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# Synthesis of $Cs_2BeSi_5O_{12}$ with a Pollucite Structure

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The new compound, $Cs_2BeSi_5O_{12}$, has been synthesized by solid state reaction at ~1200°C. It is cubic with $a = 13.406 \pm 0.001$ Å, space group $Ia3d$, and $Z = 8$. The structure was assumed to be essentially similar to that of pollucite, $CsAlSi_2O_6$, and was refined on this basis using X-ray powder intensity data to an $R$ value of 6.2% using 36 reflections. The structure has a three-dimensional beryllosilicate framework in which rings containing 4, 6, and 12 $(Be,Si)O_4$ tetrahedra, sharing corners, are present. No evidence for ordering of Be and Si was found. The $Cs^+$ ions occupy large cavities within the framework and have a coordination number of 12. $Cs_2BeSi_5O_{12}$ is thermodynamically stable and melts congruently at 1420 ± 20°C to give a glass-forming melt.

## Introduction

Pollucite, $CsAlSi_2O_6$, has recently received considerable attention as a possible host material for the immobilization of radioactive cesium present in nuclear radwaste (*1–3*). It has an aluminosilicate framework structure which contains $CS^+$ ions in large, 12-coordinate sites (*4–6*). The unit cell of pollucite is cubic with space group $Ia3d$. Similar framework structures occur in other minerals such as analcite, $NaAlSi_2O_6 \cdot H_2O$, and leucite, $KAlSi_2O_6$ (*7–12*). Leucite is cubic above ~605°C, but at lower temperatures it undergoes a tetragonal distortion (*10–12*). The mutual solid solubility of leucites and pollucites has been determined (*13*) and the tetragonal to cubic transformation studied by high temperature powder X-ray diffraction (*14*). The conditions of synthesis and thermal stability of pollucite have been investigated (*15, 16*). The iron analog of pollucite, $CsFeSi_2O_6$, has been reported (*17, 18*). In this work, we report the synthesis and structure of $Cs_2BeSi_5O_{12}$, a cubic beryllosilicate framework analog of pollucite.

## Experimental

The new phase, $Cs_2BeSi_5O_{12}$, was prepared by solid state reaction of stoichiometric amounts of $Cs_2CO_3$, BeO, and $SiO_2$. The reactants, ~10 g total, were mixed into a paste with acetone, dried, and fired in Pt crucibles, initially at ~600 to 700°C to expel $CO_2$ and finally at 1000 to 1200°C for 1 to 3 days to complete the reaction. The product was analyzed by X-ray powder diffraction using a Hägg–Guinier camera, $CuK\alpha_1$ radiation. For accurate $d$-spacing measurements, an internal standard, KCl, $a = 6.2931$ Å, was added and the films measured using the Cooksley microdensitome-

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TABLE I

X-RAY POWDER DIFFRACTION DATA ($Cs_2BeSi_5O_{12}$: $a = 13.4059 \pm 0.0011$ Å)

