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# Rietveld refinement of the low temperature crystal structures of $\text{Cs}_2\text{XSi}_5\text{O}_{12}$ ( $X = \text{Cu}, \text{Cd}$ and $\text{Zn}$ )

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## RESEARCH ARTICLE



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## ABSTRACT

The synthetic leucite silicate framework mineral analogues  $\text{Cs}_2\text{XSi}_5\text{O}_{12}$  ( $X = \text{Cu}, \text{Cd}, \text{Zn}$ ) 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  $X = \text{Cu}, \text{Zn}$ ; 10K  $X = \text{Cd}$ ) 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  $\text{SiO}_4$  and  $\text{XO}_4$  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).

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## 1. Introduction

Anhydrous synthetic analogues of the silicate framework minerals leucite  $\text{KAlSi}_2\text{O}_6$  [1] and pollucite  $\text{CsAlSi}_2\text{O}_6$  [2] can be prepared with the general formulae  $\text{ABSi}_2\text{O}_6$  and  $\text{A}_2\text{CSi}_5\text{O}_{12}$ . *A* is an alkali metal cation (K, Rb, Cs), *B* is a trivalent cation (Al, B,  $\text{Fe}^{3+}$ , Ga) and *C* is a divalent cation (Be, Mg, Mn,  $\text{Fe}^{2+}$ , 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<sub>1</sub>/a* tetragonal  $\text{KGaSi}_2\text{O}_6$  [4] and *Ia-3d* cubic  $\text{Rb}_2\text{ZnSi}_5\text{O}_{12}$  [5] have *B* and *C* cations disordered with Si over the T-sites. However, lower symmetry leucite structures are known where *C* cations and Si are ordered onto separate T-sites. The *P2<sub>1</sub>/c* monoclinic  $\text{K}_2\text{MgSi}_5\text{O}_{12}$  [6] has 12 fully ordered T-sites, 10 of these are fully occupied by Si and 2 are fully occupied by Mg. Three more *P2<sub>1</sub>/c*  $\text{K}_2\text{XSi}_5\text{O}_{12}$  structures [7] are known which are isostructural with  $\text{K}_2\text{MgSi}_5\text{O}_{12}$  and have fully ordered T-sites. The *Pbca* orthorhombic structure of  $\text{Cs}_2\text{CdSi}_5\text{O}_{12}$  [8] has 6 fully

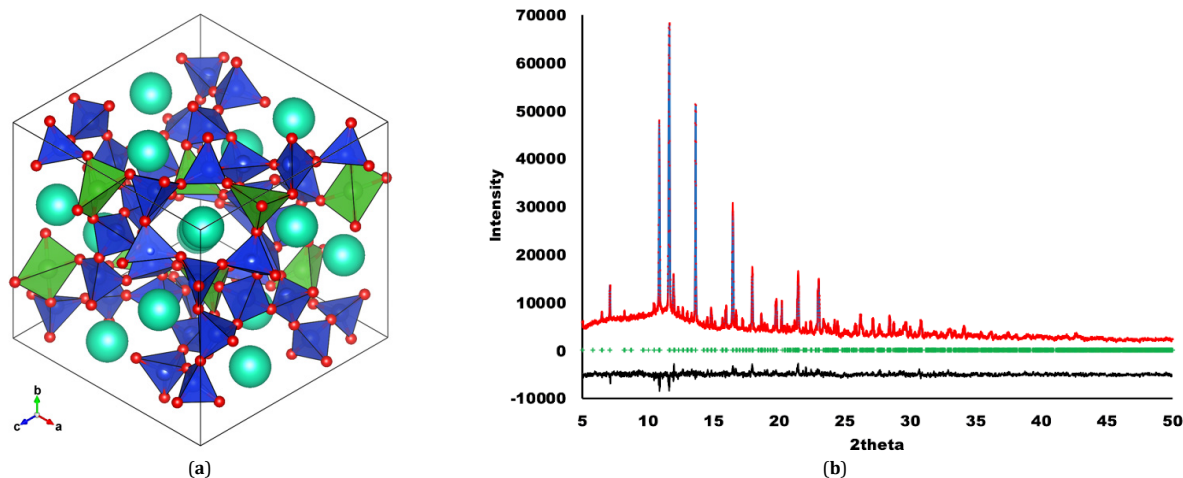
ordered T-sites, 5 of these are fully occupied by Si and 1 is fully occupied by Cd. Five more structures with the general formula  $\text{Cs}_2\text{XSi}_5\text{O}_{12}$  [9-11], four structures with the general formula  $\text{Rb}_2\text{XSi}_5\text{O}_{12}$  [9,10,12], and three structures with the general formula  $\text{RbCsXSi}_5\text{O}_{12}$  [13] are all isostructural with the fully T-site cation ordered structure of  $\text{Cs}_2\text{CdSi}_5\text{O}_{12}$ . However, NMR [14] and high-resolution synchrotron X-ray powder diffraction [10] studies on  $\text{Cs}_2\text{ZnSi}_5\text{O}_{12}$  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  $\text{K}_2\text{MgSi}_5\text{O}_{12}$  [15] showed a first-order phase transition from *P2<sub>1</sub>/c* to *Pbca*.

