Table 5. *The oxygen-surroundings of the potassium ions*

Distances to K(1) Atom	Distance	Distances to K(2) Atom	Distance
O(2) $(x, y-1, z)$	3·14 Å	O(1) $(x-1, y, z)$	2·76 Å
O(4) (x, y, z)	2·75	O(1) $(1-x, y, z)$	2·79
O(5) $(x+1, y-1, z)$	2·72	O(2) $(x, y-1, z)$	2·76
O(6) $(x-1, y, z)$	2·76	O(3) (x, y, z)	2·72
O(6) $(1-x, y, z)$	2·73	O(5) $(x-1, y, z)$	2·87
O(7) (x, y, z)	2·80	O(8) (x, y, z)	2·90

Fig. 6 shows a projection of potassium mesotartrate along a non-crystallographic axis so as to make it possible to see the hydrogen-bonded ions separately. Both water molecules have three hydrogen bonds in a distorted non-planar trigonal arrangement. All hydrogen bonds are within the anion layers except for one: O(8)–O(5). The latter bond connects ions of different sheets giving the structure, to some extent, the aspect of a three-dimensional network. The hydrogen bond distances are given in Table 4. It is noteworthy that of the corresponding distances in the two isomorphous structures only the hydrogen bonds have the same lengths, whereas there are notable differences in all other intermolecular contacts.

The arrangement of the oxygen atoms around the cations is a very irregular one. Table 5 contains the distances of the potassium ions to the oxygen atoms that can be considered as the nearest neighbours.

We are indebted to Drs A. de Vries and J. A. Kanters for valuable discussions and we wish to thank Dr J. C. Schoone for helpful advice concerning the computational work.

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The Crystal Structure of Barium Tetraborate, $BaO . 2B_2O_3$

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(*Received* 29 *December* 1964)

$BaO . 2B_2O_3$ crystallizes in the monoclinic system, $P2_1/c$. The lattice constants are $a=10·56$, $b=8·20$, $c=13·01$ Å, $\beta=104°\ 57'$, and $Z=8$.

The structure was established by Patterson projections and three-dimensional electron density syntheses utilizing the heavy atoms initially to establish some phases. The structure was refined by three-dimensional least-squares to a final $R=10·4\%$ (observed data only).

The borate network can be described as a three-dimensional linkage of alternating six-membered single rings containing two tetrahedral boron atoms and one triangular boron atom, and double rings containing two tetrahedral boron atoms, one of them being common to both rings, and three triangular boron atoms. Each single ring is directly linked only to double rings and each double ring directly links only to single rings. The barium atoms fit into channels of this network.

Introduction

The anhydrous borates with more than 50 mole % B_2O_3 are in an important glass forming region and there is much interest in the structure of the borate groups. There have been several radial distribution (Block & Piermarini, 1964; Krogh-Moe, 1962*a*) studies of various glass compositions but the only single-crystal structure studies have been of several alkali borate compounds of lithium, cesium and potassium by

Krogh-Moe (1960, 1962*b*, 1959). No alkaline earth compounds in the glass forming region have been studied. An infrared study by Weir & Schroeder (1964) of the relationship between absorption bands and borate structures indicated that Ca, Ba, and Zn 1:2 compounds with B_2O_3 could have similar structures but that the isomorphous strontium and lead compounds are quite different. The structures of the barium and the strontium (Perloff & Block, 1965) compounds have been determined.

Structure determination

Single crystals were grown on a hot wire apparatus from a melt of the stoichiometric composition. The cell dimensions and their estimated standard deviations for $BaO . 2B_2O_3$ as previously reported (Block, Perloff & Weir, 1964) are

$a = 10{\cdot}56 \pm 0{\cdot}01$ Å   Space group $P2_1/c$
$b = 8{\cdot}20 \pm 0{\cdot}01$ $Z = 8$
$c = 13{\cdot}01 \pm 0{\cdot}01$ $\varrho(\text{calc.}) = 3{\cdot}57$ g.cm^{-3}
$\beta = 104° \; 57' \pm 10'$

The set of three-dimensional *hkl* ($k = 0 - 8$) and 0*kl* data was obtained by the multiple film technique with an integrating Weissenberg camera using Mo $K\alpha$ radiation ($\lambda = 0{\cdot}7107$ Å) and read on a densitometer. Lorentz and polarization corrections were applied.

Intensity data were obtained from an irregular single-crystal fragment that approximated, very roughly, a cylinder of 0·15 mm mean diameter and 0·29 mm length. The long direction was almost parallel to the *b* axis. Based on a linear absorption coefficient of 74·9 cm^{-1} the cylindrical μR value ranges from 0·56 for the zero level to 0·60 for the eighth level. These values yield errors due to absorption which are less than the estimated 15% accuracy of the reading errors. Therefore, no absorption corrections were made.

