tetrahedra. The Al₂O₃ in the LAW and HLW glasses may be forming -B-O-Al-O-Si linkages, increasing connectivity between the B and Si sub-networks, which may be impeding the formation of NaCaPO₄ at a lower P₂O₅ content than 1.25 mol%. When P₂O₅ is added it requires charge compensation,

which based on the MAS NMR results of the simple NBSP glass series, suggests that it is charge compensated by Na^+ cations from the silicate sub-network. However, the formation of NaCaPO_4 crystal phases, suggests that these clusters formed prior to crystallisation, and the P^{5+} is being charge compensated both by Na^+ and Ca^{2+} cations, where it is unclear which sub-network the Ca^{2+} is being withdrawn from. The removal of glass modifiers as charge compensators by P^{5+} from the glass network suggests that it should re-polymerise, which is the case at 1.25 mol% P_2O_5 in the HLW glasses as supported by Raman spectroscopy. The LAW glasses had an elevated modifier content compared to HLW as well as a lower Al_2O_3 and Fe_2O_3 content. The elevated modifier content suggests that the P_2O_5 solubility limit and subsequent crystallisation occurred at a higher mol%, due to there being enough Na^+ and Ca^{2+} cations to charge compensate P, as well as participate along with Li^+ in the glass network as modifiers. The semi-quantitative analysis of the Q^n speciation of the HLW glasses suggested that the glass was de-polymerising with increasing P_2O_5 content between 0.00-0.625 mol%, suggesting that perhaps there was a conversion of $^{[3]}\text{B} \rightarrow ^{[4]}\text{B}$ generating NBØs, the minor formation of Fe^{2+} as confirmed by XANES and Mossbauer, or Li^+ presence as tetrahedra and its involvement in the glass network as opposed to acting as a glass modifier. The LAW polymerisation behaviour is less straightforward due to the non-linear behaviour exhibited with increasing P_2O_5 content. However, the increase and decrease in polymerisation may be due to a mixture of the same parameters as stated for the HLW glasses. However, based on the Fe K-edge XANES and Mössbauer spectra it is likely that Fe is not a limiting factor in the P_2O_5 solubility in the HLW and LAW glasses, where there was little change in its redox ratio, meaning that perhaps Fe was not a major factor in the conversion of the B coordination. This is further supported by Zhang et al. (2022) where they reported that per-alkaline glasses containing P_2O_5 and Fe_2O_3 , had little effect on the Fe-redox behaviour, but that P_2O_5 in peraluminous glasses oxidises Fe, where P had a tendency to form $\text{Al}^{3+}\text{-O-P}^{5+}$ units, resulting in the removal of excess Al^{3+} from competing with Fe^{3+} for alkaline/alkaline earth cations (Zhang et al., 2022).

The ILAW glass series was much harder to analyse and infer compositional component roles in the glass structure and subsequent effects on P_2O_5 solubility due to the involvement of 19 components. However, the compositional effects of individual oxide components can be suggested based on relevant literature. The

ILAW series had the additional components of ZrO_2 , Cr_2O_3 , MgO , SO_4^{2-} , SnO_2 , V_2O_5 , Cl^- , TiO_2 , F^- , and K_2O . ZrO_2 and V_2O_5 are glass formers; TiO_2 , Cr_2O_3 , SnO_2 , MgO are glass intermediates; K_2O is a glass modifier. Calahoo and Wondraczek (2020) described SO_4^{2-} in glasses as an oxoanion and F^- and Cl^- as halides. TiO_2 , ZrO_2 , Cr_2O_3 , and V_2O_5 are nucleating agents similar to P_2O_5 (Morimoto & Kuriyama, 1996; Zhang et al., 2020), where some may act to enhance nucleation and promote the formation of nuclei contributing to bulk crystallisation, or promote phase separation (Han et al., 2019). Some of the components mentioned are also multivalent species, where their redox behaviour depends on the composition and melting conditions, where the valency dictates their role in the glass structure.

TiO_2 , SnO_2 , and ZrO_2 are opacifiers, where they can promote the tendency for phase separation of a base glass when added in small quantities (Vogel, 1994). Due to their low solubilities, they form nuclei or crystallites during cooling, where their combination with SiO_2 and or B_2O_3 results in open or occluded immiscibility gaps (Vogel, 1994). This tendency to phase separate is immediately then followed by crystallisation (Vogel, 1994). Cr_2O_3 has been reported to promote crystallisation (Han et al., 2019). Therefore, the ILAW glass may be more susceptible to phase separation and crystallisation than other compositions due to the presence of these components.

TiO_2 is a multivalent species where it can be present as three-fold (Ti^{3+}), four-fold (Ti^{4+}), five-fold (Ti^{5+}), and six-fold (Ti^{6+}) oxidation states, where the ratio of each depends on the glass composition and the melting conditions (oxidised or reduced atmosphere) (El Batal et al., 2012; Nienhuis et al., 2020). Ti^{4+} acts as a glass former, whereas Ti^{6+} acts as a glass modifier (Mysen & Neuville, 1995; Nienhuis et al., 2020). Ti^{5+} has been reported to act as both a glass former and a glass modifier due to its capability of forming BO s and other terminal oxygen bonds, however, it was later reported to primarily act as a glass former (Farges et al., 1996; Henderson & St-Amour, 2004; Limbach et al., 2017; Nienhuis et al., 2020). The effects of Ti will depend on its coordination, which will alter the glass melt structure and affect the physical and thermodynamic properties (Cormier et al., 1998, 2001; Nienhuis et al., 2020). Glasses that have small additions of TiO_2 will experience alterations in the network connectivity, promoting the formation of Ti^{4+} , where the initial presence of Ti^{5+} ions act as a network modifier, breaking up the glass network (Greegor et al., 1983; Nienhuis et al., 2020). However, in

glasses that contain alkali and alkaline-earth oxides, the coordination of Ti depends on the relative sizes of the network modifier cation (Nienhuis et al., 2020). The solubility of Ti has been hypothesised to be dependent on the network rigidity and the amount of free volume available within the glass network (Nienhuis et al., 2020). It is unclear what the coordination of Ti is in the ILAW glasses without further analysis e.g., Ti K-edge or UV-Vis spectroscopy, and hence its role in the short and medium range structure. However, the discussed literature has provided an indication of the possible behaviour of Ti in the ILAW glasses.

SnO₂ is a chemical fining agent where additions to glass melts is used to reduce bubble formation (He et al., 2021). It is a glass intermediate and can take the role of either a glass former or modifier depending on the glass composition (Lu et al., 2008). The main coordination of Sn²⁺ is [SnO₃] triangular pyramid, but a proportion can be present as [SnO₄] square pyramid (Chen et al., 2018; Hoppe et al., 2019; Lu et al., 2008). Lu et al. (2008) reported that SnO₂ doped into borosilicate glasses takes the role of a conditional glass former when there are free O available, where SnO associates itself with a comparable M₂O to form structural units. If there is not enough O then SnO takes the role of a glass modifier instead, breaking up the [BO₃] and [SiO₄] sub-networks, leading to an increase in NBØs (Lu et al., 2008). The role of SnO in borosilicate glasses can be described by free oxygen/ SnO > 1.0 = network modifier and free oxygen/SnO < 1.0 = glass former (Lu et al., 2008). It is unclear in the ILAW glasses the free oxygen available, and without structural analysis e.g., XANES, UV-Vis spectroscopy, or ¹¹⁹Sn Mössbauer spectroscopy, the SnO coordination and subsequent Sn⁶⁺: Sn³⁺ ratio is unclear and can not be commented on further.

Whilst ZrO₂ may be a nucleating agent, it has been reported that it is not involved in phase separation or crystallisation due to the existence of Zr-O-Si linkages, as oppose to PO₄³⁻ mobile entities (Achigar et al., 2021). Zr ions are mainly found as six-fold coordinated [ZrO₆]⁴⁻ and octahedrally linked to other network formers e.g., Si through corner sharing (Bergeron et al., 2010; Calas et al., 2014; Lu et al., 2018). Lu et al. (2018) reported that Zr in both simplified and simulant borosilicate glasses was present in 6-fold coordination, where Zr K-edge EXAFS data and MD simulations reported that the second shell around Zr composed on average Si, B, Al, with Na, and Ca as the charge compensating ions. They

summarised that substitution of $\text{ZrO}_2/\text{SiO}_2$ increased the network connectivity, which was seen increasing the T_g , lowering the CTE, and enhancing the chemical durability in neutral pH conditions and alkali-rich environments. For a constant CaO and Na_2O content, the $\text{ZrO}_2/\text{SiO}_2$ substitution resulted in an increased number of Na^+ and Ca^{2+} cations acting as charge compensators, meaning that there were fewer glass modifiers to create NBØs. The ZrO_2 content in the ILAW glasses is lower than the nominal content due to its presence in the material left in the crucible after the pour, as confirmed by XRD. However, there was also evidence of a Zr containing crystal phase in the ILAW0.00 crucible material, i.e., $\text{Na}_4\text{Zr}_2(\text{SiO}_4)_3$. The presence of this crystal phase has removed glass forming Si tetrahedra and Na^+ modifiers, to use as charge compensators, which will affect the polymerisation behaviour of the glass, where other glass species may change function to cater for the removal of the Si, Zr, and Na. ZrO_2 may be present in a six-fold coordination in the glass structure, but would need to be confirmed with other analysis techniques not implemented in this study, e.g., XANES. Therefore, it is unclear on the coordination of Zr and its structural role and sole effect on the glass properties.

Both Cr and V are transition metals and are present in nuclear waste glasses, and can impact the crystallisation and foaming behaviour (McKeown et al., 2011; Muller et al., 2009). Depending on the glass melt composition, transition metals can increase the tendency for the crystallisation of spinel upon cooling of the glass melt or the final bulk glass (McKeown et al., 2011).

V_2O_5 is often added to the glass melt to promote SO_3 incorporation, which helps reduce the tendency for the formation of a separate salt layer (McKeown et al., 2011). However, larger concentrations of V_2O_5 can increase melt foaming, which involves the reduction of cations and generation of oxygen gas, which then affects the redox conditions (McKeown et al., 2011). Vandadium (V) can be present in the following oxidation states: 3+, 4+, and 5+, where V^{5+} acts as a glass former, whereas V^{3+} and V^{4+} acts as glass intermediates (Lu et al., 2019; Smith-Gray et al., 2021). V can be found in a tetrahedral, square pyramidal, or octahedral coordination (McKeown et al., 2002; Smith-Gray et al., 2021). When V is added to borosilicate based glass systems as V_2O_5 in increasing concentrations, it has not been found to alter the silicate network, but instead the borate network (Manara et al., 2007; Sengupta et al., 2015; Smith-Gray et al., 2021). However,

the presence of < 5 mol% V_2O_5 has been reported to promote a homogeneous melt and glass (Sengupta et al., 2015; Smith-Gray et al., 2021) and increase the incorporation of oxyanions e.g., sulphates (Kruger & Matlack, 2012; Manara et al., 2007; McKeown et al., 2017; Smith-Gray et al., 2021) and molybdates (Lian et al., 2020; McKeown et al., 2017; Smith-Gray et al., 2021; Suzuki et al., 2018), where the presence of V-O linkages cause the de-polymerisation of the silicate network, creating voids in the glass matrix, where said voids are then filled by sulphate units (Manara et al., 2007; Smith-Gray et al., 2021). Smith-Gray et al. (2021) suggested that the upper limit for V_2O_5 was ~ 5 wt% (~ 1.9 mol%) for the measured composition of a simplified US LAW glass containing SiO_2 , Na_2O , B_2O_3 , CaO , Al_2O_3 , SO_4^{2-} , V_2O_3 , and Cr_2O_3 . The Raman spectra exhibited characteristic vibrational modes for V_2O_5 within the range of $850 - 910\text{ cm}^{-1}$ (Smith-Gray et al., 2021). When compared to the literature studies, the V_2O_5 content in the ILAW glasses in this study was < 1 mol%, where it may be present as V^{5+} forming V-O linkages, contributing to the de-polymerisation of the silicate network, however, this would need to be further investigated, especially as the content was so low that it might have very little impact on the glass. The valency and coordination of V can be determined using UV-vis spectroscopy or XANES, which would inform its structural role.

Cr is added to waste glass melts to aid in the reduction of corrosion of Cr-rich refractory bricks in high Na-containing glass melts (McKeown et al., 2011). Cr can be present in glass primarily as two oxidation states, trivalent (3+) or hexavalent (6+), where both ions can co-exist depending on the glass composition and melting conditions (Aktas et al., 2019; Jin et al., 2022; Smith-Gray et al., 2021). Cr_2O_3 has a low solubility in borosilicate glasses (Huang et al., 2004), however, phosphate glass systems have been reported to easily dissolve Cr_2O_3 (Feng et al., 1996). McKeown et al. (2011) investigated the Cr redox behaviour in borosilicate LAW nuclear waste glasses based on the parent glasses, Z10-G-60C, Q10-G-136D, and DWV-G-123B, with similar compositional components to the ILAW glasses studied in this report. The Cr XANES analysis established that as the Na_2O content decreased the Cr became more reduced, which is consistent with glass basicity arguments, where less polymerised glasses or glasses with higher modifier cation content, stabilised higher cation oxidation states (McKeown et al., 2011). When the glasses had an increased bubbling time (increased oxygen fugacity), the Cr became more reduced, where there was no

evidence of Cr^{6+} , and increasing evidence of Cr^{3+} . The valency of Cr was dependant on the Na-content, where the Na-rich glass (23.13 mol% Na) had a total $\text{Cr}^{3+}/\text{Cr}_{\text{total}}$ ranging between 15 to 95% (McKeown et al., 2011). Further literature has also reported that higher Cr^{6+} proportion to Cr^{3+} is typical in high-alkali containing glasses (Brow, 1987; Hirma et al., 2006; Jin et al., 2022; Murata et al., 1997; Nath & Douglas, 1965). The Cr_2O_3 content in the ILAW glasses ranged between 0.06-0.12 mol% compared to the McKeown glasses, which were between 0.21-0.85 mol%. The valency of Cr in the ILAW glasses is unknown but may exist as both Cr^{3+} and Cr^{6+} and would be affected by the Na-content. The ILAW composition had a ~26 mol% Na-content, which would be deemed Na-rich, implying that Cr would be oxidising, and the glass structure may be re-polymerising. However, the Cr oxidation could also be affected by $\text{V}^{4+, 5+}$ or $\text{Fe}^{2+, 3+}$ present in the glass, where McKeown et al. (2011) reported their redox behaviour was also dependant on the Na-content. In Na-poor glasses where there was increased oxygen fugacity, redox coupling reactions involving electron donations occurred '*from V to Cr and from Fe to Cr where: $\text{Cr}^{3+} + \text{V}^{4+} \rightarrow \text{Cr}^{2+} + \text{V}^{5+}$ and $\text{Cr}^{3+} + \text{Fe}^{2+} \rightarrow \text{Cr}^{2+} + \text{Fe}^{3+}$* ' (McKeown et al., 2011). The Na-content in the ILAW glasses will also have reduced due to the crystallisation of $\text{Na}_4\text{Zr}_2(\text{SiO}_4)_3$, potentially leading to a reduced glass environment. As such, the transition metal valence states would need to be compared using for example, UV-vis or XANES spectroscopy.

Sulphur (S) can be stable as both sulphide (S^{2-}) and sulphate (SO_4^{2-}) in glasses, however, in reducing conditions the main species present is S^{2-} (Jin et al., 2022; McKeown et al., 2001). When the glass is melted in air and S^{6+} in the form of SO_4^{2-} is the main sulphur species present in borosilicate glasses (Brendebach et al., 2009; Jin et al., 2022; McKeown et al., 2004), it is surrounded by a shell of alkali or alkaline-earth cations, and is isolated in the borosilicate glass matrix (Jin et al., 2022; McKeown et al., 2004; Vaishnav et al., 2020). Jin et al. (2022) reported that the saturation concentration of SO_4^{2-} of simplified LAW glasses was limited by the maximum void concentration, where both CrO_4^{2-} and Cl^- anions can also both exist in the matrix voids similar to SO_4^{2-} and compete with each other for occupation of said voids. This is important to note as the ILAW glasses contain all three species. The total anions the glass matrix can host is dependent on the overall size of the anions, where Jin et al. (2022) cited Jenkins and Thankur (1979) who reported that the radii of SO_4^{2-} , CrO_4^{2-} , and Cl^- anions were 0.258,

0.256, and 0.172, respectively. Even though the radii of SO_4^{2-} and CrO_4^{2-} had a difference of 0.002, the solubilities were different in the LAW glasses, where SO_4^{2-} was 1.25 mol% and CrO_4^{2-} was 2.09 mol% (Jin et al., 2022). The Cl^- is the anion with the smallest radii and had the highest solubility of 3.76 mol% (Jin et al., 2022). There was a strong negative relationship between Cr_2O_3 and Cl^- content on SO_3 solubility, where increasing Cr_2O_3 or Cl^- concentration resulted in a decrease in the SO_3 solubility in the glass (Jin et al., 2022). However, there was variations in the total anion solubility, for which the void model cannot fully explain, where it may be due to a number of other factors (Jin et al., 2022). The first being that the model does not consider the charge compensation by cations, where different cations can be surrounding different anions, e.g., SO_4^{2-} has a preference to be charge compensated by Na^+ cations, whilst Cl^- is charge compensated by Ca^{2+} (Jin et al., 2022; McKeown et al., 2004, 2015; Vaishnav et al., 2020). Secondly, the bonding environment of both Cl and Cr may be more complex than assumed (Jin et al., 2022; McKeown et al., 2015). It should be noted that these anions in the ILAW glasses will be in competition with P_2O_5 in the glass for charge compensating cations e.g., Na^+ and Ca^{2+} , and their presence will, therefore, affect its solubility to some degree based on the arguments presented in the literature above.

The P_2O_5 solubility of the different glass series (NBSP, HLW, LAW, and ILAW) were compared to relevant literature by Vienna et al. (2014, 2016), where they reported that the P_2O_5 constraint for HLW was 4.5 wt% and LAW was 4.6 wt%. The HLW constraint was based on the compositions from tank wastes AY-101/C-104, AZ101, AZ-102, AY-102/C-106, that contributed to 747 HLW glasses, where these glasses consisted of 23 components (Al_2O_3 , B_2O_3 , Bi_2O_3 , CaO , CdO , Cr_2O_3 , F, Fe_2O_3 , K_2O , La_2O_3 , Li_2O , MgO , MnO , Na_2O , Nd_2O_3 , NiO , P_2O_5 , SiO_2 , SrO , TiO_2 , UO_3 , ZnO , and ZrO_2) (Vienna et al., 2016). The LAW glass compositional range was modelled on 253 glasses consisting of 33 components (Al_2O_3 , B_2O_3 , BaO , Bi_2O_3 , CaO , CdO , Cl , CoO , Cr_2O_3 , Cs_2O , CuO , F, Fe_2O_3 , Gd_2O_3 , K_2O , La_2O_3 , Li_2O , MgO , MnO , MoO_3 , Na_2O , NiO , P_2O_5 , PbO , Re_2O_7 , Sb_2O_3 , SiO_2 , SnO_2 , SrO , TiO_2 , ZnO , and ZrO_2) (Vienna et al., 2014). The NBSP series had a P_2O_5 solubility between 6.00-8.83 wt%, which was much higher than both the Vienna HLW and LAW glasses, however, this may have been due to its simplistic nature, where there is a distinct lack of complex behaviours inhibiting the solubility of P_2O_5 . However, the NBSP glass series provided an indication of

the highest possible P_2O_5 content in the glass and provides structural and key property behaviours that can then be inferred on more complex compositions. The HLW P_2O_5 content constraint was between 1.23-2.39 wt%, which was lower than the Vienna value of 4.5 wt%. There was a lack of main compositional components and their ranges presented in the report to compare with. The LAW solubility was 3.96-4.34 wt%, which was 0.88-1.26 wt% higher than the Vienna 2014 value of 3.08 wt% but was lower than the Vienna 2016 constraint model value of 4.6 wt% by 0.26-0.64 wt%. However, the glass compositions were not the same, where compositional differences have contributed to variation in the P_2O_5 solubility. When comparing the 8-component analysed concentrations of LAW1.875 and LAW1.94 to those in the Vienna 2014 composition, the differences were as follows:

1. The SiO_2 , B_2O_3 , Al_2O_3 , Na_2O , and CaO were within the same compositional range, whereas the Fe_2O_3 was much lower and Li_2O content was marginally lower, and the P_2O_5 content was higher.
2. The reduced Li_2O content may influence the type and amount of network modifier used as a charge compensator, which effects the P_2O_5 solubility, however, this cannot be confirmed due to the presence of other components in the ILAW glass but not present in the HLW/LAW glasses.
3. The lower Fe content may also have an influence on the P_2O_5 solubility, where it may be present as either a glass former or modifier, depending on the composition. Langawoski et al. (1996).reported that the presence of Li_2O , CaO , Nd_2O_3 , La_2O_3 , other rare earths, and SO_3 decreased the P_2O_5 solubility. The ILAW glass had a P_2O_5 solubility of >1.57 wt%, which was lower than the Vienna LAW values. The ILAW series had the closest composition to a full LAW glass, with 19 components, albeit the concentrations were different but still within the compositional range of the Vienna 2014 LAW samples. The higher P_2O_5 solubility of the Vienna 2014 and 2016 samples may be due to the addition of other components not added to this reports ILAW samples.

In summary, the P_2O_5 solubility is highly affected and dependant on the compositional components, their concentrations, and subsequent roles in the glass structure. The comparison of the solubility limits from highest to lowest were NBSP > LAW > ILAW > HLW. The ILAW had a higher P_2O_5 solubility than the

HLW glasses, but had 9 more components, suggesting that the presence of ZrO_2 , Cr_2O_3 , MgO , SO_4^{2-} , SnO_2 , V_2O_5 , Cl^- , TiO_2 , F^- , and K_2O may be having an effect of increasing the P_2O_5 solubility, where the exact mechanisms are unclear. While neither of the HLW, LAW, or ILAW series exceeded previously published P_2O_5 constraints, they have produced different values that have not yet been reported, where the solubility limits have been narrowed down to a specific range. This information should better inform compositional decisions when processing tank waste high in P_2O_5 .

