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Nitrato- and Fluoroboracites $M_3B_7O_{13}NO_3$ and $M_3B_7O_{13}F$

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New boracites containing nitrato- or fluoroanions that appear to be true low-pressure phases have been synthesized at superatmospheric pressures. The $M_3B_7O_{13}NO_3$ compounds (M = Co, Ni, Cu, Zn, Cd) transform rapidly and reversibly in the temperature region 300–500°C between probable orthorhombic and face centered cubic symmetry, while the $M_3B_7O_{13}F$ compounds (M = Mg, Mn, Fe, Co, Zn) appear to maintain rhombohedral symmetry up to their decomposition temperatures of 800–900°C. True high-pressure boracite-like phases containing F and Cr, Mn, Fe, or Co that decompose upon heating to $M_3B_7O_{13}F$ have also been isolated.

Introduction

Boracites $M_3B_7O_{13}X$ derived from the prototype mineral $Mg_3B_7O_{13}Cl$ comprise an extensive class of compounds wherein M = divalent Mg, Cr, Mn, Fe, Co, Ni, Cu, Zn, or Cd, and X = Cl, Br, or I and, in a few instances, OH. The boracite structure (*1*) consists of a boron–oxygen network in which the borons occupy two different crystallographic sites, one having tetrahedral and the other a more trigonal-like coordination. The cations lie on a cubic sublattice in this framework and are essentially octahedrally coordinated in a distorted manner to four oxygen and two halogen atoms. One or more reversible transitions occur in these materials from a high-temperature cubic ($F\bar{4}3c$), piezoelectric form to either an orthorhombic ($Pca2_1$) or trigonal ($R3c$) distortion of this phase at some lower temperature that has been observed to be as high as 798°K for the Cd–Cl compound and as low as about 10°K for the Cr–I compound. When in their noncubic forms, these boracites are pyroelectric and a number of them have also been observed to be ferroelectric. They are transparent to visible light and the Fe, Co, and Ni species also show magnetic ordering at low temperatures. This combination of optical, electrical, and magnetic properties in these materials coupled with their chemical stability has led to extensive studies on the physical properties of boracites (*2–7*).

Synthesis of boracites in a form suitable for physical studies is difficult and a vapor transport technique for crystal growth under reduced pressure developed by Schmid (*2*) is now in use. In more recent work, hydrothermal synthesis techniques have also been used for the preparation of crystals of some of the known halogenoboracites (*8*) as well as hydroxyboracites (*8–10*) of Mg, Mn, Fe, and Ni. In the course of our high-pressure studies on the synthesis and chemistry of new borates (*11*), we have now found two additional anion species that can be incorporated into the boracite lattice to give extensive series of new $M_3B_7O_{13}X$ compounds. The first of these is the nitrate anion and represents a novel expansion in the field of boracite chemistry. The second is the fluoride ion which in part gives compounds related to the known halogenoboracites.

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Experimental

Reactions were carried out (1) at pressures of 25–58[1] kbars in gold or platinum capsules containing about 0.2 g of reactants in a tetrahedral anvil device (*12*), (2) at pressures of 5–30 kbars in welded gold or platinum capsules containing about 0.6 g of reactants in a piston-cylinder device (*13*), and (3) under an external argon pressure of 1–3 kbars in 3/8–1/2 in. i.d. sealed gold tubes 4–6 in. long containing about 3 g of reactants. Reagent grade chemicals were used as reactants and were ground together in the desired ratios and pelleted prior to reaction. Following reaction at the indicated temperatures and pressure, the products were extracted with hot water to remove soluble materials including excess B_2O_3 or H_3BO_3 and were then rinsed with acetone and air dried.

X-Ray powder diffraction patterns were taken at 25°C with a Debye–Scherrer camera or a Hägg–Guinier camera which used monochromatic Cu$K\alpha_1$ radiation and a KCl internal standard ($a = 6.2931$ Å). High temperature diffraction patterns were taken with a Guinier–Lenné camera using Rh as an internal standard. Films were read on a David Mann film reader, Model No. 1222. Cell dimensions were refined by a least-squares method and showed a standard deviation of ±0.001 Å or less.

