Antimony-modified soda-lime-silica glass: towards low-cost radiation-resistant materials

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Citation:

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Antimony-modified soda-lime-silica glass: towards low-cost radiation-resistant materials

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Abstract

The development of inexpensive radiation-resistant glass is important for potential applications in displays, optics, and nuclear or space environments. This study considers the γ-ray and X-ray resistance of glasses relevant to low-cost float glass (i.e., SiO_2–Na_2O–CaO-MgO), modified with various concentrations (0 – 10 mol%) of Sb_2O_3. Various doses (0, 0.2, 2.0, and 5.0 MGy) of γ-rays from the decay of ^{60}Co nuclei, and X-rays generated by an X-ray fluorescence (XRF) spectrometer, have been applied to this series of Sb_2O_3-modified float-type glasses to study their resistance to radiation-induced damage. Irradiation leads to the formation of various defect centres (HC_2, HC_1, TE, E', and E^- types). These radiation-induced defects cause photo-darkening of the glass, which reduces its visible-wavelength optical transparency. The addition of Sb_2O_3 to these glasses led to reductions in the formation of radiation-induced defect-centres, combined with forbidden bandgap narrowing which led to non-linear changes in visible-wavelength absorption as a function of Sb_2O_3 content such that

1

26   the most transparent irradiated glasses were advantageously obtained at low (0.5 mol%)

27   Sb_2O_3 content. The mechanisms of defect-formation involve the creation of Sb^{4+}-ions which

28   assists in mitigating the effects of irradiation on the visible-wavelength transparency of the

29   glass. The 0.5 mol% of Sb_2O_3-modified float glass provided a maximized concentration of

30   Sb^{4+}-ions upon γ-ray irradiation. Combined with the smallest changes in the UV band gap

31   narrowing, it enabled this glass to retain the highest visible-wavelength transparency at all

32   doses of ionizing radiation studied (0.2, 2 and 5 MGy). This work confirms the substantially

33   enhanced radiation resistance of Sb_2O_3-modified float-type glasses compared to standard

34   float glass, which could potentially be further developed towards commercialization, for

35   example as a low-cost solution for radiation resistant applications.

36

37   **1. Introduction**

38   Photo-darkening of commercial glass systems interacting with ionizing radiation has

39   been previously studied across a range of systems and scenarios [1–10]. Both UV-Vis-NIR

40   optical absorption spectroscopy and electron paramagnetic resonance (EPR) techniques have

41   been employed to better understand radiation-induced effects in glass systems [1–10]. Based

42   on these and other articles, two interesting conclusions may be drawn regarding the

43   mechanisms involved:

44   I.   Trapping of electrons in defects existing before glass irradiation; or

45   II. Defect centres created during the irradiation process

46   The radiation-induced defects in the amorphous form of SiO_2 (a-SiO_2) and silica based

47   glass have been studied in depth by various research groups [1,3,10–14]. Electron

48   Paramagnetic Resonance (EPR) studies have confirmed the formation of paramagnetic

49   radiation-induced defects [11]. EPR studies reveal that the fundamental radiation-induced

50 defect centres in silica systems are E'-centres [15], non-bridging-oxygen hole centres

51 (NBOHC) [16], peroxy-radicals (POR) [17] and self-trapped holes (STH) [18]. The radiolytic

52 process of formation of E'-centres can be presented as $[\equiv Si:Si\equiv]^0 + h^+ \rightarrow [\equiv Si\cdot \ ^+Si\equiv]^+$, where

53 '$\equiv$' represents the bonds to 3 bridging oxygens in the glass network, ':' represents a pair of

54 electrons equally shared between two adjacent silicon atoms, the '$\cdot$' implies an unpaired

55 electron localized in a dangling sp^3 orbital of a single silicon atom, and 'h^+' defines the hole

56 interacting with the glass network [19]. The fission of strained Si-O-Si bonds causes the

57 formation of NBOHC (i.e., $\equiv$Si-O$\cdot$) defects [11]. The peroxy-radicals (POR, i.e., $\equiv$Si-O-O$\cdot$)

58 are formed via several pathways [11,19]. Self-trapped holes are of two types: STH_1 contains a

59 hole trapped in a bridging oxygen network (i.e., $\equiv$Si-$\dot{O}$-Si$\equiv$), while STH_2 comprises a hole

60 delocalized over two bridging oxygens [11,12]. In general, all of the stable paramagnetic

61 defects have half-filled energy levels located in the optical band gap, hence such defects give

62 rise to optical absorption bands [11].

63   These radiation-induced defects trap the electrons that give rise to so-called "colour

64 centres" [1–3,10,11,19–22]. The absorption peak position and relative intensity of the various

65 colour centres within irradiated soda-lime-silica glasses varies with glass-melting

66 environment (oxidizing or reducing) [1]. Ionizing radiation-induced absorption bands are

67 reported at (a) $590 – 620$ nm (i.e., $16,949$ - $16,129$ cm^{-1} or $2.0 – 2.1$ eV), (b) $430 – 450$ nm

68 (i.e., $23,256$ - $22,222$ cm^{-1} or $2.75 – 2.90$ eV), (c) $300 – 310$ nm (i.e., $33,333 – 32,258$ cm^{-1} or

69 $4.0 – 4.1$ eV), and (d) $225 – 235$ nm (i.e., $44,444$ - $42,553$ cm^{-1} $5.3 – 5.6$ eV) for soda-lime-

70 silica systems [1,19,20,23]. The origin of radiation-induced absorption band near $16,500$ cm^{-1}

71 (2.0 eV) has been attributed to both POR ($\equiv$Si-O-O$\cdot$) and NBOHC or HC_2 ($\equiv$Si-O$\cdot$) [10,23].

72 According to Zatsepin $et\ al.$ [20] and others [1, 23], the radiation-induced absorption band at

73 around $22,200$ cm^{-1} (2.75 eV) is manifested for Na_2O or K_2O modified silica glasses

74 [1,20,23]. This band has been attributed to modified NBOHC-centres (i.e., $HC_1 \rightarrow \equiv$Si—

75 $\dot{O}...Me^+$, where '…' presents the dangling bond) [20]. The absorption band near 33,300 cm^{-1}

76 (4.0 eV) has been attributed to trapped electron defects [23] and the band near 43,500 cm^{-1}

77 (5.4 eV has been attributed to E'-centres [23].

78   Radiation-hard glasses are glasses with compositional modifications, often enabled by

79 the incorporation of transition metals or lanthanides, that reduce defect centre related

80 colouration effects. Ions such as Ce^{3+}, Fe^{2+} and Mn^{2+} capture the holes, which evolve after

81 the interaction of ionizing radiations [1,24–27]. In contrast, ions including Ce^{4+}, Eu^{3+} and Ti^{4+}

82 capture the electrons after interaction with γ-rays [1,2,24,25,28,29]. Baccaro *et al.* [9]

83 reported the effects of Ce^{3+}/Ce^{4+} ion-modified borosilicate glass for radiation-resistance over

84 a wide range of γ-ray doses, with applications in radiation-resistant windows [9]. The

85 addition to oxide glasses of Ce^{3+}/Ce^{4+} has provided radiation resistance for many years and

86 commercially produced "*radiation-hard*" glasses typically use Ce^{3+}/Ce^{4+} ions in the network

87 to provide resistance from extreme high-radiation environments such as in space or the

88 nuclear industry [8,9,30,31]. Apart from cerium, only a few elements can exist in multiple

89 oxidation states within oxide glasses whilst producing little or no visible absorption

90 (colouration) when present at concentrations sufficient to provide significant added resistance

91 to radiation damage (>ca. 1 wt. %) [9,31,32]. In oxide glass, most transition metals and

92 lanthanides produce visible absorption bands due to *d-d* or *f-f* transitions [33–37] and

93 substantial levels of doping would render such glasses moderately or strongly coloured,

94 depending on the nature of the additive/s and the redox conditions associated with glass

95 preparation. Many glass applications require high visible-range transparency so the addition

96 of most of the transition metals and many of the lanthanides is not an option, hence the

97 widespread use of Ce^{3+}/Ce^{4+} for radiation resistance, since neither of these oxidation states of

98 cerium produces strong absorption bands centred at visible wavelengths. However, a number

99 of first, second and third-row transition metals, when present in oxidation states with d^0

4

configurations, produce no visible absorption bands [33–37]. A number of these have been studied for potential solar energy UV protection and downshifting applications [38,39].

Glasses with transition metal dopants present in their colourless oxidation states can, in some cases, develop extrinsic defects, by photo-oxidation or photo-reduction, which manifest as visible or UV absorption bands, for high-energy (UV, X-ray, γ-ray) and high-dose radiation [4,7,40]. Traditionally referred to as solarisation (in the context of UV from sunlight), this is a well-known phenomenon that describes radiation-induced changes in oxidation state [4,7,40–47]. For example, Mn^{3+} was used for many centuries [40,48] to decolourise glasses by oxidising Fe^{2+} to Fe^{3+} through the redox reaction $Mn^{3+} + Fe^{2+} \rightarrow Mn^{2+} + Fe^{3+}$ [4,7]. However, prolonged exposure to UV radiation could supply sufficient photons with adequate energy to measurably reverse this reaction and oxidise Mn^{2+} to Mn^{3+}, which gives rise to visible absorption bands, via the redox reaction $Mn^{2+} + Fe^{3+} + hv \rightarrow Mn^{3+} + Fe^{2+}$ [33,40]. Photo-oxidation or photo-reduction reactions have been documented for many multivalent cations in oxide glasses – principally at low ($\ll$ 1 wt %) abundance and principally for transition metals and lanthanides [2,4,5,7–9,32,33,40,42,49–58]; but also post-transition metals (e.g. Nb, Ta, W) and the so-called heavy metals including Sb, As and Pb [6,7,42,45–47,53,59,60]. These include cations which undergo "*colourless to coloured*" photo-oxidation or photo-reduction, for example, $Ti^{4+} \rightarrow Ti^{3+}$, $Mn^{2+} \rightarrow Mn^{3+}$ or $Nb^{5+} \rightarrow Nb^{4+}$. The presence of multivalent cations including Fe^{2+}/Fe^{3+} [1,4,7,21,56,61–64], Ce^{3+}/Ce^{4+} [1,4,7,52,61], $Cu^{0}/Cu^{+}/Cu^{2+}$ [4,7,54–56], Mn^{2+}/Mn^{3+} [1,4,7,55–57,61,65], Ti^{3+}/Ti^{4+} [1,2,4,7,44,46,47,52] and other transition metals, lanthanides and heavy metals [1,2,4,5,7,49,51–53,55,56,58,60,61] can have varying degrees of efficacy, depending on their abundance and distribution in the glass; the nature, energy, and dose of irradiation; the glass composition and structure; and the glass melting (redox) conditions.

