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A study of possible extra-framework cation ordering in *Pbca* leucite structures with stoichiometry $\text{RbCsX}^{2+}\text{Si}_5\text{O}_{12}$ ($X = \text{Mg, Ni, Cd}$).

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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 $A_2BSi_5O_{12}$ 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 onto tetrahedrally coordinated sites (T-sites) in the 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].

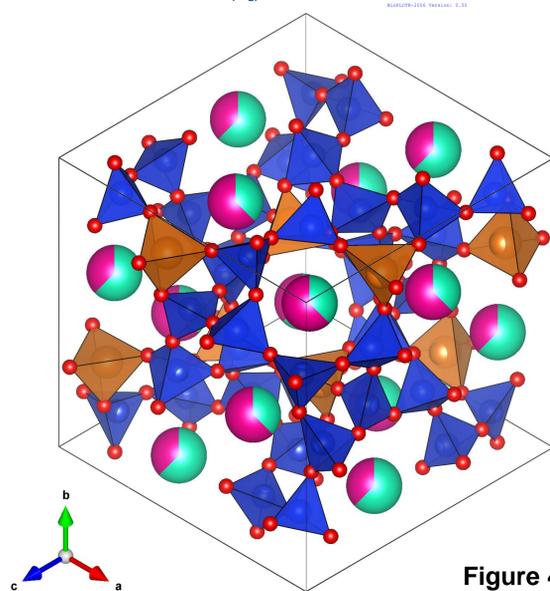
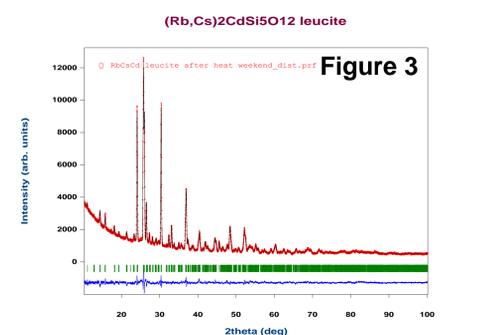
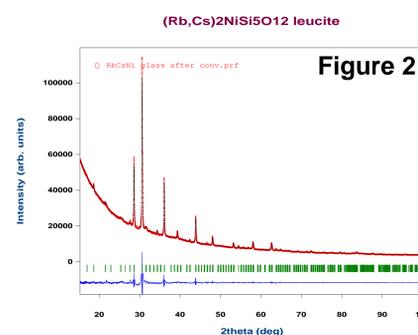
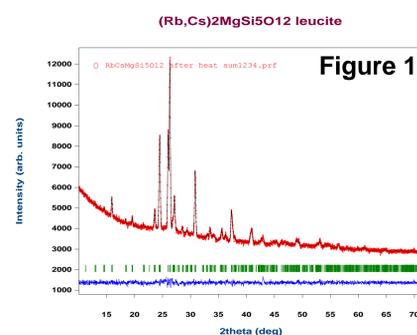
We have used X-ray and neutron powder diffraction to determine and Rietveld [2] refine the *Pbca* crystal structures of leucite analogues [3-7] with the general formulae $A_2BSi_5O_{12}$, ($A = \text{Rb, Cs}; B = \text{Mg, Mn, Co, Ni, Cu, Zn, Cd}$). These structures all have ordered T-site cations and also have A cation sites fully occupied with either Rb or Cs. In this poster we report the Rietveld refinements of the *Pbca* crystal structures of three more cation ordered leucite analogues with **both Rb and Cs** on the A cation sites, these have the stoichiometry of $\text{RbCsX}^{2+}\text{Si}_5\text{O}_{12}$ ($X = \text{Mg, Ni, Cd}$). The *Pbca* structure has **two different sites** for A cations, this study is to discover whether these sites have Rb and Cs cation order?

