Crystal Structure of $Na_2BaSi_2O_6$

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The structure of the title compound has been determined by Patterson and Fourier methods from three-dimensional *X*-ray data collected with a scintillation counter, and refined by block-diagonal least squares to *R* 0·060 for 839 observed independent reflections. Crystals are monoclinic, space group $P2_1$, with $a = 11{\cdot}440(5)$, $b = 4{\cdot}758(2)$, $c = 5{\cdot}670(2)$ Å, $\beta = 91{\cdot}42(4)°$, $Z = 2$. The structure contains infinite SiO_3 chains parallel to *b* linked through five- and six-co-ordinate sodium and eight-co-ordinate barium atoms. It is compared with the related Na_2SiO_3 and $BaGeO_3$ structures.

STUDIES on the phase equilibria in the system Na_2O–BaO–SiO_2 [1] revealed the existence of a new metasilicate, $Na_2BaSi_2O_6$. Its crystal structure has been determined in order to establish the form of the anion and to examine the relationship of the compound to the metasilicates of sodium and barium.

Metasilicates, and related compounds, may have anions which are either infinite chains or finite rings. Liebau [2] classified a number of such compounds on the basis of their unit cells. $BaSiO_3$ crystallises in two modifications; the low-temperature form appeared to be of the pseudo-wollastonite type, containing Si_3O_9 rings, while the high-temperature form appeared to be based on infinite chains with two tetrahedra per repeat distance of 4·58 Å. This latter structure type was confirmed for high-temperature $BaGeO_3$,[3] whose cell dimensions are virtually identical with those of high-temperature $BaSiO_3$ (Table 1). Similar chains, with a repeat distance of 4·82 Å, were found in sodium metasilicate, Na_2SiO_3.[4] Comparison of cell dimensions (Table 1) suggests that $Na_2BaSi_2O_6$ contains similar infinite chains.

TABLE 1

Crystal data for some metasilicates and high-temperature form of $BaGeO_3$

Compound	Cell dimensions [a]				*Z*	Space group
$BaGeO_3$ [b, c]	$c = 12{\cdot}76$	$a = 4{\cdot}58$	$b = 5{\cdot}68$		4	$P2_12_12_1$
$BaSiO_3$ [b, d]	$c = 12{\cdot}27$	$a = 4{\cdot}54$	$b = 5{\cdot}56$		4	
Na_2SiO_3 [e]	$a = 10{\cdot}48$	$c = 4{\cdot}82$	$b = 6{\cdot}07$ [f]		4	$Cmc2_1$
$Na_2BaSi_2O_6$ [g]	$a = 11{\cdot}44$	$b = 4{\cdot}76$	$c = 5{\cdot}67$	$\beta = 91{\cdot}42°$	2	$P2_1$

[a] Arranged to show resemblance with those of $Na_2BaSi_2O_6$. [b] High-temperature form. [c] Ref. 3. [d] Ref. 2. [e] Ref. 4. [f] The structural relation is closest with a cell defined somewhat differently: see Figure 3. The alternative cell has virtually identical dimensions. [g] Present work.

EXPERIMENTAL

$Na_2BaSi_2O_6$ crystals were grown from a glass of the same composition by heating it for 24 h at 800 °C. The temperature of crystal growth was carefully chosen because the compound melts incongruently at 895 °C.

Crystal Data.—$Na_2BaSi_2O_6$, $M = 335{\cdot}5$, Monoclinic, $a = 11{\cdot}440(5)$, $b = 4{\cdot}758(2)$, $c = 5{\cdot}670(2)$ Å, $\beta = 91{\cdot}42(4)°$, $U = 308{\cdot}7$ Å^3, $D_m = 3{\cdot}57(3)$, $Z = 2$, $D_c = 3{\cdot}60$. Space group $P2_1$. Cu-K_α filtered radiation, $\lambda = 1{\cdot}5418$ Å, for single-crystal oscillation, rotation and Weissenberg photographs about *b* and *c*; cell parameters refined from indexed *X*-ray powder data obtained on a diffractometer using an

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[1] R. P. Gunawardane and F. P. Glasser, *Trans. J. Brit. Ceram. Soc.*, in the press.