124   To minimise the formation of extrinsic or intrinsic visible colour centres through photo-

125   oxidation or photo-reduction, it is essential to avoid any multivalent constituents which

126   produce absorption bands centred at visible wavelengths. Most multivalent ions can access

127   various oxidation states by melting under extreme redox conditions [66,67] (e.g., sufficient to

128   reduce cations to their metallic forms), to cause visible or near-IR (for solar energy /

129   photovoltaic applications) absorption bands.

130   One such multivalent element, which produces no visible absorption bands in any

131   nonzero oxidation state, is antimony. There is evidence that Sb_2O_3 can render oxide glasses

132   more resistant to the formation of radiation-induced defects [52,60,68–70], and Sb_2O_3

133   additions can provide enhanced resistance to γ-radiation when present with other active

134   dopants [60,69,71]. The effect of radiation-induced attenuation has been studied for Sb_2O_3

135   and Nb_2O_5 modified P_2O_5–K_2O–BaO–Al_2O_3 glass [60]. The γ-irradiated base glass as well as

136   Nb_2O_5-modified glasses revealed a very broad, intense absorption band centred at $330 - 700$

137   nm ($30,300 - 14,300$ cm^{-1}). However, the Sb_2O_3-modified glasses did not show any

138   additional absorption bands. EPR analysis of those γ-ray exposed glass samples showed two

139   types of response [60]. The major EPR signal consisted of sharp hyperfine splitting

140   associated with PO_2, PO_3, PO_4, and phosphorus-oxygen hole centres (*POHC*: an unpaired

141   electron shared by two NBO atoms bonded with the same phosphorus) [3,60]. The minor

142   signal had larger hyperfine splitting with broad lines, which is associated with phosphorus-

143   oxygen electron centres (*POEC*: PO_2, PO_3, PO_4 complexes that consist of unpaired electrons

144   localized on the central P-atom). The base glass showed both major and minor EPR bands,

145   under γ-ray exposure. However, the Nb_2O_5-modified phosphate glass exhibited only the

146   major EPR response, while Sb_2O_3-modified samples showed both EPR bands were absent.

147   The γ-ray generated electron-hole pair must therefore be retained in the phosphate base glass

148   by redox reactions, (A) $PO + h^+ \rightarrow POHC$ (h^+: Hole from electron-hole pair production) and

149   (B) $PO + e^- \rightarrow POEC$ (e^-: electron from electron-hole pair production). However, the Nb^{5+}

150   ions, which act as an electron capture centre, following the redox reaction $Nb^{5+} + e^- \rightarrow Nb^{4+}$,

151   whereas some PO captures the hole in the vicinity of the Nb^{5+} ion. Further, the process of

152   electron-capture could cause the formation of Nb^{4+}–O–Nb^{4+} or Nb^{4+}–O$^-$ complexes and

153   possibly lead to the formation of Nb^{3+}–O– Nb^{5+} units [71–73]. On the contrary, for Sb$_2$O$_3$-

154   containing glasses, Sb^{3+}-ions act as a hole-trapping centre that follows the redox reaction Sb^{3+}

155    $+ h^+ \rightarrow Sb^{4+}$ [60]. The nearest PO captures the e^- to result in $POEC$, in this process [60].

156   However, Sb^{4+} has instabilities at room temperature that causes a further redox reaction, Sb^{3+}

157    $+ 2Sb^{4+} \rightarrow Sb^{5+} + 2Sb^{3+}$ [60]. Now, the electrons captured in $POEC$ must be absorbed by the

158   Sb^{5+} ions to recover Sb^{3+} by the redox reaction, $Sb^{5+} + 2POEC \rightarrow Sb^{3+} + 2PO$ [60]. By this

159   method, the Sb^{3+} ions are recovered in the process of γ-ray absorption, and the net effect on

160   the glass system is that it remains unaltered. As a result, the EPR spectra of Sb$_2$O$_3$-modified

161   phosphate glasses remain unaffected by γ-ray irradiation [60].

162   The present study investigated the radiation-resistant performance of Sb$_2$O$_3$-modified

163   soda-lime-silica (SLS) glass, building on our previous study to characterise the base glass and

164   Sb-doped glasses [74]. The radiation-resistant performance of various concentrations ($0 - 10$

165   mol%) of Sb$_2$O$_3$ modified SLS glass has been substantiated for high doses (up to 5×10^6 Gy)

166   of ^{60}Co γ-rays and for X-ray irradiation. The impacts of Sb$_2$O$_3$ on the levels and nature of

167   radiation-induced defects in soda-lime-silica type glasses, relevant to float glass manufacture,

168   were here studied by UV-Vis-nIR optical absorption EPR and ^{121}Sb Mössbauer

169   spectroscopies.

170

2. Experimental Procedures

This study explored the radiation-induced changes in a float glass-type SiO_2-Na_2O-CaO-MgO glass modified with various concentrations (0.0, 0.5, 1.0, 5.0, and 10.0 mol%) of Sb_2O_3. The detailed glass synthesis protocol, X-ray fluorescence (XRF) determined compositional analysis, thermal properties, and structural analysis were detailed in a previous publication [74]. The base glass (i.e., SLS glass modified with 0.0 mol% of Sb_2O_3) in this study was labelled sample SLS. The glasses modified with x mol% of Sb_2O_3 were denoted Sbx; on this basis, Sb0.5, Sb1.0, Sb5.0, and Sb10.0 are labelled. The undoped (SLS, Sb_2O_3-free) base glass had a nominal composition of (mol %): SiO_2 70.67; Na_2O 13.76; MgO 5.49; CaO 9.27; Al_2O_3 0.59; SO_3 0.22. Full and detailed analysis and discussion of this series of glasses can be found in [74].

To study their radiation behaviour, glass samples were irradiated with γ-rays and X-rays. The γ-ray irradiation experiments were executed employing a Foss Therapy Services 812, equipped with a ^{60}Co gamma irradiator at the Dalton Cumbrian Facility at The University of Manchester, which provides gamma photons with energies of $1.17 - 1.33 \, MeV$ [75]. In this study, glasses were irradiated with doses of 0.2, 2.0, and 5.0 MGy of γ-rays. The experimental conditions for the γ-irradiation were similar to one of our previous studies [76] to enable a consistent approach. A wavelength dispersive Philips PW2440 sequential X-ray fluorescence spectrometer (XRF) was employed as the source for X-ray irradiation. The XRF tube is a source of continuous X-rays, delivering photon energies from 0.2 keV to 35.5 keV.

Glasses were analysed using UV-Vis-nIR absorption spectroscopy and X-band electron paramagnetic resonance (EPR) spectroscopic techniques. UV-Vis-nIR absorption spectra were collected from flat and optically polished sample at room temperature, using a Varian Cary 50 Scan spectrophotometer. Absorption spectra were recorded in the range $200 - 1100$

nm. All measurements were carried out in absorption mode, using the single beam scanning technique, at a scan rate of 60 nm/min. The thickness of glass samples was ~ 2 mm for all samples. First-derivative, continuous-wave, and monolithic-specimen EPR spectra were collected for all glass samples. All EPR measurements were performed using a Bruker EMX nano EPR spectrometer, at room temperature, at an X-band frequency of ~ 9.6 GHz. The magnetic field modulation employed was 100 kHz. The microwave power used for the experiment was 0.3162 mW, with a modulation amplitude of 0.4 mT. The second-order derivative of the EPR signal was obtained by numerically differentiating the measured first-order derivative e of EPR spe(ctra, which has been used to clarify the g-values and linewidths associated with radiation-induced defect-centres.

^{121}Sb Mössbauer spectra were obtained at room temperature (293 K) in transmission geomerry using the 37.2 keV γ–rays from a 0.84 mCi CaSn(^{119}Sb)O$_3$ source mounted on a constant acceleration drive (SEECO, Edina, MN.). The gamma-rays were detected with a xenon-filled proportional counter. The velocity scale was calibrated using an α-Fe absorber and a Rh^{57}Co source. The absolute source velocity must be slightly adjusted because the Rh^{57}Co source has an isomer shift relative to α-Fe which requires subtraction of 0.1 mm s^{-1}. The resulting spectra showed two broad lines, one due to Sb^{3+} and one due to Sb^{5+}, the latter having a higher absolute velocity. The asymmetry in the Sb^{3+} component is due to the quadrupole splitting of the eight lines in the 7/2+ to 5/2+ transition in ^{121}Sb. The 5+ line has no quadrupole splitting since it is spherically symmetrical, so the extra width compared with the lifetime width of about 2 mm s^{-1} reflects the broadening by the different environments in the glass. We take the 5+ to have the same natural width. The spectra were least-square fitted to extract the hyperfine parameters centre shift (δ), quadrupole interaction (e^{2}Qq), Lorentzian linewidth (Γ), and intensities (I) and are shown in Figure 7. The velocity scale shown in Figure 7 is the as measured velocity. In the literature it is common to quote the centre shift

220   values relative to InSb by adding 8.6 mm s^{-1}. Hence the conversion here was -0.1+8.6 = +8.5

221   mm s^{-1} and the corrected values of the centre shift (δ) are given in Table 3, together with the