5.2.2 Phase Separation and Crystallisation Behaviour

When the P_2O_5 solubility was exceeded, there was evidence of phase separation at a nanoscale and crystallisation at a macro-scale. The NBSP samples showed evidence of a nucleation-type morphology associated with phase separation below at ≥ 4.0 mol% P_2O_5 , resulting in clustering and subsequent crystallisation of phosphate-bearing phases. When the solubility limit was exceeded in the HLW and LAW samples, there was evidence of larger nm droplets were suspended in an amorphous matrix, where in some cases the droplets were interconnected, where XRD and EDX confirmed these droplets to be $\text{NaCa}(\text{PO}_4)$. Raman spectroscopy confirmed the presence of P-related intensities associated with NaCaPO_4 . The visible droplets are evidence of stable phase separation, where phase domains of $0.1\text{--}5\text{ }\mu\text{m}$ size range are detectable as visible opalescence (Taylor, 1990). Macroscopically, both the NBSP, HLW, and LAW glasses exhibited opalescence at higher P_2O_5 content, which is indicative of crystallisation. Liu et al. (2011) and Schuller et al. (2017) commented that liquid-liquid phase separation is the first step of crystallisation, where liquid-liquid phase separation may aid in subsequent inhomogeneous nucleation by producing a phase that has a great tendency to nucleate more than the initial glass (Liu et al., 2011; Schuller et al., 2017). In the case of the NBSP samples, they did exhibit a morphology that resembled liquid-liquid phase separation before crystallisation of NaP_2O_7 occurred, as evidenced by different coloured droplets interspersed in an amorphous matrix. This phase separation may be due to both Si^{4+} and P^{5+} strongly attracting oxygen ions in the glass network, where the attraction of P^{5+} is stronger than that of Si^{4+} (Liu et al., 2011). These attracted oxygen ions need to be charge neutralised by network modifying ions, and as a result there is competition between the network forming ions in attracting the oxygen ions, which

results in phase separation during the cooling of the glass melt, leading to two separated phases. Schuller et al. (2017) cited work by Kracek (Kracek, 1930) who reported that '*The tendency for phase separation increases with cation field strength of alkali and alkaline earths*'. Liu et al. (2011) reported that during nucleation Ca^{2+} and Na^+ cations tend to be more strongly associated with $[\text{PO}_4]^{3-}$ units than $[\text{SiO}_4]^{4-}$, leading to the formation of the more favoured NaCaPO_4 crystal phase (Liu et al., 2011). The introduction of Li_2O into the glass system results in the likelihood of liquid-liquid phase separation and subsequent crystallisation, where Li^+ have a higher tendency to cluster around $[\text{SiO}_4]^{4-}$ units than Na^+ ions (Liu et al., 2011), which both the HLW and LAW glass systems contained. Langawoski et al. (1996) reported that the addition of CaO to a $\text{SiO}_2\text{-B}_2\text{O}_3\text{-Al}_2\text{O}_3\text{-Na}_2\text{O-As}_2\text{O}_3\text{-Sb}_2\text{O}_3$ glass system resulted in an increase in phase separated droplet sizes when P_2O_5 had a constant concentration of 2.5 wt%. CaO was found to concentrate in these droplets and caused the secondary precipitation of an apatite crystal phase. The formation of a Ca-containing phase was also the case for the HLW and LAW glasses.

The ILAW samples did not display evidence of measurable phase separation or crystallisation, where the P_2O_5 solubility was not exceeded. Whilst the ILAW glasses did not exhibit phase separation or crystallisation, it should be noted that they did crystallise upon further heat treatment replicating the glass cooling in a canister. Jantzen (1999) demonstrated that cooling of DWPF frit at different rates could enhance the extent of phase separation, where slower cooling rates resulted in a larger volume fraction of phase separated glass, and even the fastest quench rate still resulted in phase separation.

In summary, all the simplified glasses (NBSP, HLW and LAW) showed evidence of measurable phase separation and or crystallisation, whereas the most complex glass (ILAW) most closely related to a LAW waste simulant presented as X-ray amorphous, where the P_2O_5 solubility was not exceeded. The samples that did show evidence of phase separation at a nanometre scale and crystallisation of phosphate-bearing phases, had morphologies that closely resembled the nucleation and growth type mechanism, as evidenced by their droplet-like shape. It is important to characterise phase separation and subsequent precipitation of soluble crystalline phases in these materials because they could potentially negatively affect the long-term durability of the final vitrified

forms (Jantzen, 1999; Schuller et al., 2017; Taylor, 1990), because metal oxides and fission products tend to partition into the more soluble phase. The effects of phase separation and the presence of these crystal phases will be discussed later in this chapter.

5.2.3 Sulphate Solubility as a Function of P₂O₅ Content

Whilst there have been studies investigating the effects of SO₄²⁻ and P₂O₅ separately in silicate and borosilicate glass systems (Bengisu et al., 2006; Glatz et al., 2018; Muñoz et al., 2007, 2008; Mysen, 1996, 1998; Yu et al., 2017), there has been little research into how P₂O₅ effects the SO₄²⁻ solubility or vice versa in these same systems. The few studies that are available have reported that P₂O₅ can increase the retention of SO₄²⁻, where Vienna et al. (2014) reported that this was ≤ 3.0 mol% P₂O₅. The solubility limits of SO₄²⁻ before crystallisation occurred have been reported to be (i) 0.37-2.05 wt% (Vienna et al., 2014), (ii) 0.15-1.83 wt% (Xu et al., 2020), and (iii) ~1.2 wt% (Lonergan et al., 2020), respectively.

The formation of Na₃PO₄ at 1.0 mol% P₂O₅ is far lower than the solubility limit in the NBSP glasses, which was between 3.0-4.0 mol% P₂O₅, suggesting that the presence of 2.25 mol% SO₄²⁻ is affecting the solubility limit and crystallisation behaviour of the glasses. The solubility limit of SO₄²⁻ in the NBSi-Sx glass system was between 1.875-2.00 mol% (2.34 and 2.51 wt%), where excess SO₃ formed a molten salt layer on the surface of the separated sample. The solubility limit of this glass system was higher than the reported value of ~1.2 wt% by Lonergan et al. (2020) for a similar sodium borosilicate glass system, however, this may be due to the presence of other species in the glass i.e., Al₂O₃ and CaO. The tetrahedrally coordinated Al₂O₃ would also require alkali cations for charge balance (Bingham et al., 2017; Lonergan et al., 2020). In the P₂O₅-doped SO₄²⁻ containing sodium borosilicate glasses, the SO₄²⁻ solubility did not change within error, suggesting that P₂O₅ had a negligible effect.

Langowski (1996) commented that separation in a HLW glass based on the WV-182 composition occurred causing the accumulation of sulphate gall layer. This gall contained Na, P, Ca, La, S, and spinel. The accumulation of the sulphate resulted in the segregation of P₂O₅, Li₂O, CaO, and rare earths into the cold cap, where the sulphates then volatilise '*leaving behind crystalline calcium rare earth phosphates and other phosphates depending on the glass composition*' (Langowski, 1996). In comparison, the NBSiS-P glasses also formed a gall layer,

where after washing in de-ionised water the gall layer was removed, leaving behind a mixture of amorphous material and sodium phosphate crystal phase, as identified by XRD. The presence of phosphate phases can be detrimental to the long term solubility of the final vitrified form and affect other key properties e.g., melt viscosity.

5.3 Glass Structure

5.3.1 The Effects of P_2O_5 on the Glass Structure

As previously reported in literature, P_2O_5 has a tendency to cluster together and once the solubility limit has been exceeded, the glass has a propensity to phase separate and crystallise (Cheng, 2014; Krishnamurthy et al., 2020; Liu et al., 2011; Stone-Weiss et al., 2020). When P_2O_5 was added to the NBSP, NBSiS-P, HLW, and LAW glass systems, the glasses phase separated and crystallized but at different solubilities due to the overall compositional differences.

The MAS NMR analysis of the NBSP samples established that when P_2O_5 was added to the glass system it entered as Q^3_P before changing to Q^0_P , Q^1_P , and Q^2_P units. The P was then supplied O by the silicate sub-network, causing NBØs to covert to BØs, resulting in the re-polymerisation of the network, as evidenced in the decrease in Q^3_{Si} and increase in Q^4_{Si} units. When there were not enough NBØs available, the P bonded with itself resulting in its segregation and clustering, forming Q^0_P and Q^2_P clusters, which eventually led to the formation of $Na_4P_2O_7$, as revealed by the XRD patterns. Raman spectra also displayed characteristic peaks associated with phosphate-bearing crystal phases, as well as a reduction in the intensity of the reedmergnerite-like/ danburite-like structure peak at 630 cm^{-1} , further supporting the notion that the silicate sub-network was re-polymerising. This behaviour agreed with previous literature reported by Krishnamurthy et al. (2020), Muñoz et al. (2006), Schuller et al. (2020), and Stone-Weiss et al. (2020).

Both the HLW and LAW glasses exhibited the dual polymerisation behaviour associated with P_2O_5 , where it had the effect of either re- or de-polymerising the glass structure. For example, between 0.00-0.3125 mol% P_2O_5 in the HLW glass series and at 2.00 mol% P_2O_5 in the LAW series the glass network re-polymerised, which could have been attributed to the removal of modifier cations Ca^{2+} and Na^+ due to the formation of $NaCaPO_4$, resulting in a decrease in the

NBØ content. However, in these same glass series, there was evidence of the glass structure de-polymerising as well, e.g., in the HLW0.3125 sample.

Based on the NBSP structural analysis, the behaviour of P_2O_5 in the HLW and LAW samples can be inferred. Due to the occurrence of the $NaCaPO_4$ crystal phase and droplet morphology of crystallites when the P_2O_5 solubility limit was exceeded, this indicates that the initial addition of P_2O_5 to the glass system results in the formation of P-O-B linkages (yet to be confirmed by B K-edge XANES), where the remainder are present as Q^0_P and Q^1_P species, where Na^+ and Ca^{2+} are partially removed to act as charge compensators leading to an increase in the BØs. Whilst Li^+ ions remain as glass modifiers in the silicate and borate sub-networks due to its higher tendency to cluster around $[SiO_4]^{4-}$ units when compared to Na^+ ions (Liu et al., 2011). However, Achigar et al. (2021) reported that Ca^{2+} and Li^+ ions have a higher tendency than Na^+ to separate from the silicate sub-network, resulting in the de-mixing or crystallisation of the glass, which was not the case in this work's HLW and LAW series, where there was a distinct lack of Li-bearing crystal phases. The Raman spectroscopy of both the HLW and LAW series supports this suggestion, where there was an increase in $(Q3 + Q4) / (Q1 + Q2)$ ratio. However, the presence of the alkali and alkaline earth ions may compete against P_2O_5 for the negative charge of the Al_2O_3 tetrahedra, where they would form P-O-Al linkages, reducing the amount of P_2O_5 which can be incorporated into the glass (Langowski, 1996). There is also the competition induced by the presence of AlO_4 tetrahedra, where they compete alongside the FeO_4^- , BO_4^- , SiO_4^{4-} , and PO_4^- units for the charge compensating cations Na^+ , Ca^{2+} , and Li^+ .

In both the HLW and LAW glasses, Fe_2O_3 is present, where the effects of P_2O_5 on the redox behaviour of iron have not been widely reported. However, a more recent study by Zhang et al. (2022) attempted to structurally characterise the effects of Fe_2O_3 and P_2O_5 in sodium aluminoborosilicate glasses using MAS NMR, where this study may aid in explaining some of the structural behaviour of the HLW and LAW glasses, due to its similar compositions. They reported using ^{23}Na MAS NMR that there was an increase in the average Na-O bond distance with increasing P_2O_5 content due to the changing role of Na^+ cations, where they either changed from being network modifiers to charge compensators, or there was an increase on the fraction of phosphate units associated with NBØs created

by Na^+ cations, where these units are known to have a larger bond distance compared to $\text{Na-NB}\emptyset$ (Lee & Stebbins, 2003; Zhang et al., 2022). The ^{11}B MAS NMR spectra displayed a decrease in the N_4 fraction with the addition of P_2O_5 , which was deduced to be caused by phosphate species being in close proximity to Na^+ cations, decreasing their availability for BO_4 units. However, there was also evidence of a shoulder at $\sim -2\text{ppm}$, which may be ascribed to either the formation of B-O-Si or B-O-P linkages, as both Si and P induce a shielding effect. The ^{27}Al MAS NMR spectra exhibited a slight increase in the shielding of AlO_4 peaks centred at 50 and 60 ppm with increasing P_2O_5 content, suggesting that Al atoms are gradually becoming surrounded by P atoms instead of Si atoms (Brow, 1993; Brow et al., 1993; Zhang et al., 2022), further suggesting the formation of Al-O-P linkages. The ^{31}P MAS NMR spectra evidenced that the phosphate species present in the Fe-free glasses were P^0 at 16 ppm, P^1 species with one Na site replaced by either BO_4 or AlO_4 unit at 8ppm, pure P^1 species at 3 ppm, P^2 species associated with either one BO_4 or AlO_4 unit and one PO_4 unit at -9 ppm where there may have been overlap with other P species, and pure P^2 species at -16 ppm. It was observed that the increase in P_2O_5 content resulted in an increase in the silicate and phosphate sub-network connectivity. The ^{29}Si MAS NMR further complemented the other MAS NMR spectra, where there was a single broad peak centred -87 ppm characteristic of an amorphous material, where the upshift of the peak with increasing P_2O_5 supported the hypothesis of a near-fully polymerised silicate sub-network. When Fe was added to the P_2O_5 containing glasses, it preferentially associated with the phosphate units, resulting in the formation of P-O-Fe linkages over Fe-O-Al/ -Si/ -B linkages. There was a decrease in the fraction of $\text{Fe}^{3+}/\text{total Fe}$ ratio, where Fe^{3+} moved towards a higher coordination and the Fe^{2+} moved towards a six-fold coordination. In the P_2O_5 -free glasses there was a propensity for AlO_4 and FeO_4 tetrahedra to avoid each other, where Fe preferentially bonded to silicate and borate units. However, in the presence of P_2O_5 , Fe instead preferred to associate with phosphate units instead, resulting in the formation of Fe-O-P linkages instead of Fe-O-Si, Fe-O-B, and Fe-O-Al linkages. Hence, additions of P_2O_5 to an Fe-bearing sodium aluminosilicate glass had a minimal impact on the connectivity of the glass network (Zhang et al., 2022). The marginal change in the Fe redox of the HLW and LAW glasses may be due to some of the arguments presented by Zhang et al. (2022), however,

without further analysis by B, P, or Al K-edge XANES, it is not possible to comment further.

SO_4^{2-} is a glass modifier and when added to a sodium borosilicate glass system enters the glass network as isolated tetrahedra in interstitial spaces. S is a multi-valent species, but under oxidising conditions will be present as S^{6+} (sulphate), as is the case in the NBSiS-P glass system, as shown by the distinct lack of sulphite Raman bands in the Raman spectra. P_2O_5 is a glass former and enters the glass network as tetrahedra, forming its own isolated network. Overall, this SO_4^{2-} and P_2O_5 bearing sodium borosilicate glass system is a mixed glass former system containing Si^{4+} , B^{3+} , and P^{5+} , where the Na^+ , added as a glass modifier, results in the de-polymerisation of the glass network by increasing the formation of NBØs in the silicate and borate network. Both SO_4^{2-} and P_2O_5 scavenge Na^+ cations to charge compensate themselves, which in turn re-polymerises the glass network by forming BØ linkages causing an increase in Q^4 units (Xu et al., 2021). The competition for the Na^+ cations is dependent on the cation field strength, which is determined by the coordination and oxidation state (Bingham & Hand, 2008). Based on Goldschmidt's ionic radius ratio rule of $R_{\text{cation}}:R_{\text{oxygen}}$ (Goldschmidt et al., 1926), the cation field strength can be estimated, where SO_4^{2-} and P_2O_5 have values of $0.21 \text{ \AA}^{-2}$ (0.29:1.4) and $0.25 \text{ \AA}^{-2}$ (0.34:1.4), respectively, suggesting that Na^+ cations preferentially charge compensate P_2O_5 .

The continued increase in the P_2O_5 content reduced the availability of Na^+ cations available to de-polymerise the silicate and borate networks, as well as partially charge compensate SO_4^{2-} , due to the low degree of polymerisation (Xu et al., 2021). Based on the structural changes exhibited by Raman spectroscopy, it can be postulated that Na^+ cations were removed from the glass network as network modifiers and used as charge compensators, initially for S existing as isolated SO_4^{2-} then for P_2O_5 , due to the formation of S-O-Na bonds having lower bond strengths than the Na-O-P bonds (Mandal et al., 2022). This leaves fewer available Na^+ cations to form NBØs, re-polymerising the glass network, which is seen effecting the bulk density, molar volume and T_g (Bingham et al., 2017; Mandal et al., 2022). Exceeding the SO_4^{2-} solubility resulted in the crystallisation and formation of the gall layer comprising Na_2SO_4 as evidenced by XRD patterns, which is mostly removed during the washing process due to it being a water-soluble phase, leaving behind the amorphous part of the sample and the insoluble

sodium phosphate phases (Na_3PO_4 and $\text{Na}_4\text{P}_2\text{O}_7$). The removal of Na^+ cations as Na_2SO_4 and sodium phosphate crystal phases, results in the formation of BØs, re-polymerising the glass network. It has been suggested that the relationship between SO_4^{2-} retention is controlled by the polymerisation of the glass network, and hence is related to the relative contents of NBØs and BØs, and free oxygens (Bingham et al., 2017).

The ILAW glasses, as previously stated, are incredibly complex where it is not possible to explain the structural-property relationships adequately. The standard analysis of the structure by MAS NMR cannot be conducted due to the presence of Fe_2O_3 , and XANES may not be possible for all elements present due to overlapping energies. The only comments that can be made on the structure of the ILAW series is based on the Raman spectroscopy which suggested the B and Si sub-networks were interconnected from the presence of the intensity at 630 cm^{-1} associated with reedmergnerite- and danburite-like rings structures. There were also characteristic peaks associated with P_2O_5 at 944 , 991 , and 1040 cm^{-1} , suggesting its incorporation in the glass network. The Fe K-edge XANES indicated that all Fe was present as Fe^{3+} in both the P_2O_5 -free base glass and P_2O_5 -doped glass. This behaviour was also presented in the simpler HLW and LAW glasses, where it was suggested that Fe formed linkages with a phosphate anion as Fe-O-P preferentially over Fe-O-Si, Fe-O-B, and Fe-O-Al. However, this has not been supported by further structural analysis i.e., P K- and $\text{L}_{2,3}$ -edge XANES.

In summary, the role of P_2O_5 in the different glass series remains the same, where it acts as a glass former, and bonds with a variety of species in the glass, where some are more preferential than others. Depending on the composition, depends on the role glass intermediates and glass modifiers have in the glass system with the additions of P_2O_5 , which subsequently dictates the formation of different crystalline phases if the P_2O_5 solubility is exceeded. It is incredibly difficult to explicitly say what effects P_2O_5 is having on each species in the glass beyond the simple NBSP glasses, due to the sheer complexity of the compositions and lack of further structural analysis that can cope with such complex systems. However, study of the NBSP samples has instead provided a starting point in understanding how P_2O_5 interacts with other major glass formers and modifiers, where the study of the HLW and LAW glasses has provided further information on the interaction

between P_2O_5 and Fe_2O_3 . Especially, as there is a distinct lack of study on both species together in waste glass relevant compositions.

5.4 Glass Properties

The Hanford Site waste compositions vary greatly where it is almost impossible to formulate an optimised waste glass for each waste composition based purely on an experimental basis (Vienna, 2014). Hence, mathematical, statistical, and optimisation methodologies are effective in developing glass compositions that meet the property constraints for all the expected range of waste compositions. Therefore, understanding the glass composition-property relationships of the glasses in this thesis are extremely important in contributing to the model databases that optimise the waste glass compositions. The properties that are of interest are the crystallisation behaviour of non-heat treated and heat-treated glasses, T_g , chemical durability, and how additions of P_2O_5 have affected these.

5.4.1 Crystallisation Behaviour of the Glasses

The crystallisation of the glass is a function of the composition of the glass-forming melt. The crystal phases that were present as identified by XRD in the different glass series differed depending on the compositions, as to be expected. The NBSP series presented Na_3PO_4 and $Na_4P_2O_7$ when the P_2O_5 solubility was exceeded, and when subjected to heat treatment the glasses exhibited the same crystal phases with the addition of cristobalite and tridymite. The NBSiS-P series also exhibited Na_3PO_4 and $Na_4P_2O_7$ crystal phases. The HLW and LAW samples had the same compositional components as each other but in differing concentrations, where the HLW series exhibited Fe_2O_3 and $NaCa(PO_4)$, and the LAW series exhibited only $NaCa(PO_4)$, but at a higher concentration of P_2O_5 . When the HLW and LAW series underwent heat treatment, they both exhibited $NaAlSiO_4$, with the addition of other crystalline phases. CCC HLW and LAW both presented $NaCa(PO_4)$, but CCC LAW also exhibited quartz and $Ca_2Al_2SiO_7$. ILAW samples were initially X-ray amorphous until they underwent heat treatment where they exhibited $Na_{5.27}Ca_3(Si_6O_{18})$ and $Na_{7.7}((Al_{5.1}Si_{6.9})O_{24})(SO_4)_{0.88}(S_3)_{0.76}$. The formation of these crystalline phases after heat treatment suggests that there were nanoscale crystallites present in the glass, and that continued heat treatment allowed nucleation and growth, thereby suggesting that the glasses may not be wholly amorphous and homogeneous. The occurrence of

these crystal phases has also been reported for similar glass compositions by Achigar et al. (2021), Langowski (1996), and Zhang et al. (2022).

When evaluating the heat treated HLW samples in this study, P_2O_5 additions also seemed to have suppressed the formation of $NaAlSiO_4$ to a certain degree based on the XRD patterns. This behaviour has also been reported and is in agreement with Lu et al. (2021), Lu et al. (2022), and Zhang et al. (2022). To quantitatively assess this behaviour, Rietveld analysis should have been implemented, and is hence, suggested for future work. Zhang et al. (2022) and Lu et al. (2022) suggested that the suppression of $NaAlSiO_4$ formation may have been due to the formation of Si-O-B and Al-O-P linkages, resulting in a reduction in the formation of Si-O-Al linkages that are paramount for the formation of $NaAlSiO_4$. The formation of Na-Ca silicate and Na-Al-silicate type phases have been reported to be present in LAW glasses, where these crystals have been reported to be detrimental to the glass durability by removing Si and Al from the glass matrix (Lonergan et al., 2021).

$NaAlSiO_4$ has been identified to be a troublesome and undesirable crystalline phase for Hanford waste compositions (Marcial et al., 2017; McCloy et al., 2015; Rodriguez et al., 2017), where it has been reported to affect the chemical durability of the final waste form (Marcial et al., 2017). Its occurrence is dependent on the presence of B_2O_3 and basic cations e.g., Ca^{2+} and Na^+ . The more basic cations present, the more likely it is they cause the formation of nepheline-like-aluminosilicates to precipitate out, where they are ready to donate their electrons resulting in their removal from the covalent glass matrix (Rodriguez et al., 2011). CaO and B_2O_3 have been reported to increase the likelihood of the occurrence of $NaAlSiO_4$, where the effect is not fully understood, but where McCloy et al. (2015) reported that the valency of the B and the connectivity of $^{[3]}B$ was a contributory factor. Fe has also been reported to promote $NaAlSiO_4$ crystallisation in sodium aluminosilicate and aluminoborosilicate (Lu et al., 2022). Lu et al. (2022) reported that when $P_2O_5 > 10$ mol%, the suppression of $NaAlSiO_4$ crystallisation occurred and may have been due to the unavailability of AlO_4 units used to form Si-O-Al linkages that are crucial for its formation (Lu et al., 2022; Marcial et al., 2019; Nizamutdinova et al., 2020). Lu et al. (2022) explained that the substitution of SiO_2 by P_2O_5 leads to the formation of PO_4^{3-} units that are charge compensated by Na^+ cations. At the same time of this is happening, Al is maintaining its four-

coordination state while present as AlO_4 units, which are also being charge compensated by Na^+ cations and Al-O-P linkages (Lu et al., 2022). The formation of the Al-O-P linkages removes the Al from the aluminosilicate glass network, resulting in the promotion of Si-O-Si over Si-O-Al linkages (Lu et al., 2022). The substitution of these linkages for weaker Al-O-P linkages saw a linear decrease in the T_g when the P_2O_5 content was ≤ 15 mol% (Lu et al., 2022). NaAlSiO_4 occurred in both the HLW and LAW glasses, where CCC LAW had the addition of $\text{Ca}_2\text{Al}_2\text{SiO}_7$, a nepheline-like-aluminosilicate phase. The effects of NaAlSiO_4 on the glass samples cannot be confirmed due to a lack of T_g and chemical durability data.

The formation of $\text{Na}_{5.27}\text{Ca}_3(\text{Si}_6\text{O}_{18})$ and $\text{Na}_{7.7}((\text{Al}_{5.1}\text{Si}_{6.9})\text{O}_{24})(\text{SO}_4)_{0.88}(\text{S}_3)_{0.76}$ may affect the chemical durability of the heat treated ILAW glasses. Both crystal phases have resulted in the removal of glass formers, intermediates, and modifiers from the glass network. Lonergan et al. (2021) studied crystallisation constrains of WTP LAW glasses and reported on their CCC impacts and PCT responses, where they reported the formation of a similar Na-Ca silicate phase after heat treatment, $\text{Na}_4\text{Ca}_4\text{Si}_6\text{O}_{18}$ amongst other phases.

