

The Crystal Structure of the High Pressure Phase, $\text{CaB}_2\text{O}_4(\text{IV})$, and Polymorphism in CaB_2O_4

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$\text{CaB}_2\text{O}_4(\text{IV})$ is a high pressure phase of calcium metaborate. Single crystals were grown at 30 kbar and 900°C . They were found to be cubic with $a=9.008 \pm 0.001 \text{ \AA}$, $Z=12$, $d_c=3.426 \text{ g.cm}^{-3}$ and space group symmetry $Pa\bar{3}$.

The structure has been determined by a three-dimensional Fourier synthesis. The positional and isotropic thermal parameters have been refined by the least-squares method based on 267 structure factors. The final conventional R value is 0.033. All the boron atoms are tetrahedrally coordinated. The mean B–O distance is 1.480 \AA . There are two independent Ca atoms. Ca(1) is surrounded by a 12-oxygen polyhedron with two sets of Ca–O distances of 2.671 \AA and 2.785 \AA . This is the first observation of coordination twelve for calcium. Ca(2) is also surrounded by twelve oxygens, but the polyhedron formed by these oxygen atoms is very irregular. There are four sets of Ca–O distances: 2.385 , 2.483 , 2.598 and 3.142 \AA . The coordination number of the oxygen atoms is five; each one is surrounded by one Ca(1), two Ca(2), and two boron atoms.

Calcium metaborate can crystallize with four different structures by varying the pressure at which the synthesis is carried out. The common trend among these structures is an increase of the cation coordination with increasing pressure. By analogy many new phases of borates and polyborates could be synthesized under pressure.

Introduction

Calcium metaborate can be prepared in four crystalline modifications by varying the pressure at which the synthesis is carried out. A detailed structure study has been reported for $\text{CaB}_2\text{O}_4(\text{I})$ (Marezio, Plettinger & Zachariasen, 1963*b*) and $\text{CaB}_2\text{O}_4(\text{III})$ (Marezio, Remeika & Dernier, 1969). The precise crystal structure of $\text{CaB}_2\text{O}_4(\text{II})$ has been determined by Zachariasen (1968). This paper reports in detail the crystal-growth and the crystal structure determination of $\text{CaB}_2\text{O}_4(\text{IV})$. In addition, a discussion of the polymorphism of CaB_2O_4 is given.

Crystal growth

The starting material for all high pressure runs was $\text{CaB}_2\text{O}_4(\text{I})$. The procedure of the high pressure experiments was the same as has been described in the preceding paper.

The high pressure phase $\text{CaB}_2\text{O}_4(\text{IV})$ was first prepared in polycrystalline form by direct application of temperature and pressure to $\text{CaB}_2\text{O}_4(\text{I})$. A temperature of 900°C and a pressure of 30 kbar for one hour was sufficient to produce the desired phase change. It should be noted that each time $\text{CaB}_2\text{O}_4(\text{IV})$ was formed during the raising of the temperature, a pressure drop of 1 kbar was observed between 450° and 500°C . After quenching to room temperature and pressure, X-ray powder photographs of the quenched material showed that a fourth phase of CaB_2O_4 had been retained metastably. The powder pattern of the new phase

could be indexed on a cubic cell of about 9 \AA . Also, the new phase could be reconverted to the low pressure phase by annealing overnight at 750°C in air. The powder photographs of the annealed CaB_2O_4 and of the starting material were identical.

In order to obtain single crystals of $\text{CaB}_2\text{O}_4(\text{IV})$, powdered $\text{CaB}_2\text{O}_4(\text{I})$ was packed into a platinum cup of dimensions 2.6 mm internal diameter by 5.5 mm high, to which $20 \mu\text{l}$ of distilled water were added as a solvent. After one hour at 30 kbar and 900°C , the sample was allowed to cool to room temperature at a rate of $30^\circ/\text{min}$. Then the pressure was released at a rate of approximately 2 kbar/min. The platinum cell was broken open and many transparent crystals were found. A few large ($\sim 1.5 \text{ mm}$ long) crystals had a didodecahedral form but most crystals were fractured and of rather poor morphology. X-ray powder photographs of these crystals were identical to those of the polycrystalline $\text{CaB}_2\text{O}_4(\text{IV})$.

