The Crystal Structure of the High Pressure Phase CaB$_2$O$_4$(III)

By M. Marezio,* J. P. Remeika and P. D. Dernier

Bell Telephone Laboratories, Incorporated, Murray Hill, New Jersey, U.S.A.

Calcium metaborate can crystallize with four different structures by varying the pressure at which the synthesis is carried out. Single crystals of CaB$_2$O$_4$(III) were grown at 20 kbar and 900°. They were orthorhombic with $a = 11\cdot380 \pm 0\cdot002$, $b = 6\cdot382 \pm 0\cdot002$, $c = 11\cdot304 \pm 0\cdot002$ Å, $Z = 12$, $d_c = 3\cdot052$ g.cm^{-3}, space group symmetry *Pna*2$_1$, and all atoms in general positions. The structure of CaB$_2$O$_4$(III) has been solved by three-dimensional Patterson and Fourier syntheses. The positional and anisotropic thermal parameters have been refined by the least-squares method based on 2118 structure factors. The final conventional R index is 0·039. The structure contains units [B$_6$O$_{12}$]$^{-6}$ consisting of four boron–oxygen tetrahedra and two boron–oxygen triangles. These units are linked together to form a three-dimensional network. The mean bond distances are B–4O = 1·480 Å and B–3O = 1·373 Å. There are three types of calcium atoms. Ca(1) and Ca(2) are each surrounded by an 8-oxygen polyhedron, Ca(3) is surrounded by a 10-oxygen polyhedron. The average Ca–O distances are Ca(1)–O = 2·530 Å, Ca(2)–O = 2·443 Å and Ca(3)–O = 2·638 Å.

Introduction

In oxide compounds the boron atom can have two kinds of coordination, triangular or tetrahedral. From the point of view of the coordination one can distinguish three kinds of boron oxide compounds: one in which the boron atom has only triangular coordination, a second kind in which it has only tetrahedral coordination, and a third kind in which the boron atom has both types of coordination. Until recently, metaboric acid was the only boron oxide compound known to crystallize with three different structures, one of each kind. α-HBO$_2$ is orthorhombic with all boron atoms triangularly coordinated (Peters & Milberg, 1964). The β form is monoclinic and two thirds of the boron atoms have coordination number 3, while one third have coordination number 4 (Zachariasen, 1963*a*). The γ form is cubic and in this structure the boron atoms have coordination number 4 only (Zachariasen, 1963*b*) The density values and the structural arrangement of these three forms seem to indicate that β-HBO$_2$ and γ-HBO$_2$ are high pressure phases.

During our study of the behavior of LiMO$_2$ compounds (with M=B, Al, Ga, In, Tl) under high pressure, (Marezio & Remeika, 1966) we found a new high pressure phase of LiBO$_2$. At atmospheric pressure this compound crystallizes with a monoclinic structure in which the lithium and the boron atoms have coordination number 5 and 3 respectively (Zachariasen, 1964). The high pressure phase is tetragonal with both cations having coordination number 4. By analogy with the polymorphism of HBO$_2$ we predicted that a third phase of LiBO$_2$ could exist, namely one in which the boron atoms would have coordination number 3 and 4.

Chang & Margrave (1967) have reported that at 15 kbar and 230°C the monoclinic phase of LiBO$_2$ transforms to a phase which is different from the tetragonal high pressure phase. The above authors have not determined the crystal structure of the new phase, but by infrared spectroscopy they have been able to see that the coordination of the boron atoms is indeed 3 and 4. Also B$_2$O$_3$ and CaB$_2$O$_4$ have been reported to crystallize with two structures. B$_2$O$_3$(I), which is stable at low pressure, is trigonal with the boron atoms triangularly coordinated (Gurr, Montgomery, Knutson & Gorres, 1967). B$_2$O$_3$(II), which is stable at high pressure, is orthorhombic with the boron atoms tetrahedrally coordinated (Prewitt & Shannon, 1968).

At atmospheric pressure CaB$_2$O$_4$ is known to crystallize with an orthorhombic structure in which all boron atoms are triangularly coordinated and the calcium atoms are each surrounded by an 8-oxygen polyhedron (Marezio, Plettinger & Zachariasen, 1963). In addition, CaB$_2$O$_4$ can crystallize with a second orthorhombic structure, which has been recently solved by Zachariasen (1967). It has one half of the boron atoms triangularly coordinated and the other half tetrahedrally coordinated. The calcium atoms are still eightfold coordinated (Zachariasen, 1968). The density values of these two phases and the coordination of the boron atoms seem to indicate that the second orthorhombic phase is a high pressure phase. Furthermore, one can speculate that at least one more phase for CaB$_2$O$_4$ could exist at higher pressure, namely the one in which all the boron atoms would be tetrahedrally coordinated. We have found that CaB$_2$O$_4$ can crystallize with two more structures at higher pressures.

It is the object of this paper to report the synthesis, the crystal growth, and the structure of CaB$_2$O$_4$(III). The data for CaB$_2$O$_4$(IV) are reported in the following paper along with a discussion of the crystal chemistry

---

* Present address: Laboratorie d'Electrostatique et de Physique du Métal, CNRS, CEDEX 166, Grenoble, France.

of the polymorphism of CaB_2O_4. In these papers the four phases of CaB_2O_4 will be called I,II,III, and IV.

