completely unrelated interatomic triangles if the associated triangle is sufficiently large. More precisely, if the associated triangle is large, it is no longer permissible to consider interatomic triangles which are only approximately congruent as belonging to the same set since the deviations from congruence are exaggerated by multiplying by the large magnitudes $|\mathbf{h}_1|$ and $|\mathbf{h}_3|$ of (3.5). Hence the conditions of our hypothesis are not, in this case, approximately fulfilled even though interatomic triangles may be almost congruent.

4. Concluding remarks

The power of the direct methods of phase determination depends on the extent to which *a priori* structural knowledge can be utilized. Thus, the earliest methods employed the positivity of the electron density to yield inequality relationships among the structure factors, while the essential discreteness of the electron density function later led to relationships of equality. Recently (Hauptman, 1964) it was shown how previous knowledge of partial or complete molecular structure could be used. In the present paper we have found new relationships among the structure factors that are valid for structures satisfying our hypothesis. If, in addition, partial or complete knowledge of molecular structure is also available, (3.10) may be employed directly to obtain a first estimate of the structure invariant $V_{\mathbf{h}_1\mathbf{h}_2\mathbf{h}_3}$, since the function $B(z,t)$ has already been tabulated (Hauptman, 1964). Standard techniques may then be used to find the phases themselves. In future publications it will be shown how to exploit other kinds of structural information as aids in phase determination, *e.g.* the tendency for interatomic distances to coincide, the existence of coplanar groupings in the crystal structure, *etc.*

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The Crystal Structure of the High Temperature Form of Barium Borate, $BaO.B_2O_3$

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The crystal structure of the high temperature form of $BaO.B_2O_3$ (m.p. 1095 ± 5°C) was determined by conventional three-dimensional Patterson and electron-density syntheses. The heavy atom technique was used to establish the initial phases. $BaO.B_2O_3$ crystallizes in the trigonal system, space group $R\bar{3}c$, with 18 formula units per hexagonal cell. Unit-cell dimensions, referred to hexagonal axes, are $a=b=7{\cdot}235$, $c=39{\cdot}192$ Å. Least-squares refinement with 498 independent reflections yielded a reliability index of 5·7%, based on the observed data only. The anion in the structure is a nearly planar $[B_3O_6]^{3-}$ group constructed of three BO_3 triangles each of which shares two of the three corners. The structure contains two crystallographically distinct barium atoms located in positions having point symmetries 32 and 3. About the barium in the 32 point symmetry position the oxygens are arranged in a trigonal prism. About the barium which lies in the 3 point symmetry position the oxygen coordination is ninefold.

Introduction

As part of a continuing program aimed at achieving a better understanding of the structural principles of anhydrous borate compounds, the structure of the high temperature form of $BaO.B_2O_3$ was selected for study. Levin & McMurdie (1949) have investigated the BaO–B_2O_3 system and found that $BaO.B_2O_3$ exists as the primary phase in mixtures containing approximately 56 to 78% BaO. They reported that this compound existed in two polymorphic forms, but the inversion temperature was not determined since the transition occurred over a range of 100°C to 400°C. The crystalline high temperature form of $BaO.B_2O_3$ (m.p. 1095 ± 5°C) can be quenched and studied at room temperature. McMurdie & Levin found this crystalline form to be highly birefringent, uniaxial negative, with $N_e=1{\cdot}528$ and $N_o=1{\cdot}667$. Preliminary unit-cell dimensions and possible space groups have been reported by Block, Perloff & Weir (1964), and the infrared spectrum has been investigated by Weir & Schroeder (1964), who suggested the presence of a $[B_3O_6]^{3-}$ ring.

