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BELL, Anthony M. T. and HENDERSON, C. Michael B.

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Rietveld refinements of the crystal structures of $\text{Rb}_2\text{XSi}_5\text{O}_{12}$ ($X = \text{Mn}, \text{Ni}$)

A.M.T.Bell¹ (Anthony.Bell@shu.ac.uk) and C.M.B.Henderson².

1. MERI, Sheffield Hallam University, Sheffield, S1 1WB. 2. SEAES, University of Manchester, Manchester, M13 9PL.

Introduction

Synthetic anhydrous analogues of the silicate framework minerals leucite (KAlSi_2O_6) and pollucite ($\text{CsAlSi}_2\text{O}_6$) can be prepared with the general formulae $\text{A}_2\text{BSi}_5\text{O}_{12}$ and ACSi_2O_6 , where A is a monovalent alkali metal cation, B is a divalent cation and C is a trivalent cation. These structures all have the same topology with B and C cations partially substituting into a tetrahedrally coordinated silicate framework and charge balancing A cations sitting in extra-framework channels. The A cations can be replaced by ion exchange and these materials are of potential technological interest as storage media for radioactive Cs from nuclear waste [1]. We have used X-ray and neutron powder diffraction to determine and Rietveld [2] refine the crystal structures of many different leucite analogues [3-10]. In this poster we report the Rietveld refinements of the crystal structures of two more leucite analogues, $\text{Rb}_2\text{XSi}_5\text{O}_{12}$ where $X = \text{Mn}$ or Ni [11].

Synthesis

The samples were made from stoichiometric mixtures of Rb_2CO_3 , SiO_2 and MnO ($X = \text{Mn}$) or NiO ($X = \text{Ni}$). These mixtures were ground together and heated overnight at 873 K to decompose the carbonates, then melted in platinum crucibles at 1673 K for 2 hours ($X = \text{Mn}$) or 1573 K for 1.5 hours ($X = \text{Ni}$) before quenching to form glasses. The glasses were dry crystallized at ambient pressure and 1193 K for 12 days.

Data collection and analysis

Ambient temperature X-ray powder diffraction data were collected on these samples with a PANalytical X'Pert Pro MPD using $\text{Cu K}\alpha$ X-rays and an X'Celerator area detector. Analyses of the powder diffraction data showed that both samples were single-phase and isostructural with the *Pbca* structure of $\text{Cs}_2\text{CdSi}_5\text{O}_{12}$ [6]. Rietveld refinements were done using FULLPROF [12], the *Pbca* crystal structures of $\text{Cs}_2\text{MnSi}_5\text{O}_{12}$ [7] and $\text{Cs}_2\text{NiSi}_5\text{O}_{12}$ [7] were used as starting models with Rb replacing Cs as the extra-framework cations. Figures 1 and 2 show the Rietveld difference plots for these structures.

Discussion

Complete tetrahedral site (T-site) cation order was present in the refined crystal structures for $X = \text{Ni}$ and Mn , X and Si were ordered onto separate T-sites with extra-framework Rb cations. However, for $X = \text{Ni}$ (Figure 3), the Ni site isotropic temperature factor was larger than expected [$B_{\text{iso}} = 7.5(9)\text{\AA}^2$]. The mean Ni—O bond length for the NiO_4 tetrahedron is $1.90(2)\text{\AA}$, shorter than that seen in tetrahedrally coordinated NiO_4 units [13-14]. The mean Si—O bond length for the SiO_4 tetrahedra is $1.643(18)\text{\AA}$, longer than seen in tetrahedrally coordinated silicate frameworks [15]. This would suggest that there may be some Si/Ni T-site disorder in the $\text{Rb}_2\text{NiSi}_5\text{O}_{12}$ structure. A higher resolution synchrotron/neutron study may be needed to determine if this structure really has T-site disorder.

For $X = \text{Mn}$ (Figure 4) the mean Mn—O bond length for the MnO_4 tetrahedron is $2.02(1)\text{\AA}$, this distance is in agreement with that seen in tetrahedrally coordinated MnO_4 units [7]. This would suggest that the refined crystal structure for $\text{Rb}_2\text{MnSi}_5\text{O}_{12}$ has complete T-site cation order.