Optical analysis confirmed that the crystals of $\text{CaB}_2\text{O}_4(\text{IV})$ are cubic. In addition to these isotropic crystals, in each run some very small, birefringent crystals were present. X-ray powder photographs showed that these crystals were $\text{Ca}_3(\text{BO}_3)_2$, meaning that a decomposition had taken place under pressure: $3\text{CaB}_2\text{O}_4 \rightarrow \text{Ca}_3(\text{BO}_3)_2 + 2\text{B}_2\text{O}_3$. More of this decomposition product was obtained at 40 kbar and 1000°C with $10 \mu\text{l}$ of distilled water as solvent. Furthermore, in the runs where a larger amount of water was used, needle-like crystals of a third phase were present. Subsequent high pressure experiments revealed that the yield of the needle-like crystals depended on the amount of water present. Most important was the fact that no reflections belonging to the needle-like phase

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were detected in any of the X-ray powder photographs of the polycrystalline $\text{CaB}_2\text{O}_4(\text{IV})$ material. These observations seem to indicate that the needle-like crystals are a hydrate of CaB_2O_4 or some product of decomposition of CaB_2O_4 .

Crystal data

The crystals of $\text{CaB}_2\text{O}_4(\text{IV})$ were found to be cubic with $a = 9.008 \pm 0.001 \text{ \AA}$ and 12 molecules per unit cell. The calculated density is 3.426 g.cm^{-3} . The symmetry and the lattice parameter were determined from a powder film taken at room temperature with a Norelco camera of 114.6 cm in diameter and Cr $K\alpha$ radiation. The lattice parameter was calculated by the least-squares refinement program of Mueller, Heaton & Miller (1960). A comparison of observed and calculated interplanar spacings and observed intensities is given in Table 1.

Table 1. Powder pattern of $\text{CaB}_2\text{O}_4(\text{IV})$

$h^2 + k^2 + l^2$	d_{obs}	d_{cal}	I
5	4.008	4.029	w
8	3.172	3.185	w
9	2.907	3.003	w
11	2.708	2.716	s
13	2.489	2.498	m
14	2.402	2.407	wm
16	2.246	2.252	w
17	2.180	2.185	wm
18	2.120	2.123	w
19	2.065	2.067	vw
20	2.011	2.014	ms
21	1.962	1.966	s
22	1.918	1.921	ms
24	1.837	1.839	vw
27	1.731	1.734	wm
29	1.669	1.673	w
30	1.641	1.645	wm
32	1.590	1.592	wm
33	1.567	1.568	vvw
34	1.544	1.545	vw
35	1.519	1.523	vw
36	1.499	1.501	w
38	1.459	1.461	m
43	1.373	1.374	w
44	1.357	1.358	w
45	1.342	1.343	w
48	1.296	1.300	m
53	1.237	1.237	m
54	1.225	1.226	w
56	1.203	1.204	ms
57	1.193	1.193	w
59	1.173	1.173	s
61	1.153	1.153	w

Precession photographs taken with Mo $K\alpha$ showed that the systematic absences are: $k = 2n + 1$ for $0kl$, $l = 2n + 1$ for $h0l$ and $h = 2n + 1$ for $hk0$ (h, k, l are not permutable). These absences lead to space group symmetry $Pa3$. Of the 12 calcium atoms, 4 are in the special positions $4(a)$ and 8 in the special positions $8(c)$. The boron atoms and the O(1) and O(2) atoms are in the general positions $24(d)$ (*International Tables for X-ray Crystallography*, 1952). The density variation

coresponding to the transition $\text{CaB}_2\text{O}_4(\text{I}) \rightarrow \text{CaB}_2\text{O}_4(\text{IV})$ is about 23%.

