

## The Structure of Potassium Barium Silicate $K_2Ba_7Si_{16}O_{40}$

BY F. J. CERVANTES-LEE, L. S. DENT GLASSER,\* F. P. GLASSER AND R. A. HOWIE

*Department of Chemistry, University of Aberdeen, Meston Walk, Old Aberdeen AB9 2UE, Scotland*

(Received 20 October 1981; accepted 18 February 1982)

### Abstract

The structure of  $K_2Ba_7Si_{16}O_{40}$  has been solved from three-dimensional single-crystal X-ray diffraction data and refined by block-diagonal least squares to  $R = 0.063$  for 993 observed independent reflections. Crystals are monoclinic, space group  $C2/m$ , with  $a = 31.991(9)$ ,  $b = 7.704(2)$ ,  $c = 8.255(2)$  Å,  $\beta = 100.60(2)^\circ$ ,  $Z = 2$ . The structure consists of infinite  $Si_2O_5$  sheets parallel to (201) linked together through eight-coordinate K and seven and nine-coordinate Ba atoms.

### Introduction

In the phase diagram of the system  $K_2O$ – $BaO$ – $SiO_2$ , Gunawardane & Glasser (1976) reported an incongruently melting phase, believed to have the formula  $K_2Ba_3Si_8O_{20}$ , and said to occur in two polymorphic modifications. The high-temperature modification of this phase was, according to their experimental evidence, capable of taking up to 4.8 mol% silica into solid solution whereas in the low-temperature polymorph solid solution was negligible.

Structural studies on both phases have been undertaken to try to establish the mechanism by which solid solution occurred in the high-temperature phase and also to determine the structural relationship between the two polymorphs. We here report the results for the high-temperature modification.

### Experimental

#### *Preparation of crystals*

Several compositions were chosen according to the phase diagram. These were prepared from reagent-grade  $K_2CO_3$ ,  $BaCO_3$  and optical-grade quartz and mixed under ethanol in an agate mortar. After drying, the mixtures were decarbonated for several hours at 1273 K and then melted twice at 1623 K for periods of

15 min with intermediate grinding, to yield a homogeneous glass by quenching in water. The glasses were then recrystallized at different temperatures until eventually suitable crystals were obtained. The runs which gave the best results were (proportions in mol%): (A) 8.3  $K_2O$ , 25  $BaO$ , 66.7  $SiO_2$ , 7 d at 1473 K; (B) 15  $K_2O$ , 15  $BaO$ , 70  $SiO_2$ , 5 d at 1273 K.

Both preparations contained some glass; the X-ray powder pattern of the crystalline phase agreed with that of Gunawardane & Glasser's high  $K_2Ba_3Si_8O_{20}$ .

#### *Intensity-data collection*

Two crystals, *A* and *B*, one from each batch, were selected for single-crystal work; both were plates of irregular shape and were approximately  $0.10 \times 0.05 \times 0.01$  mm with their longest dimension along *b*.

The cell parameters were initially determined from single-crystal rotation and Weissenberg photographs (Cu  $K\alpha$  filtered radiation  $\lambda = 1.5418$  Å) with the crystal rotating about its unique axis, *b*, and refined by a least-squares fit to indexed powder data.

Intensity data for crystal *A* were collected on a Hilger & Watts Y190 automatic linear diffractometer with Mo  $K\alpha$  radiation ( $\lambda = 0.7107$  Å) with balanced filters. Of the 1258 independent reflections measured, 931 were classed as observed [ $I > 3\sigma(I)$ ], the remainder were arbitrarily assigned an intensity equal to half the minimum observed intensity and classed as unobserved. Data for crystal *B* were collected using a Nicolet P3 four-circle single-crystal diffractometer with filtered Mo  $K\alpha$  radiation; the  $\theta$ – $2\theta$  scan technique with  $\theta \leq 40^\circ$  was used and 993 unique reflections were measured as observed [reflections for which  $I < 3\sigma(I)$  were omitted]. A Honeywell 66/80 computer was used for all calculations, mainly with programs of Dr F. R. Ahmed and collaborators, of the National Research Council of Canada, adapted for use on this machine by J. S. Knowles and R. A. Howie of the University of Aberdeen. Scattering-factor curves for  $Ba^{2+}$ , K,  $Si^{3+}$  and  $O^-$  (a compromise between the theoretically 'best' ionization states and those for which curves were given) were taken from *International Tables for X-ray Crystallography* (1968).