Crystal growth

The starting material for all high pressure experiments was CaB_2O_4(I) formed by fusion of a equimolar mixture of high purity B_2O_3 and $CaCO_3$. Comparison of observed and reported d-spacings confirmed that the low-pressure phase of CaB_2O_4 had indeed been formed.

The high pressure apparatus used was the same as has been previously described (Marezio, Remeika & Dernier, 1966). The temperature was monitored with a Pt/Pt–Rh(10%) thermocouple during each run. No correction was made for the effect of pressure on the thermocouple. For most runs the temperature fluctuation was less than $\pm 20\,^\circ$C at constant pressure. A platinum cylindrical cell was used as a container for each high pressure run.

The high pressure phase CaB_2O_4(III) was first prepared in polycrystalline form by direct application of temperature and pressure on CaB_2O_4(I). A temperature of $900\,^\circ$C and a pressure of 20 kbar for one hour was sufficient to produce the desired phase change. In this experiment the quench rate was not critical. X-ray powder photographs of the quenched material showed that CaB_2O_4(III) had been retained metastably. This new phase could be reconverted to the low pressure phase by annealing overnight at $750\,^\circ$C in air. The powder photographs of the annealed CaB_2O_4 and of the starting material were identical.

Two different methods were used to grow single crystals of the high pressure phase CaB_2O_4(III). In one method powdered CaB_2O_4(I) was mixed with LiCl as a flux in a mole weight ratio of $10:1::CaB_2O_4:LiCl$. After one hour at 20 kbar and $1000\,^\circ$C, the sample was allowed to cool to room temperature at a rate of $30\,^\circ$/min. Then the pressure was released at a rate of approximately 2 kbar/min. The platinum cell was broken open and immersed in pure ethanol. Small, transparent crystals were slowly extracted from the LiCl flux. In the second method of obtaining crystals, the conditions were essentially the same except distilled water replaced the LiCl as solvent. These crystals were on the average twice the size of the first batch. Some of the very small crystals had a prismatic habit, but in general the morphology was quite irregular and poor. X-ray powder photographs of these crystals were identical to those of the polycrystalline CaB_2O_4(III). A piezoelectric test was made on these crystals with a sensitive Giebe–Scheibe apparatus, and was negative.

Crystal data

The symmetry, the space group and the approximate lattice parameters were determined from precession photographs taken with Mo $K\alpha$. CaB_2O_4(III) was found to be orthorhombic with twelve molecules per unit cell. The systematic absences are: $k+l=2n+1$ for

$0kl$ and $h=2n+1$ for $h0l$. These absences correspond to two space groups $Pna2_1$ and $Pnam$. Analysis of the Patterson function (see *Solution of the structure*) clearly indicated that the correct choice of space group is $Pna2_1$. All atoms are in the general positions $(x,y,z; \bar{x},\bar{y},\frac{1}{2}+z; \frac{1}{2}-x,\frac{1}{2}+y,\frac{1}{2}+z; \frac{1}{2}+x,\frac{1}{2}-y,z)$. In this structure there are three types of calcium atoms, six types of boron atoms and twelve types of oxygen atoms. By the use of lattice parameters as determined from the precession photographs, a powder pattern, taken with a Norelco camera of 114·6 cm in diameter and Cr $K\alpha$ radiation, was indexed. Precise lattice parameters were obtained by accurate measurements of the 2θ values for 12 reflections in the back reflection region. The least-squares refinement program of Mueller, Heaton & Miller (1960) was used. The final values are $a=11\cdot380\pm0\cdot002$, $b=6\cdot307\pm0\cdot002$ and $c=11\cdot304\pm 0\cdot002$ Å. A comparison of observed and calculated interplanar spacings is given in Table 1. The calculated X-ray density is $3\cdot052$ g.cm^{-3}. The density increase corresponding to the transition CaB_2O_4(I) $\rightarrow CaB_2O_4$ (III) is about 12%, whereas the one corresponding to the transition CaB_2O_4(II) $\rightarrow CaB_2O_4$(III) is about 5%.

Table 1. *Powder pattern of* CaB_2O_4 (III)

hkl	d_o	d_c	I
011	5·532	5·557	w
211	3·963	3·976	m
212	3·385	3·395	m
013	3·238	3·245	vvw
020	3·180	3·191	vvw
311	3·120	3·133	m
120	3·066	3·072	m
121	2·955	2·965	m
400	2·838	2·845	m
004	2·818	2·826	s
401	2·751	2·759	m
221	2·697	2·702	ms
122		2·699	
402		2·541	
204	2·531	2·532	m
114		2·531	
313	2·463	2·466	w
321	2·382	2·387	w
412	2·358	2·361	w
322	2·238	2·242	w
510	2·140	2·144	m
130	2·090	2·091	m
031		2·091	
124	2·077	2·080	m
131	2·054	2·056	w
215	1·993	1·996	m
231	1·962	1·962	m
414	1·911	1·913	m
315	1·854	1·858	m
520		1·853	
331	1·830	1·831	w
125	1·817	1·821	w
610		1·818	
611	1·794	1·795	w
116	1·783	1·785	w
415	1·704	1·706	w
424	1·695	1·698	w
134	1·680	1·681	wm
325	1·658	1·659	wm
524	1·548	1·549	m