In summary, the different glass series produced crystalline phases that have been previously described in literature. The phases produced have been reported to potentially have detrimental effects on the chemical durability of the glasses due to the effects they have on the structure of the glass. The formation of these phases is also influenced by phase separation, where their morphologies can also affect durability, as well as other properties such as the melt viscosity.

5.4.2 Glass Transition Temperature (T_g)

The thermal properties, especially the T_g , of the glass composition are of great importance as they are crucial inputs to aid in the calculation of heat load which allow the ability to assess the heating, ventilation, and air condition (HVAC) system of the Waste Treatment Plant (Rodriguez et al., 2017, 2013). The properties can also affect or modify the design of the HVAC system which are required for the pour cave (Rodriguez et al., 2017, 2013). The Thermal properties also help to develop numerical models used to predict temperature distribution within the glass and the heat emitted from the canisters during cooling (Rodriguez et al., 2017, 2013).

T_g is strongly affected by the composition of the glass, where it is '*influenced by the average number of network constraints per atom*' (Cheng, 2014; Fujii & Kondo, 1981; Rajmohan et al., 2010) and is, therefore, sensitive to the amount of network connectivity (Cheng, 2014; Gin et al., 2012). A decrease in T_g is indicative of the fraction of NBØs in the silicate network increasing, whereas the conversion of $^{[3]}B$ to $^{[4]}B$ units increases T_g (Cheng, 2014; Gin et al., 2012). The trend exhibited by T_g as a function of P_2O_5 differed depending on the composition of the samples in this study. The T_g both increased and decreased as a function of increasing P_2O_5 in the NBSP, HLW, and LAW glasses, but exhibited only an increase in T_g in the NBSiS-P glasses. The ILAW series only had two samples, where the T_g was the same within error. The dual behaviour of both increasing and decreasing T_g has been previously reported by Cheng (2014), where they reported that the addition of 1 mol% P_2O_5 to a sodium borosilicate glass resulted in an increase in the T_g , but further additions resulted in its steady decrease until the glass phase separated. This similar behaviour had also been reported by Bengisu et al. (2006, 2008). Muñoz et al. (2008) reported that the effect of P_2O_5 on T_g was related to the type of P species present in the glass and their concentration. The T_g increased when P_2O_5 was added to the sodium borosilicate glass when compared to the base glass but then decreased when there was >38% of P-O-B species present, as calculated from MAS NMR spectra. Evaluation of the MAS NMR data of the NBSP samples demonstrated the presence of P-O-B linkages at $3.0\text{-}3.5 \pm 5$ ppm, where the T_g was the same within error between 0.0 – 3.0 mol% P_2O_5 , after which it increased gradually with further additions of P_2O_5 . Therefore, the increase in T_g suggested a reduction in the amount of NBØs, resulting in the re-polymerisation of the silicate network, insinuating that there was < 38% P-O-B linkages, which was further supported by the O distribution calculations that demonstrated that there was an increase in Q^4_{Si} units and decrease in Q^3_{Si} units as a function of increasing P_2O_5 content.

5.4.3 Chemical Durability

It is incredibly difficult to predict the dissolution of a multiple glass former containing glass due to the difference in the hydrolysis rates (Lu et al., 2018; Yu & Edén, 2016), reaction energies of different bond linkages between the network formers (Lu et al., 2018; Zapol et al., 2013), and the $^{[3]}B$: $^{[4]}B$ ratio (Lu et al., 2018). In the case of the glasses in this study, they are also different in composition,

where measured elemental mass loss and dissolution behaviour is heavily influenced by it.

The occurrence of sodium phosphate crystal phases in the pristine NBSP and CCC heat treated samples may be problematic due to the removal of glass modifiers, resulting in the polymerisation of the glass network, which will then affect the chemical durability. While there is no durability data available for the NBSP glasses, the effects of sodium phosphate phases can be inferred based on relevant literature of similar glass compositions, as sodium phosphate phases are water soluble, where the solubility of $\text{Na}_4\text{P}_2\text{O}_7$ in cold water is 3.16 g/100 ml and in boiling water 40.26 g/100 ml (National Technical Information Service, 2016). The chemical durability of the separated phase will have a different chemical durability than the homogeneous parent glass material, where it is affected by composition and morphology, and where phase separation has been shown to have an unpredictable effect of the durability of nuclear waste borosilicate glasses (Cheng, 2014; Garbev et al., 2007; Martinez-Ramirez et al., 2003). Cheng (2014) cited Jantzen et al. (2000) where they commented that glasses with higher P_2O_5 content that underwent crystalline phase separation were more chemically durable than glasses that contained <2.6 wt% P_2O_5 that underwent amorphous phase separation. Cheng (2014) reported the reduced Si concentration in the leachate solution where the high resistance of the Si-rich phase may be related to the doping of P_2O_5 , which resulted in the re-polymerisation of the silicate network through the removal of NBØs, which then incrementally promoted the formation of tridymite at higher P_2O_5 content (Cheng, 2014). This was also the case with the heat treated NBSP glasses, where they formed tridymite at higher P_2O_5 doping. Lonergan et al. (2021) reported that the general trend presented in the PCT-B response for glasses with >10 wt% total crystals exhibited a significant increase in the normalised release rate after CCC heat treatment in comparison to quenched glasses.

When comparing the minimum normalised release rate of B, Si, Na, and P for the LAW and ILAW samples, the ILAW glasses had significantly higher NL_B , NL_Si , and NL_Na release rates but lower NL_P when compared to the LAW glasses. These differences can be attributed to the different compositions, where the ILAW has more components that could affect the minimum normalised release rate. As previously stated, the presence of phase separation and crystallisation can also

affect the chemical durability of glass due to changes made to the glass structure, in particular through the polymerisation of the vitreous network, role of glass components in the glass, and distribution of network modifiers (Nicoleau et al., 2015). *'In the initial rate regime the leaching behaviour can be directly correlated with the quantity of NBØs'*, where a decrease in the initial rate is a result of a reduction in the amount of NBØs (Nicoleau et al., 2015). Jain (2000) reported that surface layers that are in contact with solution can act as sinks that reduce the concentration of corrosion species in the solution and increase the affinity for glass dissolution, where it is influenced by amorphous silica phases(s), precipitated crystalline phases, gel layer, and bulk glass components.

The LAW1.94 – 2.25 exhibited crystallisation of NaCaPO₄ which is a water soluble phase where Knabe et al. (1997) reported that it had a high solubility of 1.0 g per litre at pH 7. This crystal phase had a droplet-like morphology surrounded by an amorphous matrix. As the P₂O₅ increased in these samples, the NL_P and NL_{Na} decreased from 0.060 to 0.046 and 0.101 to 0.091 gm⁻²d⁻¹, respectively. The Raman spectroscopy also supported the suggestion that the glass structure was de-polymerising in these samples as a function of increasing P₂O₅ content. The CCC LAW glasses exhibited the crystalline phases NaAlSiO₄ and Ca₂Al₂SiO₇, which are both classified as detrimental to the durability of the final vitrified form (Lonergan et al., 2021; McCloy et al., 2015). However, PCT data is not available for the heat-treated LAW samples, where the effect of these crystal phases could be confirmed. Another contributing factor to the durability behaviour may be the presence of Fe, where Jain (2000) reported that the ratio of Fe³⁺ ions in a tetrahedra coordination that are charge compensated by alkali ions are dependent on the redox ratio, where if the ratio increases or Fe³⁺ ions decrease, then the amount of FeO₄ tetrahedra decreases. It was found that the Na concentration increased rapidly as the sample became more reduced, where the decrease in the durability was associated with the increase in the ratio where more alkali ions are attached as NBØ to Si and fewer are attached to FeO₄ units (Jain, 2000). The Mössbauer spectroscopy of the HLW samples did suggest there was a small fraction of Fe³⁺ tetrahedra that were reduced with increasing P₂O₅.

In comparison, the non-CCC ILAW samples were X-ray amorphous and did not show a decrease in the initial rate, but an increase instead with the addition of P₂O₅, where the NL_{Na}, NL_{Si}, and NL_B increased from 0.527 to 0.546, 0.135 to

0.182, and 0.258 to 0.416 $\text{gm}^{-2}\text{d}^{-1}$, respectively. Jain (2000) cited Feng (1989) where they reported that small additions of SiO_2 , Al_2O_3 , and ZrO_2 in a full waste simulant (WV-205) resulted in an increase in the durability. The effect was based on deficiencies in the network formers, where network formers present in the less durable glass regions were attacked by water. Based on the initial rate values, the ILAW glass did not exhibit an increase in durability, however, this may be due to other effects caused by other components in the glass. The CCC heat treated ILAW samples did exhibit Na-Ca silicate type crystal phases, where the NL_{Na} , NL_{Si} , and NL_{B} also increased from 0.324 to 0.688, 0.114 to 0.158, and 0.208 to 0.561 $\text{gm}^{-2}\text{d}^{-1}$, respectively. The Raman spectra was too complex to deconvolute to produce semi-quantitative data on the polymerisation behaviour of the glasses. The comparison of the pristine ILAW samples and CCC samples showed a reduction in the chemical durability of the glasses, where the heat treatment induced crystallisation of potentially soluble phases.

Nicoleau et al. (2015) reported that generic behaviours associated with aqueous alteration depending on the type of phase separation could be identified, subject to the type of mechanism by which phase separation occurred i.e., spinodal decomposition or nucleation and growth. They cited work by Tomozawa et al. (1990) that proposed a classification system: type A is connected phases within variable durability, type B is separated phases dispersed within a surrounding vitreous matrix phase, and type C which is separated phases dispersed within a mainly durable vitreous phase. The LAW glasses exhibited type C phase separation, whereas CCC ILAW could not be identified due to a lack of SEM imaging. Nicoleau et al. (2015) suggested that if the glass exhibited type C phase separation, then the glass would have low phase connectivity, as a result of the nucleation and growth process, compared to the surrounding glass, and therefore, the reactive surface variations caused by the dissolution of a soluble phase e.g., $\text{NaCa}(\text{PO}_4)$ would be small and have little effect on alteration. The opposite could be said for spinodal decomposition because when the slightly more soluble phase dissolves it leaves behind a large reactive surface area, resulting in the fast alteration of the material (Nicoleau et al., 2015).

In summary, it is not entirely clear what has caused the differences in the durability of the LAW and ILAW glasses when P_2O_5 is added in increasing increments, where the durability was seen to increase, however, the following

factors may contribute in varying degrees: the composition, structure, presence of phase separation, and precipitation of crystalline phases and their morphologies, where they can be a result of thermal treatment. The initial rate can also provide an indication on whether the polymerisation of the glass structure has been affected when coupled with information from other techniques e.g., Raman spectroscopy, and whether phase separation may be present.

5.5 Implications for The Hanford Site

The study of the composition-structure-property of P_2O_5 doped borosilicate glasses has allowed for further data to be acquired regarding key parameters of interest to the Hanford site that can be applied to future waste glass property models, where these properties generally include (Jain & Pan, 2000; Vienna, 2014):

- Natural logarithm of melt viscosity as a function of temperature at a fixed temperature.
- A normalised Si, B, Na, or Li release rate based on PCT methods.
- Specific molar volume and density.
- Thermal Parameters.
- Fraction of crystal phase at temperature C_T .

The results can then be used to aid in effectively producing glass compositions with a low processing risk but with the capacity to vitrify higher P_2O_5 -containing wastes before the occurrence of potentially detrimental crystal phases in the final vitrified form.

5.5.1 Melt Viscosity

Glass melts vitrified using the joule-heated ceramic lined melters require a viscosity between 2 and 10 Pa-s (20 and 100 p) at the melting temperature of 1150°C (Jain & Pan, 2000; Piepal et al., 1993). If the viscosity of the glass melt is below 2 Pa-s, then the glass melt could increase the erosion of the refractory lining, penetrate along refractory joints, result in the volatilisation of alkalis, B, and refractive elements e.g., Cs, and it could cause noble metals to settle at the bottom of the melt which could potentially lead to electrical shortening (Jain & Pan, 2000; Piepal et al., 1993). If the viscosity of the melt is above 10 Pa-s then it could plug the pour stout, cause crystallisation at cold spots in the melter, and result in undissolved components (Jain & Pan, 2000).

The rheological behaviour of the NBSP glasses at a very simple level inferred that if the solubility limit of P_2O_5 was exceeded and there was the formation of phase separation and/or crystals, the viscosity would not only increase as a function of P_2O_5 content, but also increase as the melting temperature decreased. Therefore, it could be suggested that more complex P_2O_5 -containing Hanford waste compositions should be processed at the melting temperature of $1150^{\circ}C$, where if the waste is a HLW composition it should not contain more than >1.25 mol% due to likely formation of P-bearing crystal phases, and if it is an LAW composition, <1.94 mol%. If the glass melt began to cool while still being processed, it may be more likely that P-bearing phases could form, decreasing the viscosity below 2 Pa-s and damaging the refractory and furnace, where processability of the glass may need to be altered.

5.5.2 PCT-B

The current PCT-B specification for Hanford LAW glasses for the normalised release rate of Na, B, and Si should be < 2 g/m² using the 7-day PCT test at $90^{\circ}C$ (Kim et al., 2003). The NL_i for Na, B, and Si of the pristine LAW glasses were all <2 g/m², even the glasses that exhibited crystallisation when the P_2O_5 solubility was exceeded. The pristine ILAW glasses also did not have NL_i for Na, B, and Si that exceeded 2 g/m², however, the values were higher than the LAW glasses, which may be accredited to its more complex composition. The initial examination of LAW based composition leachate behaviours has demonstrated that even when the P_2O_5 solubility is exceeded and crystalline phases form, the chemical durability is still within the expected limit. However, to further clarify if higher P_2O_5 contents is truly detrimental to the glass, results from longer duration PCT tests are required not only on pristine glasses but CCC heat treated samples as well. This will provide a more realistic suggestion on the effects of P_2O_5 on the final glass structure and potential long-term durability.

5.5.3 Density

Density data is an important parameter used to contribute to density models as well as numerical models for temperature distribution (Rodriguez et al., 2017; Vienna et al., 2002). Kruger et al. (2022) measured LAW glasses, where they used specific or molar volumes of constituent oxides to predict glass density. They reported for 41 density values that the density of LAW glasses varied very little and that the values were between $2.64 - 2.70$ g/cm³. The density values for LAW

and ILAW glasses in this study ranged between 2.61 – 2.63 g/cm³ and 2.65 – 2.68 g/cm³, respectively. The density of the HLW samples ranged between 2.62 – 2.63 g/cm³. The HLW and LAW glasses had density ranges that were below the Kruger et al. (2022) range, whereas the ILAW density values were within range. However, the HLW and LAW compositions were simplified with a different composition to the full simulant LAW glasses reported by Kruger et al. (2022). However, the density data collected for the samples could be used in future property-composition models, but it should be noted that the density for the glasses also included values for glasses that are classified as multi-phase i.e., crystallised or amorphous phase separated, where these values could lead to the degradation of the predictive performance models (Vienna et al., 2002). The density values of the glasses in this study are still below the 3.7 g/cm³ contractual limit and comply with the density requirement (Kruger et al., 2022).

5.5.4 Thermal Parameters

Thermal parameters are of great importance for the vitrification of Hanford waste, because the total amount of heat contained in the molten glass that can be removed and the heat release rate depend on thermal properties of the glass, which vary with composition as the glass changes upon cooling (Rodriguez et al., 2017). Knowledge of the thermal parameters are important as inputs for heat load calculations that assess the ability of the WTP heating, ventilation, and air-conditioning (HVAC) system (Rodriguez et al., 2017). Numerical models have been developed to predict the temperature distribution with the glass upon cooling in the canisters. The key parameters needed to predict the heat load are the glass heat capacity (C_p), density (ρ), and thermal conductivity (k) (Rodriguez et al., 2017).

This study did not report on these particular thermal parameters, except for the density, but did report on T_g , T_d , and CTE, which are classified as descriptive parameters, where there are no restrictions on T_g and that it only be reported (Piepal et al., 1993). CTE is also classed as a descriptive parameter, but where it is important for glass processing, where CTE of molten glass affects the convection currents in the melter, and where these convection currents control the transfer of molten glass to the cold cap (Piepal et al., 1993). CTE of solid glass provides information on the extent of internal stresses produced during the

cooling process (Piepal et al., 1993). The T_g , CTE, and T_d are recorded in Table 77 for all samples, where the T_g ranges between 441-535°C, the CTE between 6.57-15.67 1/T K, and the T_d between 490-581°C.

5.5.5 Phase Relations

Phase behaviour includes both phase separation and crystallisation, where the occurrence of both can affect the glass processability, and where insoluble and residual solid phases may increase the rate of accumulation of 'sludge' at the bottom of the melter, causing the melter to become blocked and short the electrodes (Jain & Pan, 2000; Piepal et al., 1993). This can be problematic because radionuclides can be concentrated in the separated melt phase. The NBSP and HLW samples had SEM evidence of nucleation and growth type phase separation, followed by crystallisation. It can be inferred from the formation of the same crystal phase in the LAW glasses that the phase separation mechanism was the same. The ILAW samples did not exhibit crystallisation, however, it did not include all the components in the glass melt, where there was evidence of undissolved material and crystalline material in the crucible. This may indicate problems with processing the melt in larger batches. The samples that underwent the simulated CCC treatment did not exhibit the same crystalline phases as the pristine samples, where the HLW and LAW glasses exhibited NaAlSiO_4 and $\text{NaCa}(\text{PO}_4)$, and ILAW exhibited Na-Ca silicates. NaAlSiO_4 and Na-Ca silicates have been reported to be problematic if they exceed the contents constraint in the glass, where the LAW glasses did not exceed the Na-Al silicate constraint, and ILAW glasses did not exceed the Na-Al silicate alternative or Na-Ca silicate constraints. This suggests that whilst P_2O_5 -containing glasses may produce undesirable crystal phases, their concentration are within the expected constraint, suggesting the glass may be still processable.

In summary, P_2O_5 has affected key parameters set out by the Hanford site, at varying degrees. P_2O_5 had the biggest impact on the melt viscosity and phase behaviour of the pristine and CCC heat treated glasses, however, the effects were within previously reported constraints. There are still other key parameters that need to be investigated, e.g., the heat capacity and electrical conductivity, but the data provided can be contributed to current and future composition-property models devised for the Hanford site.

Sample series	Nominal and Measured P ₂ O ₅ solubility (mol%)	Viscosity at 1150°C Log(η /dPas)	T _g onset range of glass (°C)	CTE of glass ((1/T) K)	T _d (°C)	Density (p)	Crystalline phases	Phase separation
NBSP	3.0-4.0 (N) 2.7 ± 0.02 - 4.0 ± 0.01 (M)	1.07 – 1.72	508 - 535	6.57 - 7.60	550 - 581	-	Na ₃ PO ₄ Na ₄ P ₂ O ₇ Cristobalite Tridymite	Nucleation and growth
HLW	0.625-1.25 (N) 0.69 ± 0.03 -1.19 ± 0.00 (M)	-	448 - 455	10.88 - 11.60	496 - 506	2.619 – 2.645	NaCaPO ₄ Fe ₂ O ₃ NaAlSiO ₄	Nucleation and growth
LAW	1.875-1.94 (N) 1.86 ± 0.00 -2.04 ± 0.02 (M)	-	445 - 465	12.53 - 13.79	492 - 508	2.616 – 2.630	NaCaPO ₄ NaAlSiO ₄ SiO ₂ Ca ₂ Al ₂ SiO ₇	N/A Crystalline phases had droplet morphology
ILAW	>1.53 (N) >0.71 ± 0.03 (M)	-	441 - 443	15.56 - 15.67	490 - 495	2.653 – 2.676	Na _{5.27} Ca ₃ (Si ₆ O ₁₈) Na _{7.7} ((Al _{5.1} Si _{6.9})O ₂₄) (SO ₄) _{0.88} (S ₃) _{0.76}	N/A

Table 77 – Key glass parameters as identified by (Jain & Pan, 2000; Vienna, 2014)

Chapter 6: Conclusions and Future Work

The predominant aims of this PhD were to characterise and analyse the effects of P_2O_5 on borosilicate-based compositions relevant to the Hanford site radioactive waste glasses. As previously stated, the aims of the research were to:

- Understand the effects of varying the amount of P_2O_5 on glass composition, properties, and structure.
- Identify and characterise phase separation in relevant glasses.
- Support increasing waste loading of current high-level activity and low-level activity waste.

6.1 Main PhD Results

The main project results were as follows:

6.1.1 Glass Composition

1. The P_2O_5 solubility differed depending on the glass composition and the component concentrations, which then dictated the phase separation mechanism and subsequent role of other components in the glass i.e., glass intermediates and modifiers. The series with the highest P_2O_5 solubility was as follows: NBSP > LAW > ILAW > HLW.
2. The difference in solubility of P_2O_5 between the HLW (lower solubility) and LAW (higher solubility) samples, suggested that the compositional differences may be a contributing factor i.e., increased modifier content, reduced Fe and Al content.
3. Phase separation identified occurred via the nucleation and growth-type mechanism, followed by crystallisation. There was SEM evidence that suggested that there may have been liquid-liquid phase separation before the solubility limit was reached.
4. Increasing the P_2O_5 content had a negligible effect on the S solubility.

6.1.2 Glass Structure

1. Raman spectra and MAS NMR spectral data of the NBSP samples indicated that the $^{[3]}B$: $^{[4]}B$ concentration remained constant as a function of increasing P_2O_5 content, where it was instead supplied O by the silicate

sub-network, where NBØs transformed to BØs. As a result, the silicate sub-network was re-polymerising with increasing P₂O₅ content, as evidenced by the reduction in the intensity of the reedmergnerite- / danburite-like structure peak at 630 cm⁻¹, as well as the calculated distribution of Q³_{Si} and Q⁴_{Si} species. The Raman spectra of the HLW and LAW glasses suggested that the glasses were both re-polymerising and de-polymerising as a function of increasing P₂O₅.

2. P₂O₅ had a negligible effect on the Fe redox and coordination, where it was present predominantly Fe_{Tet}^{3+} and Fe_{Oct}^{3+} with a marginal contribution of Fe_{Oct}^{2+} , as identified by Fe Mössbauer spectroscopy and Fe K-edge XANES for the HLW, LAW and ILAW samples.

6.1.3 Glass Properties

1. P₂O₅ affected the polymerisation behaviour of the glass structure, resulting in its re- and de-polymerisation, which was then seen effecting key properties i.e., the T_g, CTE, and viscosity. The polymerisation behaviour demonstrated the dual effect of P₂O₅, previously reported in literature.
2. The effect of P₂O₅ on the density of each glass series was as followed:
 - 2.1. NBSP: N/A
 - 2.2. NBSiS-P: Decreased in a linear trend
 - 2.3. HLW: Decreased in a linear trend
 - 2.4. LAW: Increased and decreased in a non-linear pattern
 - 2.5. ILAW: Decreased
3. The viscosity data of the NBSP samples demonstrated that NBSP0.0 had the lowest viscosity value of Log (η / dPas) = 1.0715 at 950°C, whilst NBSP6.0 had the highest with a viscosity value of Log (η / dPas) = 1.721. The occurrence of non-Newtonian behaviour and increase in viscosity in some of the glass melts may have been attributed to phase separation and crystallisation, where the sodium phosphate phases (ortho- and pyrophosphate) may have been acting as the major viscous phase.
4. CCC heat treatment of samples saw the development of new crystal phases, as well as previously amorphous samples developing crystallinity. The crystal phases between the HLW and LAW were similar, whilst the ILAW samples were different. This was attributed to the difference in composition.