\* To whom correspondence should be addressed.

## Solution of the structure

The symmetry and the systematic absences gave  $C2$ ,  $Cm$  and  $C2/m$  as the possible space groups. Using the  $A$  data, a three-dimensional Patterson synthesis was calculated and the coordinates of the Ba, most of the K and two Si atoms were determined using a superposition technique. Structure factor calculations using these coordinates gave  $R$  values of 0.40, 0.43 and 0.45 for  $C2$ ,  $Cm$  and  $C2/m$  respectively and  $C2$  was selected as the most likely space group for further calculations. A three-dimensional electron density map based on the resulting phases revealed the position of additional atoms in the structure, all of which were treated as O atoms at this stage. Repeated refinement of the positional parameters of the atoms located, followed by calculation of electron density maps, revealed most of the structure, but two K atoms required by the formula of Gunawardane & Glasser could not be located. Alternative interpretations of the Patterson synthesis were tried but always led to an equivalent arrangement of heavy atoms. The  $R$  value of 0.119 suggested that the structure was at least partially

Table 1. Atomic parameters and e.s.d.'s

Figures in parentheses represent e.s.d.'s corresponding to the least significant digit(s).

	$x$	$y$	$z$	Occu- pancy*	$B_{iso}$ ( $\text{\AA}^2$ )
Ba(1)	0.14912 (7)	0.0000	0.05819 (24)	—	0.8†
Ba(2)	0.26991 (7)	0.0000	0.89597 (26)	—	1.1†
Ba(3)	0.38637 (7)	0.0000	0.68866 (27)	—	1.1†
Ba(4)	0.0384 (2)	0.0000	0.2764 (7)	0.333	0.8 (1)
Ba(5)	0.5000	0.0000	0.5000	0.333	1.2 (1)
K(1)	0.0384 (4)	0.0000	0.2764 (13)	0.666	1.3 (2)
K(2)	0.5000	0.0000	0.5000	0.666	1.6 (3)
Si(1)	0.0739 (2)	0.2007 (8)	0.6545 (7)	—	0.7 (1)
Si(2)	0.2007 (2)	0.2070 (8)	0.4348 (7)	—	0.7 (1)
Si(3)	0.1674 (2)	0.2977 (8)	0.7531 (7)	—	0.5 (1)
Si(4)	0.0460 (2)	0.2971 (8)	0.9755 (7)	—	0.5 (1)
O(1)	0.2033 (6)	0.2187 (21)	0.8876 (18)	—	1.4 (3)
O(2)	0.1842 (6)	0.2761 (23)	0.2602 (19)	—	1.8 (3)
O(3)	0.0572 (8)	0.0000	0.6370 (27)	—	1.3 (4)
O(4)	0.1938 (10)	0.0000	0.4415 (36)	—	3.5 (6)
O(5)	0.3391 (8)	0.0000	0.1988 (27)	—	1.2 (4)
O(6)	0.4544 (8)	0.0000	-0.0369 (26)	—	1.2 (4)
O(7)	0.0839 (6)	0.2057 (21)	0.0865 (19)	—	1.4 (3)
O(8)	0.0674 (5)	0.2892 (21)	0.4823 (19)	—	1.5 (3)
O(9)	0.0000	0.2095 (27)	0.0000	—	0.8 (4)
O(10)	0.0453 (5)	0.2887 (21)	0.7796 (18)	—	1.1 (3)
O(11)	0.1227 (5)	0.1979 (19)	0.7592 (17)	—	0.8 (3)
O(12)	0.1741 (5)	0.2960 (20)	0.5628 (17)	—	1.0 (3)
O(13)	0.2500	0.2500	0.5000	—	3.6 (6)

\* All occupancies are 1.0 unless otherwise stated.