Experimental

The intensity measurements were made by use of the same diffractometer and by following the same procedure described in the preceding paper. The specimen was a crystal of irregular shape, the longest dimension being $\sim 0.3 \text{ mm}$. This crystal was oriented with the $[001]$ zone axis parallel to the ϕ axis of the goniostat. No absorption correction was applied because the dimensions of the crystal were such that the absorption effects were negligible. A total number of 863 independent reflections were measured; each one represents the average of at least three measurements taken on three different planes of the same crystallographic form. The symmetry of the X-ray diffraction effects for $\text{CaB}_2\text{O}_4(\text{IV})$ is $m3$, in which the hkl and khl reflections are different. Those reflections for which the peak-height was not at least twice as much as the background were regarded as unobserved. This criterion gave a total of 267 observed reflections and 596 unobserved ones.

Solution of the structure

The first step in solving the structure was based on determining the position of the Ca(2) atoms, which are in the special positions (x, x, x) of the $Pa3$ space group. It was evident from the observed structure factors that, once Ca(1) had been placed in the special positions $(0, 0, 0)$, Ca(2) was very nearly at $(\frac{3}{8}, \frac{3}{8}, \frac{3}{8})$. A three-dimensional Fourier synthesis carried out with the F_{hkl} having the signs of the relative calcium contribution gave the approximate positions of the other three atoms, B, O(1), and O(2). The Fourier synthesis was computed by the use of the program 'Four' written by Fritchie (1967) and modified by L. Guggenberger & P. B. Jamieson. Since the structural arrangement obtained was reasonable from the crystal chemistry point of view, this structure was refined by the use of the least-squares program written by Prewitt (1966) with the f -curves for neutral calcium, oxygen and boron given by Cromer & Waber (1965). The anomalous dispersion corrections were not applied to the f -curve of Ca (see the section *Anomalous dispersion* in the preceding paper: Marezio, Remeika & Dernier, 1969). All observed structure factors were weighted equally. Convergence was attained after several refinement cycles of the scale factor, the extinction correction coefficient, the positional parameters and the isotropic temperature factors. The secondary extinction correction was quite small, but still appreciable. In the final refinement anisotropic temperature factors were introduced, but, as expected, there was no appreciable anisotropy. The degree of agreement between observed and calculated structure factors is shown in Table 2, where F_c represents the calculated structure factor per unit cell. The final refinement gave a conventional R

It consists of a ring of three BO_4 tetrahedra having two of their vertices in common. The three oxygens which are shared among the three tetrahedra which form the ring are O(1), whereas the six oxygens which are shared with other units are O(2). One unit shares the six O(2) atoms with six different units. This array of boron-tetrahedra forms large empty cages in which the calcium atoms are accommodated. The mean B–O distance is 1.480 Å with individual distances varying from 1.465 to 1.495 Å. There are two types of calcium atom in this structure. Ca(1) is at the origin and is surrounded by a 12-oxygen polyhedron which is shown schematically in Fig. 3. In the polyhedron there are two sets of six Ca–O distances, $\text{Ca}(1)–\text{O}(1)=2.785$ Å and $\text{Ca}(1)–\text{O}(2)=2.671$ Å. As far as we know this is the first observation of coordination twelve for calcium in oxide compounds. Ca(2) is on a threefold axis and is surrounded by three sets of three oxygen atoms at 2.385 Å, 2.483 Å and 2.598 Å. In addition to these first nearest oxygen atoms there is one set of three oxygen atoms at 3.142 Å. These twelve oxygen atoms form a very irregular polyhedron. When there is such a large variation among the distances in the same polyhedron it is very difficult to determine the coordination number of the cation, the true coordination being between 9 and 12. In fact, the average of the first nine Ca–O distances, 2.489 Å, is much shorter than the value of 2.57 Å given by *International Tables for X-ray Crystallography* (1962) as the average Ca–O distance for 9-coordinated calcium. Furthermore, the average of the first twelve Ca–O distances, 2.652 Å, is much shorter than the average of the twelve distances $\text{Ca}(1)–\text{O}$, 2.728 Å. The coordination number of the oxygen atoms is five; each one is surrounded by one Ca(1), two Ca(2), and two boron atoms.

If one assigns a bond strength of 0.75 to each B–O bond and 0.17 to each Ca–O bond, the bond strength of both O(1) and O(2) is 2.0, indicating that in this structure the distortion of the boron and calcium polyhedra must be ascribed to next nearest neighbor interactions.