A high temperature study from 295-1173 K [16] has also been done on these three  $\text{Cs}_2\text{XSi}_5\text{O}_{12}$  ( $X = \text{Cu}, \text{Cd}, \text{Zn}$ ) leucite analogues using lower resolution synchrotron X-ray powder diffraction. For  $X = \text{Cd}$ , the *Pbca* structure, with complete T-site cation ordering, is retained up to 1173 K. For  $X = \text{Cu}$  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  $X = \text{Zn}$  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  $\text{Cs}_2\text{CdSi}_5\text{O}_{12}$  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	Cs <sub>2</sub> CuO <sub>12</sub> Si <sub>5</sub>	Cs <sub>2</sub> CdO <sub>12</sub> Si <sub>5</sub>	Cs <sub>2</sub> ZnO <sub>12</sub> Si <sub>5</sub>
Formula weight	661.78	710.64	663.61
Temperature (K)	8	10	8
Crystal system	Orthorhombic	Orthorhombic	Orthorhombic
Space group	<i>Pbca</i>	<i>Pbca</i>	<i>Pbca</i>
a, (Å)	13.56321(14)	13.6760(3)	13.6356(7)
b, (Å)	13.52837(14)	13.8008(4)	13.6440(11)
c, (Å)	13.60617(14)	13.8666(4)	13.6358(10)
Volume (Å <sup>3</sup> )	2496.57(5)	2617.17(12)	2536.9(3)
Z	8	8	8
ρ <sub>calc</sub> (g/cm <sup>3</sup> )	3.52124(7)	3.6070(2)	3.4757(5)
μ (mm <sup>-1</sup> )	54.23	53.78	55.96
Specimen shape, size (mm)	Cylinder, 10 × 0.3	Cylinder, 10 × 0.3	Cylinder, 10 × 0.3
Radiation	Synchrotron, λ = 0.687286 Å	Synchrotron, λ = 0.688000 Å	Synchrotron, λ = 0.688233 Å
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
2θ values (°)	2θ <sub>min</sub> = 5.000 2θ <sub>max</sub> = 50.000 2θ <sub>step</sub> = 0.004	2θ <sub>min</sub> = 5.000 2θ <sub>max</sub> = 50.000 2θ <sub>step</sub> = 0.004	2θ <sub>min</sub> = 5.000 2θ <sub>max</sub> = 50.000 2θ <sub>step</sub> = 0.004
R-factors	R <sub>p</sub> = 4.575, R <sub>w</sub> p = 5.968, R <sub>exp</sub> = 1.470, R <sub>Bragg</sub> = 13.734	R <sub>p</sub> = 4.937, R <sub>w</sub> p = 6.611, R <sub>exp</sub> = 1.308, R <sub>Bragg</sub> = 17.515	R <sub>p</sub> = 4.226, R <sub>w</sub> p = 5.311, R <sub>exp</sub> = 1.371, R <sub>Bragg</sub> = 16.500
Goodness-of-fit	χ <sup>2</sup> = 16.472	χ <sup>2</sup> = 25.541	χ <sup>2</sup> = 15.003
No. of parameters	74	73	73
No. of restraints	24	24	24
Ambient temperature			
Crystal system	Orthorhombic	Orthorhombic	Orthorhombic
Space group	<i>Pbca</i>	<i>Pbca</i>	<i>Pbca</i>
a, (Å)	13.58943(6)	13.6714(1)	13.6415(9)
b, (Å)	13.57355(5)	13.8240(1)	13.6233(8)
c, (Å)	13.62296(4)	13.8939(1)	13.6653(9)
Volume (Å <sup>3</sup> )	2512.847(13)	2625.83(6)	2539.6(3)

**Figure 1.** (a) The crystal structure of Cs<sub>2</sub>CuSi<sub>5</sub>O<sub>12</sub> at 8 K. Turquoise spheres show Cs cations, blue polyhedra show SiO<sub>4</sub> units, green polyhedra show CuO<sub>4</sub> units and red spheres represent O atoms. (b) Rietveld difference plot for the single-phase refinement of Cs<sub>2</sub>CuSi<sub>5</sub>O<sub>12</sub> 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.