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Experimental

Single crystals of the high-temperature form of BaO. B_2O_3 were prepared from a melt of the proper stoichiometry by heating above the melting point on a hot wire apparatus and cooling slowly. The powder pattern of the crystals used in this study agreed with that reported by Swanson, Morris & Evans (1966) for the high temperature form of BaO.B_2O_3. Accurate unit-cell dimensions were calculated by least-squares refinement of powder pattern data. The crystal data for BaO.B_2O_3 are listed in Table 1. Precession photographs showed the symmetry characteristics of the point group $\bar{3}m$ (D_{3d}). Only reflections of the type $-h+k+l=3n$ were observed (the Miller indices used throughout this article refer to the hexagonal cell) and reflections $h\bar{h}0l$ with odd l were absent. This limited the possible space groups to $R3c$ and $R\bar{3}c$. A piezoelectric test was made and found negative. This observation is consistent with a centric space group which was later confirmed by the final structure determination. The density was measured on a microbalance (Berman, 1939) using toluene as the reference liquid. The observed density requires 18 formula units of BaO.B_2O_3 per unit cell. It was also noted that all reflections with $l=2n+1$ were very weak.

Table 1. *Crystal data for the high-temperature form of* BaO.B_2O_3

Space group $R\bar{3}c$ (no. 167)

Cell dimensions, hexagonal axes

$a=b=7·235$ Å with a standard error of 0·001
$c=39·192$ Å with a standard error of 0·004
$Z=18$

Density observed, 3·74 g.cm^{-3} (mean deviation of 0·05 from four determinations)

Density calculated, 3·751 g.cm^{-3}

Systematic absences for hexagonal cell

hkl: $-h+k+l\neq 3n$
$h\bar{h}l$: $l=2n+1$

μ (linear absorption coefficient, $\lambda=0·7107$) = 102 cm^{-1}.

A crystal of approximate dimensions 0·22 × 0·18 × 0·90 mm was mounted about the a axis. Three-dimensional intensity data were collected on an integrating equi-inclination Weissenberg camera using Zr-filtered molybdenum $K\alpha$ radiation ($\lambda=0·7107$). Eight levels were recorded by taking multiple-film photographs (three films per pack separated by brass foils of 0·020 mm thickness). An interfilm ratio was determined for each level from measured values for common reflections. The majority of the intensity data were read on a densitometer and for each independent reflection two equivalent spots were measured and averaged. Intensities too small for accurate densitometry were estimated visually. Level-to-level scale constants (later refined by least squares) were estimated from equivalent spots and times of exposure. An overall scale constant and a temperature factor were calculated by a non-statistical method (Hyman, 1965) and were within 4% of the final least-squares values. The data were corrected for Lorentz and polarization factors in the usual way.

The linear absorption coefficient of BaO.B_2O_3 is 102 cm^{-1} for molybdenum radiation which causes an appreciable absorption effect with the crystal used. Therefore, for the final refinement, an absorption correction was applied using the method of Albrecht (1939). A total of 498 non-zero independent reflections were recorded and used throughout the structure determination.

Structure determination

On the basis of the negative piezoelectric test the space group was assumed to be $R\bar{3}c$. Since a satisfactory structure was found in this space group, no further consideration was given to the non-centrosymmetric possibility. After collecting intensity data, a three-dimensional Patterson map was calculated. The barium atoms must lie on special positions because the density measurements indicate that there are only 18 barium atoms in a unit cell which has a 36-fold general position. The 18(e) position could be eliminated by the fact that all $l=2n+1$ reflections are very weak relative to those with $l=2n$. Both 18(e) and 18(d) positions were found to be inconsistent with the Patterson map. However, by placing the barium atoms on either position 12(c) ($z=0·35$) and 6(a) or on 12(c) ($z=0·10$) and 6(b), all predicted Ba–Ba vector positions and peak heights were in excellent agreement with the Patterson map. Calculating structure factors (Ba only), with either configuration, gave an $R=17\%$.

Two separate Fourier maps, with the structure factors assigned phases according to each combination of barium atoms, were then calculated. However, a plausible structure from the crystal chemistry point of view was obtained only when the barium atoms were placed at the 12(c) and the 6(a) positions. The approximate positions for the light atoms were easily found from the Fourier synthesis and used as the initial positions for the least-squares refinement.