5. The CCC crystalline phases were NaCaPO_4 , Na-Al like and Na-Ca like silicates, which were calculated to be within the compositional constraints reported by PNNL.
6. The 7-day PCT-B tests established an estimate of the initial rate of dissolution as a function of increasing P_2O_5 content. The results of the LAW samples indicated that LAW1.875 was the least durable sample whilst LAW1.25 was the most durable. The results of the ILAW samples indicated a decreasing level of durability, such that CCC ILAW0.00 > ILAW0.00 > ILAW1.53 > CCC ILAW1.53. However, the CCC heat treated samples would have been affected by the presence of $\text{Na}_{7.7}((\text{Al}_{5.1}\text{Si}_{6.9})\text{O}_{24})(\text{SO}_4)_{0.88}(\text{S}_3)_{0.76}$, and $\text{Na}_{5.27}\text{Ca}_3(\text{Si}_6\text{O}_{18})$ crystal phases. The sample with the higher additions of P_2O_5 displayed decreased durability.

6.1.4 Implications for the Hanford Site

The implications of the research conducted in this thesis are the following:

1. Radioactive waste containing P_2O_5 can potentially be vitrified, but with different limits depending on the compositional components and their relative concentrations. For example, the HLW based compositions had higher Fe and lower modifier content compared to the LAW based compositions, which contributed to lower P_2O_5 solubility. Therefore, it can be inferred that HLW wastes can be vitrified with P_2O_5 content between 0.69 ± 0.03 and 1.19 ± 0.00 mol%, whereas the LAW waste is between 1.86 ± 0.00 and 2.04 ± 0.02 mol%.
2. In all series beyond the specific P_2O_5 solubility limit ranges reported, the samples initially displayed evidence of nucleation-type phase separation features as shown by SEM. When the solubility limit ranges were further exceeded, crystallisation occurred, where the crystal phases present were dependant on the compositional components. The NBSP samples exhibited Na_3PO_4 and $\text{Na}_4\text{P}_2\text{O}_7$, HLW exhibited NaAlSiO_4 and $\text{NaCa}(\text{PO}_4)$, while LAW exhibited $\text{NaCa}(\text{PO}_4)$. Upon heat treatment, replicating centre line cooling conditions the glasses exhibited Na-Ca like and Na-Al like phases, both previously identified in PNNL reports, however these did not exceed the limiting constraints (Lonergan, et al. 2021).
3. The effect of P_2O_5 on the solubility of other components in the glasses varied, it did not seem to increase the SO_4^{2-} content as reported by Vienna et al.

(2014), but did lead to the suppression of crystallisation in the HLW glasses after heat treatment, as reported by Lu et al. (2021).

4. This work has provided a baseline to allow future researchers to investigate P_2O_5 loading in glasses relevant to vitrification.

6.2 Future Research

Suggested future research is as follows:

6.2.1 Glass Composition

1. Establish the P_2O_5 solubility to within a narrower range in the ILAW glasses, which involves producing and characterising more glasses.
2. Dope full simulant (ILAW) with Cs to simulate waste loading as a function of P_2O_5 solubility, where these glasses have their composition, crystallisation, thermal, and chemical behaviours, and physical properties measured.
3. Investigate the effect of other compositional components that could increase the waste loading capacity of P_2O_5 in the HLW and LAW based compositions.

6.2.2 Glass Structure

1. Ascertain the short- and medium- range structural order of P_2O_5 -doped aluminoborosilicate glasses and full simulant glasses using B K-edge, P K – and $L_{2,3}$ -edge, Si K-edge XANES, as the glass system is too complex to be fully characterised using only Raman spectroscopy. Additionally, these glasses contain Fe and thus cannot be measured using NMR. The spectra generated will provide information about the oxidation states, coordination numbers, and local environment of the P, B, and Al, which can then be used in conjunction with Raman spectroscopy to develop a deeper understanding of the glass structure and the effects of the structure on the thermal properties and crystallisation behaviour.
2. Use SEM/EDS to confirm the presence of phase separation, assess the morphology, and characterise any crystalline phases present.
3. Use small angle neutron scattering (SANS) to measure nanometre clustering as an indication of phase separation before being detectable by NMR and XRD as clustering and crystalline phases in P_2O_5 -doped aluminosilicate and full simulant glasses.
4. Implement TEM to aid in visualisation of phase separation mechanisms e.g., nucleation and growth.

6.2.3 Glass Properties

1. Measure the viscosity of P_2O_5 -doped aluminosilicate glasses and full simulant glasses to characterise the rheological behaviour to better inform melt properties.
2. Perform CCC heat treatment on all HLW samples and characterise the crystal phases using XRD Rietveld analysis and SEM/EDS.
3. Perform irradiation experiments by bombarding the glasses with helium atoms to stimulate alpha radiation, electrons (using SEM), and X-rays (using XRF) to model the glasses self-irradiation processes and thermal degradation experienced by vitrified wastes. The samples would subsequently be analysed by electron paramagnetic resonance spectroscopy (EPR), UV-VIS spectroscopy, Raman spectroscopy, X-ray photoelectron spectroscopy (XPS), and XANES to characterise any defects or changes in multivalent species oxidation state in the glass.
4. Conduct UV-Vis spectroscopy of pristine and CCC ILAW glasses to identify oxidation state of rare-earth and transition metals in the glass composition, and to establish if additions of P_2O_5 have caused changes in the oxidation state and/or coordination.
5. Perform longer term chemical durability tests with intervals 7, 14, 28.....100 days to establish the true initial rate of dissolution and establish effects of P_2O_5 on the glass in relation to the dissolution kinetics and other stages of durability. This work needs to be conducted on both pristine and CCC heat treated samples. SEM/EDS needs to be conducted on the solid material left behind after the PCT test to assess whether there is the presence of a gel layer and what its composition may be.
6. Conduct heat capacity (C_p) measurements of all samples as a function of P_2O_5 content, as this has been highlighted as an important thermal parameter to measure in terms of contributing to numerical models used for temperature distribution within the glass.

Chapter 7: References

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Chapter 8: Appendix

8.1 Appendix: Glossary

Acronym	Meaning
QXAFS	Quick-scanning x-ray absorption fine structure
a3	0 (pure Lorentzian) to 1 (pure Gaussian)
μ	Absorption coefficient
$e^{-2k^2\sigma_j^2}$	Accounts for the effects of thermal vibration and structural disorder which alter the EXAFS oscillations at high k-region
ΔG_D	Activation energy for atomic transport across the interface
K α	Alpha radiation
α	Approximate instantaneous coefficient of linear thermal expansion at ts
E_a/R	Arrhenius activation energy
ν_4	Asymmetric bending mode
ν_3	Asymmetric stretching mode
APT	Atom probe tomography
APF	Atomic packing factor
n	Atoms per unit cell
$C_{i(\text{blank})}$	Average blank concentration, gi/l
L	Average crystallite size
λ_j	Average free pathway for excited photoelectrons
BSE	Backscattered electron image
$F_j(k)$	Backscattering amplitude
K β	Beta radiation
K or K_B	Boltzmann constant
$\text{BO}_4 / [^4\text{B}] / [^4\text{B}]^{3+}$	Boron (4+) tetrahedral ion
$\text{BO}_3 / [^3\text{B}] / [^3\text{B}]^{3+}$	Boron (3+) trigonal ion
BPP	Bismuth Phosphate Process
BØ	Bridging oxygen
C-S-H	Calcium-silica-hydrogen
CCC	Centreline cooling
$\text{P}^{(2)}_{2\text{P}}$	Chain phosphate species
$\Delta(f)$	Change in the function f
δ_{iso}	Chemical shift

$C_i(I)$	Concentration observed in the i th blank
$C_i(\text{sample})$	Concentration of element “ i ” in solution, g/l
T_c	Consolute temperature
T_b	Critical miscibility temperature
CPS	Crystalline phase separation
σ^2	Debye-waller factor – the mean square variation in the interatomic distance r
T_d	Decomposition temperature
DWPF	Defence waste processing facility
DFT	Density functional theory
f_x	Dependence on the gaseous atmosphere
R_j	Distance between the absorbing and scattering atoms
$\Delta\mu$	Edge jump
$\Delta(E)$	Energy difference
ETF	Effluent treatment facility
EQS	Electric field
EELS	Electron energy loss spectroscopy
W_0	Empty holder in distilled water to the nearest 0.1 mg
$\mu(E)$	Energy dependence of the absorption coefficient
$\ln(A_s)$	Entropic factor of Arrhenius
EPA	Environmental protection agency
EXAFS	Extended x-ray absorption fine structure
$V_f(n)$	Final volume of leachate measured in the test with n th sample replicate, l
FY	Fluorescence yield
FIB	Focused ion beam
W^*	Free energy of formation of a critical nucleus
f_a	Fugacity of the gaseous species α
FS-P	Full-simulant-phosphorus
Γ	Full-width half-maximum (FWHM)
ILAW	Fully immobilised LAW
Z	Function of the cation
a^2	FWHM
GNF	Generalised Newtonian fluids
GTS	Glass technology services
$\text{Na}_3\text{CaAl}_3\text{Si}_3\text{O}_{12}(\text{SO}_4)$	Hauyne
HVAC	Heating, ventilation, and air condition
HLW	High level waste

HTV	High temperature viscosity
K_H	Hruby parameter
HAp	Hydroxyapatite
HMF	Hyperfine magnetic field
ILAW	Immobilised low-activity waste
ICP-OES	Inductively coupled plasma optical emission spectroscopy
$V_i(n)$	Initial volume of leachate in the test with nth sample replicate
I / I_0	Integral / intensity
ILW	Intermediate level waste
IAEA	International atomic energy agency
ICDD	International centre for diffraction data
IS	Isomer shift
δ	Isomer shift (mm/s)
JHCM	Joule–heated ceramic lined melters
d	Lattice interplanar spacing of the crystal
LERF	Liquid effluent retention facility
T_{liq} or TL	Liquidus temperature
LAW/ LLW	Low level activity waste
f_i	Mass fraction of element “i” in the unleached sample, g_i/g_{glass}
T_c	Maximum crystallization temperature
K_{gl}	Maximum thermal stability and glass forming ability
T_m	Melting temperature
$P^{(2)}$	Metaphosphate
MIBK	Methyl isobutyl ketone
R_i	Minimum normalised release rate
MAE	Mixed alkali effect
MGFE	Mixed glass former effect
MLLW	Mixed low-level waste
A^+	Modifier ion
A_2O	Modifier oxide
MQ MAS NMR	Multiple Quantum MAS NMR
NBØ	Non-bridging oxygen
NL(element)	Normalised mass loss of element of interest
NCi	Normalised concentration, g_i/l
NLi	Normalised elemental mass loss, $g_{wasteform}/m^2$
NL _x	Normalised mass loss

NL(B)	Normalised mass loss of boron
I	Nuclear spin momentum
Ci(n)	Observed concentration in the test with the nth sample, g/l
ORP	Office of river protection
T _x	Onset of crystallization
P ₂ O ₇ ⁴⁻	Orthophosphate
P ⁰	Orthophosphate/monophosphate
PNNL	Pacific Northwestern National Laboratory
a ₀	Peak intensity
a ₁	Peak position
$\varphi_c(k)$	Phase-shift of the absorbing atom
LO	Phonon
E ₀	Photon energy
PUREX	Plutonium uranium extraction
ΔH_m	Positive enthalpy of mixing
PDF	Powder diffraction file
PCT-B	Product consistency test method B
PO ₄ ³⁻	Pyrophosphate
P ⁽¹⁾	Pyrophosphate
Q ⁿ	Q species
Δ	Quadrupolar splitting (mm/s)
RDS	Raman difference spectra
J	Rate of nucleation
$\lambda_j T_{rg}$	Reciprocal value of the reduced glass transition temperature
REDOR	Rotational-Echo Double-Resonance
SEM	Scanning electron microscopy
$\delta_j(k)$	Scattering phase shift of the scattering atom
SCPD-HLW	Simple-complex-phosphate-doped high-level activity
SCPD-LAW	Simple-complex-phosphate-doped low-level activity
MAS NMR	Solid state magic angle spinning nuclear magnetic resonance
C _q	Specific heat
SNF	Spent nuclear fuel
SRNL	Savannah River National Laboratory
s	Standard deviation of the blank concentrations
ν_2	Symmetric bending mode
ν_1	Symmetric stretching mode

-TΔSm	Temperature dependant entropy
TMS	Tetramethylsilane hydrogens
ν	The measure of Raman shift
c	The speed of light
k	Thermal conductivity
TEY	Total electron yield
N _j	Total number of atoms in the j-th shell
TRU	Transuranic waste
TBP	Tri-butyl phosphate
TPA	Tri-party agreement
A _{1g} / E _g	Type of phonon mode
DOE	US Department of Energy
VLLW	Very low-level waste
VSLW	Very short-lived waste
Log(η/dPas)	Viscosity
VTF	Vogel-Tammann-Fulcher
V _m	Volume of atoms
V _c	Volume per unit cell (cm ³ /unit cell)
WTP	Waste treatment and immobilisation plant
λ	Wavelength of the characteristic x-ray
ν ₀	Wavenumber of incident laser light
WT	Weight of glass and holder in distilled water to the nearest 0.1 mg
WA	Weight of glass specimen in air to the nearest 0.1 mg
W _w	Weight of specimen in water
K _w	Weinberg parameter
XANES	X-ray absorbance near edge spectroscopy
XAS	X-ray absorption spectroscopy
XRD	X-ray diffraction
XRF	X-ray fluorescence spectroscopy
θ	X-ray incidence angle (Bragg angle)
xVBF	Voight-based fitting
P ¹ _{1B(IV)}	P ¹ unit linked to one ^[4] B
P ¹ _{1P}	Pyrophosphate species
P ⁽²⁾ _{2B}	P ² units linked to one boron atom
P ⁽²⁾ _{1B, 1P}	P ² units linked to one boron atom and one phosphorus atom
P ⁽³⁾ _{2B, 1P}	P ³ units linked to two boron atoms and one phosphorus atom

$P^{(3)}_{2B}$	P^3 units linked to two boron atoms
$P^{(3)}_{1B}$	P^3 units linked to one boron atom

8.2 Appendix: IAEA radioactive waste classification

Table 78 - Six classes of Radioactive waste glass sourced and modified from
(International Atomic Energy Agency & IAEA, 2009)

Type of Waste	Description
Exempt waste (EW)	Waste that meets the criteria for clearance, exemption, or exclusion from regulatory control for radiation protection purposes.
Very Short-Lived Waste (VSLW)	Waste that can be stored for decay over a limited period (few years) and cleared from regulatory control. This includes waste containing primarily radionuclides with very short half-lives.
Very Low-Level Waste (VLLW)	Waste that does not necessarily meet the criteria of EW, but that does not need high level containment and isolation and, therefore, is suitable for disposal in near surface landfill type facilities.
Low Level Waste (LLW)	Waste that is above clearance levels, but with limited amounts of long-lived radionuclides. Such waste requires robust isolation and containment for periods of up to a few hundred years and is suitable for disposal in engineered near surface facilities
Intermediate Level Waste (ILW)	Waste that contains long-lived radionuclides, requires a greater degree of containment and isolation than that provided by near surface disposal. Where the waste in this class requires disposal at greater depths, of the order of tens of metres to a few hundred metres.
High Level Waste (HLW)	Waste with levels of activity concentration that generate significant quantities of heat by the radioactive decay process or waste with large amounts of long-lived radionuclides need to be disposed of in deep stable geological formations

usually several hundred metres or more below the
surface.

8.3 Appendix: Hanford Tank Waste

Tank	Primary Waste	Secondary waste	Tank	Primary Waste	Secondary waste
A-101	A1 saltcake	P2 sludge	C-203	HS sludge	N/A
A-102	A1 saltcake	N/A	C-204	HS sludge	N/A
A-103	A1 saltcake	AR sludge	S-101	S1 saltcake	R1 (boiling) sludge
A-104	AR sludge	P1 sludge	S-102	S2 saltcake	S1 saltcake
A-105	P2 sludge	N/A	S-103	S1 saltcake	S2 saltcake
A-106	A1 saltcake	SRR sludge	S-104	R saltcake	R1 (boiling) sludge
AN-101	A2 Saltcake	N/A	S-105	S1 saltcake	R1 (non-boiling) sludge
AN-102	A2 Saltcake	N/A	S-106	S1 saltcake	N/A
AN-103	A2 Saltcake	N/A	S-107	R1 (non-boiling) sludge	CWR1 sludge
AN-104	A2 Saltcake	N/A	S-108	S1 saltcake	R1 (non-boiling) sludge
AN-105	A2 Saltcake	N/A	S-109	S1 saltcake	R1 (non-boiling) sludge
AN-106	A2 Saltcake	N/A	S-110	S1 saltcake	R1 (boiling) sludge
AN-107	A2 Saltcake	N/A	S-111	S1 saltcake	R1 (non-boiling) sludge
AP-101	Liquid	N/A	S-112	S1 saltcake	R1 (non-boiling) sludge
AP-102	Liquid	N/A	SX-101	R1 (non-boiling) sludge	R saltcake
AP-103	Liquid	N/A	SX-102	S1 saltcake	R1 (non-boiling) sludge
AP-104	Liquid	N/A	SX-103	S1 saltcake	R saltcake
AP-105	A2 Saltcake	N/A	SX-104	S1 saltcake	R1 (boiling) sludge
AP-106	Liquid	N/A	SX-105	S1 saltcake	R1 (non-boiling) sludge
AP-107	Liquid	N/A	SX-106	S2 saltcake	S1 saltcake
AP-108	Liquid	N/A	SX-107	R1 (non-boiling) sludge	R saltcake
AW-101	A2 Saltcake	N/A	SX-108	R1 (non-boiling) sludge	N/A
AW-102	CWP1 sludge	N/A	SX-109	R saltcake	R1 (boiling) sludge

AW-103	CWZr2 sludge	A1 sludge	SX-110	R1 (non-boiling) sludge	R saltcake
AW-104	A2 Saltcake	PL2 sludge	SX-111	R1 (non-boiling) sludge	R saltcake
AW-105	CWZr2 sludge	N/A	SX-112	R1 (non-boiling) sludge	N/A
AW-106	A2 Saltcake	SRR sludge	SX-113	DE sludge	R saltcake
AX-101	A1 saltcake	BL sludge	SX-114	R saltcake	R saltcake
AX-102	A1 saltcake	P2 sludge	SX-115	R1 (non-boiling) sludge	N/A
AX-103	A1 saltcake	N/A	SY-101	S2 saltcake	N/A
AX-104	P2 sludge	N/A	SY-102	Unidentified sludge	Z sludge
AY-101	Unidentified sludge	N/A	SY-103	S2 saltcake	N/A
Ay-102	BL sludge	N/A	T-101	T2 saltcake	CWR2 sludge
AZ-101	P3 sludge	N/A	T-102	CWP2 sludge	MW sludge
AZ-102	P3 sludge		T-103	CWP2 sludge	CWR1 sludge
B-101	B saltcake	BL sludge	T-104	1C sludge	N/A
B-102	B saltcake	N/A	T-105	2C sludge	CWR1 sludge
B-103	B saltcake	Mixed waste (MW) sludge	T-106	CWR1 sludge	1C sludge
B-104	2C sludge	1C sludge	T-107	1C sludge	TBP sludge
B-105	B saltcake	2C sludge	T-108	T1 saltcake	1C sludge
B-106	TBP sludge	1C sludge	T-109	T1 saltcake	N/A
B-107	1C sludge	B saltcake	T-110	2C sludge	224 Post-1949 sludge
B-108	B saltcake	CWP2 sludge	T-111	2C sludge	224 Post-1949 sludge
B-109	B saltcake	CWP2 sludge	T-112	2C sludge	224 Post-1949 sludge
B-110	2C sludge	P2 sludge	T-201	224 Pre-1949 sludge	N/A
B-111	2C sludge	P2 sludge	T-202	224 Pre-1949 sludge	N/A
B-112	2C sludge	BY saltcake	T-203	224 Pre-1949 sludge	N/A
B-201	224 Pre-1949 sludge	N/A	T-204	224 Pre-1949 sludge	N/A
B-202	224 Pre-1949 sludge	N/A	TX-101	T2 saltcake	T2 saltcake

B-203	224 pre-1949 sludge	N/A	TX-102	R1 (non-boiling) sludge	MW sludge
B-204	224 pre-1949 sludge	N/A	TX-103	T2 saltcake	T1 saltcake
BX-101	CWP2 sludge	TBP sludge	TX-104	T2 saltcake	T2 saltcake
BX-102	DE sludge	CWP2 sludge	TX-105	T2 saltcake	MW sludge
BX-103	CWP2 sludge	TBP sludge	TX-106	T2 saltcake	R1 (non-boiling) sludge
BX-104	CWP2 sludge	MW sludge	TX-107	1C sludge	R saltcake
BX-105	CWP2 sludge	TBP sludge	TX-108	T2 saltcake	TBP sludge
BX-106	CWP2 sludge	TBP sludge	TX-109	T2 saltcake	N/A
BX-107	1C sludge	N/A	TX-110	T2 saltcake	1C sludge
BX-108	TBP sludge	1C sludge	TX-111	T2 saltcake	1C sludge
BX-109	TBP sludge	N/A	TX-112	T2 saltcake	T1 saltcake
BX-110	BY saltcake	A2 saltcake	TX-113	T2 saltcake	1C sludge
BX-111	BY saltcake	1C sludge	TX-114	T2 saltcake	T1 saltcake
BX-112	1C sludge	N/A	TX-115	T2 saltcake	TBP sludge
BY-101	BY saltcake	CWP2 sludge	TX-116	T1 sludge	T2 saltcake
BY-102	BY saltcake	PFeCN sludge	TX-117	T2 saltcake	T1 saltcake
BY-103	BY saltcake	PFeCN sludge	TX-118	T2 saltcake	Unidentified saltcake
BY-104	BY saltcake	PFeCN sludge	TY-101	1CFeCN sludge	T1 saltcake
BY-105	BY saltcake	PFeCN sludge	TY-102	T2 saltcake	T1 saltcake
BY-106	BY saltcake	PFeCN sludge	TY-103	TBP sludge	1CFeCN sludge
BY-107	BY saltcake	PFeCN sludge	TY-104	1CFeCN sludge	TBP sludge
BY-108	BY saltcake	PFeCN sludge	TY-105	TBP sludge	N/A
BY-109	BY saltcake	CWP2 sludge	TY-106	DE sludge	TBP sludge
BY-110	BY saltcake	PFeCN sludge	U-101	R1 (non-boiling) sludge	S2 saltcake
BY-111	BY saltcake	N/A	U-102	T2 saltcake	S2 saltcake
BY-112	BY saltcake	MW sludge	U-103	S1 saltcake	R1 (non-boiling) sludge
C-101	CWP1 sludge	TBP sludge	U-104	DE sludge	T2 saltcake

C-102	CWP1 sludge	CWP1 sludge	U-105	S2 saltcake	N/A
C-103	CWP1 sludge	AR sludge	U-106	S1 saltcake	CWR1 sludge
C-104	CWP1 sludge	CWP2 sludge	U-107	S2 saltcake	S2 saltcake
C-105	CWP1 sludge	TBP sludge	U-108	S1 saltcake	S2 saltcake
C-106	AR sludge	N/A	U-109	S1 saltcake	CWR1 sludge
C-107	1C sludge	SRR sludge	U-110	R1 (boiling) sludge	S1 saltcake
C-108	1C sludge	TBP sludge	U-111	S2 saltcake	CWR1 sludge
C-109	TFeCN sludge	CWP1 sludge	U-112	R1 (non-boiling) sludge	N/A
C-110	1C sludge	N/A	U-201	CWR1 sludge	N/A
C-111	TFeCN sludge	CWP1 sludge	U-202	CWR1 sludge	N/A
C-112	TFeCN sludge	CWP1 sludge	U-203	CWR1 sludge	N/A
C-201	HS sludge	N/A	U-204	CWR1 sludge	N/A
C-202	HS sludge	N/A			