Transition temperatures were determined by differential scanning calorimetry using a Du Pont Differential Thermal Analyzer.

Nitratoboracites

Results

$Co_3B_7O_{13}NO_3$. The reaction of hydrated transition metal nitrates with B_2O_3 at high pressure was undertaken to ascertain the types of borate products formed in a strong oxidizing environment. Reaction of 1 mole equiv of $Co(NO_3)_2 \cdot 6H_2O$ with 0.6 to 3 mole equiv of B_2O_3 was carried out at 58 kbars under thermal conditions such as 1000°C—2 hr/cool 4 hr to 400°C/quench, or 800°C (or 600°C)—6 hr/quench. The primary water insoluble phase isolated consisted of deep-red crystals varying in habit from irregular polycrystalline segments to discrete polyhedra up to 1 mm in cross section. The X-ray diffraction powder pattern of this material, which consisted of extremely sharp lines, related to that of the mineral boracite, $Mg_3B_7O_{13}Cl$, but extensive line splitting was noted. Attempts to

TABLE I

X-RAY DIFFRACTION POWDER PATTERN OF $Co_3B_7O_{13}NO_3$

I/I_0	$h\,k\,l$[a]	d
5	1 1 0 0 0 2	6.1031
5	0 2 0	4.3799
15	1 1 2	4.3163
40	0 2 2	3.5579
25	2 0 2	3.4897
100	0 0 4 2 2 0	3.0521
10	1 3 0 3 0 1	2.7621
45	1 1 4 2 2 2	2.7303
20	3 1 0	2.6974
15	1 3 2	2.5166
10	0 2 4	2.5050
5	2 0 4	2.4831
10	3 1 2	2.4690
10	0 1 5 2 3 1	2.3553
15	0 4 0	2.1899
55	2 2 4	2.1586
20	4 0 0	2.1273
15	1 4 1	2.0903
25	2 3 3 1 2 5	2.0714
20	2 1 5 3 2 3 0 4 2	2.0578
15	4 1 1 0 0 6 3 3 0	2.0383
5	3 1 4	2.0220
5	4 0 2	2.0087
2	2 4 0	1.9452
10	1 1 6 3 3 2	1.9308
40	2 4 2	1.8553
25	0 2 6 4 1 3 3 0 5	1.8467
25	2 0 6	1.8366
40	4 2 2	1.8262
20	0 4 4	1.7799
25	4 0 4	1.7459
5	2 2 6 3 3 4	1.6938
5	1 5 2	1.6543
10	0 0 8 4 4 0	1.5264
5	1 1 8 4 4 2	1.4808
5	5 3 2 1 6 1	1.4296
5	0 6 2 6 0 0	1.4192
10	4 2 6	1.3939
10	6 0 2 2 6 0	1.3813

[a] Indexing on the basis of orthorhombic symmetry (*Pca*2_1). $a = 8.509$, $b = 8.761$, $c = 12.213$ Å.

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[1] Pressures of 65 kbars, as reported in earlier publications from this laboratory, have now been changed to a value of 58 kbars in view of a redetermination of the barium transition at 55 rather than 59 kbars.

define the space group failed since all crystals examined were highly twinned. Careful indexing of a Guinier powder pattern (Table I), however, strongly suggested that the $Pca2_1$ orthorhombic symmetry established (*1*) for the room temperature form of boracite pertains for this compound.

An infrared spectrum indicated the presence of boron in two different coordination sites as occurs in the boracite framework (*1*). Thermal analysis showed a sharp and reversible transition around 456°C in the manner observed (*2*) in the known boracites $M_3B_7O_{13}X$. A powder pattern on this compound at room temperature following a heating to 770°C was identical to that of the original material and confirmed the reversibility of the transition, as well as indicating the thermal stability of the compound. These data suggested a new boracite-type compound in which halogen was replaced by the nitrate anion. Analyses were in agreement with the proposed formula $Co_3B_7O_{13}NO_3$.

Anal. Calcd: O, 49.00; N, 2.68. Found: O, 50.22; N, 2.60.

