

Crystal synthesis of a new cesium aluminosilicate, CsAlSi₅O₁₂

JUN ITO

The James Franck Institute, The University of Chicago
5640 South Ellis Avenue, Chicago, Illinois 60637

Abstract

Small single crystals of a new cesium aluminosilicate, ideally CsAlSi₅O₁₂, have been grown by slow cooling of the melt containing Ba-,Cs-vanadate flux (1420-750°C). The compound is orthorhombic, with space group *Bbm2*; $a = 13.785(1)$, $b = 16.727(1)$, $c = 5.0130(5)$; $V = 1155.9(1)$ Å³; $Z = 4$. Electron microprobe and atomic absorption chemical analysis gave SiO₂ 65.0, Al₂O₃ 10.2, Cs₂O 25.0, BaO 0.16, and Fe₂O₃ 0.06 wt percent. The formula computed on the basis of 12 oxygen atoms per unit formula gave Ba_{0.005} Cs_{0.834} Fe³⁺_{0.004} Al_{0.939} Si_{5.084} O₁₂. There may be some partial solid solubility of BaAl₂Si₄O₁₂ (hypothetical) in CsAlSi₅O₁₂.

Introduction

During the course of the investigation of flux growth of single crystals of the feldspar type structure (Grove and Ito, 1973), a new anhydrous cesium aluminosilicate, having the ideal formula CsAlSi₅O₁₂, was obtained by a slow cooling of the clear melt containing a large amount of Ba-,Cs-vanadate flux. A brief account of the method used and the crystal data that have been obtained is presented.

Synthesis

Small crystals of CsAlSi₅O₁₂ have been synthesized by spontaneous nucleation from the clear melt. Initial charge of the melt was: reagent grade BaCO₃ 4.00 g, Cs₂CO₃ 4.91 g, H₂SiO₃ 3.60 g, Al₂O₃ 0.500 g, Fe₂O₃ 33.3 mg, and V₂O₅ 10 g. The charge was placed in a platinum crucible of 50 ml capacity which was gradually heated up to 1360°C, and kept for 48 hours in a muffle furnace with silicon carbide heating elements. The melt was then brought up to 1420°C to ensure the complete dissolution of the solid, then cooled at 2°C per hour using an on-off program-controller. The heating was terminated at 750°C; then the furnace was brought to room temperature.

The crystals apparently grew from a few nuclei either floating on the surface of the melt or adhering to the upper wall of the crucible, since a temperature gradient was maintained throughout the experiment with the bottom of the crucible hotter than the top. Countless thin platy crystals elongated parallel to (100) with well-developed (010) grew into the melt, thus forming several clusters of radially grown crystals. Separation of the crystals from the flux was

easily done by soaking the melt in a hot dilute NaOH (5%) solution followed by rapid rinsing with a dilute cold HCl (5%) solution. The yield was approximately 1.0 g of the single phase crystalline CsAlSi₅O₁₂.

Results of characterization

X-ray precession photographs, using MoK α radiation, taken on the three crystallographic axes, showed the presence of *mmm* symmetry with the following extinction criteria: $0kl$, $k = 2n$, $k + l = 2n$ and hkl , $h + l = 2n$. The space group was determined by Dr. T. Araki, using a four circle X-ray diffractometer, as orthorhombic *Bbm2*. Unit-cell dimensions obtained from the indexed powder data (Table 1) collected from the fine-grained material (CuK α ₁ radiation with Si standard) were refined using a computer program written by Appleman and Evans (1973). These are $a = 13.785(1)$, $b = 16.727(1)$, $c = 5.0130(5)$ Å; $V = 1155.9(1)$; $Z = 4$.

The only known Cs-aluminosilicate, pollucite, has a framework structure with 4-, 6-, and 8-membered loops of tetrahedra and resembles the analcite structure NaAlSi₂O₆·H₂O (Náray-Szabó, 1938; Beger, 1969). However, the structure of the new cesium aluminosilicate consists of a single layer framework containing 5-membered rings of the Al and Si tetrahedra (T. Araki, private communication). Another example of a single layer framework is found in the mordenite-type structure (Meier, 1961).