[2] F. Liebau, *Neues Jahrb. Mineral.*, 1960, **94**, 1209.

[3] W. Hilmer, *Acta Cryst.*, 1962, **15**, 1101.

[4] W. S. McDonald and D. W. J. Cruickshank, *Acta Cryst.*, 1966, **22**, 37.

internal standard. Mo-K_α radiation for intensity data collection, $\lambda = 0{\cdot}7107$ Å; μ(Mo-K_α) = 70·6 cm^{-1}.

Intensity Data.—The crystal chosen for data collection approximated to a lath, with its largest dimension 0·3 mm, corresponding to the *b* axis. It was mounted about this axis for the collection of three-dimensional intensity data on a Hilger and Watts Y190 automatic linear diffractometer with Mo-K_α radiation and a scintillation counter; the crystal was oscillated through 2°. Each reflection in one half of reciprocal space was measured four times, and the final intensities (obtained in general by averaging two equivalent reflections) were corrected for Lorentz and polarisation effects. Of the 1001 independent reflections measured, 846 were observed. Reflections considered not to be significantly above background were arbitrarily assigned a value equal to half the minimum observed intensity. An empirical check showed that absorption errors were not likely to be serious and no correction was applied.

Computing.—An ICL 4/50 computer was used, 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 of the Department of Computing, University of Aberdeen. Scattering-factor curves for Ba, Na$^+$, Si, and O$^-$ (a compromise between the theoretically 'best' ionisation states and those for which curves were given) were taken from ref. 5.

Structure Determination and Refinement.—The observed symmetry and systematic absences together with the presence of a piezoelectric effect fixed the space group as $P2_1$. *x* and *z* Co-ordinates for the Ba atom were determined from the three-dimensional Patterson synthesis, the *y* co-ordinate being fixed at 0·25 for the purpose of origin definition. A three-dimensional electron-density map based on the resulting phases revealed all of the remaining ten atom positions, eight of which had approximately the same *y* co-ordinate as the Ba atom. A structure-factor calculation with all atoms included gave *R* 0·195. From this point the structure was refined by least squares, using the block-diagonal approximation; initially the positional parameters and scale factors were refined, then isotropic temperature factors. After several cycles it became evident that the refinement was not converging satisfactorily: the positional parameters of some atoms, especially *y* co-ordinates, were oscillating through *ca.* 2σ. Full-matrix least-squares refinement did not improve the situation, so the block-diagonal method was resumed. It was thought that the trouble was largely caused by the fact that atoms in the two SiO$_4$ tetrahedra, not related by symmetry, nevertheless have *y* co-ordinates which differ by almost exactly *b*/2, and the difficulty is compounded by the fact that so many of the light atoms have approximately the same *y* co-ordinate as the Ba atom. It was also apparent from an error analysis that interlayer scaling was necessary to increase the contribution of the higher layers. After correcting for this, the light atoms were divided into two groups [Si(1), O(1), O(2), O(5), and Si(2), O(3), O(4), O(6), corresponding to the two tetrahedra] which were refined separately. The refinement converged with *R* 0·074. An error analysis showed that the unit weights used in the analysis were satisfactory. The geometry of the structure at this stage was reasonable, except for rather large discrepancies in the Si–O(bridging) bond lengths [Si(1)–O(5), Si(1)–O(6), Si(2)–O(5), and Si(2)–O(6)], all of which had large components along the polar axis (*b*). Correction for the anomalous dispersion of the Ba atom was therefore made, and structure factors calculated for each of the two polarities. However, since there was little difference between the *R* factors for the two models (0·077 and 0·075), and no convincing improvement in the bond lengths in question, it was decided to continue without the anomalous dispersion correction.