Polymorphism of CaB_2O_4

Data for the polymorphism of CaB_2O_4 are summarized in Table 5. Calcium metaborate can crystallize with four different structures, three orthorhombic and one cubic. In the phase stable at normal pressure all boron atoms are triangularly coordinated, while the calcium atoms are each surrounded by an 8-oxygen polyhedron (Marezio, Plettinger & Zachariasen, 1963b).

In the structure of $\text{CaB}_2\text{O}_4(\text{II})$ 50% of the boron atoms are triangularly coordinated and 50% tetrahedrally coordinated. The calcium atoms have the same coordination number 8 as in $\text{CaB}_2\text{O}_4(\text{I})$ (Zachariasen, 1968). Therefore, in the transition (I) \rightarrow (II) the only cations that increase their coordination are $\frac{1}{2}$ of the boron atoms. The density variation corresponding to this transition is 6.5%. The high pressure experiments made in order to prepare $\text{CaB}_2\text{O}_4(\text{II})$ seem to indicate

that the pressure range of stability of this phase is very narrow, around 12–15 kbar. We have not been able to obtain pure $\text{CaB}_2\text{O}_4(\text{II})$, but always together with the starting material, namely $\text{CaB}_2\text{O}_4(\text{I})$.

$\text{CaB}_2\text{O}_4(\text{III})$ can be synthesized at 900°C under a pressure of about 15–25 kbar. In this phase $\frac{1}{3}$ of the boron atoms are triangularly coordinated and $\frac{2}{3}$ tetrahedrally coordinated, while $\frac{2}{3}$ of the calcium atoms are

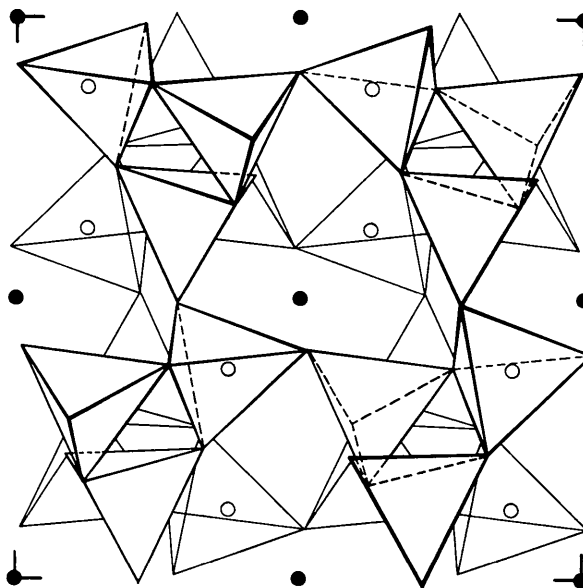


Fig. 1. The structure of $\text{CaB}_2\text{O}_4(\text{IV})$ viewed along the c axis. The boron atoms at the centers of the tetrahedra are omitted for clarity. The filled and open circles represent Ca(1) and Ca(2) respectively. Note that a left-handed system of axes has been used.

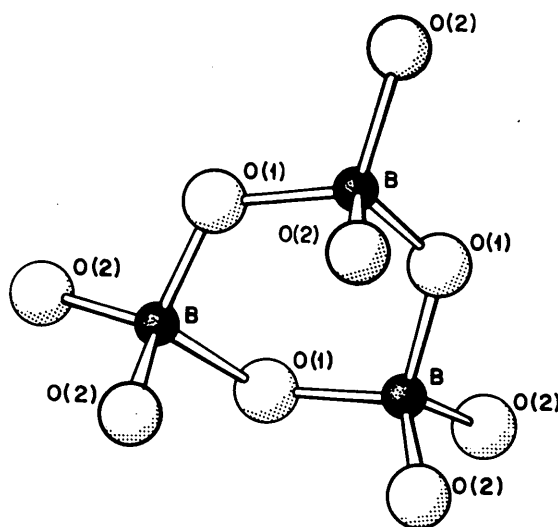


Fig. 2. A projection on the (110) plane of the three-tetrahedra unit $[\text{B}_3\text{O}_6]^{3-}$. As can be seen from Fig. 1, these units are linked together to form a three-dimensional network.