Magnetic susceptibility measurements indicated Curie–Weiss-type behavior for $Co_3B_7O_{13}NO_3$ from room temperature to 140°K, with a value of p_{eff} of 4.99 μ_B/Co atom based on this formula. This effective moment is compatible with that for high-spin Co^{2+} in an octahedral environment. At lower temperatures, magnetic ordering set in and a magnetic moment μ_S of 2.6 emu/g was observed at 4.2°K.

$Ni_3B_7O_{13}NO_3$. Reaction of a 1/1 mole ratio of $Ni(NO_3)_2 \cdot 6H_2O/B_2O_3$ at 58 kbars/1000°C—2 hr/cool 4 hr to 400°C/quench gave a mixture of irregularly shaped, orange-brown crystallites plus a lesser amount of yellow-green platelets. The X-ray pattern of the orange-brown phase was isotypic with that of $Co_3B_7O_{13}NO_3$ and could be indexed in the same manner on the basis of an orthorhombic unit cell (Table II). Again, twinning precluded a single crystal study. Analyses were consistent for the formula $Ni_3B_7O_{13}NO_3$.

Anal. Calcd: O, 49.06; density, 3.88 g/cm^3 (based on 4 molecules per orthorhombic unit cell). Found: O, 47.93; density, 3.71 g/cm^3.

Both trigonally and tetrahedrally coordinated boron were evident from the infrared spectrum. Thermal analysis showed a sharp and reversible transition around 427°C. This compound was piezoelectric and a sharp increase in capacitance was observed on heating through this transition.

$(Co,Ni)_3B_7O_{13}NO_3$. Reaction of $Co(NO_3)_2 \cdot 6H_2O/Ni(NO_3)_2 \cdot 6H_2O/B_2O_3$ in a 1/1/2 mole ratio at 58 kbars/800°C—6 hr/cool 2 hr to 400°C/quench gave irregularly shaped red crystallites of $(Co,Ni)_3B_7O_{13}NO_3$ as the main phase.

Anal. Calcd: O, 49.03; N, 2.68. Found: O, 48.97; N, 2.39, 2.50.

Crystals were twinned and the powder pattern was indexed as before (Table II). A sharp, reversible transition occurred at 442°C. A high-temperature X-ray powder diffraction pattern of $(Co,Ni)_3B_7O_{13}NO_3$ taken on film

TABLE II

$M_3B_7O_{13}NO_3$ BORACITES

Cation M	Orthorhombic $Pca2_1$ indexing of room temp. powder pattern			Color of crystals	Transition temp. °C (by DSC)
	a, Å	*b*, Å	*c*, Å		
Co	8.509	8.761	12.213	Deep red	456
(Co, Ni)	8.476	8.729	12.177	Red	442
Ni	8.441	8.716	12.141	Orange-brown	427
Cu	8.445	8.663	12.102	Straw yellow	329
Zn	8.510	8.775	12.222	White	468
Cd	8.806	8.981	12.603	White	513

at 300°C with a Unicam camera appeared to have the same symmetry as seen at room temperature. At 500°C, a simpler pattern was obtained. This was difficult to read but face centered cubic symmetry was suggested with a cell dimension $a \simeq 12.2$ Å.

Piezoelectricity and a change in capacitance were observed as for $Ni_3B_7O_{13}NO_3$. Curie–Weiss type magnetic behavior from room temperature to 100°K gave a value of p_{eff} of 4.4 μ_B per average $\overline{Co,Ni}$ atom. In contrast to $Co_3B_7O_{13}NO_3$, no magnetic ordering was observed to 4.2°K.

$Cu_3B_7O_{13}NO_3$. Reaction of $Cu(NO_3)_2 \cdot 3H_2O/B_2O_3$ in a 1/1 mole ratio at 58 kbars/800°C—6 hr/quench gave irregularly shaped light straw-yellow crystals of $Cu_3B_7O_{13}NO_3$.

Anal. Calcd: O, 47.73; N, 2.61. Found: O, 48.45; N, 2.34, 2.40.