TABLE 2

Atomic parameters, with estimated standard deviations in parentheses

Atom	*x*/*a*	*y*/*b*	*z*/*c*	B_{iso}
Ba	0·09715(9)	0·25	0·2533(2)	*
Na(1)	0·4869(6)	0·247(5)	0·1863(12)	1·0(1)
Na(2)	0·3221(6)	0·754(6)	0·2887(13)	1·4(1)
Si(1)	0·3447(5)	0·291(1)	0·6778(9)	0·8(1)
Si(2)	0·1933(5)	0·799(1)	0·7758(9)	0·8(1)
O(1)	0·3222(9)	0·243(7)	0·400(2)	0·6(2)
O(2)	0·4736(10)	0·260(8)	0·774(2)	0·8(2)
O(3)	0·1169(11)	0·754(9)	0·537(2)	1·0(2)
O(4)	0·1226(11)	0·739(8)	1·009(2)	1·0(2)
O(5)	0·2414(13)	0·127(4)	0·820(3)	0·9(2)
O(6)	0·3194(13)	0·635(4)	0·755(3)	1·0(2)

* Anisotropic temperature factors in the form: exp-$[-(B_{11}h^2 + B_{22}k^2 + B_{33}l^2 + B_{23}kl + B_{13}hl + B_{12}hk)]$

10^5B_{11}	10^5B_{22}	10^5B_{33}	10^4B_{23}	10^5B_{13}	10^5B_{12}
109(6)	1073(37)	702(22)	12(15)	−190(17)	−105(69)

TABLE 3

Interatomic distances (Å) and bond angles (°)

(*a*) Si–O tetrahedra

(i) Interatomic distances

Si(1)–O(1)	1·61(1)	Si(2)–O(3)	1·61(1)
Si(1)–O(2)	1·57(1)	Si(2)–O(4)	1·59(1)
Si(1)–O(5)*	1·65(2)	Si(2)–O(5′)*	1·67(2)
Si(1)–O(6)*	1·72(2)	Si(2)–O(6)*	1·65(2)
O(1)–O(2)	2·70(2)	O(3)–(O4)	2·68(2)
O(1)–O(5)*	2·64(2)	O(3)–O(5′)*	2·76(3)
O(1)–O(6)*	2·74(3)	O(3)–O(6)*	2·66(2)
O(2)–O(5)*	2·75(2)	O(4)–O(5′)*	2·55(3)
O(2)–O(6)*	2·51(3)	O(4)–O(6)*	2·75(2)
O(5)–O(6)*	2·61(2)	O(5′)–O(6)*	2·54(2)

(ii) Bond angles

O(1)–Si(1)–O(2)	117·0(12)	O(3)–Si(2)–O(5′)*	114·8(11)
O(1)–Si(1)–O(5)*	108·2(10)	O(3)–Si(2)–O(6)*	109·6(11)
O(1)–Si(1)–O(6)*	111·2(10)	O(4)–Si(2)–O(5′)*	102·3(11)
O(2)–Si(1)–O(5)*	117·8(11)	O(4)–Si(2)–O(6)*	116·0(11)
O(2)–Si(1)–O(6)*	99·5(11)	O(5′)*–Si(2)–O(6)*	99·6(8)
O(5)*–Si(1)–O(6)*	101·6(8)		
		Si(1)–O(5)*–Si(2′)	127·5(10)
O(3)–Si(2)–O(4)	113·5(13)	Si(1)–O(6)*–Si(2)	128·5(10)

(*b*) Cation–Oxygen co-ordination (polyhedra)