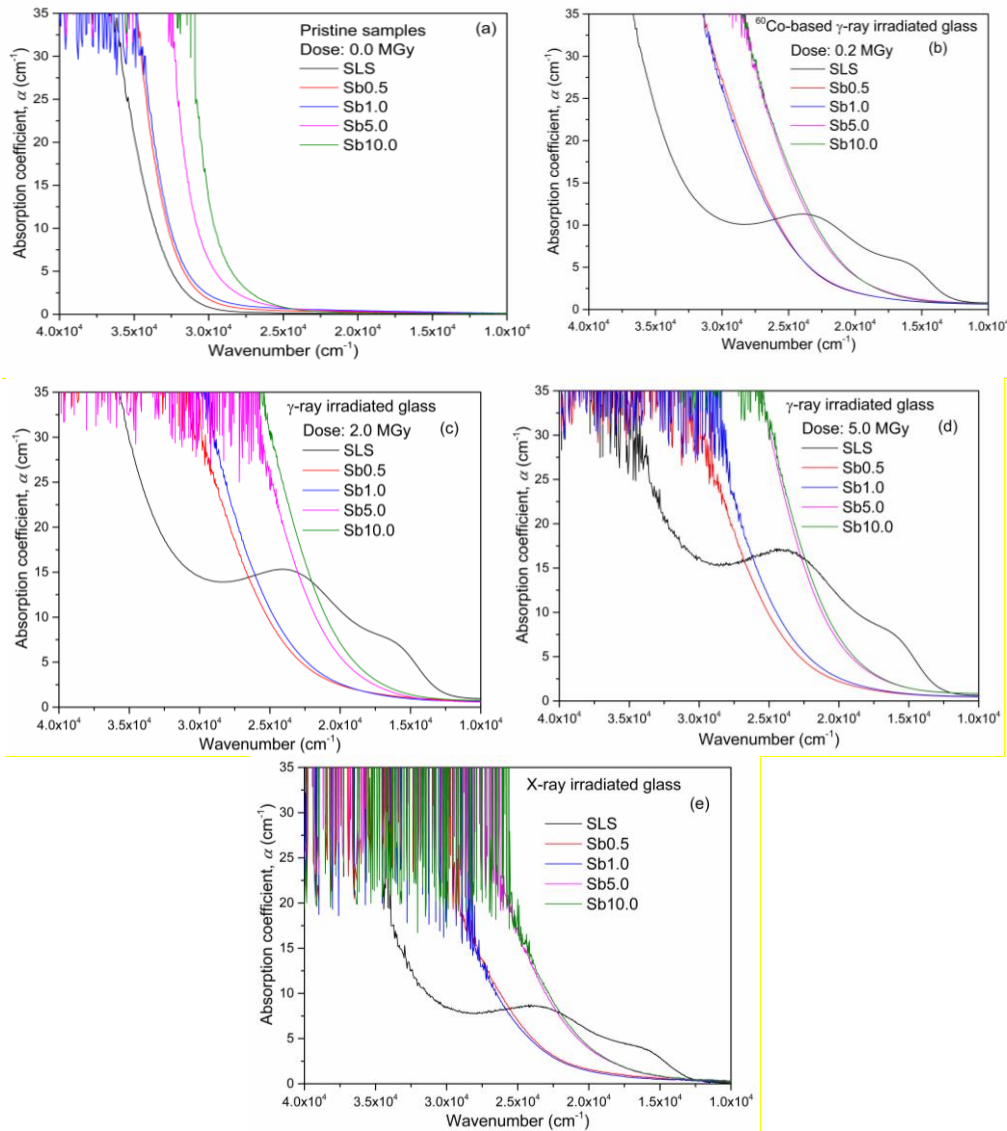222   other fitted Mössbauer parameters.

3. Results

223

Figure 1: Absorption coefficient spectra of (a) pristine (i.e., 0.0 MGy), (b) 0.2 MGy, (c) 2.0 MGy, and (d) 5.0 MGy dose of γ-ray, and (e) X-ray irradiated glass samples.

224

225   The interactions of high energy ionizing radiation (e.g., γ-ray, X-ray) with matter resulted in

226   generation of free electrons and holes in the network [1,7]. These free electrons and holes

227   were trapped either at vacancies, interstitial atoms, and non-bridging oxygens, or captured by

228   multivalent ions in the network [5]. The incorporation of holes and electrons in the network

229   leads to *defect centres* in the glass, which preferentially absorb the UV and visible radiation

230   [1,10,11,19,20,23,29]. *Defect centres* have commonly been labelled *colour centres* by some

231   authors [1,4,10,11,19,20,23,29]. In several prior studies, UV-visible-nIR optical absorption

232   spectroscopy and electron paramagnetic resonance (EPR) have been used to analyse

233   radiation-induced defect centres in glass networks [1,3,11,12,16,18–20,23]. The characteristic

234   energies and linewidths of radiation-induced optical absorption bands, together with the line

235   shapes and "*g*" values from EPR spectra, have been utilized to decipher the origins of specific

236   defect centres [1,11,12,18–20,23].

237   The absorption spectra of glass samples are influenced by their thickness, governed by

238   Beer's law. The influence of sample thickness on the absorption spectra was excluded by

239   calculating the absorption coefficient for each sample. The absorption coefficient (α) was

240   evaluated using (1):

241     $$\alpha(\varepsilon) = \frac{2.303 \times A(\varepsilon)}{t} \qquad\qquad (1)$$

242   where $A(\varepsilon)$ and t represent the measured absorbance as a function of wavenumber (i.e., ε) and

243   thickness of each sample in cm, respectively. The absorbance is measured directly using the

244   absorption spectrophotometer device. The origin of the constant multiplication factor of

245   2.303 is described in the Supplementary Information. The induced absorption coefficient for

246   each irradiated glass was evaluated by subtracting the absorption coefficient of pristine glass

247   (α_p) from the absorption coefficient of its counterpart irradiated glass (α_i). Therefore, the

248   induced absorption coefficient ($\Delta\alpha$) was calculated according to (2):

249     $$\Delta\alpha(\varepsilon) = \alpha_i(\varepsilon) - \alpha_p(\varepsilon) \qquad\qquad (2)$$

250 The radiation-induced absorption spectra for multicomponent glasses show the

251 superposition of several absorption bands from *defect centres*. To assess the contribution of

252 each *defect centre* to the induced absorption, the spectra were resolved into multiple Gaussian
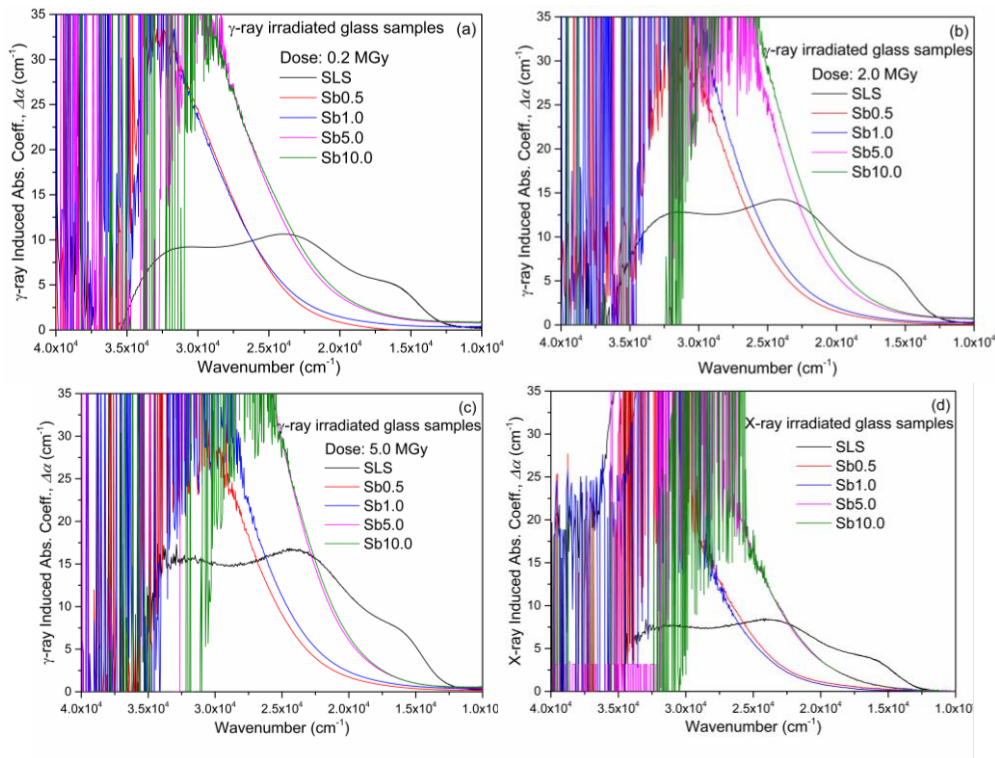

Figure 2: Radiation induced absorption coefficient ($\Delta\alpha$) spectra of (a) 0.2 MGy, (b) 2.0 MGy, and (c) 5.0 MGy dose of γ-ray, and (d) X-ray irradiation.

253 bands using OriginPro 9.1 software [1,21,23]. The deconvoluted induced absorption spectra

254 reveal the characteristic energy and bandwidth of specific *defect centres* [21,23]. According

255 to various reports the deconvolution of radiation-induced absorption coefficients of soda-

256 lime-silica glass was resolved into four Gaussian bands [1,23].

257 First-derivative, continuous-wave monolithic sample EPR spectra at room temperature

258 were recorded, probing an X-band frequency of ~ 9.6 GHz. The second derivative of the EPR

259 signal was calculated to obtain the peak of the EPR absorption signal that was utilized to

260 evaluate the *g* value of the respective *defect centres*.