Domains could be observed optically in these crystals at room temperature. Their powder pattern was indexed as before (Table II). Thermal analysis showed a sharp reversible transition at 329°C. A high-temperature diffraction pattern taken with a Guinier–Lenné camera showed a reversible transition to occur at a temperature of 337 ± 9°C, in excellent agreement with the thermal data obtained for this compound. The high temperature X-ray diffraction pattern as measured above this transition at a temperature of 450°C could be indexed on the basis of face centered cubic symmetry with a cell dimension of 12.300 Å (±0.005).

$Zn_3B_7O_{13}NO_3$. Beige-colored crystals of $Zn_3B_7O_{13}NO_3$ showing striated, domain-like growth were prepared in the manner used to synthesize the Cu isotype.

Anal. Calcd: N, 2.58. Found: N, 2.26.

The powder pattern was indexed as before (Table II). A sharp reversible transition was observed at 468°C. Other phases always formed with this Zn nitratoboracite.

$Cd_3B_7O_{13}NO_3$. Reaction of $Cd(NO_3)_2 \cdot 4H_2O/B_2O_3$ in a 1/1 mole ratio at 58 kbars/700 to 900°C—4–8 hr/cool 1–5 hr to 400°C/quench gave colorless to cloudy crystals of $Cd_3B_7O_{13}NO_3$.

Anal. Calcd: N, 2.1. Found: N, 2.4.

Orthorhombic indexing of the powder pattern applied (Table II). A reversible thermal transition around 513°C was observed.

Discussion

The nitratoboracites $M_3B_7O_{13}NO_3$ (Co, Ni, Cu, Zn, Cd) appear to require high pressure for their synthesis since all formed at 58 kbars pressure but none were isolated from reactions carried out at 3–30 kbar. The divalent cations of Fe and Cr, which readily form halogenoboracites, failed to give the nitrato analogs at 58 kbars, however, due to their extreme ease of oxidation by NO_3^- to Fe^{3+} and Cr^{3+} and/or Cr^{4+} species. The high-pressure environment is presumed to prevent decomposition of the NO_3 group prior to attainment of a kinetically favorable reaction temperature allowing formation of the boracite lattice with incorporation of the NO_3 group therein. Once formed, the thermal stability of the nitratoboracites is high and they undergo reversible, first-order transitions in the temperature range 300–500°C.

Domain structure has been observed in thin sections of these new boracites under the polarizing microscope. Although multiple twinning in their room temperature form has precluded single crystal studies, careful indexing of their powder patterns strongly suggests the $Pca2_1$ orthorhombic symmetry observed in some of the halogenoboracites. The normal $F\bar{4}3c$ cubic symmetry appears to occur in the high-temperature form above the first-order transition. Presuming the point groups $mm2 \leftrightarrow \bar{4}3m$ to pertain below and above the observed transitions in the nitratoboracites, these materials have the potential of being multiaxial ferroelectric–ferroelastics in the same manner as the orthorhombic halogenoboracites. The degree of distortion from cubic symmetry at room temperature in the nitratoboracites, however, as expressed by the ratio of the two smaller orthorhombic cell dimensions b/a, is approximately 1.03 as compared to a value of 1.001 or less for the halogenoboracites. This indicates that the spontaneous shear strain around the c axis is appreciably larger in these new boracites and shear angles in the order of 1.7° are calculated.

Phases other than the $M_3B_7O_{13}NO_3$ boracites were also obtained in a number of these high-pressure reactions and will be reported separately.

Fluoroboracites

Natural borates containing fluorine such as the mineral fluoborite, $Mg_3(F,OH)_3BO_3$, are rare and there is little work in the literature directed toward synthesis of transition metal fluoroborates. Accordingly, pressure reactions were carried out between transition metal fluorides and B_2O_3 or H_3BO_3 and a number of new fluoroborate compounds have been isolated including two distinct fluoroboracite-type species. The first was prepared at pressures of 3–30 kbars and relates to the known halogenoboracites $M_3B_7O_{13}X$ having rhombohedral (*4*) or cubic symmetry while the second was prepared at a pressure of 58 kbars and is metastable at room temperature. The transition metal/B/F fusion-charge ratio proved to be critical to the synthesis of boracite-type phases and other fluoroborate compounds were also obtained in many of these syntheses. Their preparation and study will be reported separately.

