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Published version

BELL, Anthony Martin Thomas (2021). Rietveld refinement of the low temperature crystal structures of Cs2XSi5O12 (X = Cu, Cd and Zn). European Journal of Chemistry, 12 (1), 60-63.

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Rietveld refinement of the low temperature crystal structures of Cs₂XSi₅O₁₂ (X = Cu, Cd and Zn)

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ABSTRACT

The synthetic leucite silicate framework mineral analogues Cs₂XSi₅O₁₂ (X = Cu, Cd, Zn) were prepared by high-temperature solid-state synthesis. The results of Rietveld refinement, using 18 keV synchrotron X-ray powder diffraction data collected at low temperatures (8K X = Cu, Zn; 10K X = Cd) show that the title compounds crystallize in the space group Pbca and are isostructural with the ambient temperature structures of these analogues. The structures consist of tetrahedrally coordinated SiO₄ and XO₄ sharing corners to form a partially substituted silicate framework. Extraframework Cs cations sit in channels in the framework. All atoms occupy the 8c general position for this space group. In these refined structures, silicon and X atoms are ordered onto separate tetrahedrally coordinated sites (T-sites).

KEYWORDS

Cesium
Rietveld refinement
Solid-state structures
Synchrotron radiation
X-ray powder diffraction
Silicate framework structure

1. Introduction

Anhydrous synthetic analogues of the silicate framework minerals leucite KAlSi₄O₁₂ [1] and pollucite CsAlSi₄O₁₂ [2] can be prepared with the general formulae ABSiO₄ and A-CsSi₅O₁₂. A is an alkali metal cation (K, Rb, Cs), B is a trivalent cation (Al, B, Fe³⁺, Ga) and C is a divalent cation (Be, Mg, Mn, Fe²⁺, Co, Ni, Cu, Zn, Cd). These structures consist of a tetrahedrally coordinated silicate framework structure with B or C cations partially substituting for Si on the tetrahedrally coordinated silicon sites (T-sites). A cation sits in the extraframework channels, these extraframework cations can be removed by ion exchange which makes them of technological interest as possible storage media for radioactive Cs from nuclear waste [3].

Leucite analogues with high symmetry structures such as I₄/a tetragonal KagSiO₄ [4] and la-3d cubic Rb₂ZnSi₅O₁₂ [5] have B and C cations disordered with Si over the T-sites. However, lower symmetry leucite structures are known where cations disordered with Si over the T-sites. The Pbca monoclinic K₂MgSi₅O₁₂ [6] has 12 fully ordered T-sites, 10 of these are fully occupied by Si and 2 are fully occupied by Mg. Three more P2₁/c K₂XSi₅O₁₄ structures [7] are known which are isostructural with K₂MgSi₅O₁₂ and have fully ordered T-sites. The Pbca orthorhombic structure of Cs₂CdSi₅O₁₂ [8] has 6 fully ordered T-sites, 5 of these are fully occupied by Si and 1 is fully occupied by Cd. Five more structures with the general formula Cs₂XSi₅O₁₂ [9-11], four structures with the general formula Rb₂XSi₅O₁₂ [9,10,12], and three structures with the general formula RbCsXSi₅O₁₂ [13] are all isostructural with the fully T-site cation ordered structure of Cs₂CdSi₅O₁₂. However, NMR [14] and high-resolution synchrotron X-ray powder diffraction [10] studies on Cs₂ZnSi₅O₁₂ described a Pbca structure where Zn is partially disordered over 2 of the 6 T-sites. A high temperature X-ray powder diffraction study on K₂MgSi₅O₁₂ [15] showed a first-order phase transition from P2₁/c to Pbca.

A high temperature study from 295-1173 K [16] has also been done on these three Cs₂ZnSi₅O₁₂ (X = Cu, Cd, Zn) leucite analogues using lower resolution synchrotron X-ray powder diffraction. For X = Cd, the Pbca structure, with complete T-site cation ordering, is retained up to 1173 K. For X = Cu the Pbca structure is retained up to 1173 K, but there is a first-order transition to a less distorted structure with a larger unit-cell volume at ~333 K.