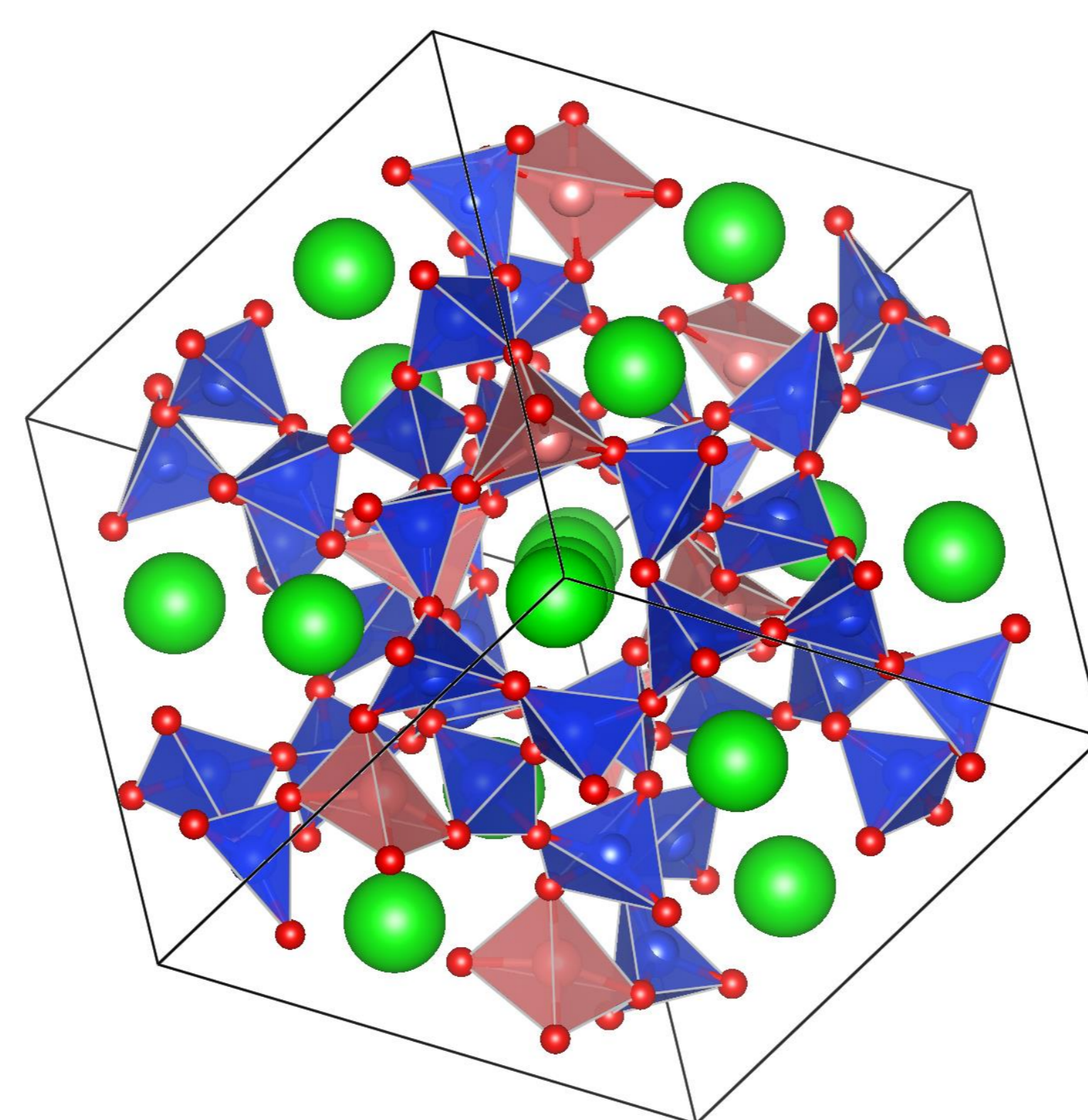


Figure 3
crystal structure for $\text{Rb}_2\text{NiSi}_5\text{O}_{12}$

Inclusion of the larger Mn cation in the silicate framework, compared to Ni, causes the central channel of the framework to be slightly more distorted for $\text{Rb}_2\text{MnSi}_5\text{O}_{12}$ (Figure 4) compared to $\text{Rb}_2\text{NiSi}_5\text{O}_{12}$ (Figure 3).