Ba–O(1)	2·69(1)	Na(1)–O(1)	2·27(1)
Ba–O(3)	2·89(4)	Na(1)–O(2′)	2·34(1)
Ba–O(3′)	2·86(4)	Na(1)–O(2″)	2·37(4)
Ba–O(3″)	2·75(1)	Na(1)–O(2‴)	2·49(4)
Ba–O(4′)	2·73(3)	Na(1)–O(6′)	2·30(2)
Ba–O(4″)	2·82(3)	Na(2)–O(1)	2·51(4)
Ba–O(4‴)	2·89(1)	Na(2)–O(1′)	2·41(4)
Ba–O(5′)	3·05(1)	Na(2)–O(2′)	2·37(1)
		Na(2)–O(3)	2·77(1)
		Na(2)–O(4′)	2·75(1)
		Na(2)–O(6)	2·71(2)

Primed atoms are symmetry-related atoms.

* Bridging oxygen atoms.

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[5] 'International Tables for *X*-Ray Crystallography,' vol. III, Kynoch Press, Birmingham, 1962.

Several axial reflections with $F_o > F_c$ due to white radiation streaks were excluded from the refinement. A difference-Fourier map showed large positive and negative regions in the vicinity of the Ba atom, indicating anisotropic thermal motion. Anisotropic temperature factors were introduced for the Ba atom and allowed to refine until the shifts were a fraction of the estimated standard deviations. Further cycles were calculated, the two tetrahedra being refined separately as before. After two further cycles in which all atoms were allowed to refine, the refinement converged with R 0·060 for 839 observed reflections. A final difference-Fourier synthesis showed electron-density values in the range ± 2 eÅ^{-3}, with values in the range ± 4 eÅ^{-3} in the region of the Ba atom.

Tables 2 and 3 give respectively the final parameters and the more important interatomic distances and angles. Observed and calculated structure factors are listed in Supplementary Publication No. SUP 20791 (4 pp., 1 microfiche).

DISCUSSION

Description of the Structure.—The structure comprises infinite single chains of silicate tetrahedra parallel to the b axis, with two tetrahedra per chain repeat; each chain is linked to its neighbours through the Ba^{2+} and Na^{+} ions. Figures 1 and 2 show projections of the structure down the b and c axes respectively. Individual chains have no symmetry, but each is related to neighbouring chains by the screw axis. This results in a pairing of chains in the direction of the a axis. The Ba^{2+} ions occupy the larger cavities between adjacent pairs of chains while the Na^{+} ions are held in the smaller cavities within.

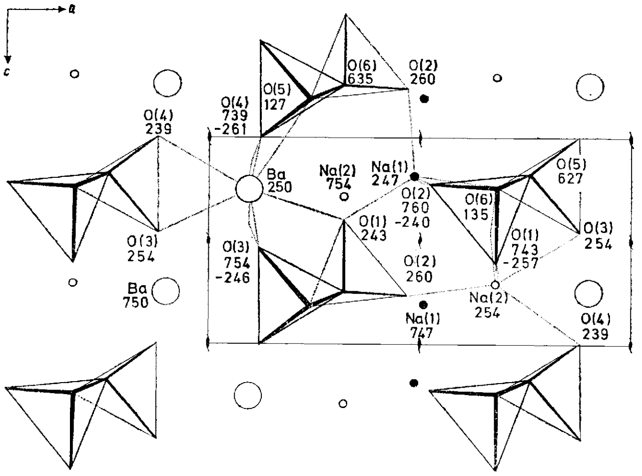

FIGURE 1 The structure projected down b, heights in b/1000. Large open circles indicate Ba atoms, small filled and open circles Na(1) and Na(2) respectively

There are two groups of Si–O bond lengths involving (i) bridging and (ii) non-bridging oxygens. For (i) the mean Si–O distance is 1·60 Å with a range of 1·57—1·61 Å while for (ii) the mean is 1·67 Å with a range of 1·65—1·72 Å. In the latter case the extreme values are just significantly different if the errors from the least squares (0·02 Å) are accepted. In fact, these are probably too low for various reasons, of which the most important is that errors in the polar direction should be increased if corrections for anomalous scattering are not made, a point discussed in the Na$_2$SiO$_3$ structure determination.[4] Since the Si–O(bridge) bonds have a large component along the polar axis, it seems reasonable to assume that they are not in fact significantly different; certainly there seems to be no good chemical reason why they should be.