Table 1 (cont.)

hkl	d_o	d_c	I
235	1·492	1·494	w
721	1·434	{ 1·437	w
335		1·434	
342	1·422	1·423	w
615	1·415	{ 1·417	w
516		1·415	
440	1·390	1·392	wm
208	1·370	1·371	wm
442	1·350	{ 1·351	wm
244		1·350	
517	1·289	1·290	w
731	1·283	1·283	w
804	1·270	1·271	w
444	1·248	1·248	w
814	1·246	{ 1·246	w
250		1·245	
911	1·232	{ 1·233	wm
019		1·232	
046	1·217	1·218	wm
153	1·202	1·202	wm
830	1·183	1·183	w
450	1·165	1·165	w
346	1·159	1·159	wm
922	1·151	1·151	w

Experimental

The intensity measurements were made with a General Electric automatic diffractometer, using Zr-filtered Mo K radiation and a scintillation counter. The specimen was a crystal with a prismatic habit which was oriented with the [010] zone axis parallel to the φ axis of the goniostat. The dimensions of the prism were $0·08 \times 0·17 \times 0·36$ mm. The integrated intensities were obtained with the stationary-crystal stationary-counter technique, with a single filter. The take-off angle was $8°$. The background was measured on each side of the peak at $2°$ off the peak itself and the average was subtracted from the peak-height. All reflections included within an octant in reciprocal space having $2\theta \leq 90°$ were measured. The total number of independent reflections measured was 3439. Those reflections for which the peak-height was not at least twice as much as the background were regarded as unobserved. This criterion gave 2175 observed reflections and 1264 unobserved. The integrated intensities were converted to structure factors using a computer program written by

Table 2. *Comparison of observed and calculated structure factors*

Table 2 (cont.)

Prewitt (1966a). No absorption correction was applied since the dimensions of the crystal were such that the absorption effect was negligible.

Solution of the structure

The first step toward the solution of the structure was based on calculating a three-dimensional Patterson synthesis which was carried out by using the program 'Four' written by Fritchie (1967) and modified by L. Guggenberger & P. B. Jamieson. The squares of the 2175 observed structure factors on an arbitrary scale were the input terms. From the concentration of vectors of the sections $xy\frac{1}{2}, x\frac{1}{2}z$ and $\frac{1}{2}yz$ it was readily seen that the correct space group was the noncentrosymmetric one, namely $Pna2_1$. All major peaks in the Patterson synthesis could be explained by placing Ca(1) at 0·07,0·05,0·00; Ca(2) at 0·03,0·66,0·24; and Ca(3) at 0·25,0·11,0·28. Structure factors based on these coordinates, assuming isotropic temperature factors of 0·4 Å² correspond to $R = \Sigma\,||F_o| - |F_c||/\,\Sigma\,|F_o| = 0\cdot47$ which reduced to 0·30 after three cycles of refinement

with the least-squares program ORFLS (Busing, Martin & Levy, 1962). The f-curves for neutral Ca and later O and B given by Cromer & Waber (1965) were used. A three-dimensional Fourier synthesis, computed with the signs of three calcium atoms, gave the positions of the 12 oxygen and 6 boron atoms. After a preliminary check that the structural arrangement was reasonable from the crystal chemistry point of view, this structure was refined with the least-squares program written by Prewitt (1966b). In the first cycle isotropic temperature factors were assumed. All observed structure factors were weighted equally, with the exception of those reflections whose $\sin\theta/\lambda < 0\cdot25$. Because of the high background errors for these reflections, zero weight was assigned to the corresponding structure factors. Several cycles gave complete refinement, with $R = 0\cdot054$. In the final refinement the temperature factors of all atoms were allowed to vary anisotropically. Convergence was achieved after two cycles with $R = 0\cdot039$. The final observed and calculated structure factors are given in Table 2. Note that the reflections which were assigned zero weight are listed at the end of

Table 2 (cont.)

the Table. The positional and thermal parameters are given in Tables 3 and 4 respectively.

Table 3. Final positional parameters

	x	y	z
Ca(1)	0·07351 (7)	0·05043 (12)	(0)
Ca(2)	0·03257 (6)	0·65995 (12)	0·23386 (10)
Ca(3)	0·25309 (7)	0·11288 (13)	0·27955 (10)
B(1)	0·1401 (3)	0·2529 (6)	0·5390 (4)
B(2)	0·2510 (4)	0·4193 (6)	0·0515 (4)
B(3)	0·2131 (3)	0·1191 (6)	0·7403 (4)
B(4)	0·3222 (3)	0·1006 (6)	0·9442 (4)
B(5)	0·4658 (4)	0·0183 (6)	0·4800 (4)
B(6)	0·4748 (3)	0·3758 (6)	0·2477 (4)
O(1)	0·2657 (2)	0·1944 (4)	0·0459 (3)
O(2)	0·2171 (2)	0·4704 (4)	0·1734 (3)
O(3)	0·0717 (3)	0·0297 (5)	0·2009 (3)
O(4)	0·4547 (3)	0·1715 (5)	0·2567 (3)
O(5)	0·2009 (2)	0·3750 (4)	0·4486 (3)
O(6)	0·1456 (2)	0·0322 (4)	0·5116 (3)
O(7)	0·0061 (2)	0·3009 (4)	0·5305 (3)
O(8)	0·1734 (2)	0·2946 (4)	0·6635 (3)
O(9)	0·1069 (3)	0·0220 (5)	0·7981 (3)
O(10)	0·2870 (2)	0·2046 (4)	0·8336 (3)
O(11)	0·4563 (2)	0·1370 (4)	0·9458 (3)
O(12)	0·1504 (2)	0·4768 (4)	0·9668 (3)

