

# Rietveld refinements of the crystal structures of Rb<sub>2</sub>XSi<sub>5</sub>O<sub>12</sub> (X = Mn, Ni)

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### Introduction

Synthetic anhydrous analogues of the silicate framework minerals leucite (KAISi<sub>2</sub>O<sub>6</sub>) and pollucite (CsAISi<sub>2</sub>O<sub>6</sub>) can be prepared with the general formulae  $A_2BSi_5O_{12}$  and ACSi<sub>2</sub>O<sub>6</sub>, 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,  $Rb_2XSi_5O_{12}$  where X =Mn or Ni [11].

11000 -10000 -9000 -8000 -7000 -6000 -

Figure 1 Rietveld difference plot for Rb<sub>2</sub>NiSi<sub>5</sub>O<sub>12</sub> brought to you by

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# **Synthesis**

The samples were made from stoichiometric mixtures of  $Rb_2CO_3$ ,  $SiO_2$  and MnO(X = Mn) or NiO (X = 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 = Mn) or 1573 K for 1.5 hours (X = 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 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 Cs<sub>2</sub>CdSi<sub>5</sub>O<sub>12</sub> [6]. Rietveld refinements were done using FULLPROF [12], the *Pbca* crystal structures of Cs<sub>2</sub>MnSi<sub>5</sub>O<sub>12</sub> [7] and Cs<sub>2</sub>NiSi<sub>5</sub>O<sub>12</sub> [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 = Ni and Mn, X and Si were ordered onto separate T-sites with extra-framework Rb cations. However, for X = Ni (Figure 3), the Ni site isotropic temperature factor was larger than expected  $[B_{iso} = 7.5(9)A^2]$ . The mean Ni—O bond length for the NiO<sub>4</sub> tetrahedron is 1.90(2)Å, shorter than that seen in tetrahedrally coordinated NiO<sub>4</sub> units [13-14]. The mean Si—O bond length for the SiO₄ tetrahedra is 1.643(18)Å, longer than seen in tetrahedrally coordinated silicate frameworks [15]. This would suggest that there may be some Si/Ni T-site disorder in the  $Rb_2NiSi_5O_{12}$  structure. A higher resolution synchrotron/neutron study may be needed to determine if this structure really has T-site disorder. For X = Mn (Figure 4) the mean Mn—O bond length for the MnO<sub>4</sub> tetrahedron is 2.02(1)Å, this distance is in agreement with that seen in tetrahedrally coordinated  $MnO_4$  units [7]. This would suggest that the refined crystal structure for Rb<sub>2</sub>MnSi<sub>5</sub>O<sub>12</sub> has complete T-site cation order.



Inclusion of the larger Mn cation the silicate in framework, compared to Ni, causes the central channel of the framework to be slightly distorted for more  $Rb_2MnSi_5O_{12}$ (Figure 4) Rb<sub>2</sub>NiSi<sub>5</sub>O<sub>12</sub> compared to (Figure 3).

Crystal structures were plotted with VESTA [16].

Rb cations - green SiO<sub>4</sub> units - blue NiO<sub>4</sub> units - pink MnO<sub>4</sub> units - purple





O anions - red

## Conclusions



Two new crystal structures for have been refined for the synthetic leucite analogues  $Rb_2XSi_5O_{12}$  where X = Mn or Ni. These refined structures have complete T-site cation ordering and are isostructural with the *Pbca* structure of  $Cs_2CdSi_5O_{12}$ .

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