† Calculated from the anisotropic temperature factors of the form  $\exp[-(B_{11}h^2 + B_{22}k^2 + B_{33}l^2 + B_{23}kl + B_{13}hl + B_{12}hk) \times 10^{-5}]$ .

	$B_{11}$	$B_{22}$	$B_{33}$	$B_{13}$
Ba(1)	5 (3)	308 (28)	634 (30)	66 (16)
Ba(2)	5 (3)	272 (28)	968 (34)	101 (17)
Ba(3)	6 (3)	408 (29)	798 (31)	63 (16)

$$B_{12} = B_{23} = 0.$$

correct, and it was then decided to collect a better set of intensity data using crystal  $B$  (which was slightly larger than  $A$ ) and a four-circle diffractometer. The final positional parameters from the previous attempt to solve the structure were refined using the new data and

Table 2. Interatomic distances ( $\text{\AA}$ ) and bond angles ( $^\circ$ )

E.s.d.'s in the least significant digits are given in parentheses. Non-bridging O atoms are denoted by an asterisk.

## (a) Silicate tetrahedra

Si(1)—*O(8)	1.56 (2)	*O(8)—Si(1)—O(3)	110 (1)
O(10)	1.65 (2)	O(10)	113 (1)
O(11)	1.64 (2)	O(11)	116 (1)
O(3)	1.63 (1)	O(3)—Si(1)—O(10)	104 (1)
		O(11)	107 (1)
		O(10)—Si(1)—O(11)	105 (1)
Si(2)—*O(2)	1.54 (2)	*O(2)—Si(2)—O(4)	110 (1)
O(4)	1.61 (1)	O(12)	109 (1)
O(12)	1.63 (2)	O(13)	113 (1)
O(13)	1.60 (1)	O(4)—Si(2)—O(12)	108 (1)
		O(13)	109 (1)
		O(12)—Si(2)—O(13)	107 (1)
Si(3)—*O(1)	1.57 (2)	*O(1)—Si(3)—O(5)	108 (1)
O(5)	1.63 (1)	O(11)	109 (1)
O(11)	1.63 (2)	O(12)	118 (1)
O(12)	1.63 (2)	O(5)—Si(3)—O(11)	107 (1)
		O(12)	107 (1)
		O(11)—Si(3)—O(12)	107 (1)
Si(4)—*O(7)	1.55 (2)	*O(7)—Si(4)—O(6)	107 (1)
O(6)	1.64 (1)	O(9)	111 (1)
O(9)	1.67 (1)	O(10)	116 (1)
O(10)	1.62 (2)	O(6)—Si(4)—O(9)	107 (1)
		O(10)	110 (1)
		O(9)—Si(4)—O(10)	105 (1)

## Summary of values

	Mean	Range
Si—*O	1.555	1.54–1.57
Si—O	1.63	1.60–1.67
O—Si—*O	112	107–118
O—Si—O	107	104–110

## (b) Cation—oxygen polyhedra

Ba(1)—*O(1) [ $\times 2$ ]	2.95 (2)	Ba(2)—*O(1) [ $\times 2$ ]	2.71 (2)
*O(2) [ $\times 2$ ]	2.81 (2)	*O(1') [ $\times 2$ ]	2.84 (2)
O(4)	3.22 (3)	*O(2) [ $\times 2$ ]	2.74 (2)
*O(7) [ $\times 2$ ]	2.66 (2)	O(5)	3.02 (2)
O(11) [ $\times 2$ ]	2.89 (1)		
		K(1)/Ba(4)—O(3)	2.93 (2)
		O(3')	3.27 (3)
Ba(3)—*O(2) [ $\times 2$ ]	2.93 (2)	*O(7) [ $\times 2$ ]	2.81 (2)
O(6)	2.84 (2)	*O(8) [ $\times 2$ ]	2.85 (2)
*O(7) [ $\times 2$ ]	2.97 (2)	O(9) [ $\times 2$ ]	2.88 (1)
*O(8) [ $\times 2$ ]	2.75 (2)		
O(12) [ $\times 2$ ]	3.01 (2)	K(2)/Ba(5)—*O(8) [ $\times 4$ ]	2.72 (2)
		O(10) [ $\times 4$ ]	2.97 (2)