Table 4. Anisotropic thermal parameters

	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
	\($\times 10^5$\)					
Ca(1)	138 (4)	473 (12)	99 (3)	−48 (6)	−1 (4)	19 (7)
Ca(2)	99 (3)	397 (11)	93 (3)	−16 (5)	−18 (3)	14 (6)
Ca(3)	80 (3)	489 (12)	194 (4)	−1 (6)	−24 (4)	−29 (7)
	\($\times 10^4$\)					
B(1)	7 (2)	30 (6)	10 (2)	2 (3)	−1 (2)	3 (3)
B(2)	9 (2)	30 (6)	9 (2)	1 (3)	−4 (2)	2 (3)
B(3)	10 (2)	33 (6)	9 (2)	1 (3)	0 (2)	−2 (3)
B(4)	8 (2)	23 (5)	8 (2)	0 (3)	−2 (1)	2 (3)
B(5)	10 (2)	27 (6)	13 (2)	0 (3)	1 (2)	−1 (3)
B(6)	11 (2)	37 (6)	12 (2)	2 (3)	2 (2)	0 (3)
O(1)	14 (1)	24 (4)	11 (1)	−1 (2)	4 (1)	1 (2)
O(2)	12 (1)	34 (5)	15 (2)	−5 (2)	5 (1)	−10 (2)
O(3)	10 (1)	56 (5)	15 (1)	1 (2)	0 (1)	−4 (2)
O(4)	18 (2)	36 (5)	35 (2)	−1 (2)	−1 (1)	2 (2)
O(5)	9 (1)	26 (4)	15 (1)	1 (2)	3 (1)	3 (2)
O(6)	10 (1)	17 (4)	12 (1)	4 (2)	−1 (1)	2 (2)
O(7)	8 (1)	38 (4)	14 (1)	5 (2)	0 (1)	3 (2)
O(8)	16 (1)	30 (4)	11 (1)	2 (2)	−2 (1)	1 (2)
O(9)	16 (1)	67 (5)	15 (2)	−15 (2)	0 (1)	−3 (2)
O(10)	8 (1)	30 (4)	9 (1)	−2 (2)	−2 (1)	0 (2)
O(11)	7 (1)	33 (5)	15 (1)	1 (2)	−1 (1)	6 (2)
O(12)	6 (1)	75 (6)	17 (2)	10 (2)	−2 (1)	7 (2)

Table 5. *Interatomic distances* (Å)*

B(1) – Tetrahedron

B(1)–O(5)	1·460 (5)	O(5)–O(6)	2·385 (4)
–O(6)	1·444 (5)	O(5)–O(7)	2·448 (4)
–O(7)	1·558 (5)	O(5)–O(8)	2·502 (4)
–O(8)	1·481 (5)	O(6)–O(7)	2·346 (4)
Average	1·486	O(6)–O(8)	2·419 (4)
		O(7)–O(8)	2·426 (4)

B(2) – Tetrahedron

B(2)–O(1)	1·446 (5)	O(1)–O(2)	2·342 (4)
–O(2)	1·468 (5)	O(1)–O(6)	2·412 (4)
–O(6)	1·451 (5)	O(1)–O(12)	2·474 (4)
–O(12)	1·537 (5)	O(2)–O(6)	2·438 (4)
Average	1·476	O(2)–O(12)	2·456 (4)
		O(6)–O(12)	2·403 (4)

B(3) – Tetrahedron

B(3)–O(2)	1·451 (5)	O(2)–O(8)	2·418 (4)
–O(8)	1·487 (5)	O(2)–O(9)	2·472 (4)
–O(9)	1·507 (5)	O(2)–O(10)	2·349 (4)
–O(10)	1·456 (5)	O(8)–O(9)	2·432 (4)
Average	1·475	O(8)–O(10)	2·388 (4)
		O(9)–O(10)	2·391 (4)

B(4) – Tetrahedron

B(4)–O(1)	1·447 (5)	O(1)—O(5)	2·347 (4)
–O(5)	1·465 (5)	O(1)—O(10)	2·413 (4)
–O(10)	1·471 (5)	O(1)—O(11)	2·474 (4)
–O(11)	1·544 (4)	O(5)—O(10)	2·477 (4)
Average	1·482	O(5)—O(11)	2·449 (4)
		O(10)–O(11)	2·347 (4)

B(5) – Triangle

B(5)–O(7)	1·366 (5)	O(7)—O(11)	2·388 (4)
–O(11)	1·385 (5)	O(7)—O(12)	2·388 (4)
–O(12)	1·357 (5)	O(11)–O(12)	2·337 (4)
Average	1·369		

B(6) – Triangle

B(6)–O(3)	1·364 (5)	O(3)–O(4)	2·410 (4)
–O(4)	1·328 (5)	O(3)–O(9)	2·335 (4)
–O(9)	1·436 (5)	O(4)–O(9)	2·391 (5)
Average	1·376		