For X = Zn the ambient temperature crystal structure shows (unlike for the high-resolution synchrotron X-ray powder diffraction study) that the Pbca structure is also isostructural with Cs₂CdSi₅O₁₂ with complete T-site cation ordering.
Table 1. Crystal data and details of the structure refinement for all low temperature leucite analogues. Ambient temperature lattice parameters are given for comparison.

| Parameters | X = Cu | X = Cd | X = Zn |
|------------|--------|--------|--------|
| Chemical formula | Cs2Cu5Si3O12 | Cs2Cd5Si3O12 | Cs2Zn5Si3O12 |
| Formula weight | 661.78 | 710.64 | 663.61 |
| Temperature (K) | 8 | 10 | 8 |
| Crystal system | Orthorhombic | Orthorhombic | Orthorhombic |
| Space group | Pnca | Pnca | Pnca |
| a (Å) | 13.5623(14) | 13.6760(3) | 13.6356(7) |
| b (Å) | 13.5287(14) | 13.8800(4) | 13.6440(11) |
| c (Å) | 13.6061(14) | 13.8666(4) | 13.6365(10) |
| Volume (Å³) | 2696.57(5) | 2617.17(12) | 2536.16(9) |
| Z | 8 | 8 | 8 |
| μ (µm⁻¹) | 5.423 | 5.378 | 5.596 |
| Diffractometer | In-house design | In-house design | In-house design |
| Specimen mounting | Borosilicate glass capillary | Borosilicate glass capillary | Borosilicate glass capillary |
| Data collection mode | Transmission | Transmission | Transmission |
| Scan method | Step | Step | Step |
| q values (°) | 2θmin = 5.000 | 2θmin = 5.000 | 2θmin = 5.000 |
| 2θmax = 50.000 | 2θmax = 50.000 | 2θmax = 50.000 |
| R-factors | Rp = 4.575, Rwp = 5.968, Rexp = 1.470, RBragg = 13.734 | Rp = 4.937, Rwp = 6.611, Rexp = 1.308, RBragg = 17.515 | Rp = 4.226, Rwp = 5.311, Rexp = 1.371, RBragg = 16.500 |
| Goodness-of-fit | x² = 16.472 | x² = 25.541 | x² = 15.003 |
| No. of parameters | 74 | 73 | 73 |
| No. of restraints | 24 | 24 | 24 |

Figure 1. (a) The crystal structure of Cs2Cu5Si3O12 at 8 K. Turquoise spheres show Cs cations, blue polyhedra show SiO₄ units, green polyhedra show CuO₆ units and red spheres represent O atoms. (b) Rietveld difference plot for the single-phase refinement of Cs2Cu5Si3O12 from synchrotron X-ray powder diffraction data collected at 8 K. The red, blue and grey lines show respectively the observed, calculated and difference plots. Calculated Bragg reflection positions are indicated by green crosses.

However, the sample with X = Zn shows evidence for a transition to a previously unknown Pn-3 cubic structure, with some T-site cation disorder, at 566 K on heating. This transition is reversible on cooling to 633 K.

2. Experimental

2.1. Sample preparation

The samples were made from stoichiometric mixtures of Cs₂CO₃, SiO₂, and CuO (X = Cu) or CdO (X = Cd) or ZnO (X = Zn). For X = Cu sample a mixture was prepared by hydrothermal synthesis, the X = Cu and Zn samples were prepared by dry synthesis. The X = Cu [11], X = Cd [8] and X = Zn [9] sample mixtures were heated in platinum crucibles overnight at 873 K to decompose the carbonates. These mixtures were reground, returned to the crucibles and melted at 1473 K (X = Cu, Cd) or 1683 K (X = Zn) before quenching by dipping the bases of the crucible into water. The resultant X = Cu sample was sealed in a platinum capsule with 2% added water and heated in a cold-seal pressure vessel at 683 K, 500 bar pressure, for 6 days to produce a hydrothermally synthesised sample. The resultant X = Cd sample mixture was heated at ambient pressure in a platinum crucible at 1123 K for 5 days to produce a dry synthesised sample. The resultant X = Zn mixture was heated at ambient pressure in a platinum crucible at 1373 K for 4.5 days to produce another dry synthesised sample. Full synthetic details are given in [11, X = Cu; 8, X = Cd; 9, X = Zn].

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2.2. Synchrotron X-ray powder diffraction

Each sample was loaded into 0.3 mm diameter borosilicate glass capillaries and mounted on the liquid helium cryostat on the DORIS-III synchrotron B2 powder diffraction beamline [17]. Synchrotron X-Ray powder diffraction data, using 18keV energy X-rays, were collected at the lowest possible temperature for each sample (8 K, \( X = \text{Cu, Zn}; 10 K \ X = \text{Cd} \)) using the OBI image plate detector [18].