| *hkl* | $d_{Obs}$ (Å) | $d_{Calc}$ (Å) | $I_{Obs}$ | $F_{Obs}$ | $F_{Calc}$ |
|---|---|---|---|---|---|
| 112 | 5.492 | 5.473 | 9.4 | 11.3 | 14.1 |
| 123 | 3.588 | 3.583 | 49.1 | 28.6 | 29.7 |
| 004 | 3.355 | 3.352 | 100 | 124.0 | 123.7 |
| 024 | 3.004 | 2.998 | 1.9 | 9.6 | 9.2 |
| 233 | 2.860 | 2.858 | 42.5 | 48.1 | 50.4 |
| 134 | 2.631 | 2.629 | 2.6 | 9.2 | 10.4 |
| 125 | 2.4484 | 2.4476 | 10.4 | 20.1 | 20.6 |
| 044 | 2.3747 | 2.3699 | 27.2 | 67.2 | 68.4 |
| 116 | 2.1748 | 2.1747 | 20 | 13.9 | 11.3 |
| 235 | | 2.1747 | | 30.3 | 28.5 |
| 136 | 1.9773 | 1.9766 | 7.2 | 21.3 | 20.7 |
| 444 | 1.9356 | 1.9350 | 4.1 | 40.3 | 34.2 |
| 046 | 1.8591 | 1.8591 | 1.7 | 15.8 | 15.7 |
| 127 | 1.8243 | 1.8243 | 16.3 | 22.7 | 22.6 |
| 255 | | 1.8243 | | 22.2 | 22.3 |
| 336 | | 1.8243 | | 31.3 | 32.4 |
| 156 | 1.7024 | 1.7026 | 17.5 | 12.8 | 12.5 |
| 237 | | 1.7026 | | 37.8 | 38.2 |
| 008 | 1.6758 | 1.6757 | 5.3 | 63.4 | 63.0 |
| 147 | 1.6502 | 1.6502 | 2.5 | 15.7 | 11.6 |
| 356 | 1.6025 | 1.6023 | 3.1 | 18.2 | 17.4 |
| 138 | 1.5585 | 1.5584 | 2.5 | 15.0 | 10.9 |
| 347 | | 1.5584 | | 7.6 | 3.7 |
| 257 | 1.5176 | 1.5179 | 5.3 | 25.3 | 23.5 |
| 048 | 1.4987 | 1.4988 | 6.9 | 41.4 | 38.8 |
| 556 | 1.4449 | 1.4456 | 2.5 | 13.3 | 13.3 |
| 129 | | 1.4456 | | 6.7 | 6.8 |
| 167 | | 1.4456 | | 14.4 | 16.8 |
| 239 | 1.3824 | 1.3827 | 3.6 | 6.7 | 6.3 |
| 367 | | 1.3827 | | 22.5 | 24.7 |
| 448 | 1.3679 | 1.3682 | 1.9 | 24.1 | 22.9 |
| 277 | 1.3271 | 1.3274 | 5.0 | 32.0 | 31.9 |
| 1110 | | 1.3274 | | 25.4 | 25.9 |
| 1310 | 1.2776 | 1.2782 | 4.1 | 19.5 | 22.3 |
| 567 | | 1.2782 | | 13.4 | 16.3 |
| 259 | | 1.2782 | | 13.2 | 13.8 |

*Note.* KCl, $a = 6.2931$ Å, added as internal standard.

ter (*19*). Powder intensities were measured using a Philips 1020 diffractometer with a slow scan speed, 0.5° $2\theta$ $\min^{-1}$, Cu$K\alpha$ radiation. For structure determination the intensities were corrected for Lp factors and multiplicities. For refinement and $R$-factor calculations, $F$ values were used.

Unit cell dimensions and space group were determined by selected area electron diffraction using an AEI EM 802 electron microscope fitted with a 60° double tilt specimen stage.

The density of several grams of powder was measured by displacement of toluene in an S.G. bottle. Melting behavior was studied by suspending small samples in the hot zone of a vertical tube quench furnace.

## Results

$Cs_2BeSi_5O_{12}$ was synthesized as a new phase by solid state reaction of the oxide starting materials at ~1200°C. The product was a white powder, free from BeO and $SiO_2$ according to its X-ray powder pattern, which is given in Table I. $Cs_2BeSi_5O_{12}$ melts congruently at 1420 ± 20°C. Melt of the same composition readily forms a glass on cooling.

The unit cell of $Cs_2BeSi_5O_{12}$ was determined by selected area electron diffraction of a powdered sample to be cubic with systematic absences of the type

$$hkl\colon\ h + k + l = 2n$$

$$hhl\colon\ 2h + l = 4n$$

$$0kl\colon\ k = 2n.$$

These absences indicated a body centred lattice type with **a** and **d** glide planes. A search through *International Tables for Crystallography* (*20*) showed the space group to be $Ia\bar{3}d$ (No. 230). The unit cell obtained by electron diffraction enabled a list of possible $d$ spacings to be calculated. From this, the powder pattern, Table I, was indexed and accurate cell dimensions obtained by least squares refinement, $a = 13.406 \pm 0.001$ Å. Assuming that the unit cell contains eight formula units, a theoreti-

TABLE II

Atomic Parameters for $Cs_2BeSi_5O_{12}$

| Atom | Position | $x$ | $y$ | $z$ | $B_{iso}$ |
|---|---|---|---|---|---|
| O | 96$h$ | 0.107 ± 0.001 | 0.136 ± 0.001 | 0.720 ± 0.001 | 0.7 |
| Si,Be | 48$g$ | 0.125 | 0.663 ± 0.001 | 0.587 ± 0.001 | 3.1 |
| Cs | 16$b$ | 0.125 | 0.125 | 0.125 | 4.3 |

cal density of 3.35 g $cm^{-3}$ is obtained which compares well with the experimentally observed value of 3.32 g $cm^{-3}$.