Ca(1) – Polyhedron / Ca(2) – Polyhedron

Ca(1)–O(1)	2·428 (3)	Ca(2)–O(2)	2·518 (3)
–O(3)	2·275 (3)†	–O(3)	2·430 (3)
–O(5)	2·860 (3)	–O(4)	2·308 (3)
–O(6)	2·552 (3)	–O(7)	2·354 (3)
–O(7)	2·443 (3)	–O(8)	2·492 (3)
–O(9)	2·321 (3)†	–O(9)	2·677 (3)
–O(11)	2·476 (3)	–O(10)	2·360 (3)
–O(12)	2·883 (3)	–O(11)	2·430 (3)
Average	2·530	Average	2·443

Ca(3) – Polyhedron

Ca(3)–O(1)	2·696 (3)
–O(2)	2·611 (3)
–O(3)	2·309 (3)
–O(4)	2·339 (3)
–O(5)	2·609 (3)
–O(6)	2·940 (3)
–O(8)	2·559 (3)
–O(9)	3·066 (3)
–O(10)	2·715 (3)
–O(12)	2·538 (3)
Average	2·638

* These interatomic distances and their standard deviations were obtained with the Busing, Martin & Levy program *ORFFE* (1964). The standard deviations reflect the use of unit weights in the least-squares refinement of the structure.

† These two standard deviations do not include the uncertainty due to the anomalous dispersion (for explanation see the corresponding paragraph).

Anomalous dispersion

In all the refinements previously described the real and imaginary anomalous dispersion corrections were not applied to the Ca f-curve. This was done because of the small values of $\Delta f'$ (0·20) and $\Delta f''$ (0·36) for Ca with Mo radiation (Cromer, 1965). In order to determine what effect this omission would have on the positional and thermal parameters, additional refinements were made in which the real and imaginary anomalous dispersion corrections were applied to the f-curve of
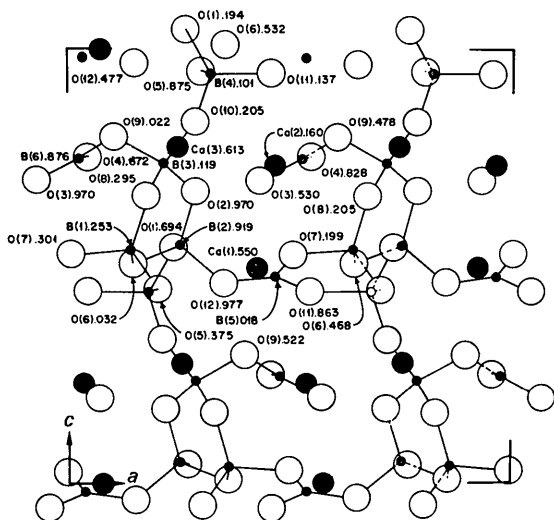

Fig. 1. The projection of one unit cell on the XZ plane. The heights of the atoms as fractions of the b parameter are given. Note that a left-handed system of axes has been used.
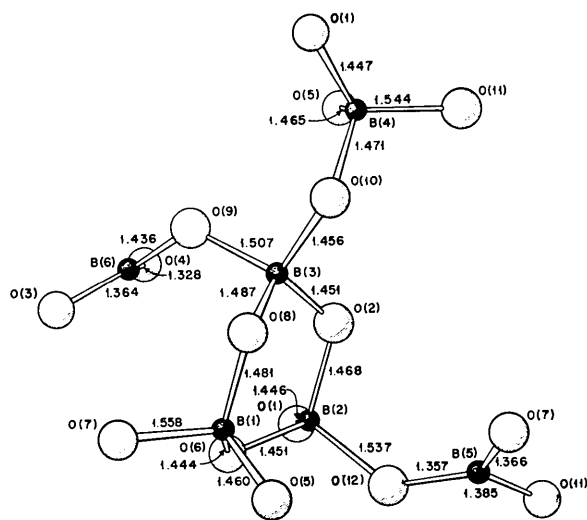

FIG. 2

Fig. 2. The projection of the unit $[B_6O_{12}]^{6-}$ on the XZ plane. The bond lengths in Å are given. As can be seen from Fig. 1, these units are linked together to form a three-dimensional network.

Ca. Since all the intensity measurements were made on one side of the Friedel mirror, two refinements were done, one assigning positive signs to the indices of the reflections and the other negative signs. After two cycles, convergence was attained in both cases. The two refinements yielded the same R index, indicating that with our experimental data it was not possible to determine whether we had measured the hkl reflections or the $\bar{h}\bar{k}\bar{l}$ ones. Very small differences were observed for the positional parameters along the z axis (the polar axis) between the two refinements, whereas no differences were observed for the x and y coordinates and thermal parameters. The z-values reported in Table 3, which were obtained without the anomalous dispersion corrections, actually correspond to the average of the two z-values obtained from the additional refinements in which the anomalous dispersion corrections had been applied. These differences in the z-coordinates did not yield any appreciable changes in the interatomic distances with the exception of two Ca–O distances, namely Ca(1)–O(3) and Ca(1)–O(9). These two distances have large components along the polar axis. The values of Ca(1)–O(3) and Ca(1)–O(9) obtained from the refinement in which positive signs were assigned to the indices of the reflections were 2·283 Å and 2·313 Å respectively, whereas 2·268 Å and 2·328 Å were obtained when negative signs were assigned to the indices of the reflections. The values of these two distances corresponding to the refinement in which the anomalous dispersion corrections were not applied, are 2·275 Å and 2·321 Å for Ca(1)–O(3) and Ca(1)–O(9) respectively. (See Table 5).