Electron microprobe and atomic absorption analysis of the flux-grown crystals gave: SiO₂ = 65.0, Al₂O₃ = 10.2, Fe₂O₃ = 0.06, Cs₂O = 25.0, BaO = 0.16. Total 100.42 wt percent. Analyzed Tanco pollucite

TABLE I. X-Ray Powder Data for a New Cesium Aluminosilicate, CsAlSi₅O₁₂*

h	k	l	I/I ₀	d(calc)	d(obs)	h	k	l	I/I ₀	d(calc)	d(obs)
1	0	1	3	4.711	4.713	6	3	0	15	2.124	2.124
1	1	1	2	4.535	4.530	0	8	0	10	2.091	2.092
2	3	0	2	4.335	4.333	5	4	1	f	2.092	
0	4	0	5	4.182	4.178	2	4	2	5	2.052	2.052
1	2	1	30	4.105	4.108	4	1	2	5	2.012	2.013
1	3	1	100	3.598	3.597	5	5	1	3	1.958	1.958
2	4	0	60	3.575	3.577	3	7	1	5	1.952	1.952
4	0	0	20	3.446	3.447	2	5	2	3	1.926	1.926
3	0	1	10	3.387	3.386	4	3	2	5	1.905	1.905
4	1	0	40	3.375	3.375	6	5	0	8	1.894	1.894
3	1	1	20	3.320	3.319	0	6	2	2	1.864	1.863
4	2	0	10	3.186	3.185	7	0	1	3	1.833	1.832
3	2	1	8	3.140	3.140	5	6	1	8	1.826	1.826
2	5	0	25	3.010	3.010	4	4	2	5	1.824	1.823
4	3	0	15	2.931	2.932	7	2	1	5	1.790	1.791
3	3	1	10	2.895	2.896	3	8	1	5	1.779	1.779
0	6	0	15	2.788	2.787	7	3	1	5	1.741	1.741
1	5	1	15	2.728	2.728	4	5	2	5	1.734	1.735
4	4	0	3	2.659	2.658	1	9	1	5	1.729	1.729
3	4	1	5	2.632	2.632	5	7	1	3	1.699	1.699
2	6	0	15	2.584	2.584	6	0	2	3	1.694	1.695
0	0	2	5	2.506	2.506	8	2	0	5	1.688	1.687
5	0	1	5	2.415	2.415	6	1	2	5	1.685	1.684
4	5	0	10	2.400	2.400	2	7	2	8	1.677	1.677
1	6	1	f	2.399		0	10	0	10	1.673	1.673
2	0	2	5	2.355	2.355	4	9	0	5	1.636	1.635
5	2	1	5	2.321	2.321	2	10	0	8	1.625	1.624
6	1	0	5	2.276	2.278	6	3	2	5	1.620	1.621
2	2	2	5	2.267	2.268	1	3	3	5	1.590	1.590
2	7	0	10	2.258	2.258	5	8	1	5	1.581	1.581
2	3	2	8	2.170	2.169	1	10	1	15	1.576	1.576
4	6	0	f	2.167							
3	6	1	8	2.153	2.153						
0	4	2	f	2.150							
1	7	1	15	2.131	2.130						

*Diffractometer with CuK α_1 radiation with Si standard. Refined unit-cell dimensions are $a = 13.785(1)$, $b = 16.727(1)$, $c = 5.0130(5)$ Å; $V = 1155.9(1)$ Å³; $Z = 4$. Space group orthorhombic $Bm\bar{2}$.

(U39-95.5), kindly supplied by Dr. P. Czerny of the University of Manitoba, was used as a probe standard. Spectrographic analysis of the hand-picked sample showed V as a significant impurity and a trace quantity of Ti, Cr, and Ca. Atomic absorption analysis gave V₂O₅ = 0.4 wt percent in the bulk sample, but it is not certain whether it is incorporated in the crystal structure or is a mere inclusion, since a large number of vanadate flux-grown crystals are known to contain vanadium oxide as an essential component as well as an inclusion (Flanigen *et al.*, 1969; Grandin de L'eprevier, 1972). The amount of BaO incorporated into the crystal was low, considering the high BaO content in the melt. The above analysis without V₂O₅ was computed on the basis of 12 oxygens according to the structure analysis. The formula is thus given as:



A small solid solubility of the hypothetical BaAl₂Si₄O₁₂ was indicated by the analysis of the Ba-bearing crystal (BaO 1.76 wt%). This was obtained from a Ba-rich run which resulted in a large amount of celsian crystals (Cs₂O 0.72 wt%). The extent of solid solution may be limited by the large difference in cation size between Cs¹⁺ and Ba²⁺. Specific gravity determined by flotation in a mixture of methylene iodide and carbon tetrachloride was found to be 2.709 (20°C) which agrees well with the calculated value of 2.710.

The crystals of the new Cs-aluminosilicate melt at a temperature above 1420°C; however, slow cooling of the resulting clear melt from 1460° to 1360°C failed to nucleate crystals. Clear glass was obtained. Therefore, direct growth from the pure liquid may be difficult.

Large single crystals, up to 5 mm in length, of Cs-containing celsian (monoclinic $C2/m$ and $I2/c$) and hexacelsian (hexagonal $P6mm$) have been successfully grown in the Ba-rich (Cs-poor) range using similar conditions and technique. Detailed structure work has been completed by Dana Griffen at Virginia Polytechnic Institute and State University.

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