## (c) Coordination of bridging O atoms (second column gives symmetry at O)

	Si—O	Other contacts	
Si(2)—O(13)—Si(2')	$\bar{1}$ 180	1.60 [ $\times 2$ ]	—
Si(2)—O(4)—Si(2'')	$m$ 163 (1)	1.61 [ $\times 2$ ]	3.22 (Ba)
Si(3)—O(5)—Si(3')	$m$ 146 (1)	1.63 [ $\times 2$ ]	3.02 (Ba)
Si(2)—O(12)—Si(3)	144 (1)	1.63, 1.63	3.01 (Ba)
Si(4)—O(6)—Si(4')	$m$ 144 (1)	1.64 [ $\times 2$ ]	2.84 (Ba)
Si(1)—O(3)—Si(1')	$m$ 142 (1)	1.63 [ $\times 2$ ]	3.27, 2.93 (K/Ba)
Si(1)—O(10)—Si(4)	138 (1)	1.65, 1.62	2.94 (K/Ba)
Si(1)—O(11)—Si(3)	137 (1)	1.64, 1.63	2.89 (Ba)
Si(4)—O(9)—Si(4'')	2 132 (1)	1.67 [ $\times 2$ ]	2.88 [ $\times 2$ ] (K/Ba)

a new three-dimensional electron density map was calculated. The results were almost identical to those using the  $A$  data and confirmed that the rather high electron density noted at the location of the  $K^+$  atoms in the earlier synthesis was real and not due to poor-quality intensity data. This, together with the unusually high density noted by Gunawardane & Glasser for the so-called 'high  $K_2Ba_3Si_8O_{20}$  solid solution' compared with that of the low polymorph, suggested that the six 'potassium' sites were in fact statistically occupied by both K and Ba. Occupancies of  $\frac{2}{3}$  and  $\frac{1}{3}$  for K and Ba respectively were estimated from the electron density map giving the revised formula  $K_2Ba_7Si_{16}O_{40}$ . With this modification refinement improved from  $R = 0.119$  to  $R = 0.067$ . Moreover it became apparent that the true space group was  $C2/m$  and this gave a final  $R$  factor of 0.063 for 993 observed reflections.\* A final difference synthesis showed electron density values in the range  $\pm 2 e \text{ \AA}^{-3}$ , with values in the range  $\pm 3 e \text{ \AA}^{-3}$  in the regions of the Ba atoms. Final parameters are given in Table 1, and the more important interatomic distances and angles in Table 2.

### Description of the structure

The structure consists of infinite sheets of silicate tetrahedra parallel to (201) with four tetrahedra in the asymmetric unit. Si atoms in tetrahedra 1 and 2 of Fig. 1 are just below the  $a$ -glide plane and have  $y$  approximately equal to 0.2 whereas those in tetrahedra 3 and 4 are just above with  $y$  approximately equal to 0.3. The tetrahedra point up and down from the glide plane at  $y = \frac{1}{4}$  with their apices alternating in the mirror planes at  $y = 0$  and  $y = \frac{1}{2}$ . This pattern of repetition is broken at  $a/2$  and similar positions, which results in the structure having a relatively long  $a$  dimension compared with  $b$  and  $c$ . Individual sheets could be classified according to Liebau's (1972) system as a special type of *Zweier-Einfachschicht* with the unshared O atoms pointing alternately to each side of the corrugated *Zweierschicht*. However, the sequence of six-membered rings usual in such a sheet is interrupted at the twofold axes, which generate four- and eight-membered rings (Fig. 2). This discontinuity changes the actual repeat along the chains from which the sheet is built from two to sixteen tetrahedra.

All the cations lie on the mirror planes at  $y = 0$  and  $y = \frac{1}{2}$  and themselves form layers which link adjacent silicate sheets as shown in Fig. 3.