Table 79 - Primary and secondary Hanford waste types for individual tanks
taken from (Wells et al., 2011)

Waste type	Definition
1C sludge	BiPO ₄ first cycle decontamination waste (1944–1956)
1CFeCN sludge	Ferrocyanide sludge from in-farm scavenging of 1C supernatants in TY-Farm (1955–1958)
224 post-1949 sludge	Lanthanum fluoride process 224 Building waste (1950–1956)
224 pre-1949 sludge	Lanthanum fluoride process 224 Building waste (1944–1949)
2C sludge	BiPO ₄ second cycle decontamination waste (1944–1956)
A1 saltcake	Saltcake from first 242-A Evaporator campaign using 241-A-102 feed tank (1977–1980)
A2 saltcake	Saltcake from the second 242-A Evaporator campaign (1981–1994)
AR sludge	Washed plutonium uranium extraction (PUREX) sludge (1967–1976)
B saltcake	Saltcake from 242-B Evaporator operation (1951–1953)
BL sludge	Low-level waste from B Plant Sr and Cs recovery operations (1967–1976)
BY saltcake	Saltcake from in-tank solidification (ITS) in BY-Farm (1965–1974)
CWP1 sludge	PUREX cladding waste, aluminium clad fuel (1956–1960)
CWP2 sludge	PUREX cladding waste, aluminium clad fuel (1961–1972)
CWR1 sludge	Reduction oxidation (REDOX) cladding waste, aluminium clad fuel (1952–1960)

CWR2 sludge	REDOX cladding waste, aluminium clad fuel (1961–1966)
CWZr2 sludge	PUREX zirconium cladding waste (1983–1989)
DE sludge	Diatomaceous earth
HS sludge	Hot semi-works ⁹⁰ Sr recovery waste (1962–1967)
MW sludge	BiPO ₄ process metal waste (1944–1956)
P1 sludge	PUREX HLW (1955–1962)
P2 sludge	PUREX HLW (1963–1967)
P3 sludge	PUREX HLW (1983–1990)
PFeCN sludge	Ferrocyanide sludge from in-plant scavenged supernatant
PL2 sludge	PUREX LLW (1983–1988)
R saltcake	Saltcake from self-concentration in S- and SX-Farms (1952–1966)
R1 (boiling) sludge	Boiling REDOX HLW
R1 (non-boiling) sludge	Non-boiling REDOX HLW
S1 saltcake	Saltcake from the first 242-S Evaporator campaign using 241-S-102 feed tank (1973–1976)
S2 saltcake	Saltcake from the second 242-S Evaporator campaign using 241-S-102 feed tank (1977–1980)
SRR sludge	Sr recovery waste from sluiced P sludge
T1 saltcake	Saltcake from the 242-T Evaporator campaign (1951–1956)
T2 saltcake	Saltcake from the last 242-T Evaporator campaign (1965–1976)
TBP sludge	Tributyl phosphate waste (from solvent based uranium recovery operations)
TFeCN sludge	Ferrocyanide sludge produced by in-tank or in-farm scavenging
Z sludge	Z Plant waste

Table 80 – Waste type definitions taken from (Wells et al., 2011)

8.4 Appendix: Density

According to ASTM C693-93 density of glass is calculated by (ASTM International, 2003):

1. Determine the density, ρ_A , of the air from the provided table in ASTM C693-93
2. -Weigh the glass specimen in air to the nearest 0.1 mg and record it as W_A
3. Calculate the weight of the specimen in water, W_w , as follows:

$$W_w = W_T - W_0 \quad (35)$$

Where W_w is the weight of the specimen in water, W_T is the weight of glass and holder in distilled water to the nearest 0.1 mg, W_0 is the weight of the empty holder in distilled water to the nearest 0.1 mg.

4. Read the distilled water temperature to the nearest 0.1°C and determine the water density, recording this as ρ_w
5. Calculate the glass density, ρ , at the average air-water laboratory temperature, T_L , as follows:

$$\rho = \frac{(W_A \rho_w - W_W \rho_A)}{(W_A - W_W)} \quad (36)$$

Where W_A is the Weight of glass specimen in air to the nearest 0.1 mg

6. Calculate the glass density, ρ_s , at a standard reference temperature, T_s , as follows:

$$\rho_s = \frac{\rho}{1 + 3\alpha(T_s - T_L)} \quad (37)$$

Where α is the approximate instantaneous coefficient of linear thermal expansion at T_s .

8.5 Appendix: Step-by-step XANES and EXAFS data reduction

In order to reduce the XANES data, the following steps need to be followed:

1. Deglitch the raw data to remove sharp structures in the line shape often caused by fake reflections from the crystal monochromator or from diffraction signals of the sample.
2. Convert the measured intensities to $\mu(E)$ to correct any measurement errors such as self-absorption effects and detector deadtime.
3. Identify E_0 , with is the maximum derivative of $\mu(E)$.
4. Subtract a smooth pre-edge function from $\mu(E)$ to remove instrumental background and absorption from other edges.
5. Determine the edge jump, $\Delta\mu$, at the threshold energy and normalise $\mu(E)$ so that the subtracted pre-edge and normalised $\mu(E)$ changes from 0 below the threshold energy to 1 above the threshold energy.
6. Remove a smooth post-edge background function.
7. The data is at a point where the XANES data can be processed by fitting the pre-edge feature with Gaussian line shapes with integrated intensities,

to establish the pre-peak centroid that is associated with a particular species and its associated coordination.

In order to reduce the EXAFS data, the following steps need to be followed:

1. To process the EXAFS region, convert χ from energy E to photoelectron wavenumber, $k = \sqrt{2m(E - E_0)/\hbar^2}$.
2. K-weight the XAFS $\chi(k)$ and Fourier transform (FT) into R-space. The R-space spectrum shows the radial distribution from isolated neighbouring atoms with different shells. However, the peak position in the FT curve will not be identical to the interatomic distance produced by the radial distribution function (RDF), because the phase-shift term used for EXAFS, shortens the actual peak position by approximately 0.3-0.5 Å for first shell atoms.
3. Inversely transform the R-space peak that corresponds to a single shell to K-space. The specific oscillation of this shell is filtered from the overall spectrum to extract structural information pertaining to that shell through a curve-fitting procedure.
4. Once the single-shell oscillation has been isolated, it can be fitted into what is termed the 'standard EXAFS equation' to obtain quantitative structural parameters. However, before this can be done, the amplitude and phase-shift relations need to be established and can be determined experimentally from a model compound. The filtered EXAFS data can then be fitted using an EXAFS function, such as a least-squares algorithm.

a. Standard EXAFS equation (Eq 24) (Sun et al., 2013):

$$\chi(k) = \sum_j \frac{N_j S_0^2 f_j(k)}{k R_j^2} e^{-2k^2 \sigma_j^2} e^{-\frac{2R_j}{\lambda_j(k)}} \sin[2kR_j + \delta_j(k) + 2\varphi_c(k)] \quad (24)$$

Symbol	Meaning
N_j	Total number of atoms in the j -th shell
S_0^2	Amplitude reduction factor
R_j	Distance between the absorbing and scattering atoms
λ_j	Average free pathway for excited photoelectrons
$F_j(k)$	Backscattering amplitude
$\delta_j(k)$	Scattering phase shift of the scattering atom

σ^2	Debye-Waller factor – the mean square variation in the interatomic distance R
$\varphi_c(k)$	Phase-shift of the absorbing atom
$e^{-2k^2\sigma_j^2}$	Accounts for the effects of thermal vibration and structural disorder which alter the EXAFS oscillations at high K-region

Table 81 - standard EXAFS formula symbol nomenclature

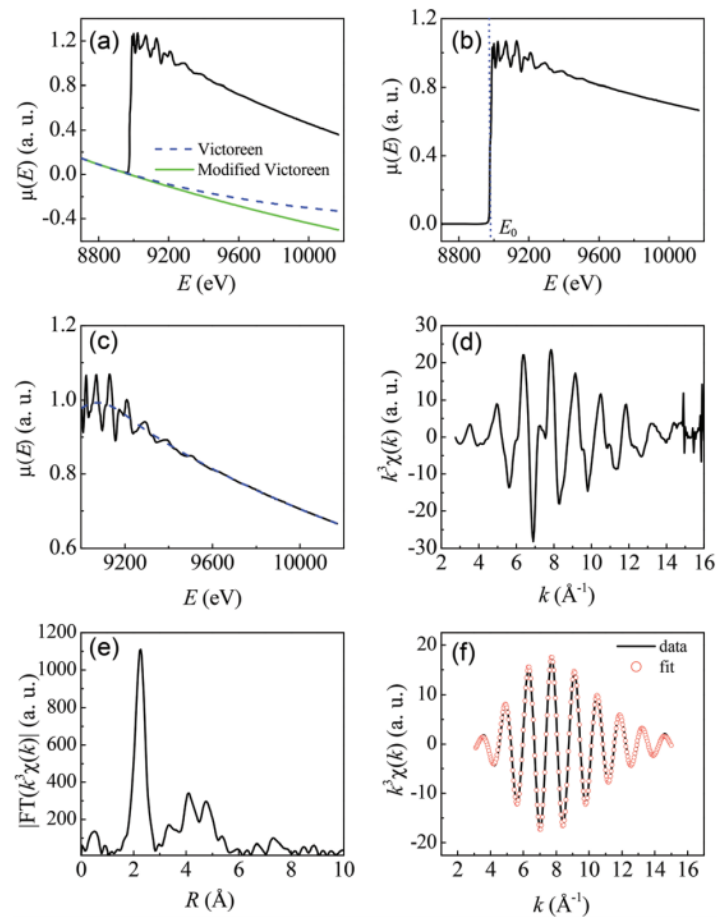


Figure 149 – ‘EXAFS data processing and analysing procedure: (a) pre-edge background removal, (b) normalisation, (c) curve fitting of μ_0 , (d) conversion to K-space and weighting, (e) Fourier Transformation to R-space, and (f) reverse Fourier Transform and fitting’ taken from (Sun et al., 2013)

8.6 Appendix: MAS NMR oxygen distribution calculations for [OB] and [OP]

¹¹B calculations

Glass species ^[4]B³⁺

Calculate uncertainty associated with B groups i.e. ^[4]B and ^[3]B.

^[4]B = $\frac{I_4}{I_4 + I_3}$, where I is the integral/intensity fraction in the spectra

$$^{[4]}B = \frac{I_4}{I_4 + I_3} = \frac{I_4 + I_3 - I_3}{I_4 + I_3}$$

$$= \frac{I_4 + I_3}{I_4 + I_3} - \frac{I_3}{I_4 + I_3}$$

$$= 1 - \frac{I_3}{I_4 + I_3}$$

$$= 1 - I_3 [I_4 + I_3]^{-1}$$

Now '^[4]B = 1 - I₃[I₄ + I₃]⁻¹' needs to be differentiated, where $\frac{\partial [4]B}{\partial I_4}$ represents the change of ^[4]B with respect to I₄, and where I₃ is only considered as a constant.

$$\frac{\partial [4]B}{\partial I_4} = 1 - I_3 [I_4 + I_3]^{-1}$$

$$= I_3 [I_4 + I_3]^{-2}$$

$$= \frac{I_3}{[I_4 + I_3]^2}$$

Now consider $\frac{\partial [4]B}{\partial I_3}$, where I₃ is now the variable and I₄ is the constant.

$$^{[4]}B = \frac{I_4}{I_4 + I_3} = I_4 [I_3 + I_4]^{-1}$$

$$\frac{\partial [4]B}{\partial I_3} = -I_4 [I_4 + I_3]^{-2}$$

$$\frac{\partial [4]B}{\partial I_3} = \frac{-I_4}{(I_4 + I_3)^2}$$

Glass species ^[3]B

And now consider the above calculations and apply to ^[3]B.

$$^{[3]}B = \frac{I_3}{I_4 + I_3} = \frac{I_3 + I_4 - I_4}{I_4 + I_3}$$

$$= 1 - \frac{I_4}{I_3 + I_4}$$

$$= 1 - I_4 [I_3 + I_4]^{-1}$$

Therefore,

$$\frac{\partial [3]B}{\partial I_4} = I_4 (I_3 + I_4)^{-2}$$

$$\frac{\partial [3]B}{\partial I_4} = \frac{I_4}{(I_3 + I_4)^2}$$

Error Propagation of [OB]

The equation used for error propagation of error values which have been multiplied and divided is as follows (Eq 43):

$$\Delta f = \sqrt{\left(\frac{\partial f}{\partial x}\right)^2 (\Delta(x))^2 + \left(\frac{\partial f}{\partial y}\right)^2 (\Delta(y))^2 + \dots} \quad (43)$$

Errors of the $\Delta(B[4])$ and $\Delta(B[3])$ intensities

Substitute in the partial derivatives for $[4]B$ with respect to I_4 and I_3 :

$$\begin{aligned} & \sqrt{\left(\frac{\partial [3]B}{\partial I_4}\right)^2 (\Delta(I_4))^2 + \left(\frac{\partial [3]B}{\partial I_3}\right)^2 (\Delta(I_3))^2} \\ &= \sqrt{\left(\frac{I_3}{(I_4 + I_3)^2}\right)^2 (\Delta(I_4))^2 + \left(\frac{-I_4}{(I_4 + I_3)^2}\right)^2 (\Delta(I_3))^2} \\ &= \sqrt{\left(\frac{1}{(I_4 + I_3)^4}\right)^2 (I_3^2 (\Delta(I_4))^2 + I_4^2 (\Delta(I_3))^2)} \end{aligned}$$

Where $\Delta(I_4) = \Delta(I_3) = \Delta I$

$$\begin{aligned} &= \left(\frac{1}{(I_4 + I_3)^2}\right) \sqrt{I_3^2 (\Delta I)^2 + I_4^2 (\Delta I)^2} \\ &= \left(\frac{1}{(I_4 + I_3)^2}\right) \sqrt{(\Delta I)^2 (I_3^2 + I_4^2)} \\ &= \left(\frac{\Delta I}{(I_4 + I_3)^2}\right) \sqrt{I_3^2 + I_4^2} \end{aligned}$$

Next, using the error propagation formula for error values which have been multiplied and divided, substitute [OB] into the formula:

Error Propagation: $\Delta f = \sqrt{\left(\frac{\partial f}{\partial x}\right)^2 (\Delta x)^2 + \dots}$

[OB]: $[OB] = \left(\frac{3}{2}[3]B + \frac{4}{2}[4]B\right)B = \frac{3}{2}B(3)B + \frac{4}{2}B(4)B$

So, the formula is ...

$$\Delta f = \Delta[OB] = \sqrt{\left(\frac{\partial[OB]}{\partial[3]B}\right)^2 (\Delta[3]B)^2 + \left(\frac{\partial[OB]}{\partial[4]B}\right)^2 (\Delta[4]B)^2 + \left(\frac{\partial[OB]}{\partial B}\right)^2 (\Delta B)^2}$$

Where $\left(\frac{\partial[OB]}{\partial B(3)}\right) = \frac{3}{2}B$, $\left(\frac{\partial[OB]}{\partial[4]B}\right) = \frac{4}{2}B$, and $\frac{\partial[OB]}{\partial B} = \frac{3}{2}B + \frac{4}{2}B$

The relationship between $\Delta^{[3]}B = \Delta^{[4]}B = \Delta^{[i]}B$

Therefore, $\Delta B(i)$ will be substituted into the equation for $\Delta^{[3]}B$ and $\Delta^{[4]}B$

$$\Delta[OB] = \sqrt{\left(\frac{3}{2}B\right)^2 (\Delta B(i))^2 + \left(\frac{4}{2}B\right)^2 (\Delta B(i))^2 + \left(\frac{3}{2}[3]B + \frac{4}{2}[4]B\right)^2 (\Delta B)^2}$$

$$\Delta[OB] = \sqrt{(\Delta B(i))^2 \left(\left(\frac{3}{2}B\right)^2 + \left(\frac{4}{2}B\right)^2\right) + \left[\frac{3}{2}[3]B + \frac{4}{2}[4]B\right]^2 (\Delta B)^2}$$

$$\Delta[OB] = \sqrt{\frac{25}{4}B^2(\Delta B(i))^2 + \left[\frac{3}{2}[3]B + \frac{4}{2}[4]B\right]^2 (\Delta B)^2}$$

$$\Delta[OB] = \sqrt{\frac{25}{4}(B * \Delta B(i))^2 + \left[\frac{3}{2}[3]B + \frac{4}{2}[4]B\right]^2 (\Delta B)^2}$$

Where $OB = \left(\frac{3}{2} * [3]B + \frac{4}{2} * [4]B\right) * B$

Therefore, let $\frac{OB}{B} = \frac{3}{2}[3]B + \frac{4}{2}[4]B$

Hence, $\Delta[OB] = \sqrt{\frac{25}{4}(B * \Delta B(i))^2 + \left(\frac{OB}{B}\right)^2 (\Delta B)^2}$

Which results in the following values (Table 82).

Sample	[³ B]	[⁴ B]	[B]	[OB]
NBSP0.0	0.23 (0.02)	0.77 (0.02)	32.6 (0.3)	61.3 (1.7)
NBSP1.0	0.22 (0.02)	0.78 (0.02)	32.2 (0.3)	60.9 (1.7)
NBSP2.0	0.21 (0.02)	0.79 (0.02)	31.9 (0.3)	60.4 (1.7)
NBSP3.0	0.22 (0.02)	0.78 (0.02)	31.6 (0.3)	59.7 (1.7)
NBSP4.0	0.20 (0.02)	0.80 (0.02)	31.3 (0.3)	59.3 (1.7)
NBSP5.0	0.23 (0.02)	0.77 (0.02)	3.9 (0.3)	58.4 (1.7)
NBSP5.5	0.24 (0.02)	0.76 (0.02)	30.8 (0.3)	57.9 (1.6)
NBSP6.0 (opalescence)	0.23 (0.02)	0.77 (0.02)	30.6 (0.3)	57.7 (1.6)
NBSP6.0 (translucent)	0.24 (0.02)	0.76 (0.02)	30.6 (0.3)	57.5 (1.6)

Table 82 - Boron analysis and uncertainties

³¹P calculations

Following the same methodology as above for boron, $\Delta[OP]$ can be calculated to be:

$$[OP] = (Q_P^0 * 4 + Q_P^1 * 3.5 + Q_P^2 * 3.0) * [P]$$

$$[OP] = (4Q_P^0 + 3.5Q_P^1 + 3.0Q_P^2) * [P]$$

Therefore, the formula is ...

$$\Delta f = \Delta[OP]$$

$$= \sqrt{\left(\frac{\partial[OP]}{\partial Q_P^0}\right)^2 (\Delta Q_P^0)^2 + \left(\frac{\partial[OP]}{\partial Q_P^1}\right)^2 (\Delta Q_P^1)^2 + \left(\frac{\partial[OP]}{\partial Q_P^2}\right)^2 (\Delta Q_P^2)^2 + \left(\frac{\partial[OP]}{\partial P}\right)^2 (\Delta P)^2}$$

$$\text{Where } \left(\frac{\partial[OP]}{\partial Q_P^0}\right) = 4P, \left(\frac{\partial[OP]}{\partial Q_P^1}\right) = 3.5P, \frac{\partial[OP]}{\partial Q_P^2} = 3.0, \left(\frac{\partial[OP]}{\partial P}\right) = 4P + 3.5P + 3P$$

$$\text{Also, } \Delta Q_P^0 = \Delta Q_P^1 = \Delta Q_P^2 \equiv \Delta(P[i])$$

Therefore, ΔQ_P^0 , ΔQ_P^1 , and ΔQ_P^2 can be substituted for $\Delta(P[i])$.

$$\Delta[OP]$$

$$= \sqrt{(4.0P)^2 \Delta(P[i])^2 + (3.5P)^2 \Delta(P[i])^2 + (3.0P)^2 \Delta(P[i])^2 + (4.0 + 3.5 + 3.0P)^2 \Delta(p)^2}$$

$$\Delta[OP] = \sqrt{\Delta(P[i])^2 (((4.0P)^2 + (3.5P)^2 + (3.0P)^2) + (4.0 + 3.5 + 3.0P)^2 \Delta(p)^2)}$$

$$\Delta[OP] = \sqrt{37.25P^2 \Delta(P[i])^2 + (10.5P)^2 \Delta(p)^2}$$

$$\Delta[OP] = \sqrt{37.25(P * \Delta(P[i]))^2 + (10.5P)^2 \Delta(p)^2}$$

Now let $10.5P = \frac{[OP]}{[P]}$. This will result in the following:

$$\Delta[OP] = \sqrt{37.25(P * \Delta(P[i]))^2 + \left(\frac{[OP]}{[P]} (\Delta P)\right)^2}$$

Which results in the following values (Table 83)

Sample	Q ⁰ _P	Q ¹ _P	Q ² _P	[P]	O-used/P	[OP]
NBSP0	-	-	-	0	-	-
NBSP1	0.11 (0.02)	0.89 (0.02)	0.00 (0.02)	2.00 (0.02)	3.55	7.1 (0.3)
NBSP2	0.07 (0.02)	0.39 (0.02)	0.00 (0.02)	4.00 (0.04)	3.54	14.1 (0.5)
NBSP3	0.09 (0.02)	0.85 (0.02)	0.06 (0.02)	6.00 (0.06)	3.51	21.1 (0.8)
NBSP4	0.48 (0.03)	0.48 (0.03)	0.05 (0.03)	8.00 (0.08)	3.71	29.7 (1.5)
NBSP5	0.20 (0.04)	0.76 (0.04)	0.04 (0.04)	10.00 (0.10)	3.58	35.8 (2.5)
NBSP5.5	0.22 (0.04)	0.76 (0.04)	0.02 (0.04)	11.00 (0.11)	3.6	39.6 (2.7)
NBSP6 (opalescence)	0.10 (0.04)	0.90 (0.04)	0.00 (0.04)	12.00 (0.12)	3.55	42.6 (3.0)
NBSP6 (translucent)	0.17 (0.04)	0.81 (0.04)	0.02 (0.04)	12.00 (0.12)	3.58	42.9 (3.0)

Table 83 – ³¹P analysis and uncertainties

8.7 Appendix: Atom Probe Tomography

Figure 150 shows the atom maps of specific elements present in both the NBSP3.0 and 4.0 samples. Where the highlighted orange boxes for Na and PO₂ exhibit denser regions representative of clustering.