Description and discussion of the structure

The interatomic distances and their standard deviations are reported in Table 5. These values correspond to the final refinement in which the anomalous dispersion corrections were not applied.

Fig. 1 shows a projection of the structure of $CaB_2O_4(III)$ on the xz plane. There are six types of boron atoms, four of them are tetrahedrally coordinated and two triangularly coordinated. The four tetrahedra and two triangles form a unit $[B_6O_{12}]^{6-}$ which is repeated throughout the structure and which is shown in Fig. 2. These units are linked together to form a three-dimensional network. In the unit $[B_6O_{12}]^{6-}$ there are three tetrahedra which have two of their four corners in common. These are the tetrahedra around B(1), B(2) and B(3). These groups of three tetrahedra are bound together by the B(4) tetrahedra and by the B(5) triangles. In addition to the oxygen-sharing, the units $[B_6O_{12}]^{6-}$ are linked together by the Ca–O bonds. The B(6) triangle shares only one of its vertices with the rest of the unit. Therefore, there are two oxygen atoms, namely O(3) and O(4), which are bonded only to one boron atom.

All oxygen atoms with the exception of O(4) and O(9) have a fourfold coordination. O(1), O(2), O(5), O(6),

O(8) and O(10) are bonded to two tetrahedral boron atoms and two calcium atoms, whereas O(7), O(11) and O(12) are bonded to one tetrahedral boron, one triangular boron and two calcium atoms. O(3) is bonded to a triangular boron and to three calcium atoms. O(4) and O(9) have a threefold and fivefold coordination respectively. O(4) is bonded to one triangular boron and two calcium atoms whereas O(9) is bonded to one triangular boron, one tetrahedral boron and three calcium atoms.

The mean boron–oxygen distances are B–4O = 1·480 Å and B–3O = 1·373 Å, with individual lengths varying from 1·444 Å to 1·558 Å and from 1·328 Å to 1·436 Å, respectively. Zachariasen (1963a) who summarized some of the data on the B–O distances gives 1·475 Å as the most probable average value for B–O in

Table 6. *Valence balance for* CaB₂O₄ (III)

	Ca(1)	Ca(2)	Ca(3)	B(1)	B(2)	B(3)	B(4)	B(5)	B(6)	Σ	Σ*
O(1)	0·28		0·17		0·82		0·81			2·08	1·95
O(2)		0·24	0·21		0·76	0·80				2·01	1·95
O(3)	0·35	0·28	0·33						1·00	1·96	1·70
O(4)		0·33	0·32						1·11	1·76	1·45
O(5)	0·12		0·21	0·78			0·77			1·88	1·95
O(6)	0·23		0·09	0·82	0·80					1·94	1·95
O(7)	0·27	0·31		0·56				1·00		2·14	2·25
O(8)		0·25	0·23	0·74		0·72				1·94	1·95
O(9)	0·32	0·18	0·04			0·67			0·84	2·05	2·25
O(10)		0·31	0·17			0·79	0·76			2·03	1·95
O(11)	0·26	0·29					0·59	0·95		2·08	2·25
O(12)	0·11		0·24		0·61			1·02		1·98	2·20
Σ	1·94	2·19	2·01	2·90	2·99	2·98	2·93	2·97	2·95		

* These values are obtained when the distortions of the calcium and boron polyhedra are not taken into account.
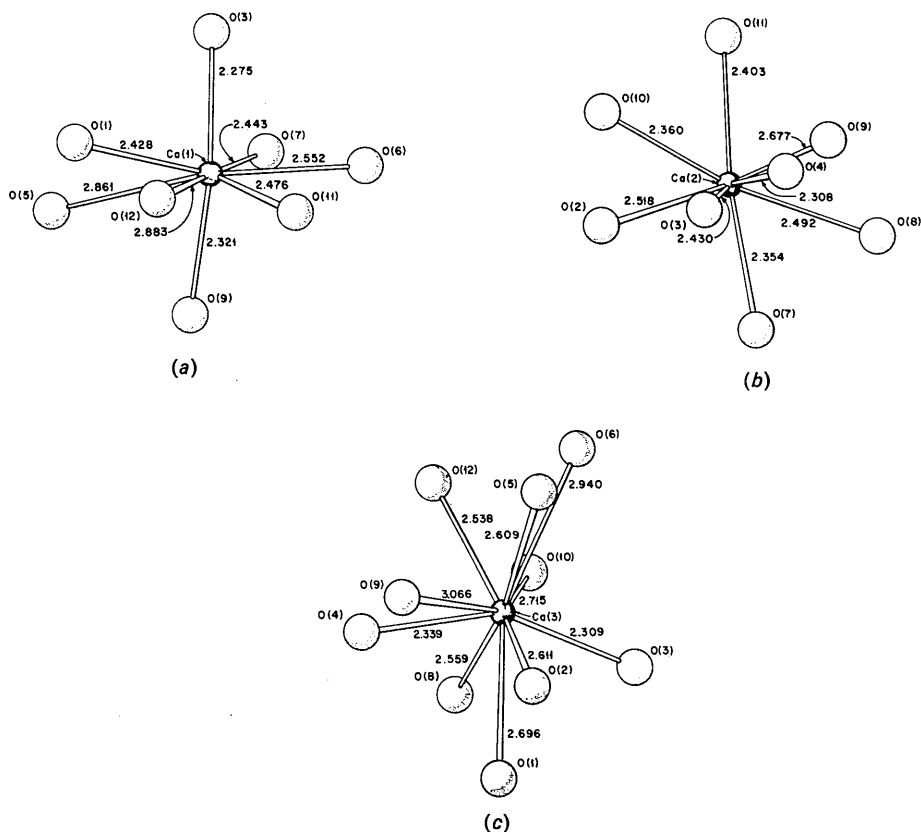