Synthesis

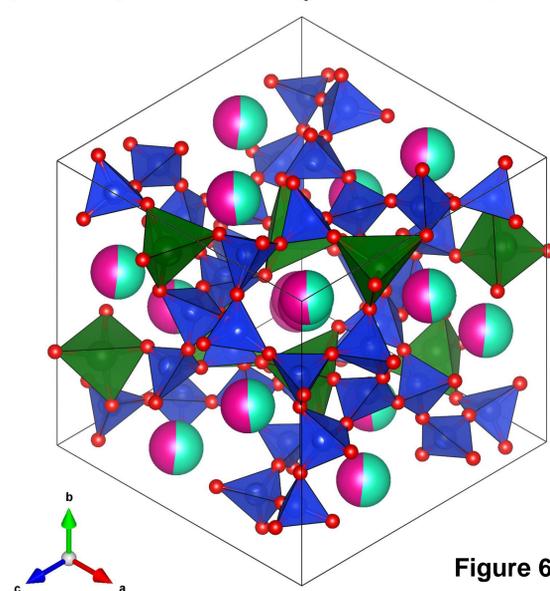
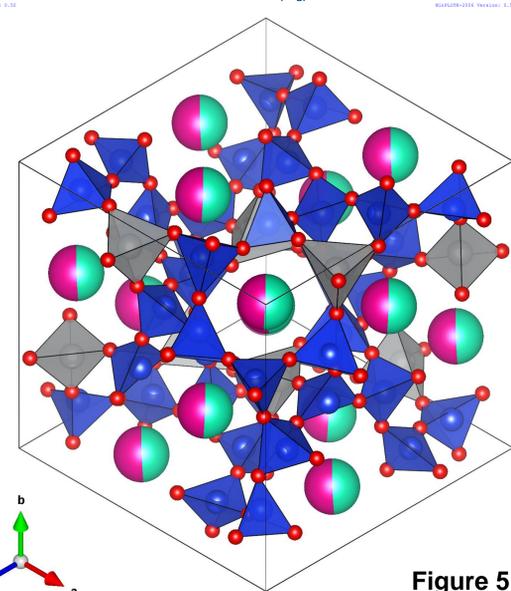
$\text{Rb}_2\text{X}^{2+}\text{Si}_5\text{O}_{12}$ and $\text{Cs}_2\text{X}^{2+}\text{Si}_5\text{O}_{12}$ were prepared from appropriate stoichiometric mixtures of Rb_2CO_3 , Cs_2CO_3 , SiO_2 , and XO ($X = \text{Mg, Ni, Cd}$) [3-5, 7] and then 50:50 mixtures of the Rb and Cs samples were made. For $X = \text{Ni}$ the starting materials were both glasses, the mixture was sealed in a gold capsule and heated in a furnace at 1173 K for a week. For $X = \text{Cd}$ and Mg the starting materials were both crystalline, the mixtures were sealed in a gold capsule ($X = \text{Cd}$) or a Pd-Ag alloy capsule ($X = \text{Mg}$) these were heated in a furnace at 1173 K for 6 hours.

Data collection and analysis

After heating the samples were removed from the metal capsules and mounted on low-background silicon wafers prior to ambient temperature X-ray powder diffraction. Data were collected for the $X = \text{Mg}$ and Cd samples on a PANalytical X'Pert Pro MPD using $\text{Cu K}\alpha$ X-rays and an X'Celerator area detector. For the $X = \text{Ni}$ sample data were collected on a PANalytical Empyrean diffractometer using $\text{Co K}\alpha$ X-rays with a PIXCEL-3D area detector. Analyses of the powder diffraction data showed that all samples were single-phase and isostructural with the *Pbca* structure of $\text{Cs}_2\text{CdSi}_5\text{O}_{12}$ [3]. Rietveld refinements were done using FULLPROF [8], using the structures of $\text{Rb}_2\text{XSi}_5\text{O}_{12}$ [4, 5 and 7] as starting models with both A cation sites occupied 50:50 with Rb and Cs. Figures 1 ($X = \text{Mg}$), 2 ($X = \text{Ni}$) and 3 ($X = \text{Cd}$) show the Rietveld difference plots for these structures. Table 1 shows the comparison of the refined lattice parameters and A cation site occupancies for $\text{RbCsX}^{2+}\text{Si}_5\text{O}_{12}$ compared to the published values for $\text{Rb}_2\text{XSi}_5\text{O}_{12}$ and $\text{Cs}_2\text{XSi}_5\text{O}_{12}$.



Figures 4 ($X = \text{Mg}$), 5 ($X = \text{Ni}$) and 6 ($X = \text{Cd}$) show VESTA [9] structure plots for $\text{RbCsX}^{2+}\text{Si}_5\text{O}_{12}$. SiO_4 tetrahedra are shown in blue with O^{2-} anions are shown in red. MgO_4 tetrahedra are shown in orange. NiO_4 tetrahedra are shown in grey. CdO_4 tetrahedra are shown in green. Light blue (Cs^+) and pink (Rb^+) shadings show the occupancies of the two A cation sites.