261 Employing the optical absorption spectra, the absorption coefficients (i.e., α) of the

262 present series of glass samples were assessed using (1). The absorption coefficient spectra of
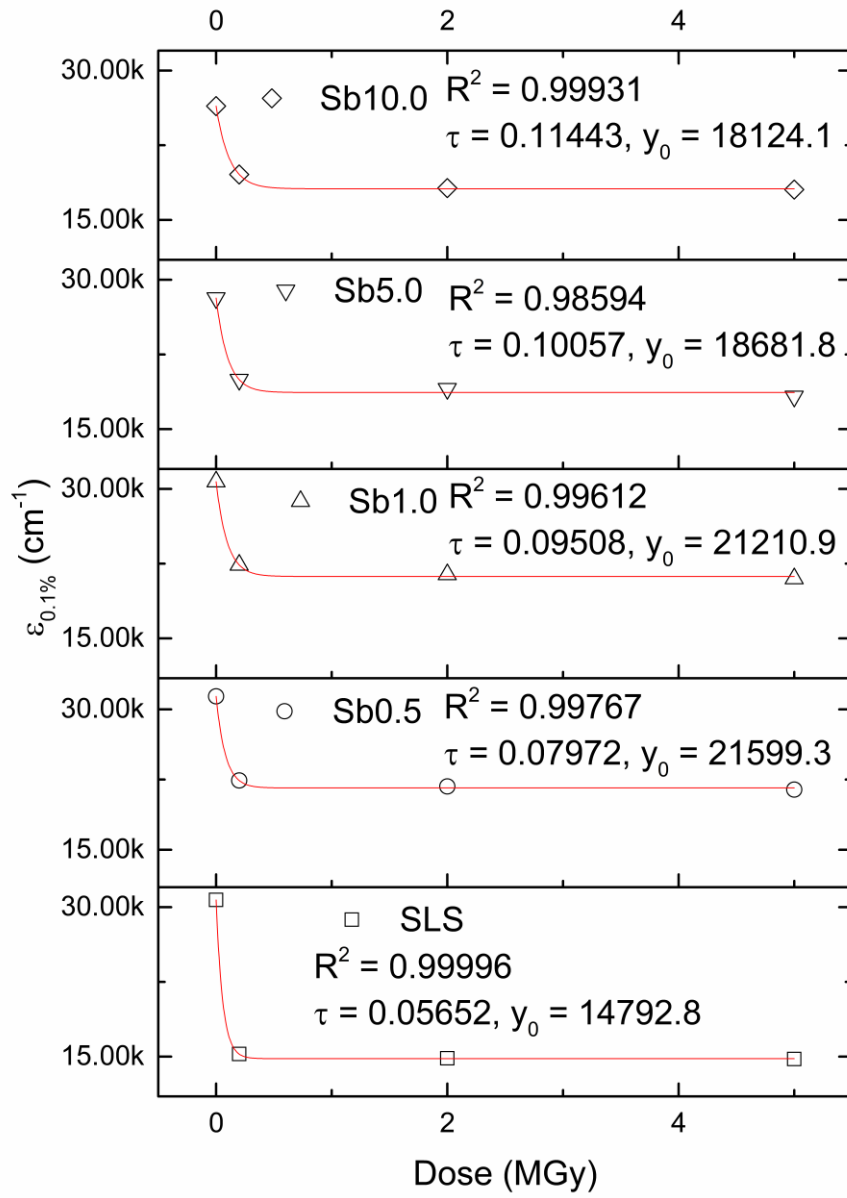
Figure 3: Plot of 0.1% transmittance wavenumber (i.e., $\varepsilon_{0.1\%}$) as a function of the γ-ray doses of studied glass samples, fitted with $y = A \exp(-x/\tau) + y_0$ function.

263

264 the glass samples before and after various doses of ionizing radiation are illustrated in Figure

265 1 (a – e). The absorption coefficient spectra of pristine (0.0 MGy) glass samples are shown in

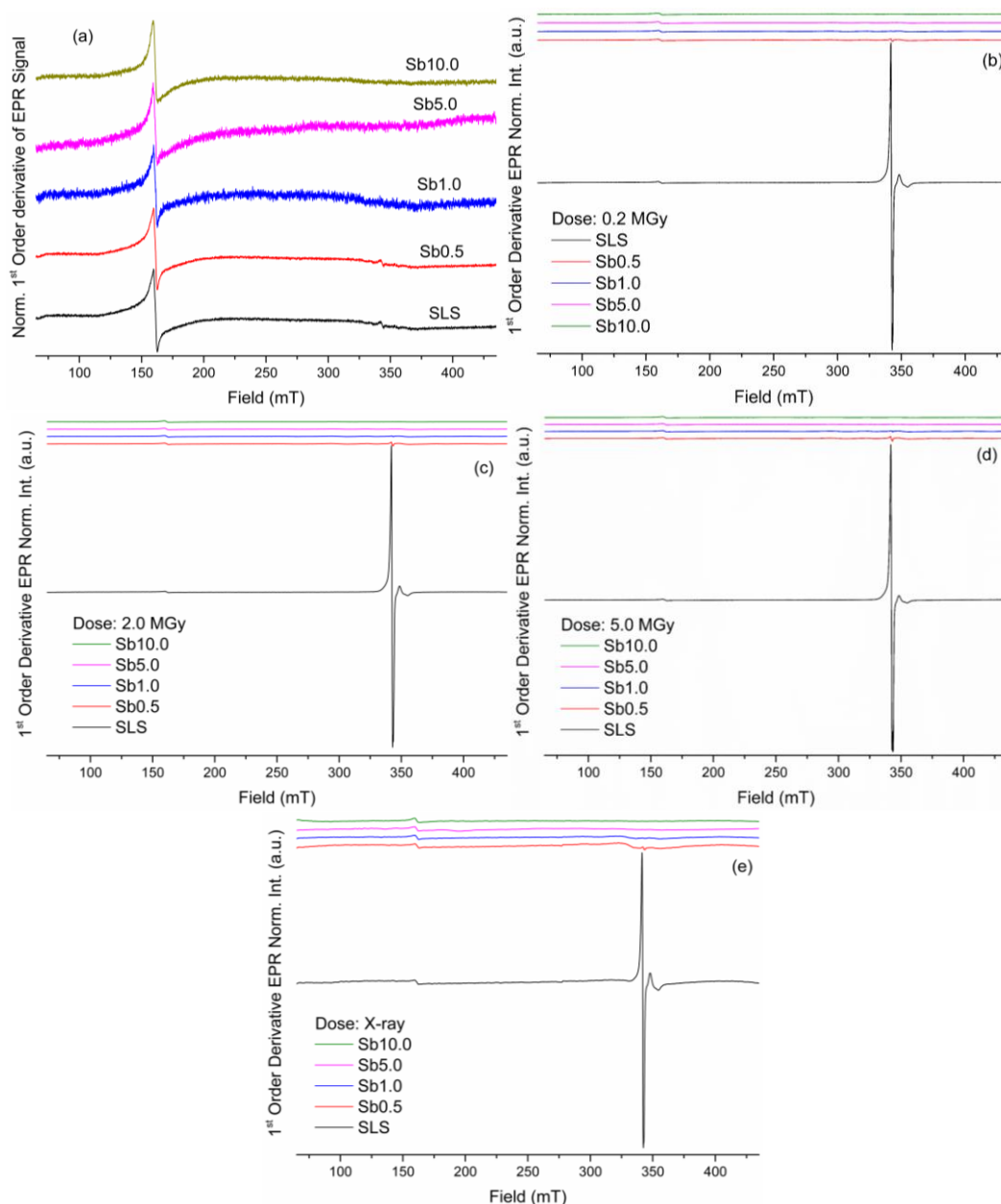266 Figure 1(a), which reveals the steady redshift of the UV band-edge wavelength with the

Figure 4: Background compensated and normalized first-order derivative of X-band EPR response of (a) pristine, (b) 0.2 MGy, (c) 2.0 MGy, (d) 5.0 MGy dose of γ-ray, and (e) X-ray irradiated glass samples at 298 K.

267 addition of Sb_2O_3 to the glass. The exposure of the glass to γ-rays then resulted in a

14

significant modification of the shape function of the absorption coefficient spectra, which are shown in Figures 1 (b – d). The effects of X-ray exposure to the glass samples are presented in Figure 1 (e). The glasses manifested the formation of radiation-induced absorption bands of defect-centres at visible wavelengths following both γ-ray and X-ray exposure. Increasing dose of γ-rays increased the absorption coefficient of the radiation-induced defect centres. Notably, the radiation-induced visible optical absorption bands disappeared when Sb_2O_3 was introduced into the glass at all levels of Sb_2O_3 addition studied here. To offer a quantitative analysis of the radiation-induced effects in glass samples, the radiation-induced absorption coefficient (i.e., $\Delta\alpha$) spectra were assessed using (2).

Figures 2 (a – d) show the radiation-induced absorption coefficient spectra of the glass samples for γ-ray doses of 0.2, 2.0, and 5.0 MGy, and for X-ray irradiation, respectively. Notably, the γ-ray and X-ray irradiated SLS glasses reveal a similar pattern of shape functions, which supports the superposition of several Gaussian bands. The addition of Sb_2O_3 to the glass causes a significant modification of the shape function of the absorption coefficient spectra. The Sb0.5 sample developed a broad and intense absorption band associated with defect-centres, which possibly has a peak at a deep UV wavelength. However, the UV band-edge of Sb0.5 glass masked the peak of the respective absorption band. Further addition of Sb_2O_3 to the glass did not alter the shape function of the induced-absorption spectra. However, increasing of the dose of γ-rays enhanced the width of the radiation-induced optical absorption band, suggesting an increase in intensity.

Figure 3 reveals the effects of irradiation dose of γ-rays on the transmittance of the glass samples. The wavenumber at which the transmittance of the glass sample (path length of 1 cm) becomes 0.1% is measured and designated as $\varepsilon_{0.1\%}$. The factor $\varepsilon_{0.1\%}$ is plotted as a function of the γ-ray dose, which closely follows a first-order exponential decay function, as

292   evidenced by the very high fit R^2 values (Figure 3). Figure 3 also confirms the retention of

293   the transmittance of the glass samples after being subjected to ionizing radiation.