\* A list of structure factors has been deposited with the British Library Lending Division as Supplementary Publication No. SUP 36790 (7 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

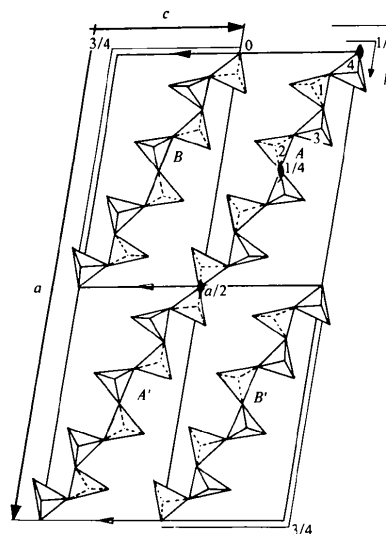


Fig. 1. The silicate sheets of  $K_2Ba_7Si_{16}O_{40}$ . The area of the projection is two unit cells.  $A$  shows that part of the sheet in the bottom half of the cell between the mirror planes at 0 and 0.5;  $B$  shows the related part in the upper half of the cell.

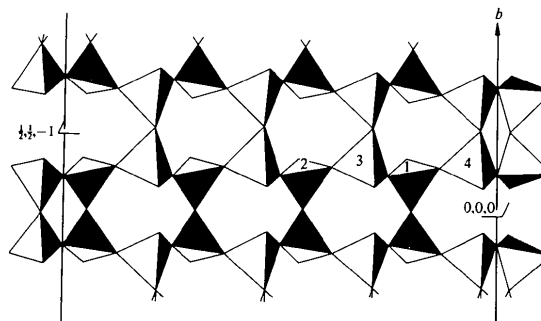


Fig. 2. Configuration of the corrugated sheet of silicate tetrahedra in  $K_2Ba_7Si_{16}O_{40}$  [(201) projection].

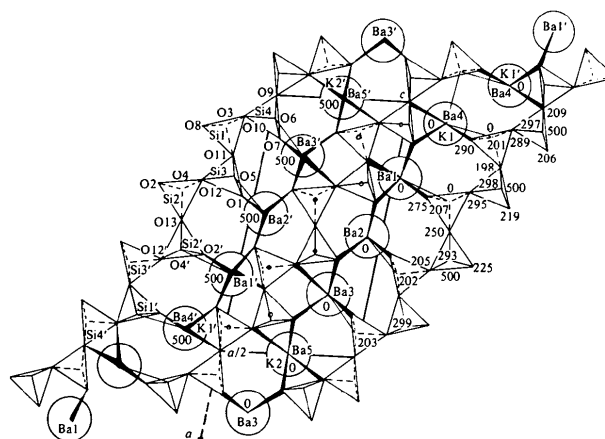


Fig. 3. A quarter of the structure of  $K_2Ba_7Si_{16}O_{40}$  [(010) projection]. Large circles are Ba and K/Ba, small circles are Si. O positions are represented by the corners of the tetrahedra. Y coordinates for the silicate sheet on the right of the diagram (thousandths of the unit-cell height) refer to the atoms designated on the equivalent sheet on the left. Half of the cations are omitted, for clarity.

The silicate tetrahedra are all somewhat distorted. Bond lengths to non-bridging O atoms are shorter than the others, and angles at Si involving them are generally larger than the rest (Table 2a). The Si—O—Si angles (Table 2c) are quite variable: adjacent Si—O distances increase with decrease in angle, and additional contacts to the O atoms increase. All of this is quite consistent with what is normally observed in silicate structures.

All the cations are irregularly coordinated (Fig. 3 and Table 2). Ba(1) and Ba(3) are each coordinated to similar geometrical arrangements of nine O atoms, four at  $y \sim \frac{1}{4}$  and four at  $y \sim -\frac{1}{4}$  forming distorted square prisms, and one at  $y = 0$ . The coordination of K(1)/Ba(4), one of the statistically occupied sites, consists of eight O atoms surrounding the site in a completely irregular fashion as shown in Fig. 3. The other statistically occupied site, K(2)/Ba(5), has a more regular coordination with eight O atoms at the corners of a parallelepiped, four of which are at  $y \sim \frac{1}{4}$  and the other four at  $y \sim -\frac{1}{4}$ . Finally, Ba(2) has a coordination number of seven with groups of three O atoms above and three below, forming a distorted trigonal prism and one more in the same plane as Ba(2). The bonds from the cations to non-bridging O atoms are, as expected, shorter (mean 2.81, range 2.66–2.97 Å) than those to bridging ones (mean 2.98, range 2.84–3.27 Å).