Discussion

Crystal structures have been refined for $\text{RbCsX}^{2+}\text{Si}_5\text{O}_{12}$ ($X = \text{Mg, Ni, Cd}$) leucite analogues from X-ray powder diffraction data. All are isostructural with their *Pbca* $\text{Rb}_2\text{XSi}_5\text{O}_{12}$ and $\text{Cs}_2\text{XSi}_5\text{O}_{12}$ analogues, with divalent X cations ordered onto separate T-sites than those occupied by Si. For $X = \text{Mg}$ and Ni the $\text{RbCsX}^{2+}\text{Si}_5\text{O}_{12}$ structures have unit cell volumes intermediate between that for the pure Rb and pure Cs analogues. However, for $X = \text{Cd}$ the $\text{RbCsX}^{2+}\text{Si}_5\text{O}_{12}$ structures has a unit cell volume much closer to that for the pure Cs analogue. For $X = \text{Mg}$ the $\text{RbCsX}^{2+}\text{Si}_5\text{O}_{12}$ structure has partial A site ordering of the alkali metal Cs^+ and Rb^+ cations. However, for $X = \text{Ni}$ and Cd the $\text{RbCsX}^{2+}\text{Si}_5\text{O}_{12}$ structures have complete A site disorder of the alkali metal Cs^+ and Rb^+ cations.

Table 1 - refined lattice parameters and A site occupancies

| A^+ cations | Rb | Rb Cs | Cs | Rb | Rb Cs | Cs | Rb | Rb Cs | Cs |
|-------------------|-----------|------------|------------|-----------|------------|------------|------------|------------|------------|
| X^{2+} cations | Mg | Mg | Mg | Ni | Ni | Ni | Cd | Cd | Cd |
| $a(\text{\AA})$ | 13.422(1) | 13.5676(9) | 13.6371(5) | 13.469(3) | 13.5399(5) | 13.6147(3) | 13.4121(1) | 13.6935(3) | 13.6714(1) |
| $b(\text{\AA})$ | 13.406(1) | 13.7115(1) | 13.6689(1) | 13.480(3) | 13.563(1) | 13.6568(5) | 13.6816(1) | 13.8031(3) | 13.8240(1) |
| $c(\text{\AA})$ | 13.730(1) | 13.5366(9) | 13.7280(5) | 13.442(2) | 13.560(1) | 13.6583(5) | 13.8558(1) | 13.8592(4) | 13.8939(1) |
| $V(\text{\AA}^3)$ | 2470.5(4) | 2518.2(3) | 2559.0(2) | 2440.6(8) | 2490.1(3) | 2539.5(1) | 2542.53(5) | 2619.6(1) | 2625.86(6) |
| A1 Rb occ. | 1 | 0.63(3) | 0 | 1 | 0.49(6) | 0 | 1 | 0.52(2) | 0 |
| A1 Cs occ. | 0 | 0.37(3) | 1 | 0 | 0.51(6) | 1 | 0 | 0.48(2) | 1 |
| A2 Rb occ. | 1 | 0.37(3) | 0 | 1 | 0.51(6) | 0 | 1 | 0.48(2) | 0 |
| A2 Cs occ. | 0 | 0.63(3) | 1 | 0 | 0.49(6) | 1 | 0 | 0.52(2) | 1 |

Conclusions

Crystal structures have been refined for $\text{RbCsX}^{2+}\text{Si}_5\text{O}_{12}$ ($X = \text{Mg, Ni, Cd}$) leucite analogues. These are isostructural with their *Pbca* $\text{Rb}_2\text{XSi}_5\text{O}_{12}$ and $\text{Cs}_2\text{XSi}_5\text{O}_{12}$ analogues. For $X = \text{Mg}$ there is partial ordering of the Rb and Cs cations over the alkali metal cation A sites. However, for $X = \text{Ni}$ and Cd these alkali metal cations are completely disordered.

References:- [1] Gatta, G. D. *et al.* (2008). *Phys. Chem. Miner.* 35, 521–533. [2] Rietveld, H. M. (1969). *J. Appl. Cryst.* 2, 65–71. [3] Bell, A. M. T. *et al.* (1994). *Acta Cryst.* B50, 560–566. [4] Bell, A. M. T. & Henderson, C. M. B. (1996). *Acta Cryst.* C52, 2132–2139. [5] Bell, A. M. T. & Henderson, C. M. B. (2009). *Acta Cryst.* B65, 435–444. [6] Bell, A. M. T. *et al.* (2010). *Acta Cryst.* B66, 51–59. [7] Bell, A. M. T. & Henderson, C. M. B. (2016). *Acta Cryst.* E72, 249–252. [8] Rodríguez-Carvajal, J. (1993). *Phys. B: Condens. Matter*, 192, 55–69. [9] Momma, K. & Izumi, F. (2008). *J. Appl. Cryst.* 41, 653–658.