Table 2. *Final atomic parameters and their estimated standard deviations*

	Position	x/a	$\sigma\times 10^3$	y/b	$\sigma\times 10^3$	z/c	$\sigma\times 10^5$	B	$\sigma\times 10^2$
O(1)	36(f)	0·174	2	0·205	2	0·04000	28	1·22	16
O(2)	36(f)	0·405	2	0·059	2	0·03650	24	1·11	13
B	36(f)	0·967	3	0·178	3	0·03796	47	1·46	26
Ba(1)	12(c)	0		0		0·34983	2	0·89	2
Ba(2)	6(a)	0		0		$\frac{1}{4}$		0·92	2

Table 3. *Final observed and calculated structure factors**

All structure factors have been reduced by a factor of three.

k	ℓ	F_o	F_c
		h=0	
0	6	106	97
0	12	48	-33
0	18	196	-185
0	24	60	47
0	30	134	-136
0	36	66	-76
0	42	101	-112
0	48	77	74
0	54	43	44
0	60	68	74
1	2	114	-113
1	8	117	114
1	20	247	250
1	26	74	72
1	32	96	88
1	38	97	-94
1	50	90	-92
1	62	52	-51
2	4	61	-63
2	10	250	-264
2	16	51	-51
2	22	111	-111
2	28	106	97
2	34	21	29
2	40	133	130
2	52	58	57
2	70	54	-57
3	0	230	249
3	6	63	61
3	12	115	117
3	15	122	-120
3	21	37	-35
3	30	154	-150
3	35	31	-29
3	42	76	-74
3	46	53	48
3	60	71	75
4	2	120	-126
4	8	78	81
4	14	37	40
4	20	185	198
4	26	35	42
4	32	69	61
4	38	84	-73
4	50	77	-78
4	62	53	-46
5	10	188	-197
5	16	54	-60
5	22	59	-65
5	28	85	91
5	40	91	87
5	52	57	55
6	0	155	162
6	6	28	26
6	12	63	65
6	18	68	-68
6	30	111	-113
6	36	25	-33
6	42	64	-52
6	48	53	46
6	60	45	50
7	2	83	-84
7	8	61	61
7	14	39	35
7	20	122	120
7	32	44	44
7	38	52	-42
7	50	61	-62
8	10	83	-85
8	22	67	-66
8	40	74	75
9	0	79	82
9	12	47	50
9	18	35	-39
9	30	83	-72
10	2	31	-38
10	8	39	40
10	20	70	65
11	10	58	-53
12	0	59	48
		h=1	
0	10	333	-315
0	16	94	-86
0	22	115	-108
0	28	115	117
0	40	123	127
0	46	32	30
0	52	65	64
0	58	46	-42
0	70	49	-56
1	0	272	252
1	3	31	-28
1	6	60	52
1	9	42	-37
1	12	175	166
1	18	113	-109
1	21	34	26
1	24	50	-52
1	30	201	-185
1	36	32	-30
1	42	68	-65
1	48	55	55
1	60	64	75
2	2	165	-157
2	5	27	25
2	8	169	160
2	11	42	38
2	14	73	66
2	20	196	186
2	23	25	-23
2	26	23	22
2	32	97	96
2	38	58	-56
2	50	91	-107
2	62	43	-34
3	4	40	-42
3	10	197	-185
3	16	37	-39
3	22	121	-114
3	28	67	75
3	34	36	35
3	40	123	126
3	52	46	45
3	58	37	-35
3	70	51	-51
4	0	220	213
4	3	18	-21
4	6	42	44
4	12	78	78
4	15	22	19
4	18	94	-95
4	24	19	-17
4	30	122	-127
4	36	27	-35
4	42	70	-65
4	48	54	49
4	60	51	62
5	2	56	-63
5	8	79	85
5	11	35	33
5	20	135	135
5	26	44	41
5	32	72	70
5	38	59	-59
5	44	24	-22
5	50	65	-73
6	4	33	-29
6	10	137	-134
6	16	27	-28
6	22	60	-63
6	28	57	56
6	40	80	85
6	52	40	38
6	70	33	-39
7	0	107	112
7	6	35	28
7	12	56	64
7	18	55	-59
7	24	22	-24
7	30	80	-86
7	42	44	-43
7	60	50	49
8	2	54	-53
8	8	53	55
8	20	75	82
8	32	47	44
8	38	36	-32
8	50	50	-53
9	10	75	-83
9	22	35	-35
9	28	40	38
9	40	52	50
10	0	65	69
10	12	25	31
10	30	53	-52
11	20	54	52
12	10	46	-42
		h=2	
0	2	135	-147
0	8	147	153
0	14	54	51
0	20	208	206
0	26	41	36
0	32	107	98
0	38	67	-66
0	50	98	-107
1	1	41	42
1	4	85	-85
1	7	41	37
1	10	221	-228
1	13	33	-28
1	16	18	-23
1	19	35	-32
1	22	112	-113
1	28	83	74
1	34	27	31
1	40	135	138
1	52	52	47
1	58	38	-39
2	0	173	183
2	3	23	22
2	6	40	42
2	9	26	24
2	12	153	150
2	18	92	-90
2	24	56	-56
2	30	163	-165
2	42	62	-55
2	48	52	44
2	60	64	72
3	2	92	-96
3	8	107	110
3	14	28	31
3	20	150	157
3	26	33	35
3	32	78	82
3	38	62	-58
3	50	84	-89
4	4	42	-43
4	10	167	-172
4	16	37	-29
4	22	72	-70
4	28	67	65
4	40	107	100
4	52	46	44
5	0	135	138