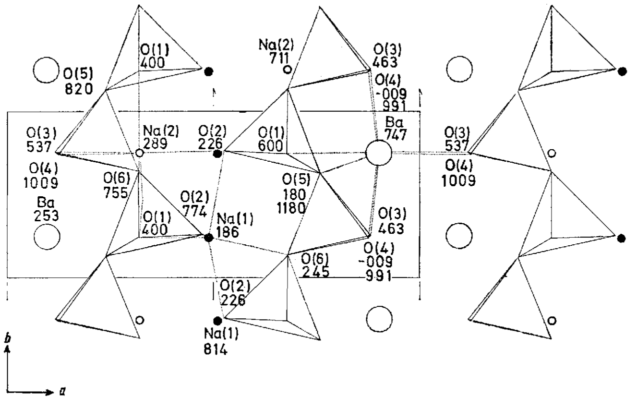

FIGURE 2 The structure viewed along c, heights in c/1000; atoms are indicated as in Figure 1

The angles at Si(1) and Si(2) are rather distorted from ideal tetrahedral geometry, varying between 99·5 and 117·8°. While it is evident that the angles involving bridging oxygens are among the smallest and those involving non-bridging among the largest, the pattern is not wholly consistent.

Both the Si–O–Si angles are equal to 128° within the limits of error; the equivalent value for Na$_2$SiO$_3$ is 133·7°. The Si–O distances found in Na$_2$SiO$_3$ of 1·672 and 1·592 Å for bridging and non-bridging oxygens respectively are also similar to those found in Na$_2$BaSi$_2$O$_6$ (1·67 and 1·60 Å). The latter thus fits in with the general observation that differences between the two types of Si–O bond are likely to be more extreme for smaller Si–O–Si angles.

The Ba atom is co-ordinated to eight oxygens (Figures 1 and 2) within 3·5 Å which are arranged approximately at the corners of a cube. Seven of these co-ordinating oxygens are non-bridging and lie at distances of 2·69—2·89 Å from the Ba, while the eighth, a bridging oxygen, is at 3·05 Å.

The Na(1) atoms have five neighbours within 3·0 Å forming a distorted trigonal prism with its axis lying nearly parallel to the b axis. The Na(2) atoms are roughly octahedrally co-ordinated, with three Na–O bonds shorter (2·57—2·51 Å) than the others (2·71—2·77 Å).

The electrostatic valency rule is reasonably well obeyed. Attempts to explain the differences between

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[*] See Notice to Authors No. 7 in *J.C.S. Dalton*, 1972, Index issue. (Items less than 10 pp. are sent as full-size copies.)

the various Si–O(bridge) distances in terms of Baur's method [6] produced an explanation which was qualitatively correct but too small by an order of magnitude. This supports the assertion (see earlier) that the differences are probably not significant.

Relationships with Other Structures.—The structure of $Na_2BaSi_2O_6$ shows marked similarities to those of Na_2SiO_3 and high-temperature $BaGeO_3$ (Figure 3). All contain single chains of tetrahedra parallel to the shortest axis, with two tetrahedra per chain repeat. They differ in the chain configuration, and in the relationship between adjacent chains. In all the chains, the individual tetrahedra have one face roughly perpendicular to the chain direction; this is the reason for the considerable shortening of the chain repeat (4·54—4·82 Å) relative to that in pyroxenes (5·2—5·3 Å) in which the tetrahedra have one edge parallel to the chain direction. In both $BaGeO_3$ and Na_2SiO_3 the chains have 2_1 symmetry, but it can be seen from Figure 3 that whereas in $BaGeO_3$ alternate chains have their tetrahedra pointing in opposite directions, in Na_2SiO_3 and $Na_2BaSi_2O_6$ all the chains are pointing the same way.