The number of formula units per unit cell was originally assumed to be eight on the basis of the volume of the cell. This assumption was verified by the final structure. There are 2 formula groups per asymmetric unit. The coordinates of the two independent Ba atoms were readily obtained from [100] and [010] Patterson projections. However, there was considerable overlap and the borate configuration could not be obtained from these projections. As the data were obtained, the various levels were scaled with the Ba contributions and the three-dimensional electron-density maps computed. When the 0*kl* and *hkl* through $k = 4$ were obtained, the oxygen positions were found. The boron positions were obtained from an electron-density map of the Ba and oxygen contributions, using data through $k = 8$.

The structure was refined by full-matrix least-squares analysis (Busing & Levy, 1959) of the complete data (3658 observed and 1467 unobserved reflections). The program minimizes the quantity $R' = \Sigma w\,(F_o - F_c)^2$. The weighting factor ($w$) was taken as unity for all reflections with a scaled $F_o \le 70$ and as 70/scaled F_o for reflections with a scaled $F_o > 70$. Refinement was terminated when both R' and the conventional R ceased changing significantly. All of the final shifts for the positional parameters were less than the estimated standard deviations, but a few of the final shifts for the temperature factors of the light atoms were greater, by as much as a factor of three, than the corresponding errors. The final conventional R value, based on the 3658 observed data, was 0·104. A difference map was computed as a final check and revealed no peculiarities.

The final parameters are presented in Table 1. A complete list of the final least-squares refinement output of parameters, shifts, errors, correlation matrix, scaled F_o and F_c values has been deposited with the Library of Congress*.

The atomic scattering factors used were O^- and neutral B (*International Tables for X-ray Crystallography*, 1962) and Ba^{2+} (Thomas & Umeda, 1957). The barium form factors were corrected for dispersion, using the values of Dauben & Templeton (1955).

Structure description

The structure of $BaO . 2B_2O_3$ consists of a borate network of six-membered rings with Ba atoms located in channels of the network. The borate network consists

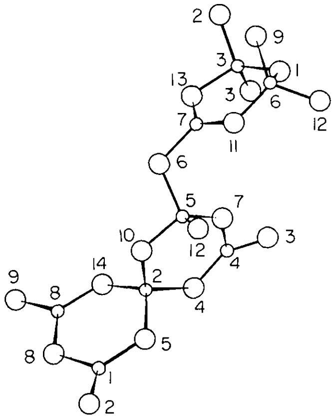

Fig. 1. The basic borate repeat unit found in $BaO . 2B_2O_3$. The smaller circles are boron atoms and the larger ones are oxygen atoms. Non-ring oxygen atoms have been repeated to provide complete coordination for all borons. The numbering corresponds to the designations in Table 1.

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* The output from the final cycle of least-squares refinement has been submitted with the manuscript and has been deposited with the U.S. Library of Congress as Document No. 10532. The list contains the final parameters, shifts, errors, correlation matrix, and a complete listing of observed and calculated structure factors. Requests for copies should be addressed: Photoduplication Service, Library of Congress, Washington, D.C. 20540. A copy may be secured by citing the Document number and by remitting $ 2·50 for microfilm or $ 13·81 for electrostatic positive prints. Advance payment is required. Make checks or money orders payable to: Photoduplication Service, Library of Congress.