5	6	29	29
5	12	78	82
5	18	67	-64
5	30	108	-113
5	42	49	-43
5	60	57	54
6	2	71	-67
6	8	65	67
6	14	30	26
6	20	103	105
6	32	53	53
6	50	64	-66
7	4	36	-28
7	10	105	-102
7	22	55	-47
7	28	49	40
7	40	66	68
8	0	86	86
8	12	46	45
8	18	49	-43
8	30	66	-67
9	2	34	-33
9	20	70	65
10	10	63	-60
		h=3	
0	6	48	46
0	12	118	119
0	18	106	-109
0	24	34	-38
0	30	157	-157
0	42	77	-69
0	48	37	46
0	60	68	77
1	2	139	-146
1	8	98	104
1	14	66	60
1	20	197	194
1	26	32	26
1	32	80	71
1	38	69	-59
1	50	85	-93
2	4	45	-44
2	10	197	-198
2	16	39	-39
2	22	85	-82
2	28	81	78
2	40	105	108
2	52	44	50
3	0	158	163
3	6	37	35
3	12	96	97
3	18	80	-78
3	24	37	-33
3	30	126	-128
3	42	54	-52
3	60	51	61
4	2	99	-100
4	8	72	69
4	14	55	44
4	20	138	140
4	32	53	50
4	38	45	-44
4	50	77	-73
5	4	32	-30
5	10	119	-117
5	16	25	-20
5	22	69	-66
5	28	40	46
5	40	84	86
6	0	100	101
6	12	61	61
6	18	43	-44
6	30	97	-91
6	60	41	42
7	2	42	-46
7	8	38	43
7	20	89	84
8	10	70	-71
9	0	66	62
		h=4	
0	4	26	-24
0	10	172	-180
0	16	47	-46
0	22	106	-108
0	28	83	76
0	34	34	35
0	40	120	120
0	52	34	42
0	58	44	-35
0	70	38	-48
1	3	15	15
1	6	41	39
1	9	17	-17
1	12	73	76
1	18	91	-91
1	30	126	-129
1	36	36	-37
1	42	71	-65
1	48	54	51
1	60	54	61
2	2	80	-84
2	8	92	97
2	14	24	28
2	20	135	138
2	26	29	31
2	32	71	72
2	38	55	-53
2	50	82	-79
3	4	28	-28
3	10	120	-123
3	16	32	-26
3	22	85	-86
3	28	57	53
3	34	33	31
3	40	106	99
3	52	37	32
4	0	130	133
4	6	31	29
4	12	65	63
4	18	66	-65
4	24	31	-21
4	30	87	-93
4	42	56	-48
4	48	42	31
4	60	49	53
5	2	60	-59
5	8	61	60
5	20	95	96
5	32	51	47
5	50	58	-60
6	10	98	-98
6	22	45	-40
6	28	50	45
6	40	65	57
7	0	84	89
7	12	41	31
7	18	50	-42
7	30	59	-57
7	36	27	-18
7	42	40	-35
7	60	36	34
8	2	38	-39
8	20	59	61
9	10	52	-52
10	0	37	42
		h=5	
0	2	55	-62
0	8	71	76
0	20	158	159
0	26	56	57
0	32	70	69
0	38	76	-75
0	50	75	-68
0	62	33	-41
1	4	24	-28
1	10	176	-180
1	13	29	-29
1	16	40	-43
1	22	64	-57
1	28	73	77
1	40	92	84
1	52	54	52
2	6	29	30
2	9	19	-15
2	12	76	80
2	18	65	-66
2	24	32	-26
2	30	112	-111
2	42	47	-47
2	48	35	38
3	2	68	-74
3	8	64	68
3	14	31	29
3	20	113	112
3	32	48	53
3	38	39	-42
3	50	64	-64
4	4	28	-26
4	10	108	-109
4	16	26	-21
4	22	53	-50
4	28	49	45
4	40	72	70
4	46	24	17
5	0	97	95
5	6	22	20
5	12	52	48
5	18	49	-44
5	30	75	-75
6	2	37	-40
6	8	34	40
6	20	67	72
6	50	47	-42
7	10	58	-62
7	40	55	47
8	0	52	49
8	12	40	35
9	20	44	38
		h=6	
0	6	38	38
0	12	69	70
0	18	77	-76
0	30	115	-108
0	42	62	-52
0	48	39	40
0	60	53	54
1	2	72	-72
1	8	71	72
1	14	28	25
1	20	117	120
1	32	58	57
1	38	48	-46
1	50	69	-68
2	4	28	-28
2	10	114	-118
2	16	18	-24
2	22	58	-58
2	28	51	51
2	40	76	77
2	52	33	35
3	6	25	27
3	12	61	62
3	18	53	-53
3	30	87	-84
3	42	39	-37
3	60	37	44
4	2	35	-41
4	8	44	46
4	20	80	83
4	32	42	42
4	38	35	-39
4	50	50	-46
5	10	81	-80
5	22	32	-37
5	28	41	36
5	40	52	52
6	0	61	62
6	12	44	40
6	30	57	-57
7	2	32	-29
7	8	28	32
7	20	48	48
8	10	47	-44
9	0	40	39
		h=7	
0	4	29	-27
0	10	109	-106
0	16	16	-19
0	22	72	-74
0	28	43	42
0	40	83	91
1	6	19	21
1	12	59	63
1	18	54	-52
1	30	92	-91
1	42	38	-39
1	60	52	48
2	2	52	-55
2	8	60	60
2	20	84	86
2	32	49	47
2	50	58	-58
3	10	94	-89
3	16	32	-23
3	22	42	-43
3	28	40	42
3	40	52	57
4	18	42	-43
4	30	54	-56
4	60	37	34
5	2	43	-40
5	8	36	36
5	20	60	61
5	50	46	-40
6	10	49	-56
6	40	49	40
7	0	57	49
7	30	40	-37
8	20	40	38