8-coordinated and $\frac{1}{3}$ 10-coordinated (Marezio, Remeika, & Dernier, 1969). In the transition (I) \rightarrow (III) $\frac{2}{3}$ of the boron and $\frac{1}{3}$ of the calcium atoms increase

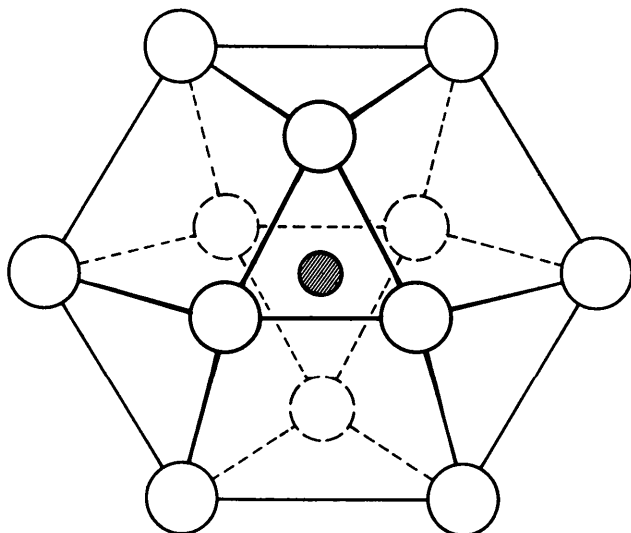


Fig. 3. The oxygen-polyhedron around Ca(1). If one considers the calcium atom as part of the array, this polyhedron forms a cubic close-packed array.

their coordination, while in the transition (II) \rightarrow (III) $\frac{1}{3}$ of the boron and $\frac{1}{3}$ of the calcium atoms increase their coordination. The density variations corresponding to these two transitions are 12.2% and 5.6%, respectively.

The structure of CaB_2O_4 (III) contains $[\text{B}_6\text{O}_{12}]^{2-}$ units consisting of two triangular and four tetrahedral boron oxygen groups (see Fig. 2 of the preceding paper: Marezio *et al.* 1969). In this unit there is a ring of three tetrahedra which have two of their four corners in common. These rings are maintained in the structure of CaB_2O_4 (IV) (see Figs. 1 and 2). In the transition (III) \rightarrow (IV) $\frac{1}{3}$ of the boron atoms increase their coordination from 3 to 4, whereas $\frac{2}{3}$ of the calcium atoms increase their coordination to 9–12 and $\frac{1}{3}$ to 12. The density variation corresponding to this transition is 11.5%.

Polymorphism in borates

Many classifications have been proposed for borates. The latest to appear is the one by Bokii & Kravchenko (1966). It is not our intention to propose new criteria for classifying borates, but we would like to point out that an interesting feature arises if one classifies the borates according to the coordination of the boron atoms. In Table 6 several anhydrous borates are classified according to this criterion. It should be noted

Table 5. *Polymorphism of CaB_2O_4*

CaB_2O_4	Approximate range of stability at 900°C	Density (g.cm ⁻³)	Symmetry	Lattice parameters (Å)	No. of molecules per unit cell	% B Δ	% B Δ	Ca (C.N.)
(I)	0–12 kbar.	2.702	Orthorhombic	$a = 6.214$ $b = 11.604$ $c = 4.285$	4	100	0	8
(II)	12–15 kbar.	2.885	Orthorhombic	$a = 8.369$ $b = 13.816$ $c = 5.007$	8	50	50	8
(III)	15–25 kbar.	3.052	Orthorhombic	$a = 11.380$ $b = 6.382$ $c = 11.304$	12	33	67	67% 8 33% 10
(IV)	25–40 kbar.	3.426	Cubic	$a = 9.008$	12	0	100	67% 9–12 33% 12

Table 6. *Classification of some anhydrous borates according to the boron atom coordination*