294   The absorption coefficient spectra of the series of pristine glasses confirm the

295   continuous red shift of the UV cut-off wavelength with increasing additions of Sb_2O_3 to the
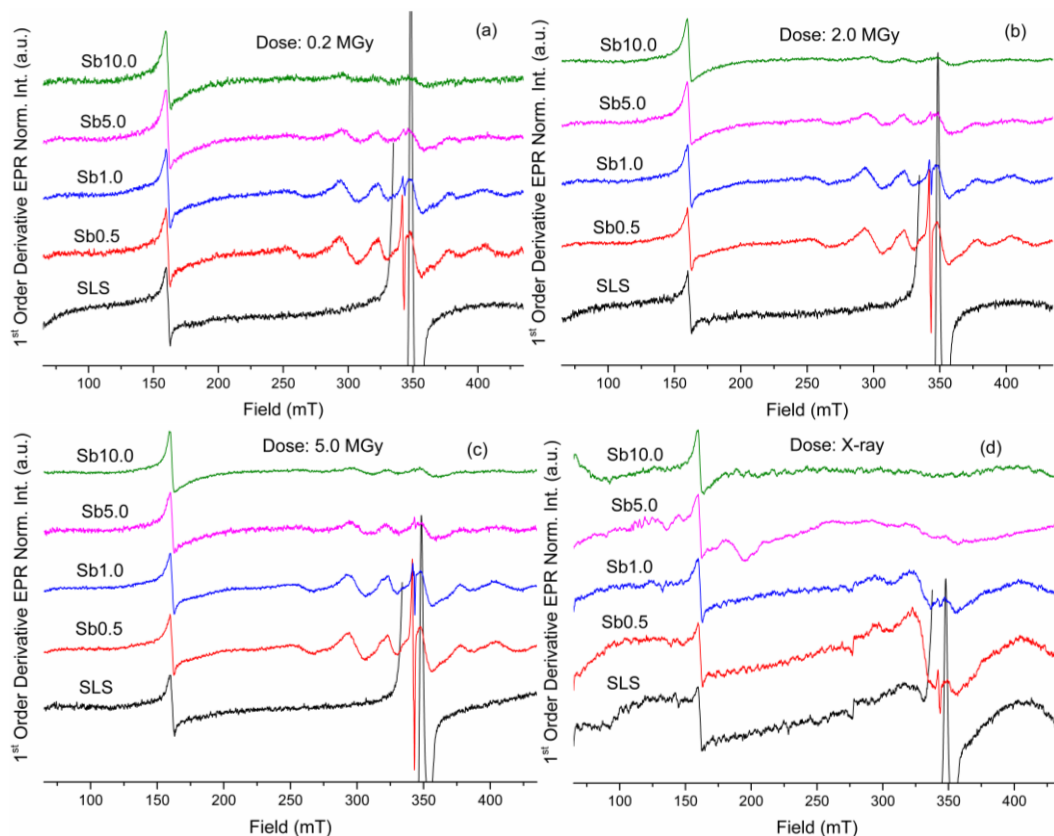

Figure 5: The magnified EPR response of glass samples irradiated with (a) 0.2 MGy, (b) 2.0 MGy, (c) 5.0 MGy dose of γ-ray, and (d) X-ray.

296   glass. Supplementary information S – I (a – e) shows the evaluation of UV band-gap energy

297   of the present series of glass, for various doses of ionizing radiation using a Tauc plot [77].

298   For the evaluation of band-gap energy, $(\alpha h v)^{1/2}$ vs. $h v$ was plotted. Supplementary

299   information S – II shows the cut-off energy as a function of nominal Sb_2O_3 content of the

300   glass, for pristine, X-ray, and γ-ray irradiated glasses. In general, increasing dose of ionizing

301   radiation steadily reduces the cut-off energy, in comparison to the pristine samples.

Figures 4 (a – e) reveal the background-compensated and normalized first-order derivatives of the X-band EPR spectra at ambient temperature (~ 298 K) for the series of glass samples, for various doses of ionizing radiation. The EPR spectra reveal the hyperfine signals in (i) the 140 – 170 mT range; and (ii) the 250 – 435 mT range. For the 140 – 170 mT range, a signal was reported around 160 mT ($g \sim 4.28$) for every sample, which is consistent with rhombically-distorted isolated sites Fe^{3+}-ion impurities [78,79]. For the present study, Fe^{3+}-ions were probably introduced as impurities in the glass making raw materials, and particularly the silica sand used in this study, at ppm levels. As a result, the
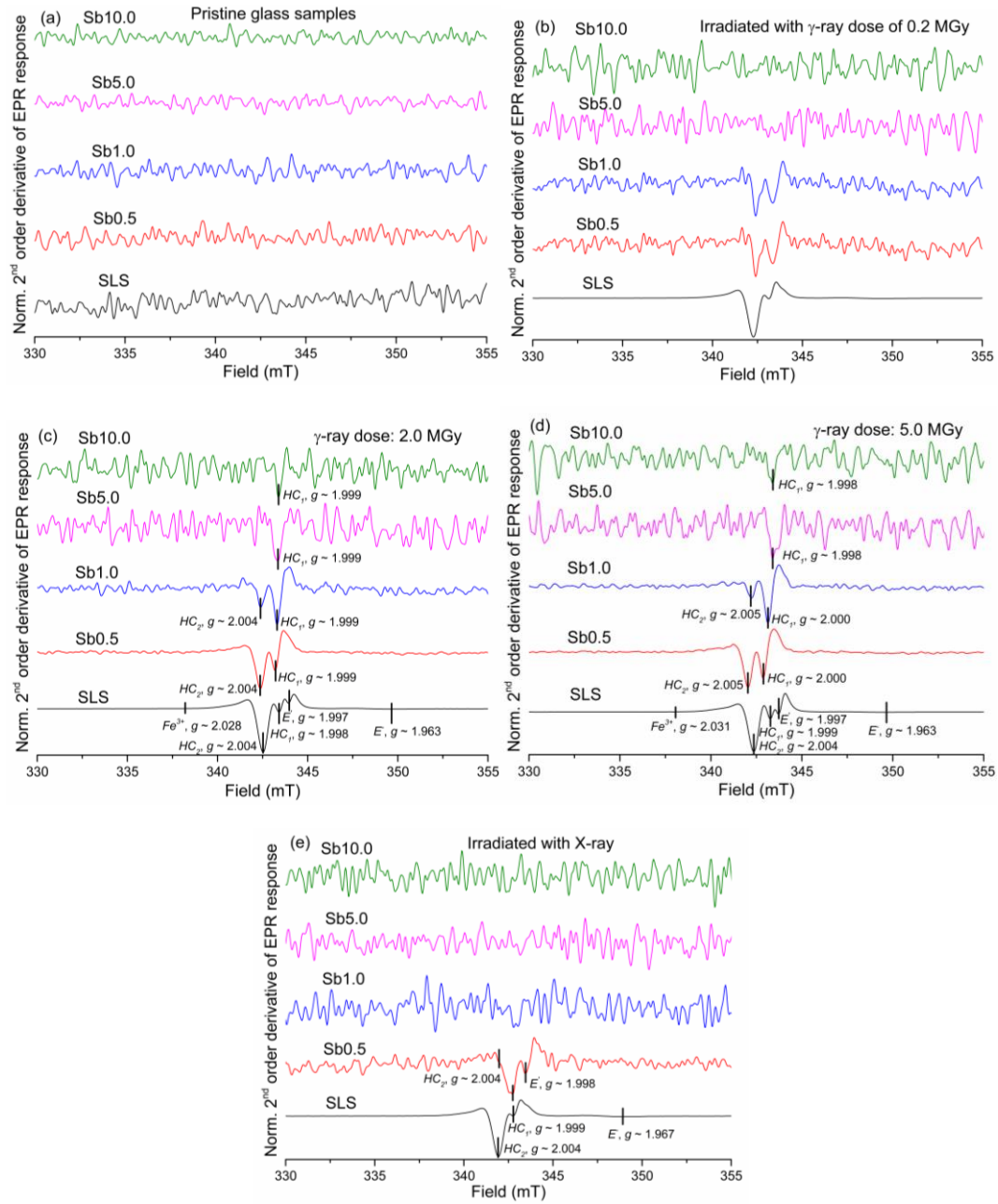
Figure 6: Normalized second-order derivative of EPR spectra of (a) pristine, (b) 0.2 MGy, (c) 2.0 MGy, (d) 5.0 MGy dose of γ-ray, and (e) X-ray irradiated glass samples.

310

normalization of the first-order derivative EPR spectra was performed for the peak-to-peak

intensity of Fe^{3+} signal (160 mT; $g \sim 4.28$). Figure 4 (a) reveals the EPR spectra of pristine

Figure 7: ^{121}Sb Mössbauer spectra (293 K) for sample Sb10.0, irradiated with 0.2, 2.0, and 5.0 MGy of γ-rays.

glass samples. Notably, for the pristine samples a very weak, asymmetric and broad EPR

trace in the range $300 - 420$ mT ($g \sim 2.0$) was detected (Figure 4(a)), which is attributed to

Fe^{3+}-Fe^{3+} interactions in the glass network [79]. Given the ppm levels of Fe in the glass, such

interactions are very weak. Nevertheless, there may be a slight decrease in the intensity of the

$g \sim 2.0$ signal with increasing Sb_2O_3 content. Figures 4 (b – d) reveal the EPR spectra of glass

samples subjected to 0.2, 2.0, and 5.0 MGy doses of γ-ray, respectively. Figure 4 (e) reveals

319   the EPR spectra of glass samples, which were exposed to X-rays. Figures 4 (b – e) have thus

320   confirmed the formation of ionizing radiation-induced defect-centres in the glass network.

321   The γ-ray or X-ray induced spectra reveal a set of intense, sharp, and overlapping EPR

Figure 8: The deconvolution of radiation-induced absorption coefficient of SLS base glass for (a) 0.2 MGy, (b) 2.0 MGy, and (c) 5.0 MGy dose of γ-rays and (d) X-rays.