Fig. 3. (a) The oxygen polyhedron around Ca(1). (b) The oxygen polyhedron around Ca(2).
(c) The oxygen polyhedron around Ca(3).

the tetrahedral coordination and 1·365Å for B–O in the triangular coordination. The large variation of the individual B–O distances found in this structure indicates that the tetrahedra and the triangles are very distorted.

There are three types of calcium atoms in this structure. Ca(1) and Ca(2) are each surrounded by an

Table 7. *Magnitudes and orientation of thermal elipsoids*

	i	r.m.s. amplitudes	Angles with respect to a	b	c
Ca(1)	1	0·079 (2)	83 (7)°	75 (6)°	163 (8)°
	2	0·088 (2)	39 (3)	55 (4)	75 (8)
	3	0·106 (1)	128 (3)	39 (3)	83 (3)
Ca(2)	1	0·071 (2)	129 (4)	90 (4)	141 (4)
	2	0·083 (2)	49 (6)	57 (6)	122 (5)
	3	0·093 (1)	65 (5)	147 (6)	110 (5)
Ca(3)	1	0·070 (2)	168 (2)	92 (3)	102 (2)
	2	0·099 (1)	96 (3)	18 (4)	73 (4)
	3	0·115 (1)	80 (2)	72 (4)	159 (3)
B(1)	1	0·060 (10)	144 (24)	62 (19)	110 (20)
	2	0·076 (9)	55 (25)	54 (30)	125 (31)
	3	0·087 (8)	94 (23)	132 (26)	138 (28)
B(2)	1	0·056 (11)	132 (10)	75 (17)	134 (9)
	2	0·080 (8)	72 (21)	18 (19)	87 (21)
	3	0·094 (7)	48 (12)	100 (23)	135 (9)
B(3)	1	0·074 (9)	67 (69)	120 (36)	140 (44)
	2	0·080 (7)	23 (69)	80 (64)	69 (65)
	3	0·085 (8)	87 (58)	32 (36)	122 (39)
B(4)	1	0·062 (10)	126 (38)	63 (55)	132 (20)
	2	0·069 (9)	60 (46)	31 (53)	83 (42)
	3	0·082 (8)	51 (21)	105 (26)	137 (17)
B(5)	1	0·075 (8)	86 (56)	172 (42)	97 (23)
	2	0·081 (8)	15 (34)	84 (57)	104 (31)
	3	0·093 (8)	104 (30)	84 (19)	164 (28)
B(6)	1	0·077 (8)	139 (20)	68 (31)	57 (29)
	2	0·087 (8)	87 (46)	142 (51)	52 (49)
	3	0·093 (7)	131 (21)	120 (53)	124 (46)
O(1)	1	0·069 (7)	108 (18)	146 (35)	62 (27)
	2	0·076 (6)	118 (14)	56 (35)	47 (23)
	3	0·104 (5)	146 (8)	90 (8)	124 (8)
O(2)	1	0·067 (7)	77 (22)	138 (19)	129 (10)
	2	0·078 (6)	33 (12)	61 (22)	106 (17)
	3	0·120 (5)	120 (5)	62 (5)	137 (5)
O(3)	1	0·084 (5)	173 (18)	85 (12)	85 (16)
	2	0·094 (5)	83 (19)	61 (13)	30 (13)
	3	0·111 (5)	92 (8)	151 (13)	61 (13)
O(4)	1	0·086 (6)	92 (11)	176 (5)	87 (4)
	2	0·110 (5)	6 (6)	91 (11)	85 (5)
	3	0·151 (5)	85 (5)	93 (4)	174 (5)
O(5)	1	0·072 (6)	148 (84)	65 (103)	72 (14)
	2	0·073 (6)	72 (77)	28 (82)	110 (4)
	3	0·103 (5)	115 (7)	101 (8)	152 (7)
O(6)	1	0·051 (8)	68 (8)	155 (9)	79 (7)
	2	0·083 (5)	32 (21)	65 (9)	71 (28)
	3	0·092 (5)	68 (26)	92 (14)	158 (26)
O(7)	1	0·066 (6)	152 (10)	62 (9)	93 (9)
	2	0·089 (5)	112 (12)	129 (16)	47 (18)
	3	0·101 (5)	106 (10)	128 (14)	137 (18)
O(8)	1	0·076 (6)	106 (12)	37 (41)	123 (39)
	2	0·082 (6)	79 (15)	53 (42)	39 (37)
	3	0·104 (5)	161 (9)	96 (10)	72 (10)
O(9)	1	0·079 (6)	143 (5)	126 (4)	98 (14)
	2	0·098 (5)	100 (12)	89 (9)	10 (11)
	3	0·134 (5)	125 (4)	36 (4)	97 (6)
O(10)	1	0·063 (7)	138 (10)	106 (16)	128 (12)
	2	0·080 (6)	89 (27)	25 (30)	115 (29)
	3	0·086 (5)	132 (10)	71 (35)	49 (23)
O(11)	1	0·066 (6)	149 (23)	66 (21)	109 (11)
	2	0·078 (6)	60 (23)	37 (17)	110 (12)
	3	0·105 (5)	83 (7)	117 (8)	152 (8)
O(12)	1	0·055 (7)	163 (3)	74 (4)	92 (6)
	2	0·101 (5)	86 (6)	67 (6)	23 (7)
	3	0·134 (5)	106 (3)	151 (6)	67 (7)