* The 740 reflection was inadvertently omitted from the table. It has the values $F_o=84$ and $F_c=89$.

Least-squares refinement

Positional parameters, individual isotropic temperature factors, and individual level scale factors were refined with a modified version of the full-matrix least-squares program of Busing, Martin & Levy (1962). The program minimizes the quantity $R' = w(F_o - F_c)^2$. The Hughes (1941) weighting scheme was used. Unit weights were applied to reflections with $F_o \leq 99$ (as listed in Table 3), and a weight of $99/F_o$ for reflections with $F_o > 99$. The scattering factors used were oxygen (O^-) and neutral boron (*International Tables for X-ray Crystallography*, 1962*a*) and barium (Ba^{2+}) (Thomas & Umeda, 1957) corrected for dispersion (*International Tables for X-ray Crystallography*, 1962*b*).

The final reliability index ($R = \Sigma \, ||F_o| - |F_c|| / \Sigma \, |F_o|$ for the 498 observed reflections was 5·7%. All final shifts were less than 1/40 of the standard deviations. The final least-squares results for the atomic parameters of the five atoms in the asymmetric unit are given in Table 2 and the final list of observed and calculated structure factors are listed in Table 3. After refinement was complete, a three-dimensional difference Fourier synthesis, based on the parameters reported in Table 2, showed no significant maxima or minima. Structure factors were calculated for all the unobserved reflections and none corresponded to a value above the barely visible region on the film.