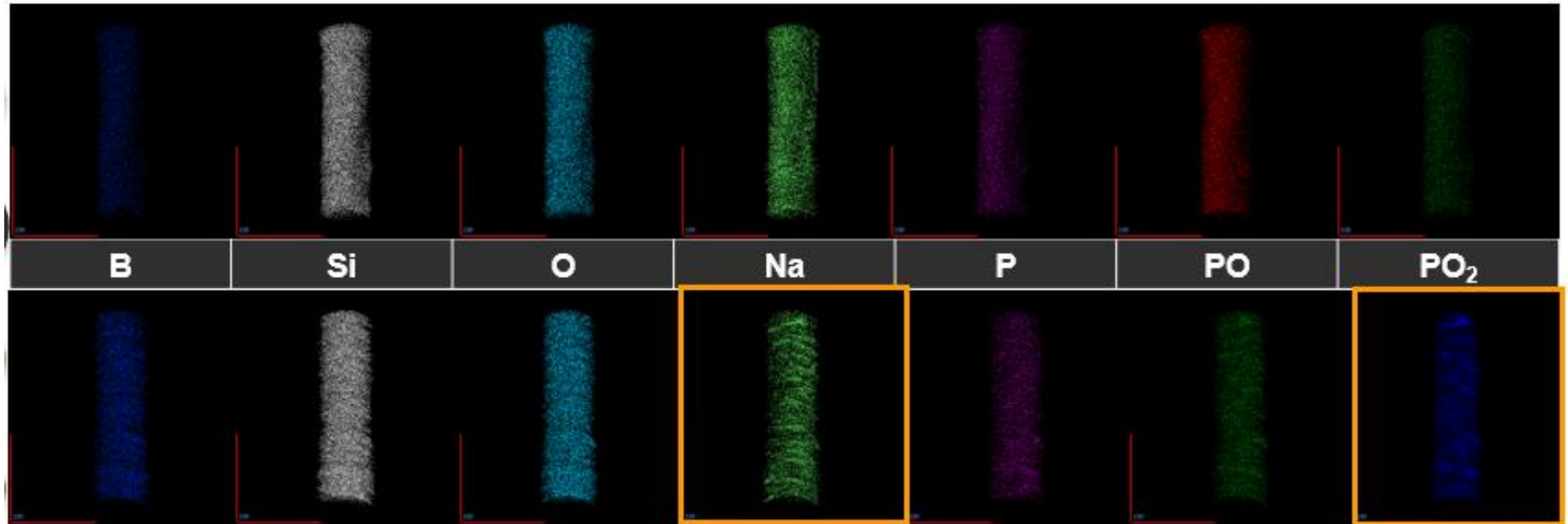


Figure 150 - Atoms maps of NBSP3.0 (top) and 4.0 (bottom) at a scale of 100 nm

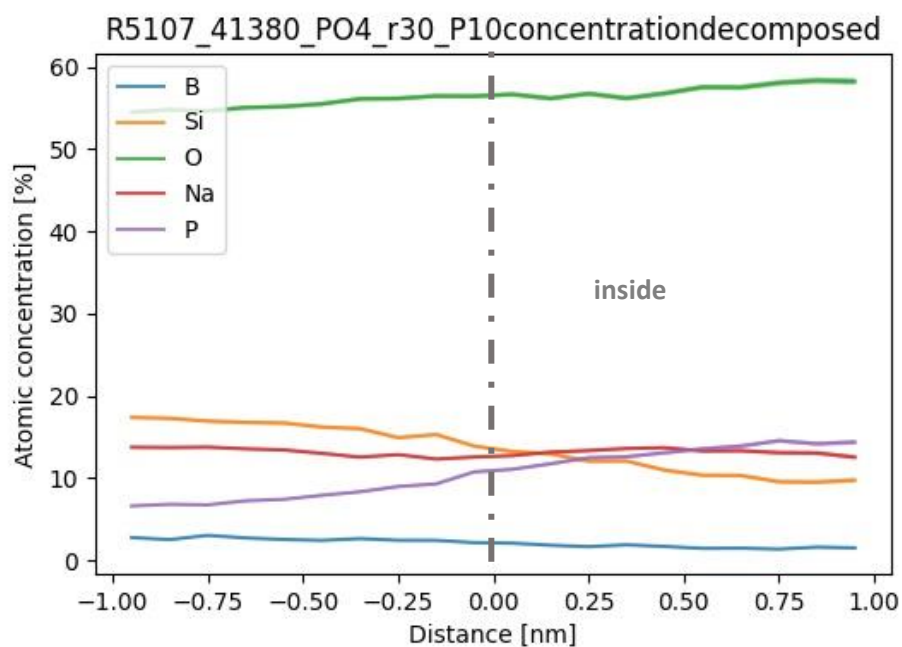
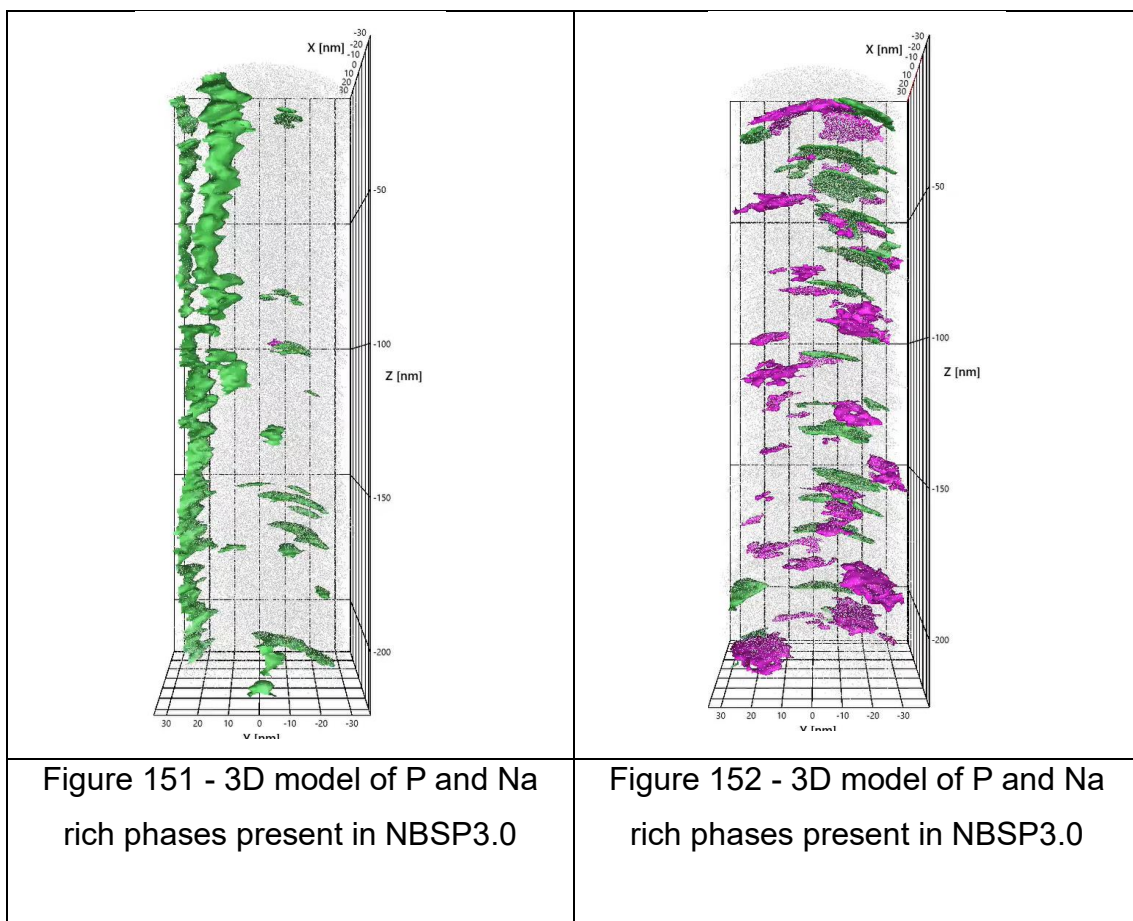


Figure 153 - Proxygram of all P-rich Isosurface for NBSP4.0

8.8 Appendix: NBSi-S and NBSiS-P XRD crystal structures

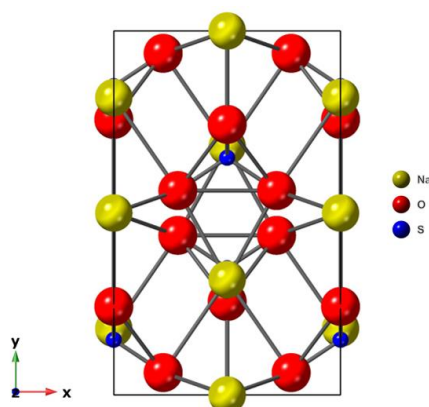


Figure 154 - Crystalline structure of Na_2SO_4

Crystal phase	Reference code	Crystal structure	Space group	Unit Cell (Å)			Reference
				a	b	c	
Na_2SO_4	24-1132 (PDF)	Orthorhombic	Amam	6.9666	8.9511	5.6109	(Swanson et al., 1974)

Table 84 - Crystalline sodium sulphate parameters

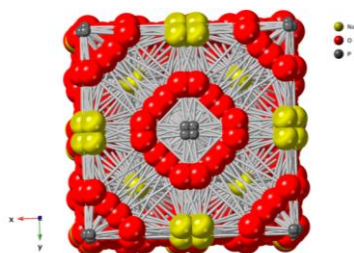


Figure 155 – Crystalline structure of Na_3PO_4

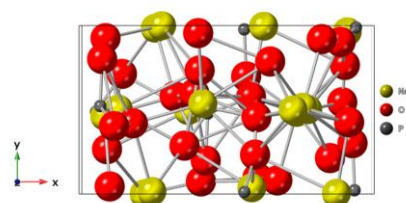


Figure 156 - Crystalline structure of $\text{Na}_4\text{P}_2\text{O}_7$

Crystal phase	Reference code	Crystal structure	Space group	Unit Cell (Å)			Reference
				a	b	c	
Na_3PO_4	04-009-5232 (ICDD)	Cubic	Fm-3m	7.5120	7.5120	7.5120	(Newsam et al., 1980)

04-018- (Leung &
 $\text{Na}_4\text{P}_2\text{O}_7$ 4331 Orthorhombic P212121 9.3670 5.3900 13.4800 Calvo,
 (ICDD) 1972)

Table 85 - Crystalline sodium phosphate parameters

8.9 Appendix: HLW crucible glass melt conditions

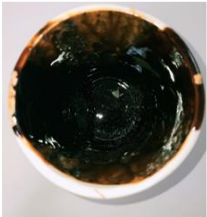
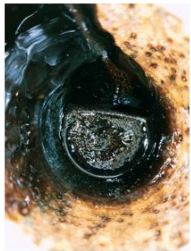
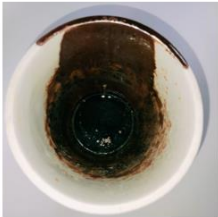
Sample	HLW0.00	HLW0.3125	HLW0.625	HLW1.25
Top view of crucible				
P_2O_5 content (mol%)	0.00	0.3125	0.625	1.25
Comments	The melt was quite fluid when poured but boiled over during melting.	The melt was quite fluid when poured. However, there was evidence of undissolved solid material at the bottom of the crucible.	The melt was slightly more viscous and there was evidence of undissolved material at the bottom of the crucible and on the sides.	The melt was slightly viscous than HLW0.625, with evidence of undissolved material in the crucible.

Figure 157 - Top view images of inside the crucibles with associated comments about the glass melts

8.10 Appendix: HLW XRD crystal structures

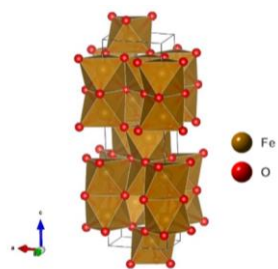


Figure 158 - ICSD 3D model of Fe₂O₃
based on PDF#: 98-018-284

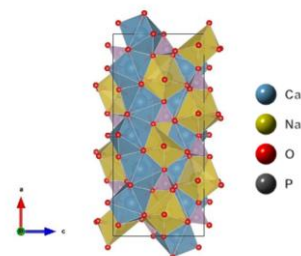


Figure 159 - ICSD 3D model of
NaCaPO₄ based on PDF#: 04-017-4455

Crystal phase	Reference code	Crystal structure	Space group	Unit Cell (Å)			Reference
				a	b	c	
Fe ₂ O ₃	04-011-9586 (ICDD)	Rhombohedral	R-3c	5.0280	5.0280	13.7300	(Hanawalt et al., 1938)
NaCaPO ₄	00-056-0816 (ICDD)	Hexagonal	P63mc	10.6400	10.6400	21.7100	(Celotti & Landi, 2003)

Table 86 - Crystalline hematite and sodium calcium phosphate parameters

8.11 Appendix: HLW Dilatometry Traces

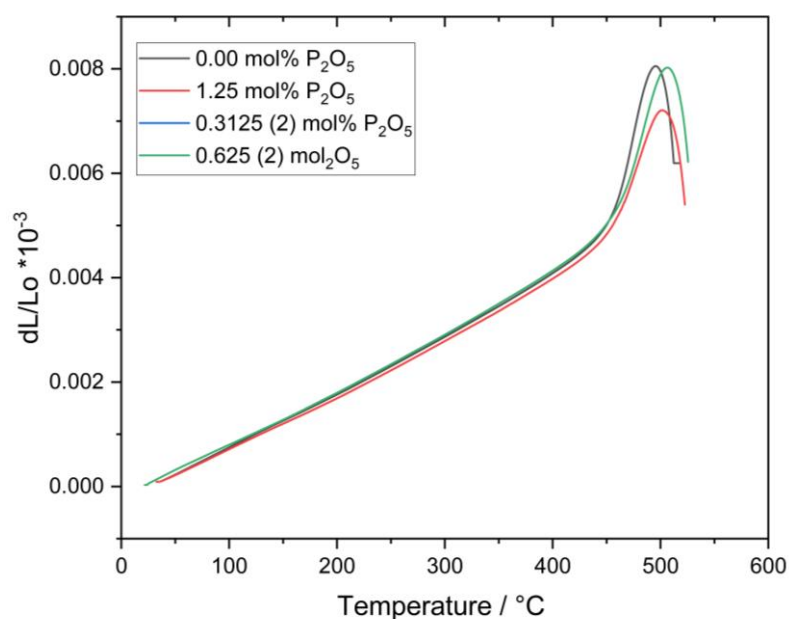


Figure 160 - Dilatometry traces of HLW0.00, 0.3125 (2), 0.625 (2), and 1.25

8.12 Appendix: HLW Raman Spectroscopy Q^n Gaussian Fittings

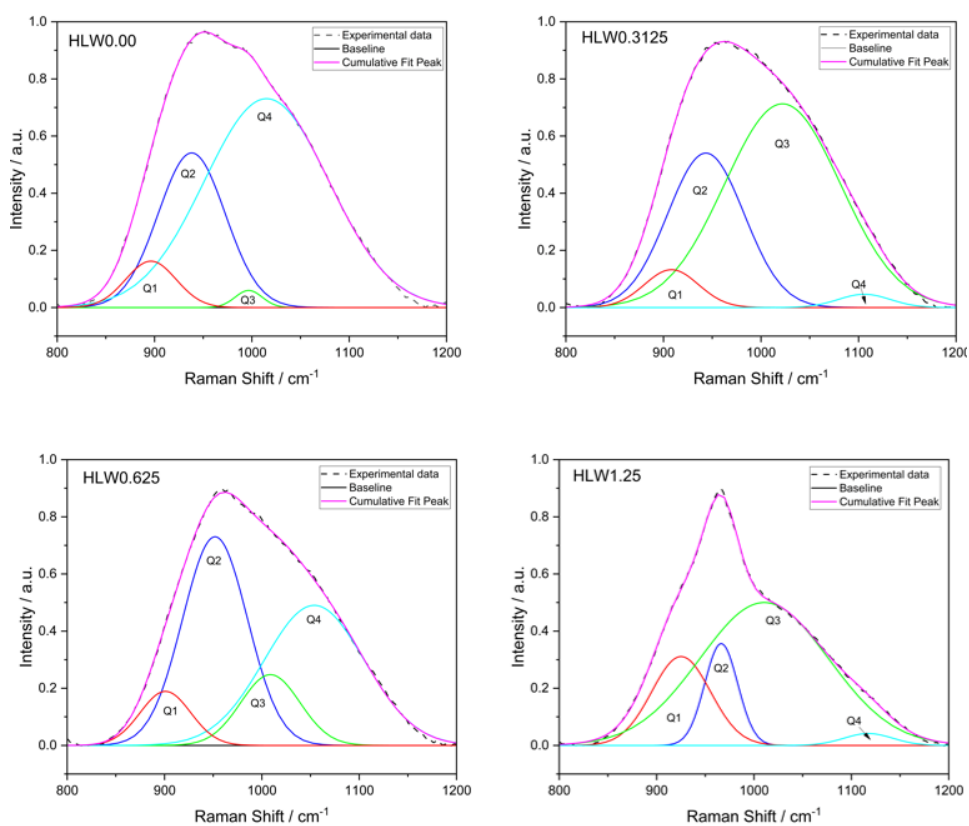


Figure 161 - HLW0.00-1.25 fitted Q^n species using Gaussian line shapes

8.13 Appendix: HLW0.3125 SEM/EDX

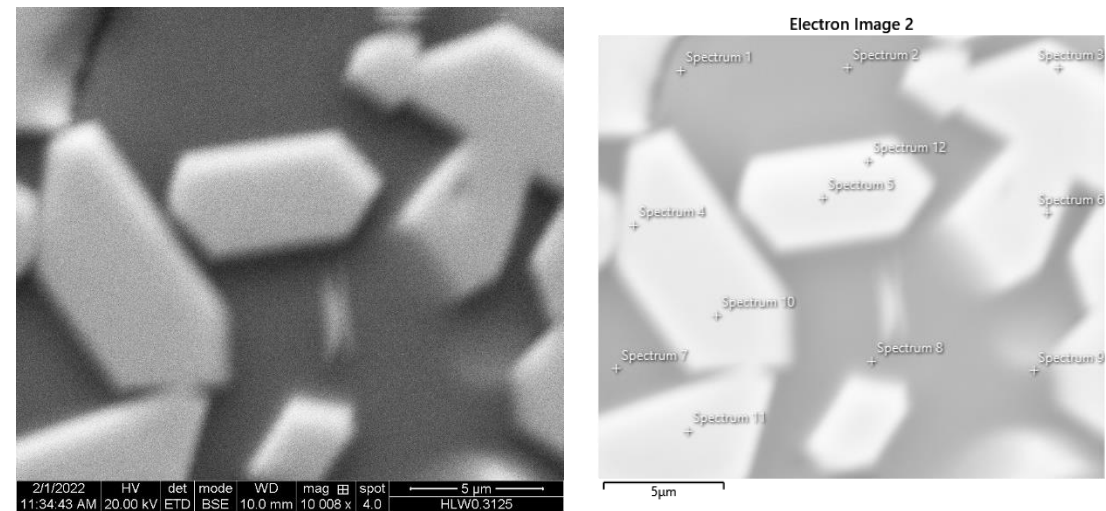


Figure 162 – BSE image (left) and point scan (right) of HLW0.3125

Element (wt%)																		
Spectrum	B	σ	Si	σ	Na	σ	Ca	σ	Al	σ	P	σ	Fe	σ	O	σ	K	σ
1	-	-	20.2	0.1	9.2	0.1	5.4	0.0	11.8	0.1	0.4	0.0	10.1	0.1	42.4	0.1	0.6	0.0
2	-	-	20.3	0.1	9.7	0.1	4.8	0.0	12.0	0.1	0.4	0.0	9.7	0.1	42.5	0.1	0.6	0.0
3	-	-	-	-	-	-	-	-	0.1	0.0	-	-	75.7	0.1	22.9	0.1	-	-
4	5.3	1.6	0.9	0.0	0.7	0.0	0.3	0.0	1.1	0.1	-	-	59.9	2.5	31.4	2.6	-	-
5	-	-	13.5	0.1	8.0	0.1	4.0	0.0	8.2	0.1	0.3	0.0	29.6	0.1	36.0	0.1	0.5	0.0
6	-	-	15.2	0.1	5.8	0.1	4.2	0.0	9.2	0.1	0.3	0.0	24.5	0.1	37.6	0.1	-	-
7	-	-	0.3	0.0	-	-	-	-	1.0	0.0	-	-	75.7	0.1	22.9	0.1	-	-

8	-	-	10.4	0.0	7.6	0.1	2.0	0.0	7.6	0.0	0.2	0.0	38.6	0.1	33.4	0.1	0.3	0.0
9	2.1	1.6	1.5	0.1	1.9	0.1	0.2	0.0	1.9	0.1	-	-	64.9	2.7	27.4	2.7	-	-
10	1.8	1.9	1.7	0.1	1.4	0.1	0.4	0.0	1.7	0.1	0.1	0.0	66.0	3.1	27.0	3.2	-	-
11	4.0	1.7	0.2	0.0	-	-	-	-			-	-	66.1	2.8	28.7	2.8	-	-
12	4.8	1.6	-	-	-	-	-	-	0.7	0.0	-	-	64.4	2.6	29.9	2.7	-	-

Table 87 – HLW0.3125 elemental point scan analysis

8.14 Appendix: HLW1.25 SEM/EDX

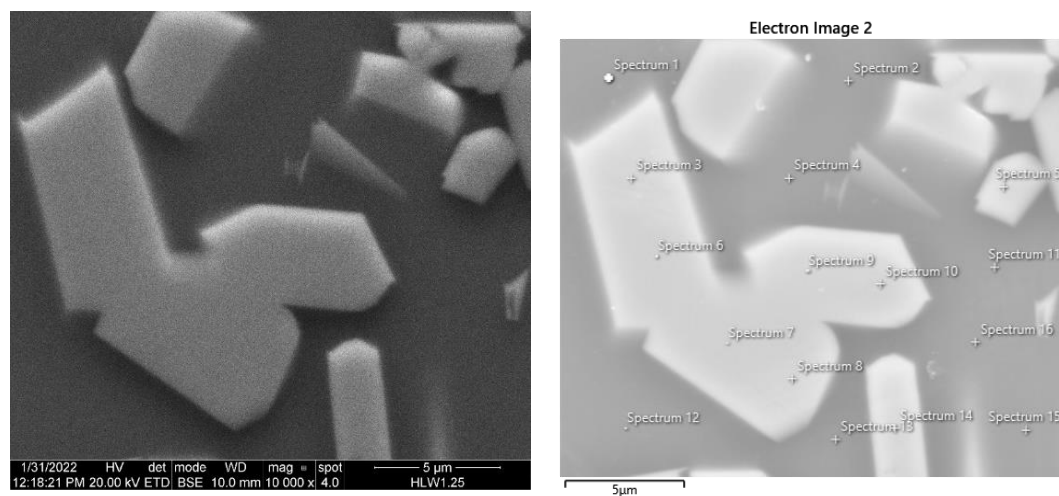


Figure 163 - BSE image (left) and point scan (right) of HLW1.25

Spectrum	Element (wt%)															
	B	σ	Si	σ	Na	σ	Ca	σ	Al	σ	P	σ	Fe	σ	O	σ
1	8.5	2.5	13.3	0.9	6.8	0.4	2.5	0.2	6.5	0.4	0.9	0.1	13.4	0.9	48.1	3.3
2	7.3	2.9	15.9	1.2	7.2	0.5	3.6	0.3	7.5	0.6	1.1	0.1	8.5	0.6	48.9	3.8
3	-	-	-	-	-	-	-	-	-	-	-	-	77.7	0.1	22.3	0.1
4	8.9	2.4	14.2	0.9	6.9	0.4	3.0	0.2	6.8	0.4	1.0	0.1	9.7	0.6	49.6	3.1
5	-	-	2.8	0.0	1.7	0.1	0.6	0.0	1.7	0.0	-	-	67.5	0.1	25.1	0.1
6	-	-	-	-	-	-	-	-	0.4	0.0	-	-	77.0	0.1	22.5	0.0
7	-	-	-	-	-	-	-	-	0.4	0.0	-	-	76.7	0.1	22.6	0.1
8	-	-	0.5	0.0	-	-	-	-	0.6	0.0	-	-	75.7	0.1	22.9	0.1
9	-	-	-	-	-	-	-	-	0.3	0.0	-	-	77.1	0.1	22.4	0.1
10	-	-	-	-	-	-	-	-			-	-	77.6	0.1	22.3	0.1
11	-	-	21.3	0.1	8.6	0.1	4.9	0.0	9.6	0.1	1.5	0.0	11.0	0.1	43.0	0.1
12	-	-	21.4	0.1	9.0	0.1	4.8	0.0	9.5	0.1	1.5	0.0	10.8	0.1	43.0	0.1
13	-	-	20.0	0.1	8.9	0.1	4.9	0.0	9.0	0.1	1.5	0.0	13.8	0.1	41.8	0.1
14	-	-	0.9	0.0	-	-	-	-	0.9	0.0	-	-	74.8	0.1	23.3	0.1
15	-	-	19.2	0.1	9.3	0.1	3.7	0.0	9.1	0.1	1.2	0.0	16.5	0.1	41.0	0.1
16	-	-	14.2	0.9	7.1	0.4	2.9	0.2	6.9	0.4	0.9	0.1	11.8	0.7	48.2	3.2