8-oxygen polyhedron with individual Ca–O varying from 2·275 Å to 2·883 Å and from 2·308 Å to 2·677 Å, respectively. Ca(3) is surrounded by a 10-oxygen polyhedron with individual Ca–O varying from 2·309 Å to 3·066 Å. The average calcium–oxygen distances are Ca(1)–O = 2·530 Å Ca(2)–O = 2·443 Å and Ca(3)–O = 2·638 Å. The three calcium-polyhedra are shown in Figs. 3(a),(b), and (c).

If one assigns a bond strength of 1·00 to each triangular B–O bond, a strength of 0·75 to each tetrahedral B–O bond, a strength of 0·25 to each 8-coordinated Ca–O bond and a strength of 0·20 to each 10-coordinated Ca–O bond, then in the CaB₂O₄(III) structure the atoms O(3) and O(4) would be underbonded, whereas the atoms O(7), O(9), O(11), and O(12) would be overbonded. It can be seen from Table 6, where the valence balance for the CaB₂O₄(III) structure is reported, that these imbalances are in large measure removed in the actual structure by the shortening of some B–O and Ca–O bonds and by the lengthening of others, thus showing that the distortions are necessary to balance the electrostatic charge in the crystal. The values given in Table 5 were obtained by the use of the bond length *versus* bond strength dependence for the B–O bond reported by Zachariasen (1963a) and a linear relationship for the Ca–O bond.

It should be remembered that valence imbalance alone cannot explain all the observed variations in bond lengths. Also, next nearest neighbor interactions affect the bond lengths and hence one cannot expect to account for observed bond length anomalies by considering only first nearest neighbor interactions. This is true especially for structures that have close-packed arrangements, and high pressure phases have such arrangements.

In Table 7 the thermal parameters of Table 4 are converted to root mean square displacements along principal axes for convenient comparison with other borates. Also shown in Table 7 are the angles that the principal axes form with the vectors **a,b,c** of the crystal. A detailed analysis of the data of Table 7 will not be presented, but it can be seen that the magnitudes and orientations of the thermal vibra-tion ellipsoids are physically reasonable when correlated with the directions of the chemical bonds.

References

Busing, W. R., Martin, K. O. & Levy, H. A. (1962). ORNL Report TM-305. Oak Ridge National Laboratory. Oak Ridge, Tennessee.
Busing, W. R., Martin, K. O. & Levy, H. A. (1964). ORNL Report TM-306. Oak Ridge National Laboratory, Tennessee.
Chang, C. H. & Margrave, J. L. (1967). *Mat. Res. Bull.* **2**, 929.
Cromer, D. T. (1965). *Acta Cryst.* **18**, 17.
Cromer, D. T. & Waber, J. T. (1965). *Acta Cryst.* **18**, 104.
Fritchie, C. J. (1967). Unpublished computer program for Fourier synthesis.
Gurr, G. E., Montgomery, P. W., Knutson, C. D. & Gorres, B. T. (1967). Paper presented at the A.C.A. summer meeting, Minneapolis, Minnesota, August 20–25, 1967.
Marezio, M., Plettinger, H. A. & Zachariasen, W. H. (1963). *Acta Cryst.* **16**, 390.
Marezio, M. & Remeika, J. P. (1966). *J. Chem. Phys.* **44**, 3348.
Marezio, M., Remeika, J. P. & Dernier, P. D. (1966). *Mat. Res. Bull.* **1**, 247.
Mueller, M. H., Heaton, L. & Miller, R. T. (1960). *Acta Cryst.* **13**, 828.
Peters, C. R. & Milberg, M. E. (1964). *Acta Cryst.* **17**, 229.
Prewitt, C. T. (1966a). Unpublished computer program for absorption corrections.
Prewitt, C. T. (1966b). Unpublished computer program for crystallographic least-squares refinement.
Prewitt, C. T. & Shannon, R. D. (1968). *Acta Cryst.* **B25**, 869.
Zachariasen, W. H. (1963a). *Acta Cryst.* **16**, 385.
Zachariasen, W. H. (1963b). *Acta Cryst.* **16**, 380.
Zachariasen, W. H. (1964). *Acta Cryst.* **17**, 749.
Zachariasen, W. H. (1967). *Acta Cryst.* **23**, (44).
Zachariasen, W. H. (1968) Private communication.