2.3. X-ray powder diffraction data analysis

All Bragg reflections in all low temperature powder diffraction patterns could be indexed in the space group \( P\bar{b}ca \) with similar but slightly smaller (due to thermal contraction) lattice parameters to the ambient temperature structures for \( \text{Cs}_2\text{XSi}_5\text{O}_{12} \ (X = \text{Cu} [11], \text{Zn} [10], \text{Cd} [9]) \). These ambient temperature structures, with complete T-site cation ordering, were used as starting models for Rietveld [19] refinements using FULLPROF [20]. In all three refinements the isotropic atomic displacement parameters were constrained to be the same for all framework sites occupied by the same element, each Si site had the same displacement parameter as did each O site, although the O site parameters were different to that for Si sites. In the refinements for \( X = \text{Cd} \) and \( \text{Zn} \) the O isotropic atomic displacement parameters could not be refined to positive values, so these parameters were kept fixed. Soft constraints were used for Si–O and \( X–O \) distances in all three refinements. For \( X = \text{Cu} \), the Si–O and Cu–O distances were constrained (±0.01 Å) to be those from the ambient temperature structure of \( \text{Cs}_2\text{CuSi}_5\text{O}_{12} [11] \). Similarly, for \( X = \text{Cd} \) the Si–O and Cd–O distances were constrained (±0.01 Å) to be those from the ambient temperature structure of \( \text{Cs}_2\text{CdSi}_5\text{O}_{12} [8] \). However, as the refined crystal structure for \( X = \text{Zn} \), from high resolution synchrotron X-ray powder diffraction data [10], did not have complete T-site cation ordering and the T–O distances from this structure were not used for soft constraints. A starting model for \( X = \text{Zn} \) with complete T-site cation ordering was used. The range of Si–O distances for silicates is 1.59–1.63 Å [21]. Therefore Si–O distances were constrained to be 1.61±0.01 Å. The Zn–O distances were constrained to be 1.93±0.01 Å as this was the soft constraint distance used at the start of the structural refinement for \( X = \text{Zn} [10] \).
3. Results and discussion

Low temperature Rietveld refinements on all three Cs₂XSiO₄ (X = Cu, Cd, Zn) leucite analogues showed that the structures were all similar to the fully T-site cation ordered ambient temperature structures, no low temperature phase transitions were observed in each sample. The only significant differences were smaller unit cell volumes due to thermal contraction. It should be noted that for X = Cd, the low temperature lattice parameter is larger than the corresponding ambient temperature parameter. Similarly, for X = Zn the low temperature b lattice parameter is larger than the corresponding ambient temperature parameter. However, for all three structures, the low temperature unit cell volumes were smaller than the corresponding ambient temperature volumes.

Table 1 shows the refined low temperature crystal structure parameters for each leucite analogue; the ambient temperature lattice parameters are also given for comparison. Figures 1a and 1b, respectively, show the VESTA [22] crystal structure plot and Rietveld difference plots for X = Cu. Similarly Figures 2a and 2b show the crystal structure plots and Rietveld difference plots for X = Cd, Figures 3a and 3b show the crystal structure plots and Rietveld difference plots for X = Zn. Table 1 and Figures 3a, 3b and 3c show that the R-factors and difference plots are larger for X = Cd than for X = Cu and Cd. This may be due to some preferred orientation in the X = Cd sample.

4. Conclusions

Low temperature synchrotron X-ray powder diffraction data collected on all three synthetic Cs₂XSiO₄ (X = Cu, Cd, Zn) leucite analogues show that in all cases the Pbcn cation ordered ambient temperature structures are retained. The only significant changes are due to thermal contraction. No low temperature phase transitions are observed. These are the first low temperature crystal structures determined for cation ordered leucite analogues.

Acknowledgements

The author wishes to thank Professor Michael Henderson of the University of Manchester for sample preparation. The author also wishes to thank Andreas Berghauser and Dr. Manuel Hinterstein for help with synchrotron X-ray powder diffraction data collection on the DORIS-III B2 powder diffraction beamline.

Supporting information

Further details of the crystal structure investigation(s) may be obtained from FIZ Karlsruhe, 76344 Eggenstein-Leopoldshafen, Germany, fax: (+49)7247-808-666; e-mail crysdata@fiz-karlsruhe.de, on quoting the deposition numbers CSD-2059131, -2059132, and -2059133.

Disclosure statement
Conflict of interests: The author declare that they have no conflict of interest.
Ethical approval: All ethical guidelines have been adhered.

Funding

No external funding was used for this work, this work was part of in-house research done when the author was employed on the DORIS-III synchrotron at the DESY Laboratory, Notkestrasse 85, 22607 Hamburg, Germany.

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