Crystal structures were plotted with VESTA [16].

Rb cations - green
 SiO_4 units - blue
 NiO_4 units - pink
 MnO_4 units - purple
 O anions - red

Conclusions

Two new crystal structures for have been refined for the synthetic leucite analogues $\text{Rb}_2\text{XSi}_5\text{O}_{12}$ where $X = \text{Mn}$ or Ni . These refined structures have complete T-site cation ordering and are isostructural with the *Pbca* structure of $\text{Cs}_2\text{CdSi}_5\text{O}_{12}$.

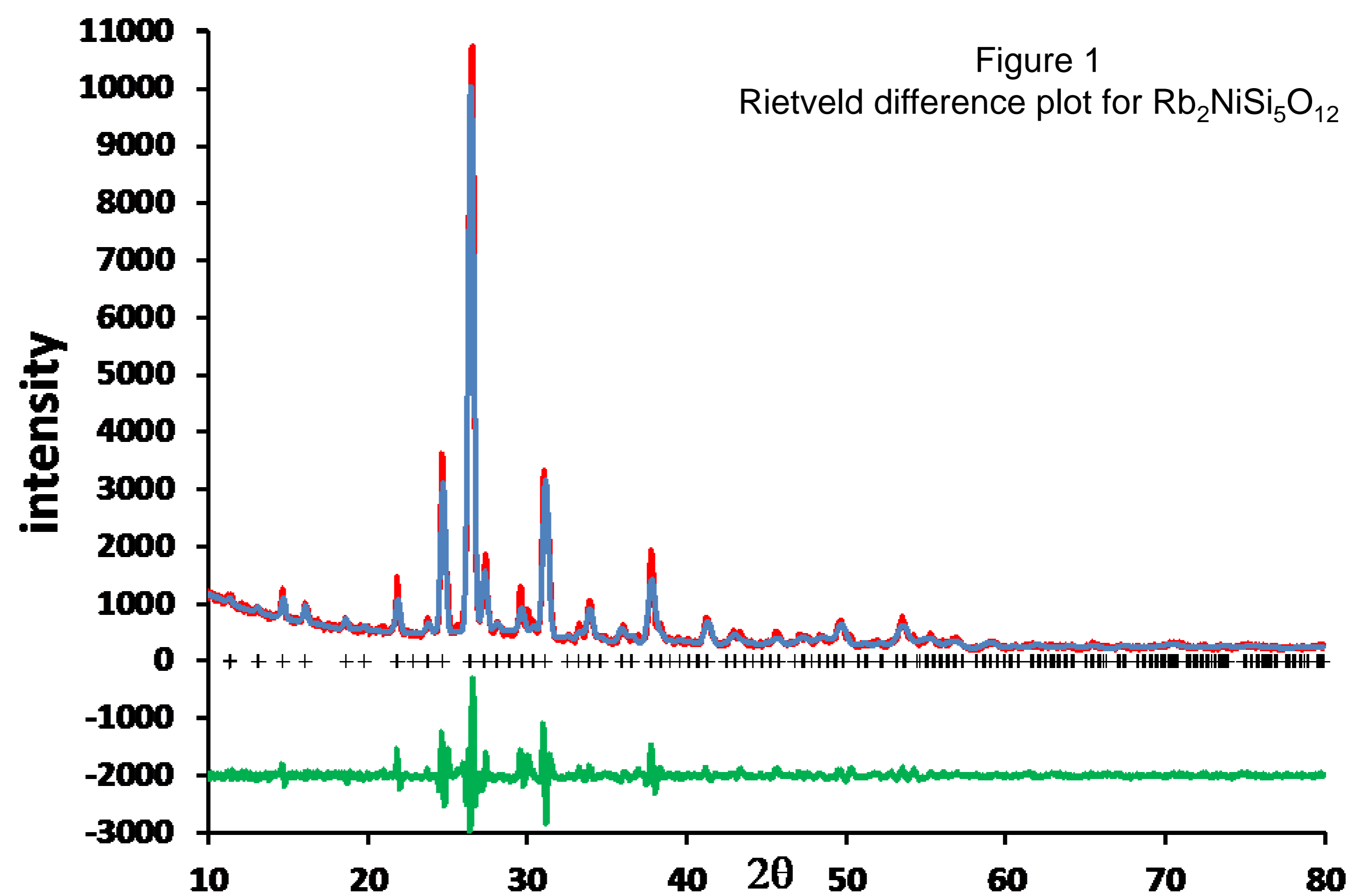


Figure 1