Table 88 – HLW1.25 elemental point scan analysis

8.15 Appendix: HLW Fe K-Edge XANES Fits

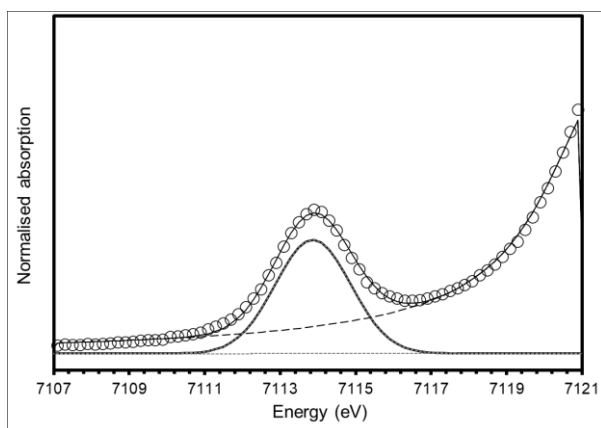


Figure 164 - Fe K-edge XANES pre-peak fitting of HLW0.00

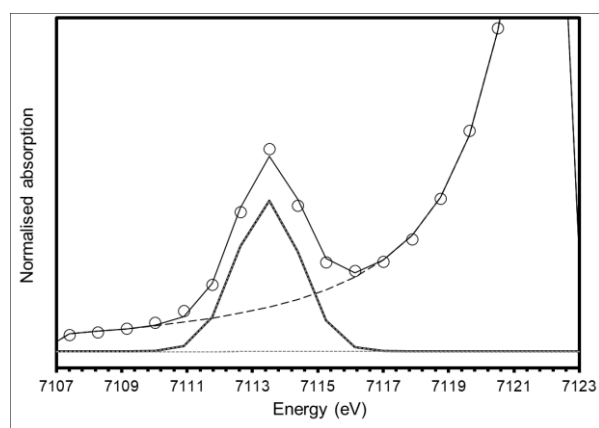


Figure 165 - Fe K-edge XANES pre-peak fitting of 0.3125 (1)

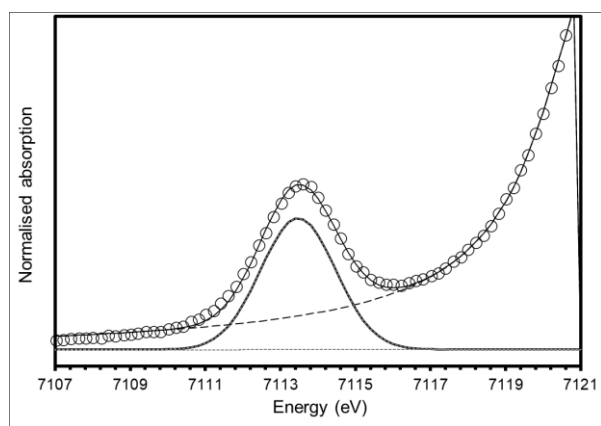


Figure 166 - Fe K-edge XANES pre-peak fitting of HLW0.625 (1)

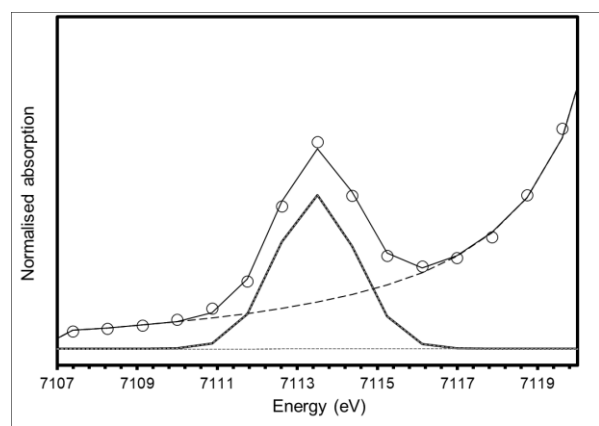


Figure 167 - Fe K-edge XANES pre-peak fitting of HLW1.25

8.16 Appendix: CCC HLW XRD Crystal Structures

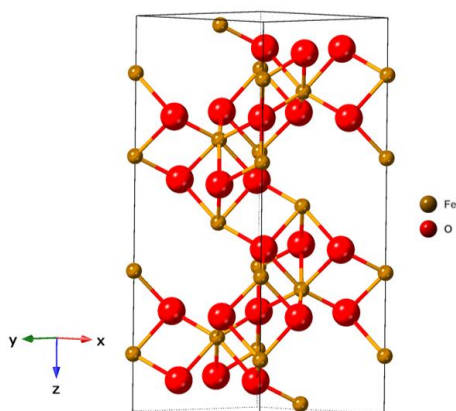


Figure 168 - ICSD 3D model of Fe_2O_3 crystal structure based on PDF#: 01-89-8103, 01-76-4579

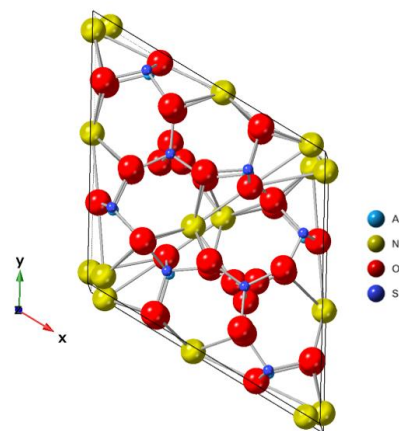


Figure 169 - ICSD 3D model of $\text{Na}_{6.41}(\text{Al}_{6.41}\text{Si}_{9.59}\text{O}_{32})$ crystal structure based on PDF#: 04-016-1739, 01-079-0994

Crystal phase	Reference code	Crystal structure	Space group	Unit Cell (Å)			Reference
				a	b	c	
Fe_2O_3	(ICDD)	Rhombohedral	R-3c				(D. Taylor, 1984)
NaAlSiO_4	(ICDD)	Hexagonal	P63				(Dimitrijevic et al., 2004)

Table 89 – Hematite and nepheline parameters

8.17 Appendix: HLW CCC RRUFF Raman Spectra of Hematite and Nepheline

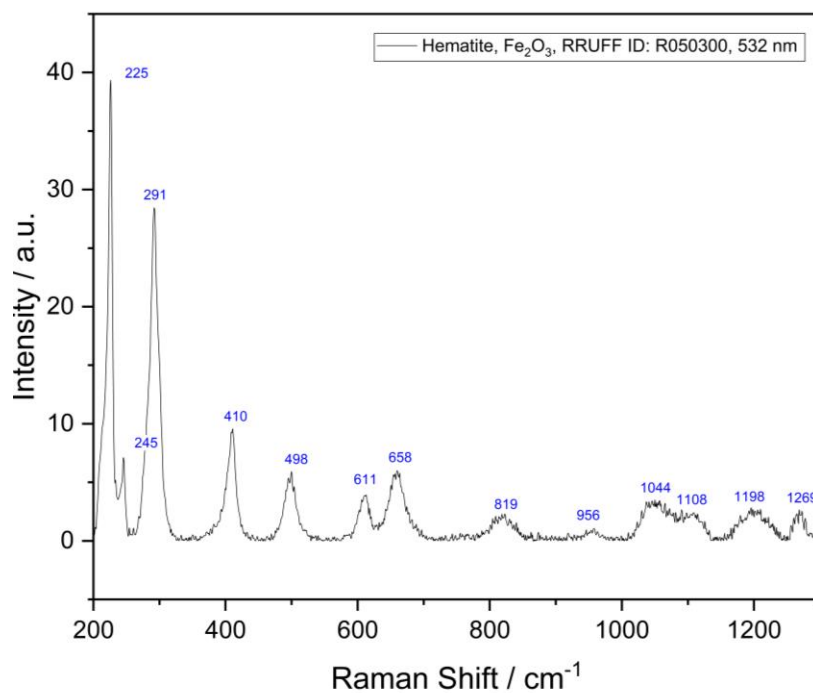


Figure 170 - Raman spectra of hematite from the RRUFF database

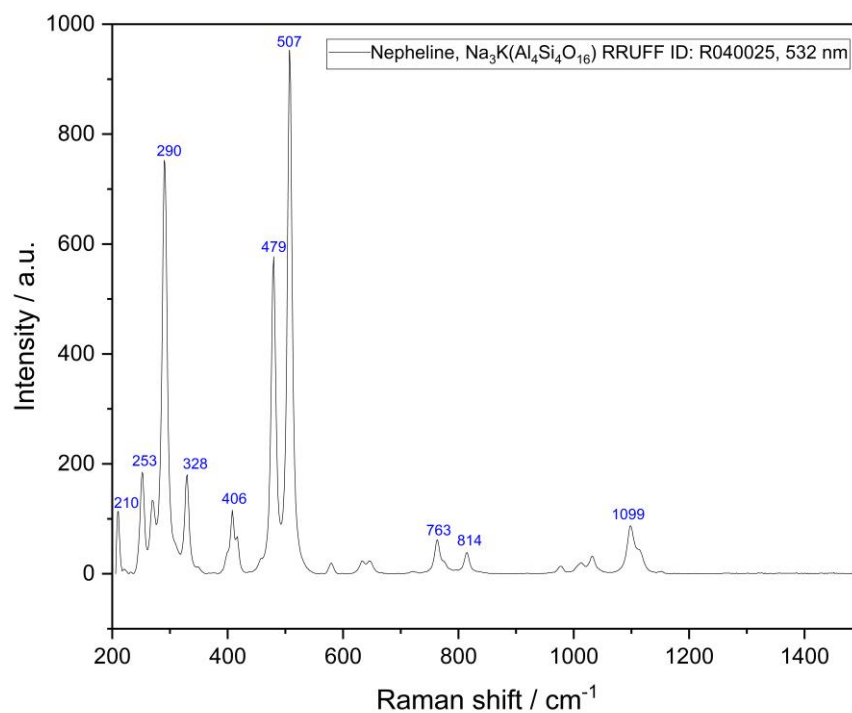


Figure 171 - Raman spectra of nepheline from the RRUFF database

8.18 Appendix: LAW Crucible Melting Conditions

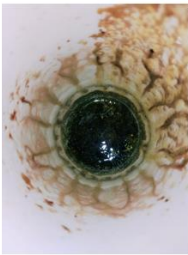
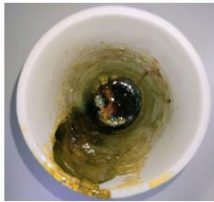
Sample	LAW0.00	LAW0.625	LAW1.25	LAW1.875
Top view of crucible				
P ₂ O ₅ content (mol%)	0.00	0.625	1.25	1.875
Comments	The melt was very fluid and easy to pour. However, the melt did bubble over the top of the crucible.	The melt was fluid and easy to pour with no evidence of undissolved material.	The melt was fluid and easy to pour with no evidence of undissolved material.	The melt became slightly more viscous than LAW1.25, but was still easy to pour. There was no evidence of undissolved material.

Figure 172 - Top view images of glass melt crucibles with associated comments for LAW0.00-1.87

8.19 Appendix: LAW Sodium Calcium Phosphate Crystal Structure and Parameters

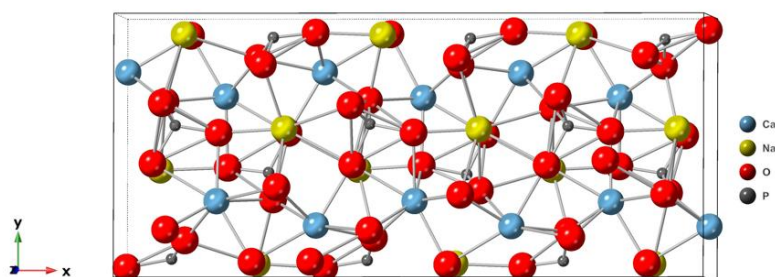


Figure 173 – ICSD 3D model of sodium calcium phosphate (NaCaPO₄) based on PDF#: 00-029-1193

Crystal phase	Reference code	Crystal structure	Space group	Unit Cell (Å)			Reference
				a	b	c	
NaCaPO ₄	(ICDD)	Orthorhombic	Pnam	6.79790	9.1650	5.4060	(Morris et al., 1978)

Table 90 - Sodium calcium phosphate parameters

8.20 Appendix: LAW Dilatometry Traces

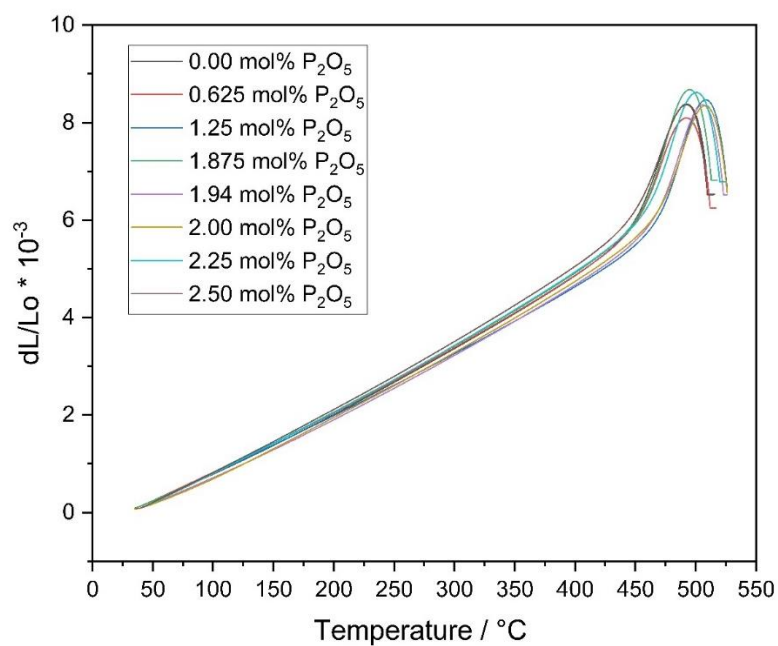


Figure 174 - Dilatometry traces of LAW samples (0.00-2.50)

8.21 Appendix: LAW Raman Spectroscopy Q^n Gaussian Line Fits

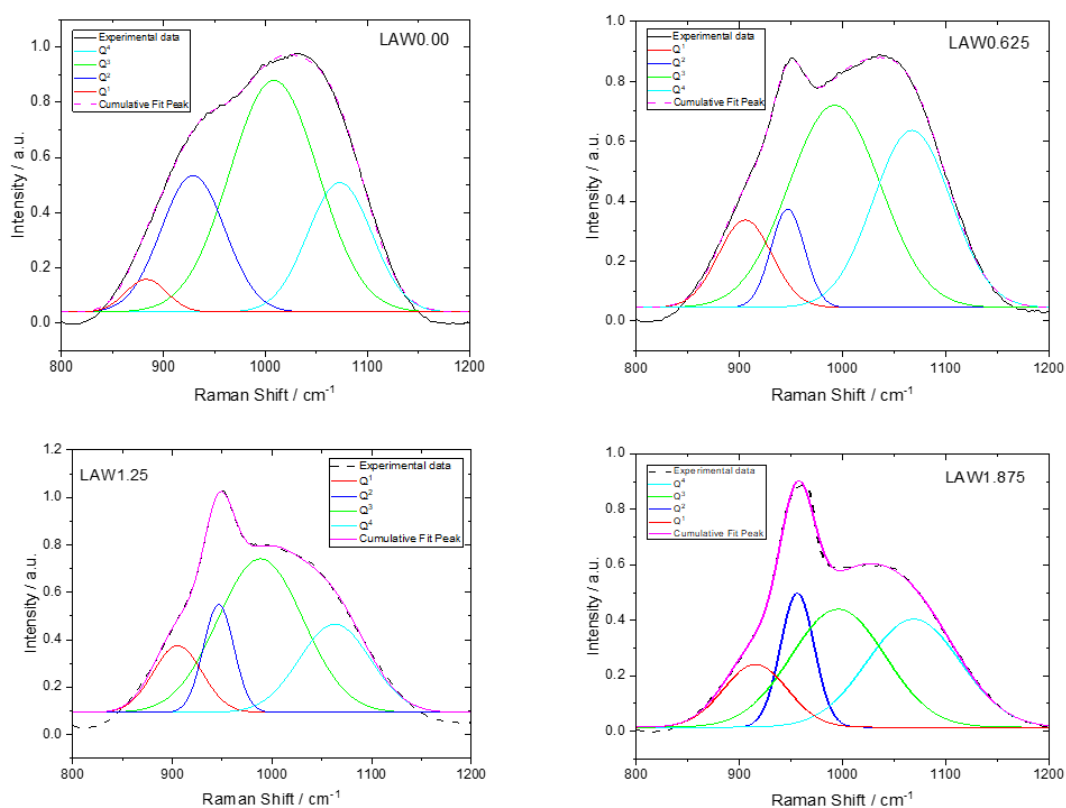


Figure 175 - LAW0.00 - 1.875 fitted Q^n species using Gaussian line shapes

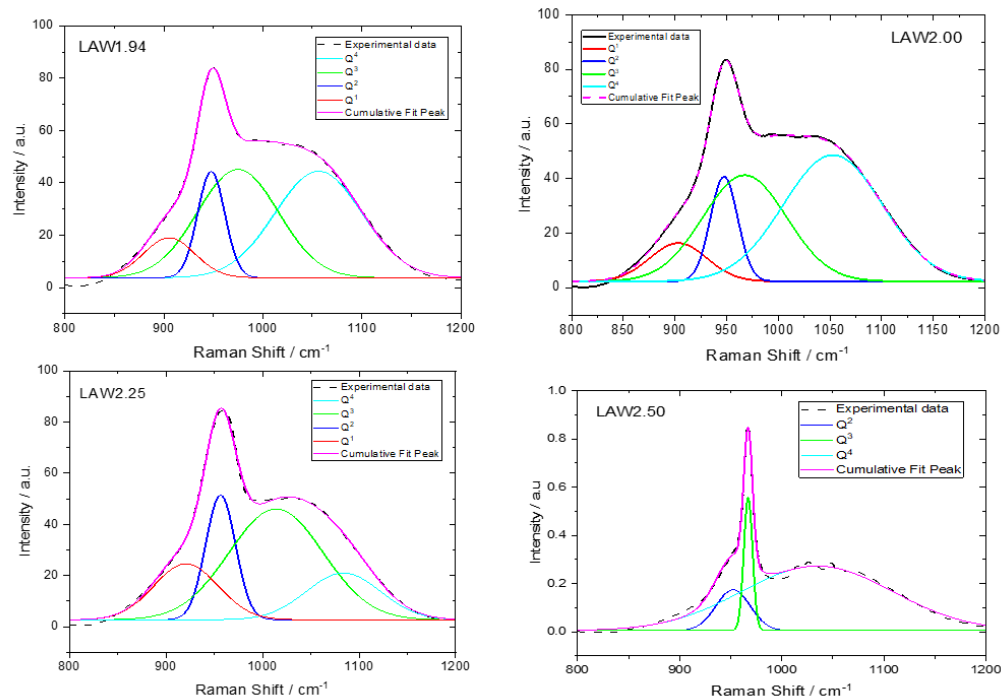


Figure 176 – LAW1.94 – 2.50 fitted Q^n species using Gaussian line shapes

8.22 Appendix: LAW Fe K-Edge XANES Fits

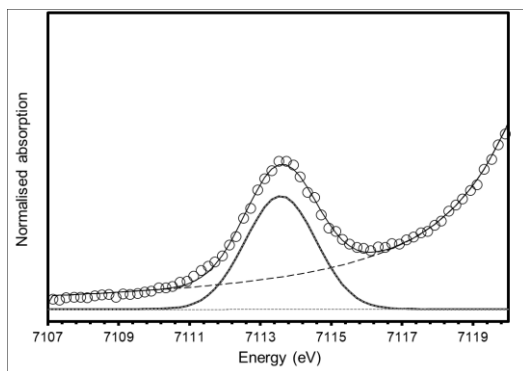


Figure 177 - Fe K-edge XANES pre-peak fitting of LAW0.00

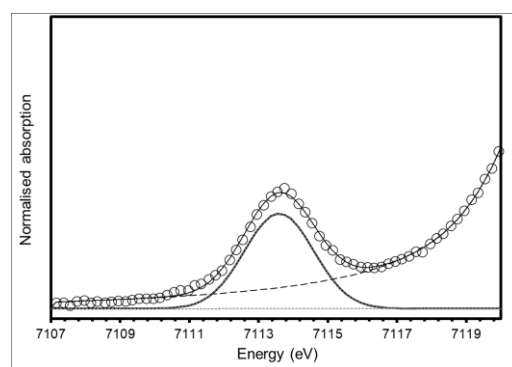


Figure 178 - Fe K-edge XANES pre-peak fitting of LAW1.875

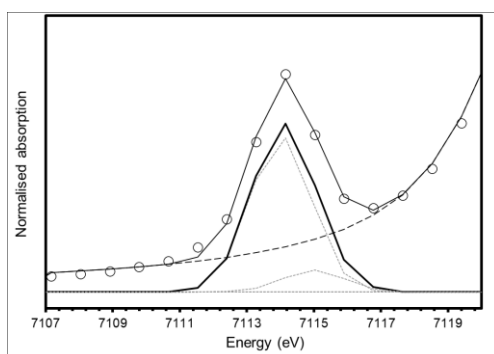


Figure 179 - Fe K-edge XANES pre-peak fitting of LAW2.00

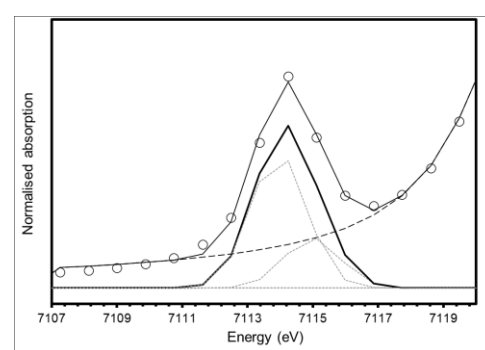


Figure 180 - Fe K-edge XANES pre-peak fitting of LAW2.25

8.23 Appendix: LAW Normalised Mass Loss and Minimum Normalised Release Rate

Sample	NL _{Si}		NL _B		NL _{Na}		NL _P		NL _{Al}		NL _{Ca}		NL _{Fe}		NL _{Li}	
LAW0.00	0.155	0.01	0.296	0.02	1.064	0.061	-	-	0.52692	0.01531	0.04817	0.00231	0.00392	9.38E-04	0.64603	0.02535
LAW0.625	0.215	0.012	0.309	0.012	0.961	0.032	-0.242	0.034	0.30925	0.05706	0.0485	0.00665	0.00194	0.00123	0.66585	0.01867
LAW1.25	0.18	0.002	0.252	0.006	0.493	0.016	0.091	0.008	0.36757	0.01008	0.0186	0.00293	0.00241	9.05E-05	0.36189	0.00681
LAW1.875	0.232	0.023	0.558	0.368	0.861	0.103	0.839	0.045	0.46947	0.15858	0.04483	0.00261	0.00652	9.59E-04	0.51758	0.01949
LAW1.94	0.131	0.201	0.289	0.039	0.708	0.106	0.42	0.131	0.3303	0.03507	0.02899	0.00666	0.00357	7.82E-04	0.41241	0.03307
LAW2.00	0.231	0.028	0.316	0.042	0.69	0.092	0.382	0.05	0.39532	0.05828	0.01825	0.00422	0.00422	8.67E-04	0.46495	0.06377
LAW2.25	0.22	0.003	0.308	0.022	0.634	0.009	0.325	0.012	0.33449	0.0022	0.01811	0.00164	0.00371	5.04E-04	0.45495	0.01902