All Δ	4 Δ :1 Δ	3 Δ :1 Δ	2 Δ :1 Δ	1 Δ :1 Δ	1 Δ :2 Δ	All Δ
NaBO_2 ⁽¹⁾	KB_5O_8 ⁽⁸⁾	$\text{Ag}_2\text{B}_8\text{O}_{13}$ ⁽¹⁰⁾	HBO_2 (II) ⁽¹¹⁾	CdB_4O_7 ⁽¹²⁾	CaB_2O_4 (III) ⁽¹⁵⁾	SrB_2O_4 (IV) ⁽¹⁶⁾
CaB_2O_4 (I) ⁽²⁾	RbB_5O_8 ⁽⁹⁾			$\text{Li}_2\text{B}_4\text{O}_7$ ⁽¹³⁾	SrB_2O_4 (III) ⁽¹⁶⁾	B_2O_3 (II) ⁽¹⁷⁾
HBO_2 (I) ⁽³⁾				CaB_2O_4 (II) ⁽¹⁴⁾		HBO_2 (III) ⁽¹⁸⁾
LiBO_2 (I) ⁽⁴⁾						SrB_4O_7 ⁽¹⁹⁾
SrB_2O (I) ⁽⁵⁾						LiBO_2 (III) ⁽²⁰⁾
BaB_2O_4 ⁽⁶⁾						CaB_2O_4 (IV) ⁽²¹⁾
B_2O_3 (I) ⁽⁷⁾						

- (1) Marezio, Plettinger & Zachariasen (1963a)
- (2) Marezio, Plettinger & Zachariasen (1963b)
- (3) Peters & Milberg (1964)
- (4) Zachariasen (1964)
- (5) Block, Perloff & Weir (1964)
- (6) Mighell, Perloff & Block (1966)
- (7) Gurr, Montgomery, Knutson & Gorres (1967)
- (8) Krogh-Moe (1965b)
- (9) Krogh-Moe (1959)
- (10) Krogh-Moe (1965a)
- (11) Zachariasen (1963a)

- (12) Ihara & Krogh-Moe (1966)
- (13) Krogh-Moe (1968)
- (14) Zachariasen (1968)
- (15) Marezio, Remeika & Dernier (1969)
- (16) Dernier (1968)
- (17) Prewitt & Shannon (1968)
- (18) Zachariasen (1963b)
- (19) Krogh-Moe (1964)
- (20) Marezio & Remeika (1966)
- (21) This paper

that all compounds in which the boron atoms have coordination number 4 have been reported to be high pressure phases with the exception of SrB_4O_7 . Krogh-Moe (1964) has reported the synthesis and the structure of this compound. Crystals of SrB_4O_7 can be prepared from a melt with a slight excess of B_2O_3 at 900°C .

One of us is studying the behavior of SrB_2O_4 under pressure (Dernier, 1969). Preliminary results seem to indicate that SrB_2O_4 behaves under pressure very much in the same way as CaB_2O_4 . One interesting difference is that $\text{SrB}_2\text{O}_4(\text{IV})$, an isomorph of $\text{CaB}_2\text{O}_4(\text{IV})$, decomposes at about 40 kbar and 900°C . One of the products of decomposition is SrB_4O_7 , as identified from an X-ray powder photograph of the quenched material. The crystals of SrB_4O_7 have been synthesized at normal pressure, but the structure (Krogh-Moe, 1964) has all the features of a high pressure structure. The cations have high coordination, all the boron atoms are tetrahedrally coordinated and the strontium atoms have 16 nearest neighbors. Although they are not all first nearest neighbors, it is a very high coordination for strontium. Furthermore, some oxygen atoms are bonded to three boron atoms. This feature has been found in the mineral tunellite (Clark, 1963), and recently in the high pressure phase $\text{B}_2\text{O}_3(\text{II})$ (Prewitt & Shannon, 1968). The calculated density, 4.02 gr.cm^{-3} , also seems to indicate that the structure of SrB_4O_7 is a compact one.

Table 6 seems to indicate that many new phases can be synthesized under pressure. New phases should exist for all those compounds in which the boron atoms are not all tetrahedrally coordinated. It is difficult to foresee how many phases exist for each compound, but by analogy to CaB_2O_4 and HBO_2 we would expect that more than one high pressure phase should exist for the metaborates, BaB_2O_4 , NaBO_2 and KBO_2 and at least one for the polyborates. For instance, at high pressure CdB_4O_7 should be isostructural with SrB_4O_7 . We also believe that more high pressure phases should exist for B_2O_3 . At present we are investigating the behavior of BaB_2O_4 under pressure.

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