Rietveld difference plot for $\text{Rb}_2\text{NiSi}_5\text{O}_{12}$

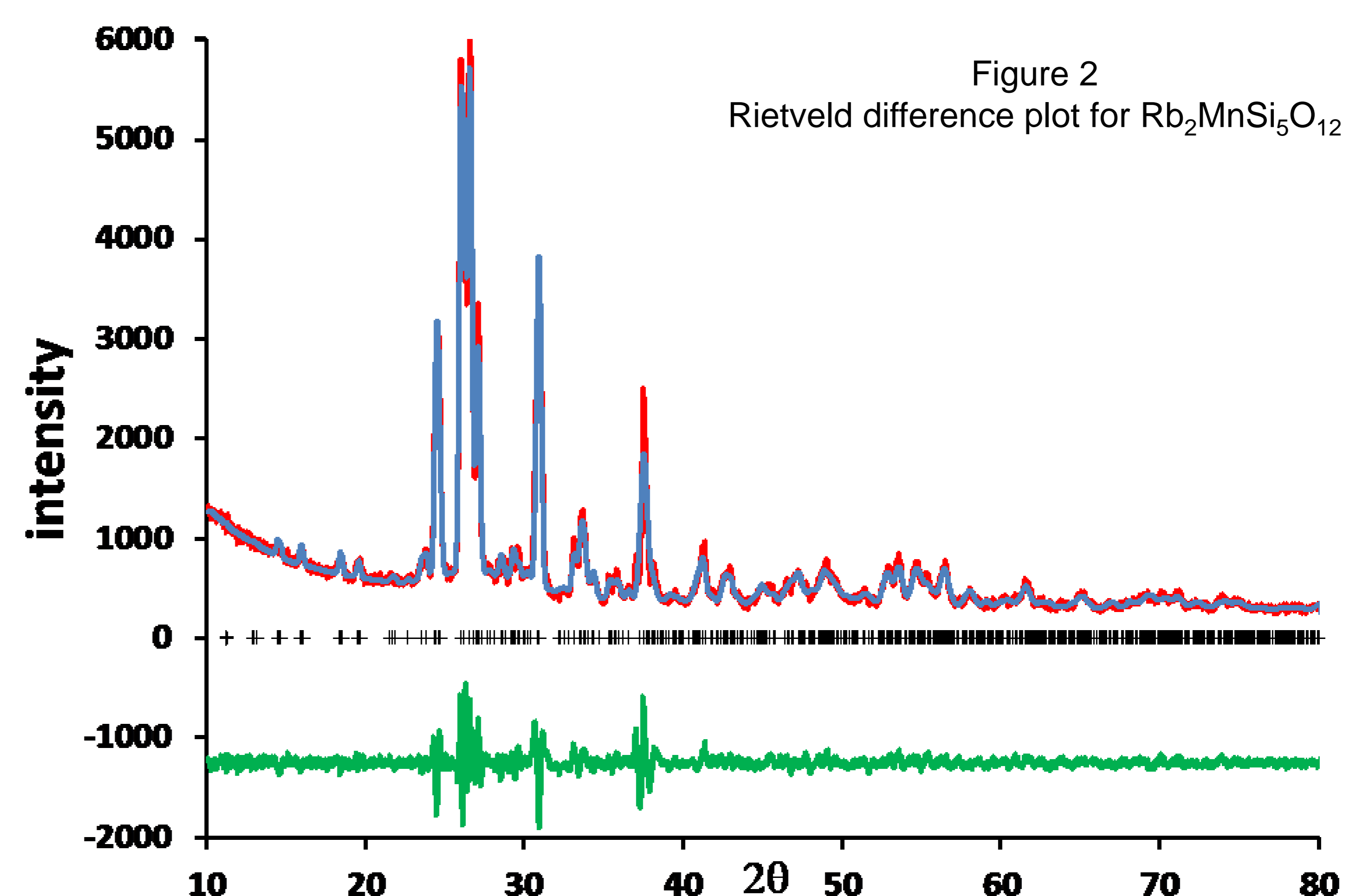


Figure 2
Rietveld difference plot for $\text{Rb}_2\text{MnSi}_5\text{O}_{12}$

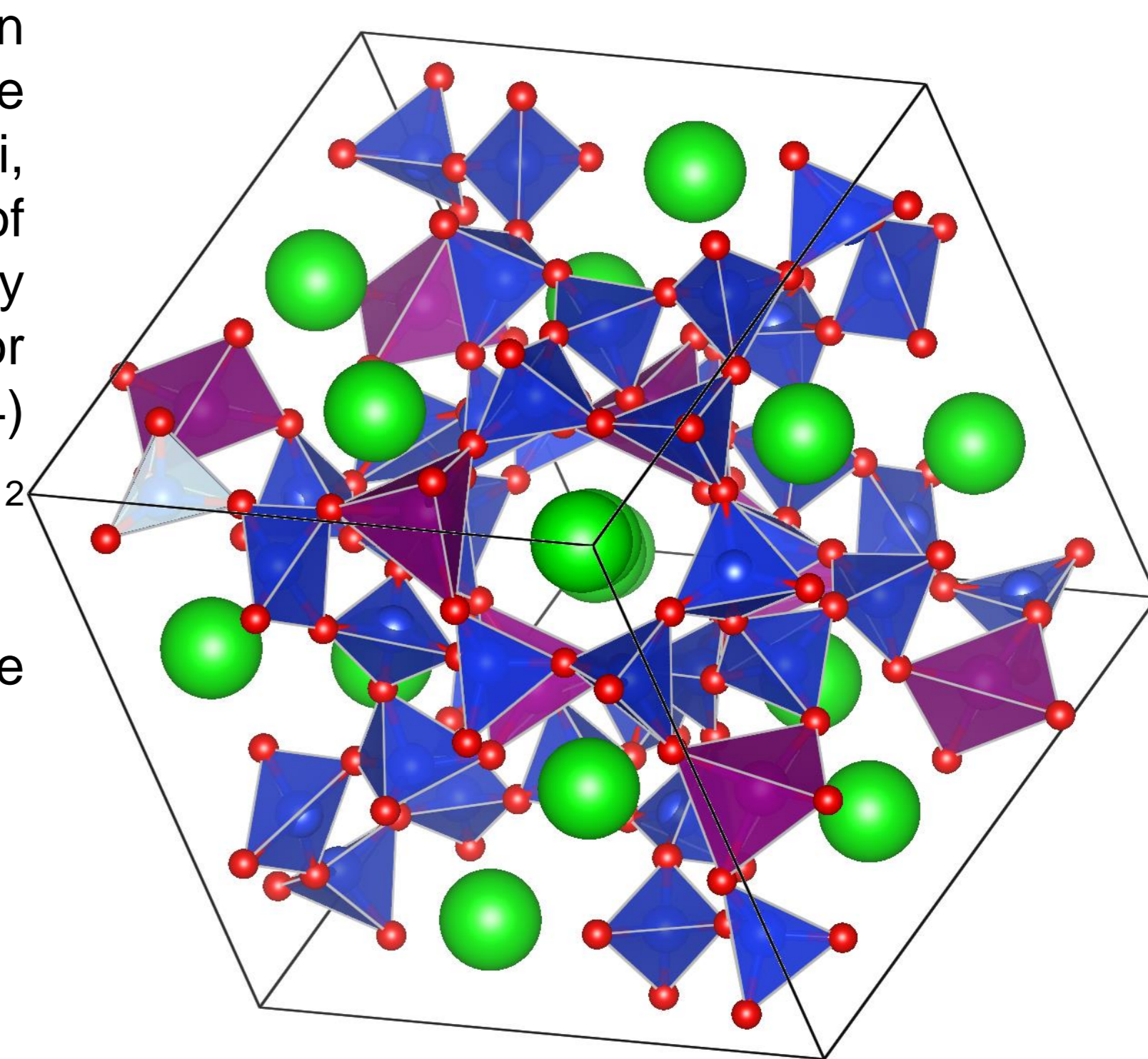


Figure 4
crystal structure for $\text{Rb}_2\text{MnSi}_5\text{O}_{12}$