The structure was also refined with the use of F_o's which were not corrected for absorption. In this case the reliability index was 11·5%. In comparing these atomic parameters with those resulting from refinement on F_o's in which the absorption correction was applied, it was observed that while the oxygen and barium parameters were within one standard deviation of each other, the boron parameters differed by two standard deviations.

All computer computations on this structure were done with the X-ray 63 system of programs developed at the University of Maryland (1964) and the University of Washington.

Structure description

The anion in the structure is a nearly planar $[B_3O_6]^{3-}$ group constructed of three BO_3 triangles with two of the three corners shared (Fig. 1). The discrete anions are perpendicular to the threefold axis which passes through the center of the ring. Fig. 2 is a schematic three-dimensional view of the unit cell, and Fig. 3 shows in greater detail the atomic arrangement in two adjacent sections. The parallel arrangement of the planes of $[B_3O_6]^{3-}$ rings perpendicular to the *c* axis is consistent with the optical data given in the introduction. The oxygen coordination about the two types of barium atom is shown in Fig. 4. About barium (2) which lies in a position having point symmetry 32 the O(2)'s are arranged in a trigonal prism. About barium (1) which lies in a position having point symmetry 3 the coordination is ninefold with 6 oxygen atoms of the O(2) and 3 oxygen atoms of the O(1) type. All distances and angles fall within the expected range (*International Tables for X-ray Crystallography*, 1962*c*).

The anion ring found confirms the prediction of Weir & Schroeder (1964), on the basis of infrared spectra, that the $[B_3O_6]^{3-}$ ring may constitute the anion in the high temperature form of $BaO.B_2O_3$. A similar anion has been found in the structure of the isomorphous pair; sodium metaborate (Fang, 1938; Marezio, Plettinger & Zachariasen, 1963) and potassium metaborate (Zachariasen, 1937).

In Table 4 and Fig. 2, it will be noted that the B–O(2) distance which is out of the ring is appreciably shorter than the B–O(1) distance in the ring. This is consistent with Zachariasen's observations of bond strength *vs.* bond lengths (Zachariasen, 1963), since the ring oxygen

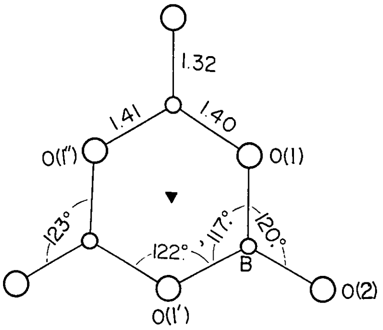

Fig. 1. The $[B_3O_6]^{3-}$ anion ring. The large circles represent oxygen atoms and the small circles boron atoms. Distances are in Å.

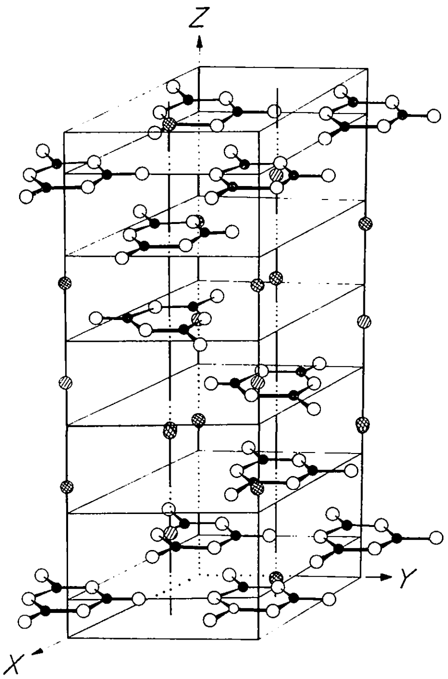

Fig. 2. Three-dimensional view of the contents of the unit cell. The cell is shown from $z=0$ to $z=\frac{1}{2}$, and a few atoms have been omitted for clarity.

is coordinated to Ba(1) as well as to two boron atoms. The shorter B–O (non-ring) distance relative to the B–O (ring) distance has been found in both the sodium (Marezio, Plettinger & Zachariasen, 1963) and potassium (Zachariasen, 1937) metaborates.