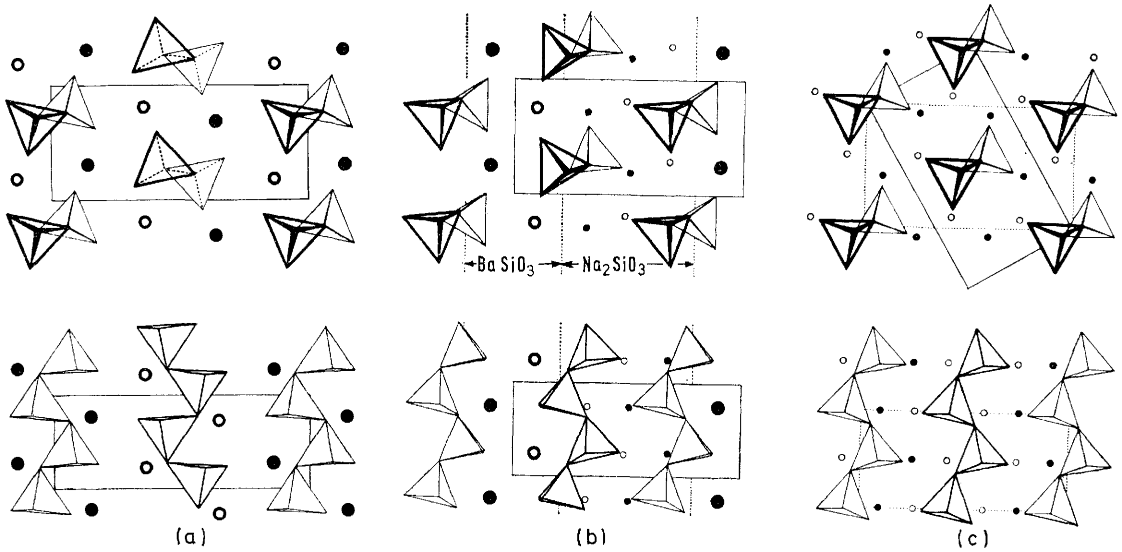

FIGURE 3 The structures of (a) high-temperature $BaGeO_3$, (b) $Na_2BaSi_2O_6$, and (c) Na_2SiO_3 viewed in equivalent directions. True unit cells are indicated by full lines; in (c), dotted lines define an alternative cell which brings out the structural similarities to (b). Large circles indicate Ba atoms, small circles, Na atoms. Heavy and light triangles, and filled and open circles indicate respectively tetrahedra and cations separated by half a cell repeat perpendicular to the paper

Figure 3 shows that $Na_2BaSi_2O_6$ can be regarded as being composed of alternating ' slices ' of high-temperature $BaSiO_3$ (assuming this to be isostructural with high-temperature $BeGeO_3$) and Na_2SiO_3. The *a* axis (11·40 Å), which is perpendicular to the alternating slices, is very close to the mean of the appropriate repeat distances in Na_2SiO_3 and $BaSiO_3$ (11·38 Å). Comparison of the repeat distances along the chains (Table 1) shows that in this respect $Na_2BaSi_2O_6$ resembles Na_2SiO_3 rather than $BaSiO_3$. This may be because each of the small sodium ions is located close to one particular chain, and thus tends to control the chain repeat distance. The larger barium ions, on the other hand, are more or less equidistant from three different chains, and appear mainly to influence the distance between chains. The $Na_2BaSi_2O_6$ *c* axis, representing the repeat distance between chains within the ' slices ' is thus similar to the corresponding distance in high-temperature $BaSiO_3$.

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[6] W. H. Baur, *Amer. Mineral.*, 1971, **56**, 1573.