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

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**Introduction**

Synthetic anhydrous analogues of the silicate framework minerals leucite (KAI(Si$_3$O$_9$) and pollucite (CsAl(Si$_3$O$_9$) can be prepared with the general formulae A$_2$BSi$_5$O$_{12}$ and ACSi$_5$O$_{12}$, 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 occupied Si site. Isostructural cloud balancing 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$_2$XSi$_5$O$_{12}$ where X = Mn or Ni [11].

**Synthesis**

The samples were made from stoichiometric mixtures of Rb$_2$CO$_3$, 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 crystalized 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 Kα 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$_2$CdSi$_5$O$_{12}$ [6]. Rietveld refinements were done using FULLPROF [12], the Pbca crystal structures of Cs$_2$MnSi$_5$O$_{12}$ [7] and Cs$_2$NiSi$_5$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 = 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)Å$^2$]. The mean Ni-O bond length for the NiO$_4$ tetrahedron is 1.90(2)Å, shorter than that seen in tetrahedrally coordinated NiO$_4$ units [13-14]. The mean Si-O bond length for the SiO$_4$ tetrahedron 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$_2$MnSi$_5$O$_{12}$ 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$_4$ 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$_2$MnSi$_5$O$_{12}$ has complete T-site cation order.

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 Rb$_2$MnSi$_5$O$_{12}$ (Figure 4) compared to Rb$_2$NiSi$_5$O$_{12}$ (Figure 3).

Crystal structures were plotted with VESTA [16].

**Conclusions**

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

**References:**