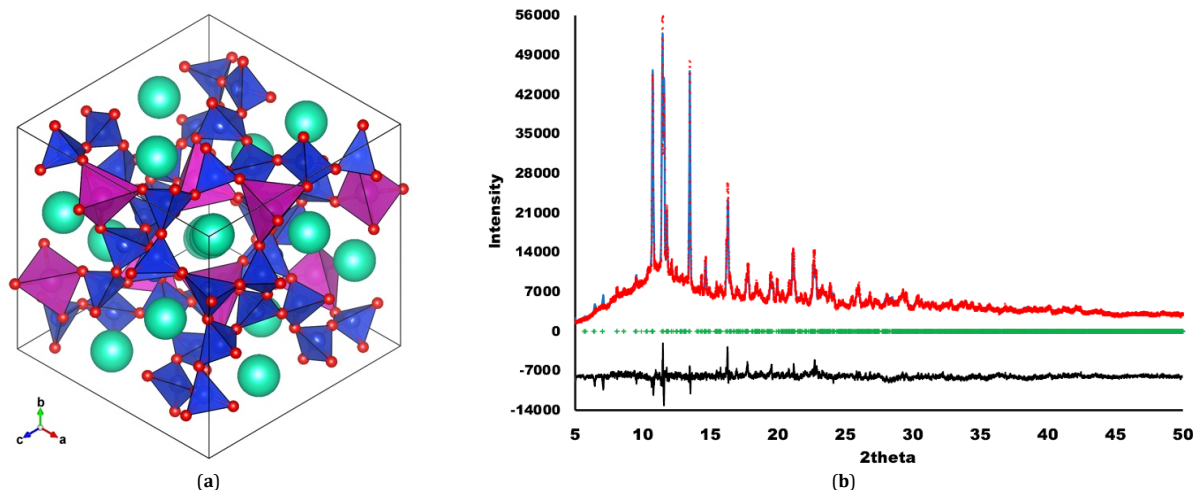
However, the sample with  $X = \text{Zn}$  shows evidence for a transition to a previously unknown *Pa-3* cubic structure, with some T-site cation disorder, at 566 K on heating. This transition is reversible on cooling to 633 K.