322   signals in the range 330 – 355 mT (Figures 4, 5 and 6). However, the systematic addition of

323   Sb_2O_3 to the glass significantly reduces the intensity of these EPR responses from irradiated

324   glasses in the 330 – 355 mT range. To aid our study of the effects of ionizing radiation for

325   Sb_2O_3-modified SLS glass samples, the series of EPR spectra were magnified and shown in

326   Figures 5 (a – d).

327   **Table 1: The parameters associated with deconvolution of radiation-induced defect centres of SLS glass:**
328   **Goodness of fit (R^2), characteristic peak energy (E), FWHM (ΔE), and area under the absorption band**
329   **(A) with the partial fraction of area under the band are in the parenthesis.**

Defect Type	Dose →	0.2 MGy	2.0 MGy	5.0 MGy	X-ray
	R^2	0.99948	0.99971	0.99959	0.99966
HC_2 + POR	E_1 (cm^{-1})	16050	16050	16050	16130
	ΔE_1 (cm^{-1})	3710	3790	3710	3870
	A_1 (eV×cm^{-1})	1.26 (6.1%)	1.64 (5.5%)	1.74 (4.7%)	1.11 (6.0%)
HC_1	E_2 (cm^{-1})	24030	23950	23950	23710
	ΔE_2 (cm^{-1})	10810	10650	10810	10160
	A_2 (eV×cm^{-1})	15.1 (72.6%)	19.7 (65.7%)	23.5 (63.1%)	11.2 (61.1%)
TE	E_3 (cm^{-1})	30810	31450	32660	32260
	ΔE_3 (cm^{-1})	4840	6130	7100	7260
	A_3 (eV×cm^{-1})	3.18 (15.2%)	6.40 (21.3%)	11.31 (30.4%)	5.98 (32.6%)
Unknown	E_4 (cm^{-1})	33150	34040	34040	32830
	ΔE_4 (cm^{-1})	2900	3870	2100	730
	A_4 (eV×cm^{-1})	1.28 (6.1%)	2.19 (7.3%)	0.70 (1.9%)	0.04 (0.2%)

330   Notably, the spectra for the γ-ray irradiated glasses confirm the presence of a second

331   type of EPR resonance, which has a very broad and diffuse EPR response across the range

332   250 – 435 mT, as shown in Figures 5 (a – c). The occurrence of these broad EPR responses

333   was verified from the integrated EPR absorption spectra of the series of γ-ray irradiated glass

334   samples, which have been shown in the supplementary information S – III (a – c). The peaks

335   of these broad EPR absorption bands of γ-ray induced Sb_2O_3-modified SLS glass were

336   observed at 260.6 mT (g ~ 2.63), 301.8 mT (g ~ 2.27), 326.6 mT (g ~ 2.10), 351.6 mT (g ~

337   1.95), 381.3 mT (g ~ 1.80), and 411.0 mT (g ~ 1.67), respectively. The peak position, shape

338   function, and relative intensity ratio of various hyperfine transitions of EPR absorption

339   spectra are consistent with the EPR spectrum of Sb^{4+} ions in a silicate glass host, as reported

340   by Schreurs and Davis [80]. The strongest relative EPR absorption intensity from these Sb^{4+}

341   ions was observed for the Sb0.5 sample, and it weakens progressively with further addition of

342   Sb_2O_3 to the glass. Figure 5 (d) also confirms the non-existence of Sb^{4+} ions in the X-ray

343   irradiated Sb_2O_3-modified SLS glass.

344   To analyse the sharp and intense EPR response in the range 330 – 355 mT, the second-

345   order derivatives of the EPR spectra were evaluated and shown in Figure 6 (a – e). The 'g-

346   values' of the defect sites were found from the local minima of the second-order derivatives

347   of EPR spectra. The ionizing radiation-induced SLS glass spectra reveal sharp and intense

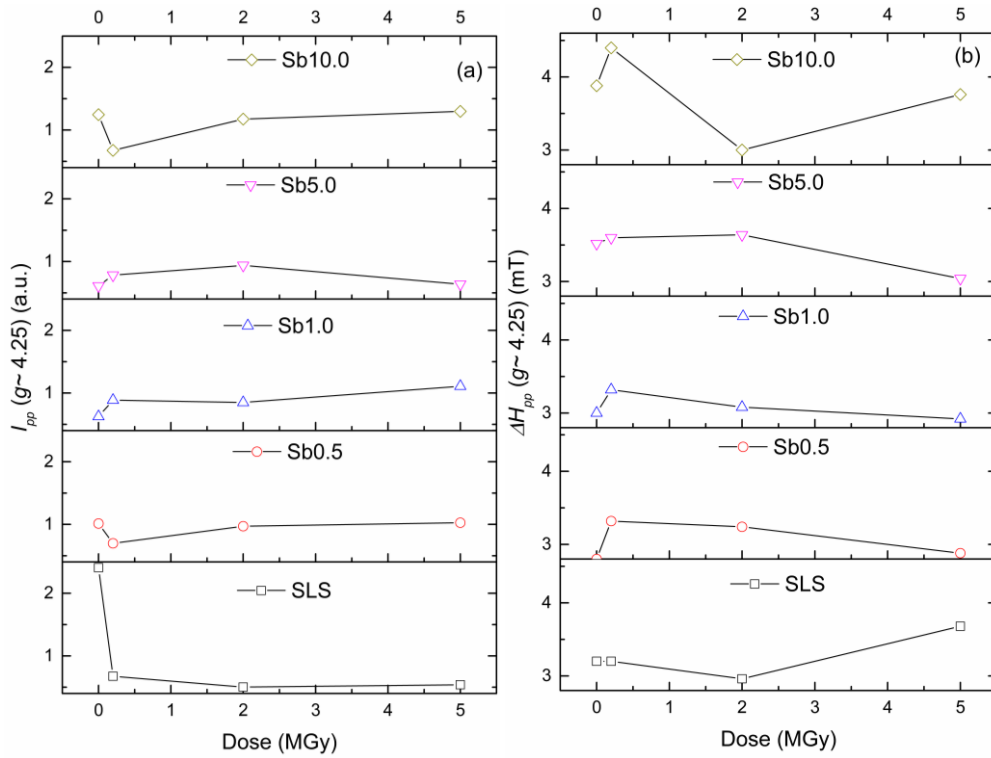**Figure 9:** EPR hyperfine signal (a) peak-to-peak intensity (I_{pp}) and (b) peak-to-peak line width (ΔH_{pp}) of ($g \sim 4.25$) signal at various doses of γ-ray irradiation.

348   bands in the EPR spectra, within the 330 – 355 mT range of the magnetic field. The addition

349   of Sb_2O_3 to the glass significantly reduces the intensity of the EPR response in the 330 – 355

350   mT range.

351 Figure 7 shows the fitted ^{121}Sb Mössbauer spectra for sample Sb10.0, irradiated with

352 0.2, 2.0, and 5.0 MGy of γ-rays. The spectra have two major components, which exhibit the

353 characteristics of Sb^{3+} (a broad asymmetric component) and Sb^{5+} (narrow symmetric

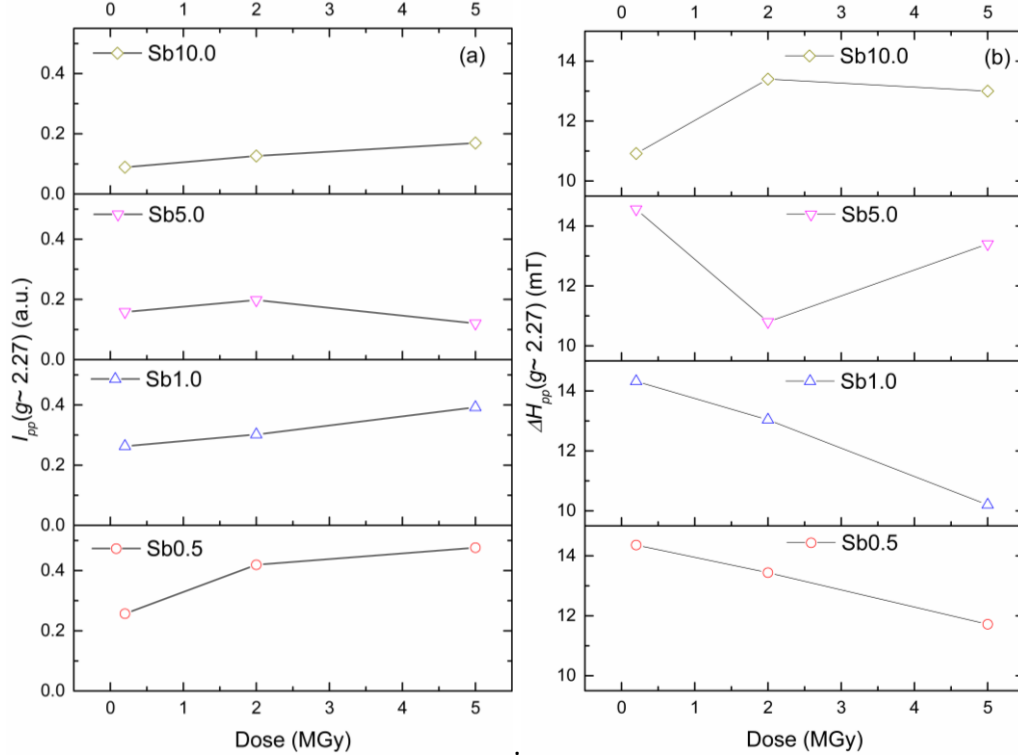354 component) ions [74]. No component representing Sb^{4+} could be reliably fitted, given its low

Figure 10: The hyperfine (a) peak-to-peak intensity (I_{pp}), (b) peak-to-peak linewidth (ΔH_{pp}) of $g \sim 2.27$ signal.

355 abundance, as indicated by EPR spectra.