Table 91 - Normalised mass loss of all elements for LAW samples

Sample	NL _{Si}	NL _B	NL _{Na}	NL _P	NL _{Al}	NL _{Ca}	NL _{Fe}	NL _{Li}	total
LAW0.00	0.022	0.042	0.152	-	0.075	0.007	0.001	0.092	0.391
LAW0.625	0.031	0.044	0.137	-0.035	0.044	0.007	0.000	0.095	0.324
LAW1.25	0.026	0.036	0.070	0.013	0.053	0.003	0.000	0.052	0.252
LAW1.875	0.033	0.080	0.123	0.120	0.067	0.006	0.001	0.074	0.504
LAW1.94	0.019	0.041	0.101	0.060	0.047	0.004	0.001	0.059	0.332
LAW2.00	0.033	0.045	0.099	0.055	0.056	0.003	0.001	0.066	0.357
LAW2.25	0.031	0.044	0.091	0.046	0.048	0.003	0.001	0.065	0.328

Table 92 - Minimum normalised release rate for all elements in LAW samples

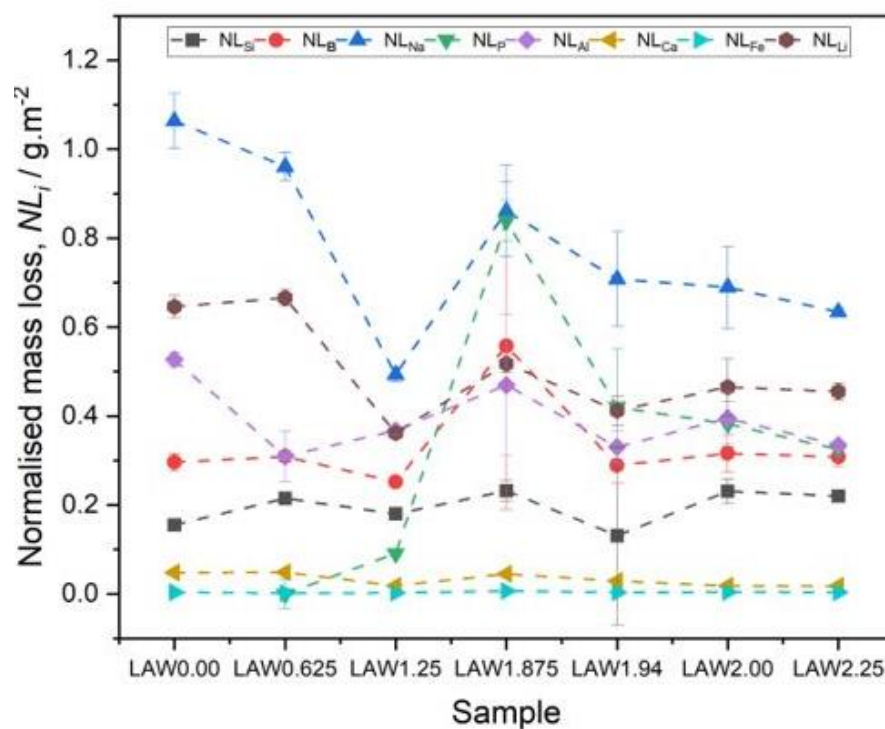


Figure 181 - Normalised mass loss of all elements in the LAW samples

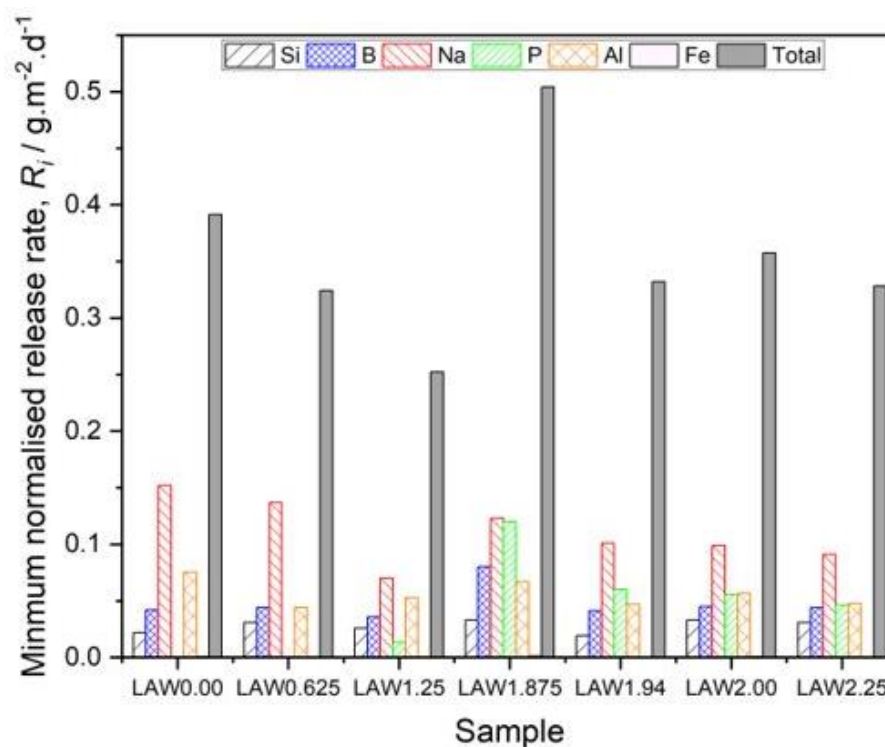


Figure 182 - Minimum normalised release rate for all elements in LAW samples

8.24 Appendix: CCC LAW Crystal Structures and Parameters

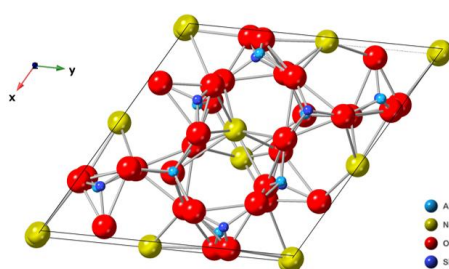


Figure 183 - ICSD model of sodium aluminium silicate

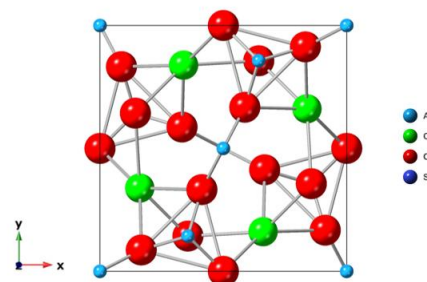


Figure 184 - ICSD model of calcium aluminium silicate

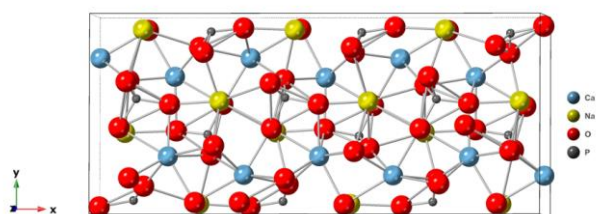


Figure 185 - ICSD model of sodium calcium phosphate

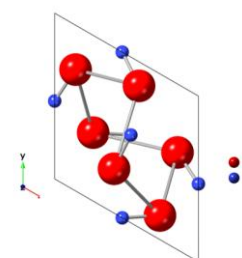


Figure 186 - ICSD model of quartz

Crystal phase	Reference code	Crystal structure	Space group	Unit Cell (Å)			Reference
				a	b	c	
NaAlSiO ₄	01-083-4382 (ICDD)	Hexagonal	P63	9.9800	9.9800	8.3500	(Xu et al., 2017)
SiO ₂	03-065-0466 (ICDD)	Hexagonal	P3221	4.9141	4.9141	5.4060	(Lager et al., 1982)
NaCa(PO ₄)	04-016-6900 (ICDD)	Orthorhombic	Pnam	20.3970	5.4120	9.1610	Ben Amara et al., 1983
Ca ₂ Al ₂ SiO ₇	04-015-7982 (ICDD)	Tetragonal	P-421m	7.6900	7.6900	5.0600	(Merlini et al., 2008)

Table 93 –Nepheline, quartz, sodium calcium phosphate, and calcium aluminium silicate parameters

8.25 Appendix: ILAW Crystal Structures and Parameters

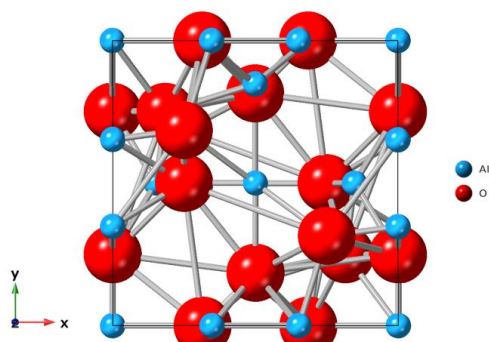


Figure 187 - ICSD 3D model of Al_2O_3
based on PDF#: 04-013-1687

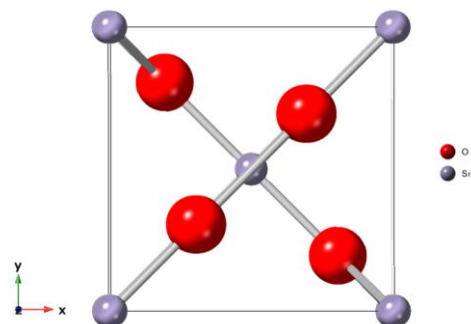


Figure 188 - ICSD 3D model of SnO_2
based on PDF#: 00-041-1445

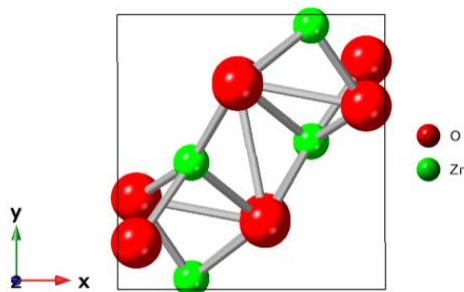


Figure 189 - ICSD 3D model of ZrO_2
based on PDF#: 01-086-1451

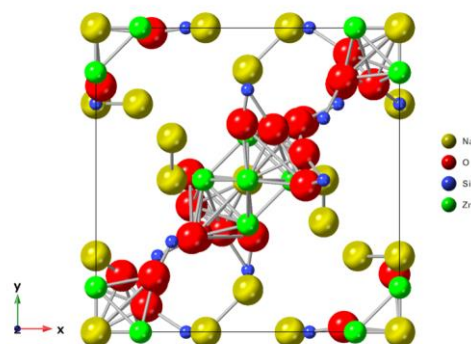


Figure 190 - ICSD 3D model of
 $\text{Na}_4\text{Zr}_2(\text{SiO}_4)_3$ based on PDF#: 04-
010-3835

Crystal phase	Reference code (ICDD)	Crystal structure	Space group	Unit Cell (Å)			Reference
				a	b	c	
Al_2O_3	04-005-4497	Rhombohedral	R-3c	4.759 1	4.759 1	12.99 73	(Cherginets et al., 2006)
SnO_2	00-041-3855	Tetragonal	P42/mnm	4.738 2	4.738 2	3.187 1	(Werner, 1956)
ZrO_2	01-086-1451	Monoclinic	P21/c	5.146 2	5.208 2	5.315 5	(Gualtieri et al., 1996)
$\text{Na}_4\text{Zr}_2(\text{SiO}_4)_3$	04-010-3835	Rhombohedral	R-3cH	9.186	9.186	22.18 6	(Kohler et al., 1983)

Table 94 – Alumina, tin oxide, zirconia, and sodium zirconium silicate parameters

8.26 Appendix: ILAW Dilatometry Traces

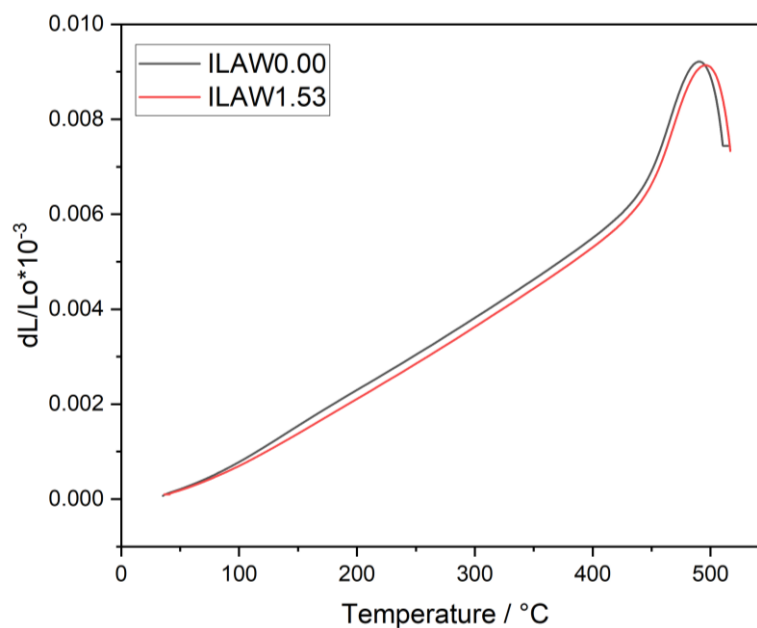


Figure 191 - Dilatometry traces of ILAW samples

8.27 Appendix: ILAW Fe K-Edge XANES Fits

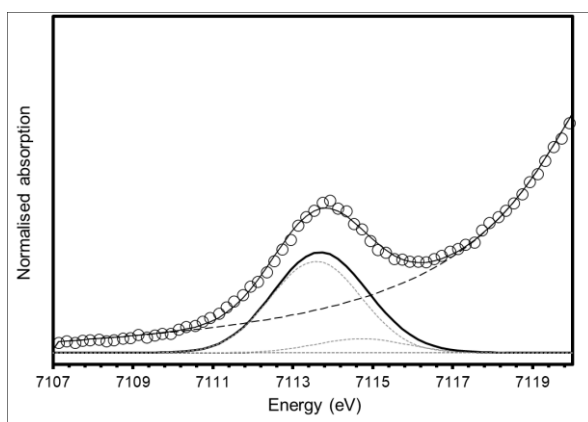


Figure 192 - Fe K-edge XANES pre-peak
fitting of ILAW0.00

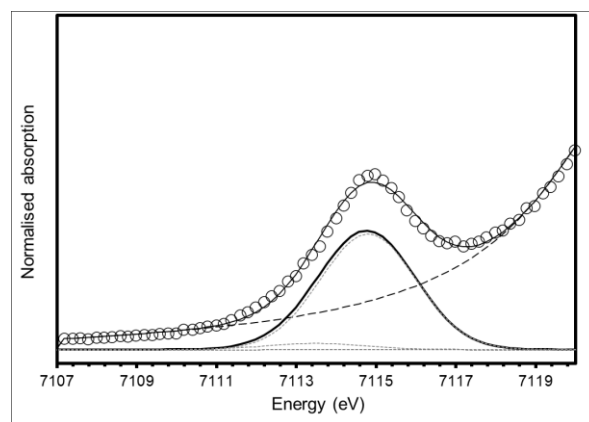


Figure 193 - Fe K-edge XANES pre-peak
fitting of ILAW1.53

8.28 Appendix CCC ILAW Crystal Structures and Parameters

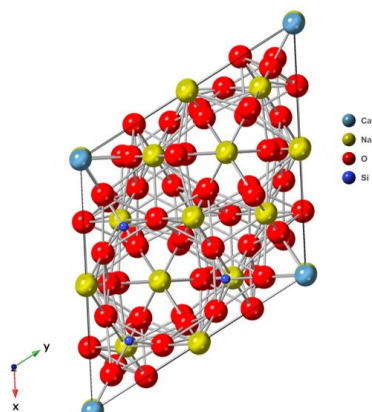


Figure 194 - ICSD 3D model of
 $\text{Na}_{5.27}\text{Ca}_3(\text{Si}_6\text{O}_{18})$

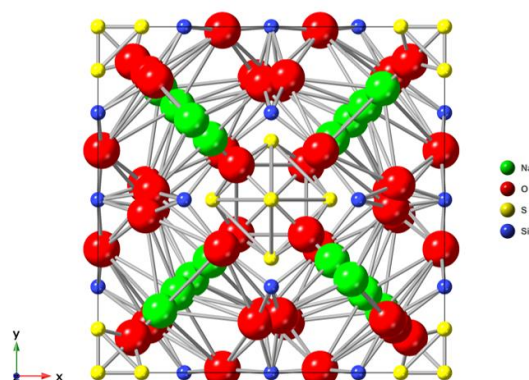


Figure 195 - ICSD 3D model of
 $\text{Na}_{7.7}((\text{Al}_{5.1}\text{Si}_{6.9})\text{O}_{24})(\text{SO}_4)_{0.88}(\text{S}_3)_{0.76}$

Crystal phase	Reference code	Crystal structure	Space group	Unit Cell (Å)			Reference
				a	b	c	
$\text{Na}_{5.27}\text{Ca}_3(\text{Si}_6\text{O}_{18})$	01-078-1650 (ICDD)	Rhombohedral	R-3m	10.4290	10.4290	13.1490	(Fischer & Tillmanns, 1987)
$\text{Na}_{7.7}((\text{Al}_{5.1}\text{Si}_{6.9})\text{O}_{24})(\text{SO}_4)_{0.88}(\text{S}_3)_{0.76}$	01-076-8976 (ICDD)	Cubic	P23	9.0928	9.0928	9.0928	(Climent-Pascual et al., 2008)

Table 95 – sodium calcium silicate and sodium sulphide aluminium silicate sulphate parameters

8.29 Appendix: ILAW Normalised Mass Loss and Minimum Release Rate Data

	NLAI	16	NLCa	16	Cl	16	Cr	16	Fe	16	K	16	Li	16	V	16	Sn	16	S	16
ILAW0.00	0.478	0.012	0.061	0.001	9.393	0.092	0.442	0.012	0.003	0.001	0.636	0.021	3.348	0.09	-	-	-	-	-	-
ILAW1.53	0.157	0.005	0.054	0.007	14.519	1.55	1.727	0.024	0.002	0.001	2.416	0.1	4.021	0.033	-	-	-	-	-	-
CCC ILAW0.00	0.253	0.002	0.05	0.003	-	-	0.544	0.008	0.001	0	1.811	0.239	3.037	0.007	1.601	0.022	0.013	0	1.661	0.033
CCC ILAW1.53	1.145	0.104	0.046	0.004	-	-	0.083	0.001	0.001	0	1.236	0.161	5.983	0.574	1.391	0.006	0.021	0.001	0.093	0.021

Table 96 - Normalised mass loss of all other elements for ILAW samples

	B	Si	Na	P	Al	Ca	Cl	Cr	Fe	K	Li	V	Sn	S
ILAW0.00	0.258	0.135	0.527	-	0.06833	0.00867	1.34183	0.06308	3.74E-04	0.09091	0.47825	0	0	0
ILAW1.53	0.416	0.182	0.546	0.01	0.02239	0.00768	2.07411	0.24676	2.79E-04	0.34509	0.57437	0	0	0
CCC ILAW0.00	0.208	0.114	0.324	-	0.03619	0.00713	0	0.07776	8.17E-05	0.25869	0.43388	0.22869	0.00186	0.23722
CCC ILAW1.53	0.561	0.158	0.688	0.001	0.16354	0.00661	0	0.01186	1.76E-04	0.17657	0.85469	0.19877	0.00303	0.01327

Table 97 - Minimum normalised release rate for all elements in ILAW samples

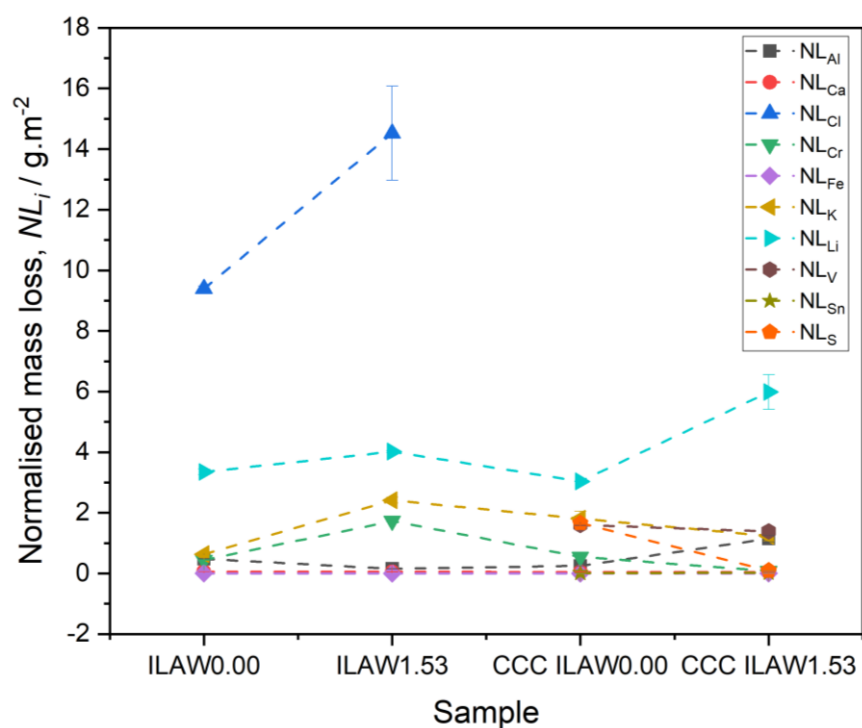


Figure 196 - Normalised mass loss of remaining analysed elements in the ILAW samples

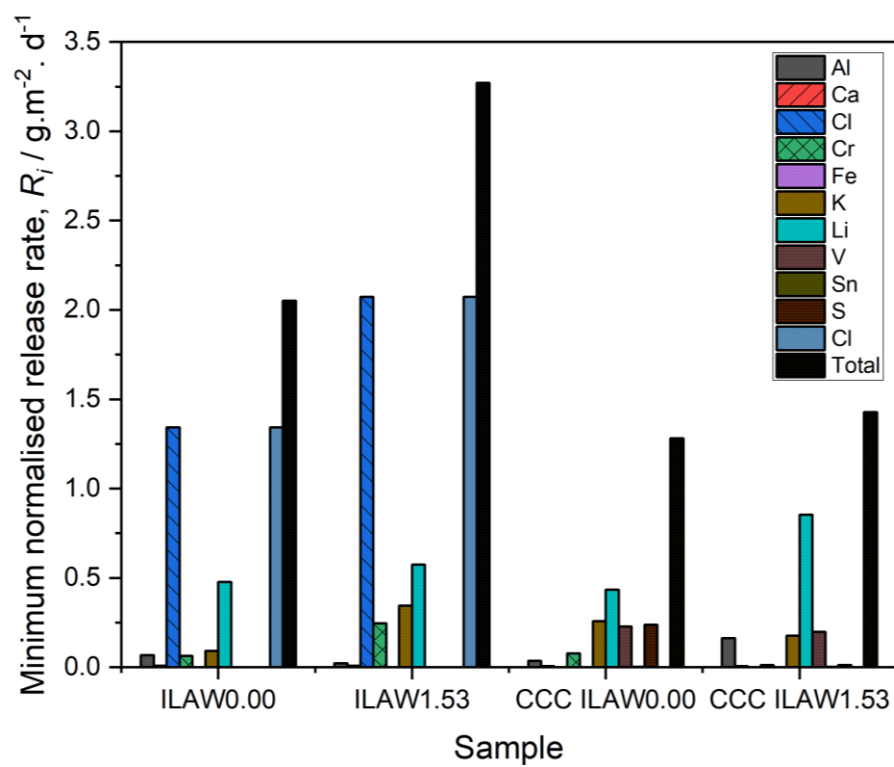


Figure 197 - Minimum normalised release rate for remaining elements in ILAW samples