From a comparison of unit cell, space group, and X-ray powder data of $Cs_2BeSi_5O_{12}$ with that reported for pollucite (*5–7*), it seemed likely that the two phases were isostructural. To confirm this, X-ray intensity data were collected by diffractometry for three different samples and the results averaged. For the initial refinement, 17 unique reflections were used. Atomic scattering factors for neutral Cs, Si, and O were taken from *International Tables* (*20*). Starting coordinates were taken as those reported for pollucite (*5*) but with Si,Be placed on the 48$g$ sites instead of Si,Al. The parameters that were allowed to refine were the three positional coordinates for oxygen, two positional coordinates for (Si,Be), and isotropic temperature factors for Cs, O, and (Si,Be). Using block diagonal least squares (*21*) the $R_F$ factor was refined to 0.039. At this stage, eight other powder lines, composed of overlapping peaks, were taken into account. The intensities of the component peaks were assigned according to their calculated $F$ values. These new reflections were included, to give a total of 36 reflections, and after further least squares cycles, a final $R_F$ value of 0.064 was obtained. The observed and calculated structure factors are included in Table I and the final atomic parameters in Table II. Interatomic distances were calculated: for the $(Be,Si)O_4$ tetrahedra the bond lengths were 1.59 and 1.62 Å. For the 12-coordinate $Cs^+$ ion, the Cs–O distances were 6 at 3.36 Å and 6 at 3.46 Å (Table III).

TABLE III

Some Bond Distances and Angles

| | |
|---|---|
| (Be,Si)–O | 1.591 ± 0.017 Å (2×) |
| | 1.620 ± 0.014 Å (2×) |
| Cs–O | 3.459 ± 0.010 Å (6×) |
| | 3.358 ± 0.010 Å (6×) |
| O–(Be,Si)–O | 110.0 ± 0.8° |
| | 108.7 ± 0.8° (2×) |
| | 112.8 ± 0.8° (2×) |
| | 103.7 ± 0.8° |

The structure of $Cs_2BeSi_5O_{12}$ is shown in Fig. 1. It is very similar to that reported for pollucite (*4–6*). It consists of rings of four and six $(Be,Si)O_4$ tetrahedra which link up to form a three-dimensional framework. Within this framework are large, 12-coordinate sites that are occupied by $Cs^+$ ions. There was no evidence in the electron dif-

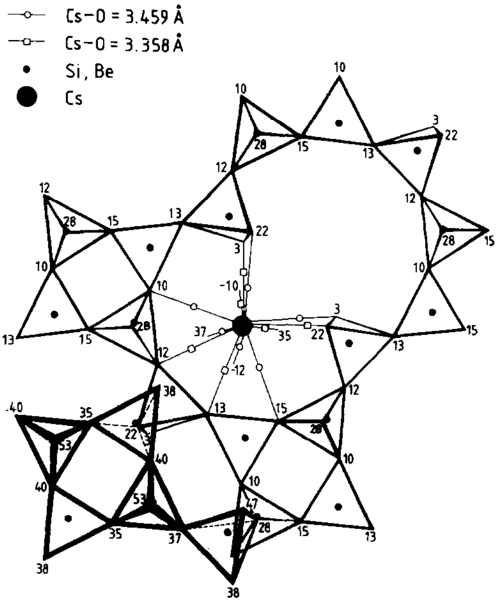

Fig. 1. Part of the crystal structure of $Cs_2BeSi_5O_{12}$ showing rings of 4, 6, and 12 $(Be,Si)O_4$ tetrahedra. Numbers correspond to heights of atoms as a percentage of the unit cell dimension.

fraction patterns of extra reflections which might be indicative of a lowering of symmetry associated with possible ordering of Be an Si. It appears therefore that the 48*g* sites contain 40 Si and 8 Be atoms which are disordered in the same way that 32 Si and 16 Al atoms are disordered in pollucite. In Fe-pollucite also, no evidence of ordering on the tetrahedral sites was found (*17*).

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