The structure obeys Pauling's rules well. Each of the non-bridging O atoms makes three contacts with the cations: if each of these is assigned a bond valence of  $\frac{1}{3}$ , the valence sum at each Ba site is 2, while at the K/Ba sites it is  $\frac{4}{3}$ , in excellent agreement with the assigned occupancies ( $\frac{2}{3}K^+ + \frac{1}{3}Ba^{2+}$ ).

### Related structures

The structure of  $K_2Ba_7Si_{16}O_{40}$  is closely related to those of high  $Ba_2[Si_4O_{10}]$  (Katscher, Bissert & Liebau, 1973) and low  $Ba_2[Si_4O_{10}]$  (sanbornite) (Douglass, 1958). These two structures consist of infinite  $[Si_4O_{10}]$  *Zweier-Einfachschichten* made up of six-membered rings of silicate tetrahedra of similar configuration to those in Fig. 2. Adjacent sheets are linked together by layers of Ba atoms. The topology of the sheets is different for each polymorph with sanbornite having the more 'folded' or 'corrugated' sheets. The silicate layers in  $K_2Ba_7Si_{16}O_{40}$  are even less folded than in high  $Ba_2[Si_4O_{10}]$ , possibly due to the thermal vibration of the K atoms, and contain six- and four-membered rings of silicate tetrahedra as shown in Fig. 2. The four-membered rings occur in the vicinity of the statistically

occupied sites and resemble those present in the structure of  $K_4Si_8O_{18}$  (Schweinsberg & Liebau, 1974).

### Discussion

According to Douglass (1958): 'In a limited substitution of two alkali ions for one barium ion in the sanbornite structure, one alkali ion could possibly occupy each former barium position, but there are apparently no holes elsewhere in this structure which can suitably accommodate the other alkali ion.' This view is further supported by our results which show that a relatively small amount (~4 mol%) of  $K_2O$  results in the formation of a different phase.

The formula derived from the structure determination was checked by microprobe analysis on several single crystals which gave an average K/Ba ratio very close to that in the proposed formula  $K_2Ba_7Si_{16}O_{40}$ . The structure does not show vacant sites or any other feature to suggest solid-solution formation with silica.

These results seem to point towards the occurrence of two closely related compounds rather than two polymorphs of the so-called ' $K_2Ba_3Si_8O_{20}$ ' reported by Gunawardane & Glasser (1976). However, there is the possibility of an order-disorder type of effect on the cation sites and also of different degrees of convolution of the silicate sheets which could account for the polymorphic changes. The structure of the 'low polymorph' may reveal more information concerning the relationship in composition and structure between these two phases.

We thank the late Mr B. G. Cooksley for collecting the intensity data for crystal *A* and Dr E. E. Lachowski for the microprobe analyses. F. Cervantes-Lee thanks CONACYT (Mexico) for financial support.

### References

- DOUGLASS, R. M. (1958). *Am. Mineral.* **43**, 517–536.  
 GUNAWARDANE, R. P. & GLASSER, F. P. (1976). *J. Am. Ceram. Soc.* **58**, 233–236.  
*International Tables for X-ray Crystallography* (1968). Vol. III, 2nd ed., pp. 203–211. Birmingham: Kynoch Press.  
 KATSCHER, H., BISSERT, G. & LIEBAU, F. (1973). *Z. Kristallogr.* **137**, 146–158.  
 LIEBAU, F. (1972). *Handbook of Geochemistry*, Vol. II/3, 14A1–14A13. Berlin: Springer-Verlag.  
 SCHWEINSBERG, H. & LIEBAU, F. (1974). *Acta Cryst.* **B30**, 2206–2213.