Table 1. *Atomic parameters*

Atom	x	$\sigma_x \times 10^5$	y	$\sigma_y \times 10^5$	z	$\sigma_z \times 10^5$	B	$\sigma_B \times 10^3$
Ba(1)	0·46306	2	0·74077	4	0·10597	0·2	0·643	5
Ba(2)	0·10503	2	0·12266	4	0·20380	0·2	0·870	5
O(1)	0·25678	27	0·25692	42	0·40344	21	0·368	31
O(2)	0·10740	30	0·39972	48	0·48533	23	0·519	36
O(3)	0·30361	31	0·52380	49	0·46822	23	0·582	36
O(4)	0·18354	27	0·59723	45	0·29272	21	0·346	32
O(5)	0·04897	32	0·77536	51	0·15911	25	0·474	38
O(6)	0·49020	37	0·36172	56	0·20244	29	0·842	46
O(7)	0·36497	31	0·74972	47	0·39562	24	0·488	38
O(8)	0·03121	32	0·80333	52	0·47576	25	0·621	38
O(9)	0·16727	31	0·99042	49	0·42674	24	0·504	37
O(10)	0·28465	30	0·81789	48	0·21238	23	0·327	35
O(11)	0·38661	26	0·43517	44	0·02502	20	0·095	30
O(12)	0·33685	29	0·02845	48	0·33648	23	0·496	35
O(13)	0·31287	33	0·19358	53	0·09501	26	0·544	41
O(14)	0·19956	28	0·58110	47	0·10866	22	0·381	34
B(1)	0·01122	43	0·28695	73	0·44819	33	0·471	49
B(2)	0·18134	42	0·69039	71	0·19241	33	0·281	50
B(3)	0·24768	39	0·36699	66	0·48418	30	0·281	44
B(4)	0·28331	35	0·62158	60	0·38255	27	0·169	39
B(5)	0·36956	39	0·86674	65	0·30991	30	0·282	44
B(6)	0·28732	47	0·08413	78	0·42625	37	0·468	55
B(7)	0·39284	35	0·32871	61	0·10612	27	0·052	40
B(8)	0·13752	39	0·59067	67	0·00895	30	0·296	43

Table 2. *Boron–oxygen bond lengths and angles*

A. Triangularly coordinated boron

Distances		$\sigma \times 10^3$	Angles		σ
B(1)–O(2)	1·365 Å	6 Å	O(2) –B(1)–O(5)	120·7°	0·4°
O(5)	1·380	5	O(2) O(3)	116·9	0·4
O(8)	1·399	6	O(5) O(8)	122·1	0·4
B(4)–O(3)	1·345	5	O(3) –B(4)–O(7)	113·7	0·3
O(4)	1·371	5	O(3) O(4)	122·9	0·4
O(7)	1·342	6	O(4) O(7)	123·3	0·4
B(7)–O(6)	1·427	5	O(6) –B(7)–O(11)	116·1	0·4
O(11)	1·358	5	O(6) O(13)	121·9	0·4
O(13)	1·378	6	O(11) O(13)	122·0	0·3
B(8)–O(8)	1·397	6	O(9) –B(8)–O(14)	126·6	0·4
O(9)	1·363	6	O(9) O(8)	113·0	0·3
O(14)	1·296	5	O(8) O(14)	120·4	0·4
Avg.	1·368			120·0	

B. Tetrahedrally coordinated boron

Distances		$\sigma \times 10^3$	Angles		σ
B(2)–O(4)	1·507 Å	6 Å	O(5) –B(2)–O(10)	107·9°	0·4°
O(5)	1·521	6	O(5) O(14)	110·9	0·3
O(10)	1·485	6	O(5) O(4)	106·6	0·3
O(14)	1·461	6	O(4) O(10)	111·0	0·3
			O(4) O(14)	110·0	0·4
			O(10) O(14)	109·3	0·3
B(3)–O(1)	1·407	6	O(1) –B(3)–O(2)	112·2	0·3
O(2)	1·509	6	O(1) O(3)	110·7	0·3
O(3)	1·452	6	O(1) O(13)	113·5	0·4
O(13)	1·512	5	O(2) O(3)	106·3	0·4
			O(2) O(13)	104·8	0·3
			O(3) O(13)	109·0	0·3
B(5)–O(6)	1·531	6	O(6) –B(5)–O(7)	106·4	0·3
O(7)	1·481	6	O(6) O(12)	110·5	0·4
O(10)	1·410	5	O(6) O(10)	107·8	0·3
O(12)	1·435	6	O(7) O(12)	111·1	0·3
			O(7) O(10)	110·9	0·4
			O(10) O(14)	110·0	0·3
B(6)–O(1)	1·466	7	O(1) –B(6)–O(9)	110·0	0·4
O(9)	1·484	6	O(1) O(11)	111·0	0·4
O(11)	1·442	5	O(1) O(12)	104·1	0·4
O(12)	1·470	6	O(11) O(9)	111·4	0·4
			O(11) O(12)	110·4	0·4
			O(9) O(12)	108·8	0·4
Avg.	1·473			109·4	

of single and double rings linked together through non-ring oxygen atoms into a three-dimensional framework. The basic borate repeat unit is shown in Fig. 1. Every non-ring oxygen atom links a single ring and a double ring. Each single ring is connected to five different double rings and each double ring is connected to five different single rings through the non-ring oxygen atoms O(2), O(3), O(6), O(9), and O(12).