Table 4. *Interatomic distances and bond angles*

The e.s.d. on each of the B–O and the O–O distances is 0·02 Å, on the B–B is 0·03 Å, and on the Ba–O is 0·01 Å. The e.s.d. on each of the bond angles is 2°.

$(B_3O_6)^{3-}$ distances		$(B_3O_6)^{3-}$ angles	
B——O(1)	1·41 Å	B——O(1′)-B	122°
B——O(1′)	1·40	O(1′)-B——O(1)	117
B——O(2)	1·32	O(2) -B——O(1′)	123
B——B	2·46	O(2) -B——O(1)	120
O(1) -O(1′)	2·40	Barium–oxygen distances	
O(1) -O(2)	2·37	Ba(1)–O(1)	3·08 Å
O(1′)-O(2)	2·38	Ba(1)–O(2)	2·84
		Ba(1)–O(2′)	2·73
		Ba(2)–O(2)	2·67

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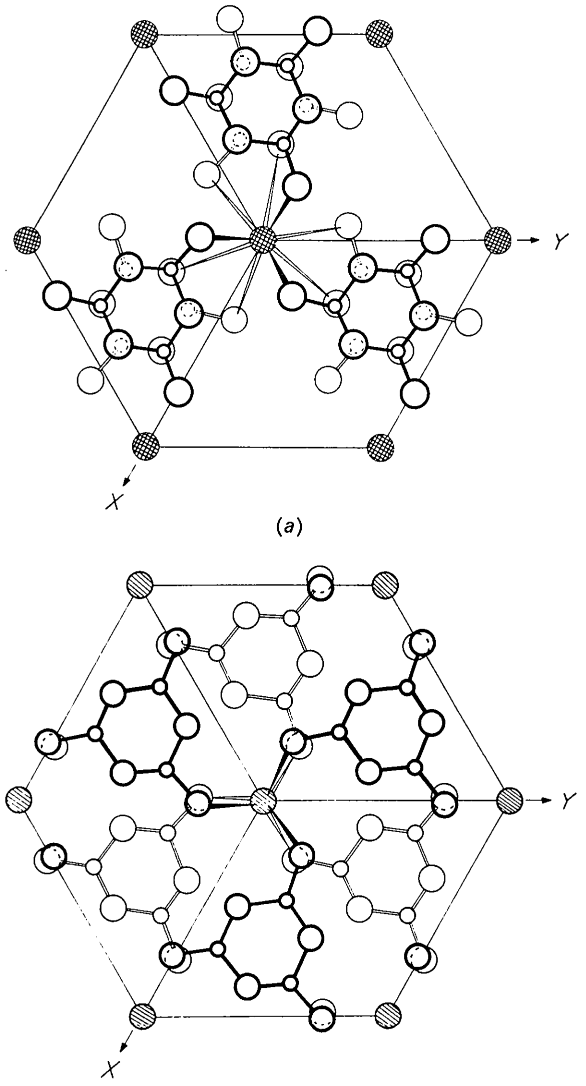

(*a*)

(*b*)

Fig. 3. Adjacent portions of the structure projected down the *c* axis to illustrate the packing of the $[B_3O_6]^{3-}$ anions and the coordination about the barium ions. The large open circles represent oxygen, and small open circles boron atoms. (*a*) Section between $z=0{\cdot}13$ $z=0{\cdot}20$ containing Ba(1). The large cross-hatched circles represent Ba(1). (*b*) Section between $z=0{\cdot}20$ and $z=0{\cdot}30$ containing Ba(2). The parallel-hatched circles represent Ba(2).

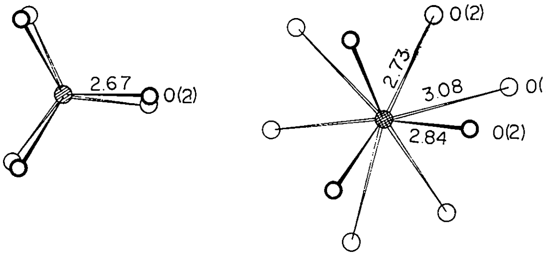

Fig. 4. Oxygen coordination to the Ba(1) and the Ba(2) atoms. The cross-hatched circles represent Ba(1), parallel-hatched circles Ba(2) and the open circles are oxygen. Only the independent interatomic distances are shown.