356 **Table 2: EPR analysis of defects induced by γ-ray irradiation, signal peak position in mT, respective g-**
357 **factor and width of the respective signal in mT.**

Sample	Defect type	0.2 MGy			2.0 MGy			5.0 MGy		
		Peak (mT)	g	W (mT)	Peak (mT)	g	W (mT)	Peak (mT)	g	W (mT)
SLS	HC_2	342.28	2.0050	1.87	342.36	2.0036	1.80	342.36	2.0045	1.94
	HC_1	343.12	2.0001	0.28	343.28	1.9985	0.42	343.28	1.9992	0.70
	E'				343.72	1.9966	0.70	343.72	1.9966	0.70
	E	349.44	1.9639	4.15	349.44	1.9628	3.88	349.44	1.9639	3.88
Sb0.5	HC_2	342.40	2.0043	1.25	342.24	2.0043	1.25	342.24	2.0052	1.39
	HC_1	343.36	1.9987	1.52	343.12	1.9989	1.52	343.12	2.0001	1.52

Sb1.0	HC_2	342.40	2.0043	1.25	342.24	2.0045	1.38	342.24	2.0052	1.38
	HC_1	343.36	1.9987	1.52	343.12	1.9989	1.66	343.12	2.0001	1.66
Sb5.0	HC_1	-	-	-	343.36	1.9985		343.40	1.9987	
Sb10	HC_1	-	-	-	343.36	1.9985		343.40	1.9987	

Figure 8 (a – d) shows the radiation-induced optical absorption spectra, which reveal the superposition of absorption bands related to different defect centres. Spectra were deconvoluted into 4 Gaussian bands, which was the minimum needed for robust fitting. Fitting parameters such as characteristic energy (E_i), bandwidth (ΔE_i), with the area (A_i) and a respective partial fraction of the area under the absorption spectrum, are presented in Table 1. A partial fraction of the area under a certain Gaussian curve associated with a specific defect-centre is roughly representing the quantitative formation of a certain defect type, although full quantification is not possible without knowledge of the extinction coefficients associated with each individual defect type. This reveals the characteristic peak energies at about 16,000 cm^{-1} (~ 620 nm) and 24,000 cm^{-1} (~ 420 nm), which remained almost unaltered for different doses of γ-rays and X-rays. The subsequent band has a characteristic wavenumber of about 30,800 cm^{-1} (325 nm) for a 0.2 MGy dose. The peak characteristic energy shifted slightly to 31,400 cm^{-1} (318 nm) and 32,600 cm^{-1} (307 nm) for 2.0 and 5.0 MGy doses, respectively. The other Gaussian band had a characteristic energy of 33,000 – 34,000 cm^{-1}. Based on prior studies, the induced absorption band at ~16,000 cm^{-1} appears to be associated with non-bridging-oxygen hole centres (*NBOHC* or HC_2) along with peroxy-radicals (*POR*) [1,9,10,23,58]. The structure of HC_2-type defect centres could be explained as a dangling oxygen atom with an unpaired electron, (i.e., $HC_2 \rightarrow \equiv$Si—$\dot{\text{O}}$, where '$\equiv$' represents three bonds with other oxygens in the network and '·' depicted as the unpaired electron) [10,14,20].

Table 3: Refined ^{121}Sb Mössbauer parameters (293 K) of the Sb10.0 sample irradiated with a various dose of γ-ray: centre shift relative to InSb (δ), Lorentzian line width (Γ), quadrupole interaction (e^{2}Qq), Intensity (I).

γ-ray dose		0.0 MGy	0.2 MGy	2.0 MGy	5.0 MGy
Sb^{3+}	δ_1 (mm s^{-1})	-3.2	-3.8	-3.4	-3.5
	Γ_1 (mm s^{-1})	3.54	3.80	3.74	3.24
	e^2Qq (mm s^{-1})	18.9	18.8	19.9	20.5
	I_1 (%)	88	83	90	85
Sb^{5+}	δ_2 (mm s^{-1})	9.1	9.4	8.6	9.2
	Γ_2 (mm s^{-1})	3.56	3.82	3.74	3.22
	I_2 (%)	12	17	10	15

381

According to Zatsepin *et al.* [20], the optical absorption band centred at ~ 16,000 cm^{-1} for the *HC$_2$* formed because of the transition of an electron from the σ-orbital to a half-filled *p*-orbital between the atoms of nonbridging oxygen and silicon [20]. The peak at ~ 24,000 cm^{-1} confirms the occurrence of an *HC$_1$*-type defect centre [3,10,21,23]. The *HC$_1$*-type defect centre is created because of the dangling bond of $\equiv$Si— $\dot{O}$ and Na$^+$ ions (i.e. *HC$_1$* $\rightarrow$ $\equiv$Si— $\dot{O}$…Na$^+$, where '…' presents the dangling bond) [14,20]. The defects induced by the self-trapped electrons (i.e., *STE* $\rightarrow$ $\equiv$Si—$\dot{O}$—Si$\equiv$) have been attributed to the absorption band at 30,800 – 32,600 cm^{-1} [10,21,23]. Unlike the *NBOHC* and *HC$_1$* defect centres, the *STE*-type defect involves bridging oxygens (i.e., *BO*), each with an unpaired electron. However, the origin of the band fitted at 33,000 – 34,000 cm^{-1} is less clear. Polaron E^--type negative electron centres originate from the capture of an electron by a silicon atom (i.e., E^- $\rightarrow$ $\equiv$Si·), which has a UV absorption band of characteristic wavenumber of 41,000 – 44,000 cm^{-1} [1,10]. However, in the present study, the UV band-edge of the host (i.e., SLS) glass was found at about 35,000 cm^{-1}, which masked any deep UV-absorption bands that may have been attributable to E^--polarons. The absolute area under defect-induced absorption bands increased steadily with radiation dose. However, the relative partial area of *HC$_2$* and *HC$_1$*-type defect centres was reduced due to the increased formation of *STE*-type defect centres

399 with increasing γ-ray dose. This implies that increased γ-ray dose resulted in more *STE*-type

400 defects, relative to the HC_2 and HC_1 defect types.

401 Figures 9 (a) and (b) reveal the effects of γ-ray exposure on the $g \sim 4.28$ EPR signal,

402 associated with Fe^{3+} impurity ions, for the present series of glasses. Figure 9 (a) reveals the

403 peak-to-peak intensity of Fe^{3+} ions using $g \sim 4.28$ signal (i.e., I_{pp}) as a function of γ-ray dose.

404 The peak-to-peak linewidth of the $g \sim 4.28$ signal of Fe^{3+} ions (i.e., ΔH_{pp}) at various γ-ray

405 doses, is shown in Figure 9 (b).

406 Figures 10 (a) and (b) show the effects of γ-ray dose on the EPR signal from Sb^{4+} ions.

407 Figure 10 (a) portrays the hyperfine signal peak-to-peak intensity (I_{pp}) of the $g \sim 2.27$ signal

408 at various doses of γ-rays. The Sb0.5 sample spectrum reveals the maximum peak-to-peak

409 intensity (I_{pp}) for the $g \sim 2.27$ signal, which implies that the relative concentration of Sb^{4+}

410 ions may be highest in the Sb0.5 sample. Increasing Sb_2O_3 content in the glass steadily

411 reduced the intensity of the EPR signal linked with Sb^{4+} ions at various doses of γ-rays (see

412 also Figure 5).

413

414 **4. Discussion**

415 One factor affecting the optical band-edge in the pristine glasses is the broad spin-

416 forbidden absorption transition of Sb^{3+}: $^1S_0 \rightarrow {}^3P_1$ centred at $40,000 - 46,000 \, cm^{-1}$ [5,7,74].

417 Increasing additions of Sb_2O_3 to the glass network have continuously red-shifted the UV

418 band-edge, as explained and discussed in our previous paper [74]. The absorption of

419 increasing doses of γ-radiation causes narrowing of the forbidden band gap. Baccaro *et al.* [9]

420 also observed the forbidden band gap narrowing with increasing dose of γ-radiation in

421 multicomponent borosilicate radiation-hard glass containing cerium [9]. This phenomenon

was explained by the accumulation of density of defect states between the valence and conduction bands of the glass matrix [9].

The inclusion of Sb_2O_3 in the glass studied here masked the absorption bands of energy greater than approximately 27,000 cm^{-1}, because of the aforementioned significant redshift of the band-edge. Therefore, the EPR analysis of the present series of glass samples is paramount. The EPR response of radiation-induced SLS glasses reveals the defect-induced signals for the 330 – 355 mT range. The second-order derivative of the EPR response was employed to decipher peak positions and evaluate their width. An EPR peak at around $g \sim$ 2.03 may be associated with clustered Fe^{3+} ions, although as noted previously the very low concentrations (ppm) of Fe in the glass make this EPR resonance extremely weak [78]. The EPR peak obtained around $g \sim$ 2.004 is attributed to the *NBOHC* or *HC$_2$* [20]. The peak obtained around $g \sim$ 1.999 is assigned to the *HC$_1$*-type of defect-centre [20]. The peak obtained at $g = 1.9966$ was identified as an E'-type defect-centre [20,81]. According to prior reports, the E'-type defect has a UV absorption band peak around 44,500 cm^{-1}, which lies within the band-edge of the studied samples [21,23]. The relatively weak signal around $g \sim$ 1.964 is recognized as the E^--centre type of defect [20]. The E^--centre signifies the polaron, which consists of a Na^+ ion with an electron trapped near it [82]. The addition of Sb_2O_3 to the glasses significantly altered the shape functions and intensity of various defect-centres. Compared to the Sb-free glass, the 0.5 mol% of Sb_2O_3 addition significantly diminished the intensity of both *HC$_1$* and *HC$_2$* defect-centres. The trace of E' and E^- defect centres is non-obvious for the Sb0.5 sample. On the other hand, the EPR study confirmed the occurrence of Sb^{4+} ions. Further increase of Sb_2O_3-content of the glass steadily reduced the intensity of *HC$_1$* and *HC$_2$* defect-centres. Unlike Sb^{4+}-ions, the Sb^{3+} and Sb^{5+} ions have no unpaired electrons, therefore give no EPR signals. However, whilst Mössbauer spectroscopy confirmed they were both present in substantial quantities, no component for Sb^{4+} could be fitted to the

447   Mössbauer spectra, indicating the relative abundance of Sb^{4+} cations in all glasses to be very

448   low (also supported by the intensity of the EPR Sb^{4+} component compared with the Fe^{3+}

449   signal at $g \sim 4.28$, known to be due to ppm levels for Fe^{3+} and hence the corresponding Sb^{4+}

450   concentrations can also be assumed to be at ppm levels).