## 2. Experimental

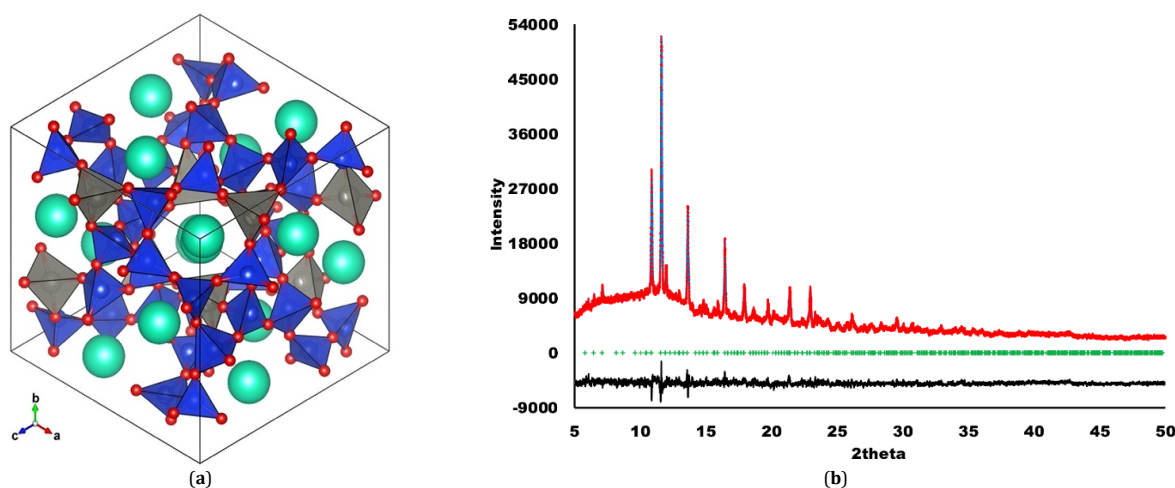
### 2.1. Sample preparation

The samples were made from stoichiometric mixtures of Cs<sub>2</sub>CO<sub>3</sub>, SiO<sub>2</sub>, and CuO ( $X = \text{Cu}$ ) or CdO ( $X = \text{Cd}$ ) or ZnO ( $X = \text{Zn}$ ). For  $X = \text{Cu}$  the sample was prepared by hydrothermal synthesis, the  $X = \text{Cu}$  and Zn samples were prepared by dry synthesis. The  $X = \text{Cu}$  [11],  $X = \text{Cd}$  [8] and  $X = \text{Zn}$  [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 ( $X = \text{Cu}, \text{Cd}$ ) or 1683 K ( $X = \text{Zn}$ ) before quenching by dipping the bases of the crucible into water. The resultant  $X = \text{Cu}$  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  $X = \text{Cd}$  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  $X = \text{Zn}$  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,  $X = \text{Cu}$ ; 8,  $X = \text{Cd}$ ; 9,  $X = \text{Zn}$ ].



**Figure 2.** (a) The crystal structure of  $\text{Cs}_2\text{CdSi}_5\text{O}_{12}$  at 10 K. Turquoise spheres show Cs cations, blue polyhedra show  $\text{SiO}_4$  units, purple polyhedra show  $\text{CdO}_4$  units and red spheres represent O atoms. (b) Rietveld difference plot for the single-phase refinement of  $\text{Cs}_2\text{CdSi}_5\text{O}_{12}$  from synchrotron X-ray powder diffraction data collected at 10 K. The red, blue and grey lines show respectively the observed, calculated and difference plots. Calculated Bragg reflection positions are indicated by green crosses.



**Figure 3.** (a) The crystal structure of  $\text{Cs}_2\text{ZnSi}_5\text{O}_{12}$  at 8 K. Turquoise spheres show Cs cations, blue polyhedra show  $\text{SiO}_4$  units, grey polyhedra show  $\text{ZnO}_4$  units, and red spheres represent O atoms. (b) Rietveld difference plot for the single-phase refinement of  $\text{Cs}_2\text{ZnSi}_5\text{O}_{12}$  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.

## 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,  $X = \text{Cu}$ ,  $\text{Zn}$ ; 10K  $X = \text{Cd}$ ) 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  $Pbca$  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],  $\text{Cd}$  [8]). 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 ( $\pm 0.01 \text{ \AA}$ ) 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 ( $\pm 0.01 \text{ \AA}$ ) 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 order 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  $1.59\text{-}1.63 \text{ \AA}$ , [21]. Therefore Si-O distances were constrained to be  $1.61 \pm 0.01 \text{ \AA}$ . The Zn-O distances were constrained to be  $1.93 \pm 0.01 \text{ \AA}$  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  $\text{Cs}_2\text{XSi}_5\text{O}_{12}$  ( $X = \text{Cu}, \text{Cd}, \text{Zn}$ ) 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  $X = \text{Cd}$ , the low temperature lattice parameter is larger than the corresponding ambient temperature parameter. Similarly, for  $X = \text{Zn}$  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  $X = \text{Cu}$ . Similarly Figures 2a and 2b show the crystal structure plots and Rietveld difference plots for  $X = \text{Cd}$ , Figures 3a and 3b show the crystal structure plots and Rietveld difference plots for  $X = \text{Zn}$ . Table 1 and Figures 3a, 3b and 3c show that the R-factors and difference plot fit for  $X = \text{Cd}$  is slightly worse than for  $X = \text{Cu}$  and  $\text{Zn}$ . This may be due to some preferred orientation in the  $X = \text{Cd}$  sample.

### 4. Conclusions

Low temperature synchrotron X-ray powder diffraction data collected on all three synthetic  $\text{Cs}_2\text{XSi}_5\text{O}_{12}$  ( $X = \text{Cu}, \text{Cd}, \text{Zn}$ ) leucite analogues show that in all cases the *Pbca* 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.

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### 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: [crysdta@fiz-karlsruhe.de](mailto:crysdta@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.

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