The single ring is reminiscent of that found in $Li_2O.3B_2O_3$ (Krogh-Moe, 1960) and the double ring of that found in $K_2O.5B_2O_3$ (Krogh-Moe, 1959.) However, in each case the relative numbers of triangular and tetrahedral boron coordinations are different. The single ring contains two tetrahedrally coordinated and one triangularly coordinated boron atoms, whereas the ring in $Li_2O.3B_2O_3$ has one tetrahedral and two triangular coordination. The double ring in the $BaO.2B_2O_3$ structure contains two tetrahedrally and three triangularly coordinated boron atoms, while the $K_2O.5B_2O_3$ double ring has one tetrahedrally and four triangularly coordinated boron atoms.

All of the boron–oxygen distances and angles fall within the range usually found in borate structures. The mean triangular boron–oxygen bond distance is 1·368 ± 0·02 Å* and tetrahedral boron–oxygen is 1·473 ± 0·03 Å. The respective mean O–B–O angles are 120·0 ± 3·3° and 109·4 ± 1·9°. The individual distances, angles, and standard deviations are presented in Table 2.

The borate network has channels wherein the Ba ions are located. This can be seen in Fig. 2 which is a projection along [010]. The projection along [100] is shown in Fig. 3. The coordination polyhedra about the barium ions are shown in Fig. 4. Ba(1) is coordinated by 9 oxygen atoms with distances ranging from 2·609 to 3·084 Å. Ba(2) is coordinated by 10 oxygen atoms and the Ba–O distances range from 2·718 Å to 3·122 Å. All the Ba–O distances and standard deviations are presented in Table 3.

Table 3. *Barium–oxygen distances*

Ba(1)–O(11)	2·757 ± 0·003 Å	Ba(2)–O(12)	2·718 ± 0·003 Å
O(10)	2·686 ± 0·003	O(13)	2·960 ± 0·004
O(6)	2·609 ± 0·004	O(2)	2·855 ± 0·003
O(12)	2·691 ± 0·003	O(8)	2·826 ± 0·004
O(1)	2·995 ± 0·003	O(5)	2·936 ± 0·004
O(11)	2·984 ± 0·003	O(4)	3·066 ± 0·003
O(7)	2·666 ± 0·003	O(5)	2·982 ± 0·003
O(14)	3·084 ± 0·003	O(10)	3·122 ± 0·004
O(3)	2·867 ± 0·004	O(1)	2·895 ± 0·003
		O(9)	3·006 ± 0·003

The authors wish to thank Miss Ellen J. Bailey for her valuable assistance, particularly in the exacting job of film reading.

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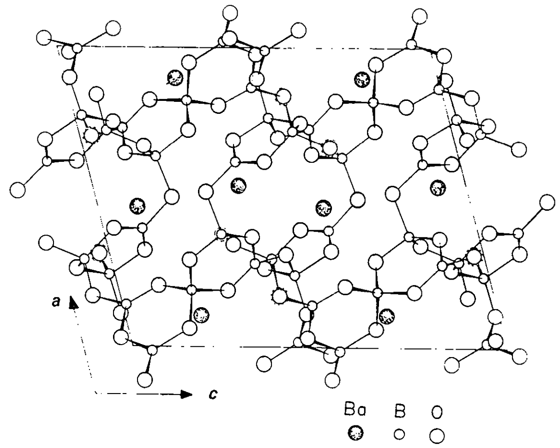

Fig. 2. [010] projection of the $BaO.2B_2O_3$ structure.

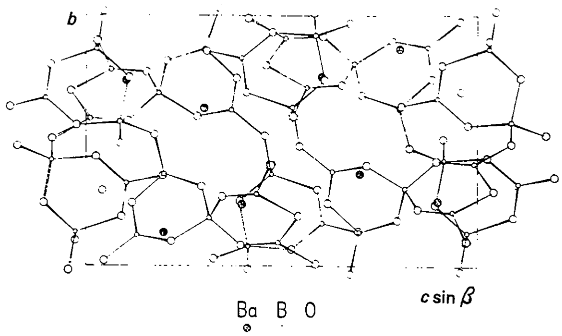

Fig. 3. [100] projection of the $BaO.2B_2O_3$ structure.

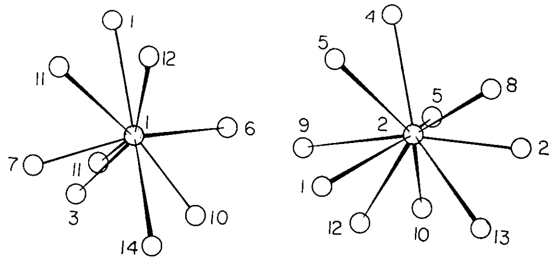

Fig. 4. Nearest neighbor coordination for each type of barium ion.

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* The limits quoted for these average values are average deviations from the mean.