451   The peak-to-peak intensity of the Fe^{3+} EPR resonance at $g \sim 4.28$ is proportional to the

452   concentration of Fe^{3+} ion present in the network at such concentrations. Notably, compared to

453   the pristine glass, 0.2 MGy dose of γ-ray exposure caused a decrease of Fe^{3+} intensity for the

454   present series of samples. This implies that the Fe^{3+} ions in the glass network may initially act

455   as electron trapping centres to follow the $\mathbf{Fe^{3+} + \mathit{e}^- \rightarrow Fe^{2+}}$ redox reaction. The growth of

456   Fe^{2+}-ions over Fe^{3+} could be confirmed from the absorption spectra reported [79,83].

457   Supplementary information S-IV (a – e) revealed the absorption coefficient spectra extended

458   up to the infrared region with the Urbach's band tail to obtain the background compensated

459   absorption coefficient of trace elements (i.e., Fe^{3+} and Fe^{2+} ions) [84]. The background

460   compensated absorption coefficient spectra of Fe^{3+} and Fe^{2+} ions are depicted in

461   supplementary information S-V (a – c). Ades *et al.* [85] and Bingham *et al.* [83,84] have

462   linked various absorption bands of Fe^{3+} and Fe^{2+} ions for the soda-lime-silica network [85].

463   The major absorption transitions are designated as: A. Fe^{3+}: $^6\Gamma_1 (S) \rightarrow {}^4\Gamma_5 (D) \sim 26300$ cm^{-1},

464   B. Fe^{3+}: $^6\Gamma_1 (S) \rightarrow {}^4\Gamma_1 (G) \sim 24200$ cm^{-1}, and C. Fe^{2+}: $^5\Gamma_5 (D) \rightarrow {}^5\Gamma_3 (D) \sim 9400$ cm^{-1}. For the

465   present study, UV absorption bands of Fe^{3+} ions (i.e., Fe^{3+}: $^6\Gamma_1 (S) \rightarrow {}^4\Gamma_5 (D)$ and Fe^{3+}: $^6\Gamma_1$

466    $(S) \rightarrow {}^4\Gamma_1 (G)$) are identified for the pristine glass samples, which become masked by the γ-

467   ray induced defect-centres. But the absorption band of Fe^{2+}: $^5\Gamma_5 (D) \rightarrow {}^5\Gamma_3 (D)$ in the infrared

468   region is identified for the pristine and γ-ray exposed samples. Notably, 0.2 MGy dose of γ-

469   rays caused significant enhancement of the absorption coefficient of Fe^{2+}: $^5\Gamma_5 (D) \rightarrow {}^5\Gamma_3 (D)$

470   band for all the glass samples. This is consistent with the decrease of EPR peak-to-peak

471   intensity of the $g \sim 4.28$ resonance, which implies a decrease of Fe^{3+} ion concentration and

472   increase in Fe^{2+} concentration for 0.2 MGy dose. Figure S-V (a) reveals the decrease of the

473   absorption coefficient of Fe^{2+}: $^5\Gamma_5 (D) \rightarrow {}^5\Gamma_3 (D)$ band with the enhanced dose (i.e., 2.0 and

474   5.0 MGy) of γ-rays, which is consistent with the EPR peak-to-peak intensity of $g \sim 4.28$

475   signal. The absorption bandwidth of Fe^{2+} ions has reduced considerably with the γ-ray

476   exposure of the glass network. The evolution of the peak-to-peak intensity of $g \sim 4.28$ signal

477   of EPR for Sb0.5 and Sb1.0 sample for various doses of γ-rays has supported the background

478   compensated absorption coefficient of Fe^{2+} ion. For the Sb5.0 and Sb10.0 samples the

479   absorption band tail does not follow Urbach's equation, and the absorption contribution of

480   Fe^{2+} ions are reported in the supplementary information. The peak-to-peak linewidth (ΔH_{pp})

481   of the $g \sim 4.28$ signal results from the separation of three Kramer's doublet transitions d_{xx}, d_{yy},

482   and d_{zz}, which are not overlapping with each other [79]. The linewidth of $g \sim 4.28$ signal for

483   SLS glass has reduced for 0.2 MGy dose and increased for 5.0 MGy dose of radiation. For

484   Sb0.5 and Sb1.0 samples the linewidth of the $g \sim 4.28$ signal has not varied considerably at

485   various doses of γ-rays. For the Sb5.0 sample, the linewidth of $g \sim 4.28$ signal remains

486   roughly unaltered up to 2.0 MGy of γ-ray, then it reduced at 5.0 MGy dose.

487   In this study, the decay of the ^{60}Co nucleus, employed as the source of γ-rays, offers γ-

488   photons of 1.17 and 1.33 MeV [86], with γ-photons with energy more than 1.02 MeV being

489   necessary to trigger pair-production [87]. The pair-production process causes the creation of

490   an electron (e^-) and positron/hole (h^+) pair. The Sb^{3+}-ions in the SLS network operate as hole

491   (h^+) trapping centres in the network. The hole in the glass network follows the redox reaction

492     $\mathbf{Sb^{3+} + h^+ \rightarrow Sb^{4+}}$ [60]. As a result, the ^{60}Co nucleus related γ-rays interacting with Sb_2O_3-

493   modified SLS glass form the Sb^{4+}-ions. At the lowest concentrations of Sb_2O_3 in the glass,

494   there is large Sb-Sb ion-ion separation, which prevents the majority of Sb^{4+} ions from

495   interacting with nearby or adjacent Sb^{4+}/Sb^{3+}-ions. As a result, newly-formed Sb^{4+} ions

496   cannot readily transform to Sb^{3+} or Sb^{5+} ions. An increased amount of Sb in the SLS glass

497 network reduces the average Sb-Sb ion-ion separation: as demonstrated, for example, by prior

498 studies of Fe^{3+} in SLS type glass, exchange interactions become dominant at concentrations

499 greater than approximately 1 mol% [88,89,90]. Therefore, we can surmise that as the Sb_2O_3

500 content of the glasses studied here increases, the Sb^{4+} ions are increasingly likely to have

501 nearby Sb^{3+} ions to enable the redox exchange reactions, which effectively reduces the

502 number of Sb^{4+} ions in the network. This explains why the highest EPR intensity of Sb^{4+}-ions

503 was observed for the lowest Sb_2O_3 content (Sb0.5) sample.

504   Offering different results, to a degree, were the X-ray irradiated glasses. The lab-scale

505 XRF tube used for X-ray irradiations in the present study is a continuous source of X-rays,

506 with photons of energy up to 35 keV. This X-ray energy is well below 1.02 MeV and hence

507 inadequate for pair-production to generate electron (e^-) and positron/hole (h^+) pairs. Hence,

508 the lack of holes (h^+) from the X-ray irradiated samples prevented execution of the $\mathbf{Sb^{3+} + \mathit{h}^+}$

509 $\rightarrow \mathbf{Sb^{4+}}$ redox reaction. This explains why the EPR spectra of X-ray irradiated samples did

510 not reveal the formation of Sb^{4+} ions in the X-ray irradiated glass network (Figure 5).

511   The optical absorption spectra of Sb_2O_3-modified SLS glasses reveal the non-obvious

512 formation of radiation-induced colour centres at UV and visible wavelengths. This implies

513 that the addition of Sb_2O_3 to the SLS network reduced the possibility of HC_1 and HC_2 type of

514 defect centre formation. The Sb^{3+}-ions in the glass network play the role of hole-trapping

515 centres. The nearest Si-ion captures the electron (e^-) that gives rise to the E^--polaron in the

516 network. Now, the electrons captured in the E^--polaron must be absorbed by the Sb^{5+} ions to

517 recover Sb^{3+}. As a result, the EPR spectra have shown a steady decrease of response intensity

518 with Sb_2O_3-concentration in the glass network for various doses of γ-rays.

519

520 **5. Conclusions**

Laboratory simulant float glasses modified with Sb_2O_3 has been studied for their high-energy ionising radiation performance. The radiation-resistant performance of these glasses was confirmed by irradiating with multiple doses (0.2, 2.0, and 5.0 MGy) of γ-rays (^{60}Co nucleus decay) as well as with X-rays. The interaction of ionizing radiation with the undoped base glass (i.e., SLS) caused the formation of hole-centres (HC_1 and HC_2) and electron-centres (E' and E^-), which produce strong, dark visible colouration. The increase of Sb_2O_3 concentration steadily reduces the formation of radiation-induced defects. As a result, this continuously reduces the radiation-induced colouration effects of the float glass. EPR spectra confirm that Sb^{3+}-ions are acting as hole-trapping centres to interact with the holes originating from the pair-production of γ-rays through the redox reaction of $Sb^{3+} + h^+ \rightarrow Sb^{4+}$. However, the X-rays have lower energy than γ-rays, which prevents the creation of Sb^{4+}-ions. Notably, the Sb0.5 sample (0.5 mol% Sb_2O_3) shows the optimum EPR response for Sb^{4+}-ions, which can be explained by ion-ion separation. Moreover, the introduction of Sb^{3+}-ions in the network significantly reduced the ionizing radiation-induced defect-centres (e.g., HC_1, HC_2, E' and E^-) for the Sb0.5 sample. This significant reduction of ionizing radiation-induced colour centres has greatly improved the transparency of Sb_2O_3-modified float glass. The Sb^{3+} ions in the float glass network are working as hole-trapping centres, which confirms their radiation-resistant behaviour. Study of radiation resistance of float glass doped with lower concentrations of Sb_2O_3 (i.e., lower than 0.5 mol%) is currently underway. This will enable optimal concentrations of Sb_2O_3 to provide the greatest radiation resistance for the minimum Sb additions to be identified. In short, this study confirms the addition of Sb_2O_3 in the low-cost float-type soda-lime-silica glass proves beneficial in enabling the radiation-resistance behaviour that retains its transparency under an ionizing radiation environment. Therefore, Sb_2O_3-modified float glass is a more radiation-resistant type of float

glass that could potentially be applied in nuclear industries, consumer electronics, and other

extreme environments.

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