Results—$M_3B_7O_{13}F$ Phases

$Co_3B_7O_{13}F$. Reaction of a 1/2 mole ratio of $CoF_2 \cdot 4H_2O/B_2O_3$ in a sealed gold tube at 3 kbars/700°C—24 hr/quench gave deep red-purple crystals of cubic growth habit about 0.1 mm in size. Reaction at 30 kbars/1000°C—2 hr/cool 4 hr to 400°C/quench gave the same product with crystals up to 2 mm in size. Their X-ray diffraction powder patterns related to that of the mineral boracite but line splitting was observed. All crystals examined were twinned, but indexing of a Guinier powder pattern (Tables III and IV) suggested that the *R*3*c* rhombohedral symmetry established (*4*) for $Fe_3B_7O_{13}Cl$ at room temperature applies for this compound. An infrared spectrum again indicated boron to be in two different coordination sites. These data suggested the fluoro analog of the halogenoboracites and the analyses were in agreement with the formula $Co_3B_7O_{13}F$.

Anal. Calcd: Co, 36.87; B, 15.78; O, 43.38; F, 3.96. Found: Co, 36.94, 37.08; B, 15.99; O, 43.51, 43.68; F, 4.06.

TABLE III

X-Ray Diffraction Powder Pattern of Rhombohedral $Co_3B_7O_{13}F$

I/I_0	$h\,k\,l$[a]	d	I/I_0	$h\,k\,l$	d
50	0 1 2	6.0261	20	1 2 8	1.9117
75	1 0 4	4.2799	2	1 3 4	1.9030
25	1 1 0	4.2467	50	0 2 10	1.8278
80	0 0 6	3.5086	20	0 4 2	1.8129
70	2 0 2	3.4727	10	0 0 12	1.7553
100	0 2 4	3.0155	35	4 0 4	1.7369
20	1 1 6	2.7051	10	2 1 10	1.6787
60	1 2 2	2.6891	40	2 3 2	1.6674
15	0 1 8	2.4782	35	3 2 4 4 1 0	1.6078
60	3 0 0 2 1 4	2.4533	10	1 0 13	1.5811
40	2 0 8	2.1407	15	4 1 6	1.4603
40	2 2 0	2.1243	15	5 0 2	1.4579
30	1 1 9	2.0495	20	3 0 12	1.4273
35	2 1 7	2.0422	20	2 3 8	1.4214
50	2 2 3 1 3 1	2.0327	15	0 5 4 3 3 0	1.4179
20	1 0 10	2.0248	10	2 2 12	1.3526
40	3 0 6	2.0107	10	2 4 4	1.3444
15	3 1 2	2.0038			

[a] Indexing on the basis of rhombohedral symmetry (*R*3*c*) using the hexagonal indices $a = 8.498$, $c = 21.055$ Å.

These crystals gave a positive test for piezoelectricity. In contrast to the known halogenoboracites and the new nitratoboracites, no sharp and reversible thermal transition was noted by DSC to 475°C nor by DTA to about 880°C, at which temperature decomposition had occurred to a solid having an X-ray pattern suggesting conversion to $Co(BO_2)_2$. A high-temperature X-ray diffraction pattern taken with a Guinier–Lenné camera showed retention of the same rhombohedral pattern from room temperature up to a decomposition temperature of 805 ± 8°C.

$Fe_3B_7O_{13}F$. Reactions of $FeF_2/1.5\ B_2O_3$ at 10 kbars/1000 or 800°C—2 hr/cool 4 hr to 400°C/quench, or $FeF_2/FeO/1.6\ B_2O_3$ at 25 kbars/1000°C gave pale yellow-green to blue-green crystals of irregular growth habit up to 1 mm in size having a crazed appearance. The X-ray pattern of these crystals was isotypic

TABLE IV

$M_3B_7O_{13}F$ BORACITES

Cation M	Rhombohedral $R3c$ indexing of room temp. powder pattern		Color of crystals	Max. temp., °C, in rhombohedral form
	a, Å	α, °		
Mg	8.566	59.34	White	> 500
Mn	8.682	59.53	Pink	> 500
Mn[a]	8.68	59.5	Beige	> 500
Fe	8.615	59.59	Yellow green to Blue green	> 500
Co	8.563	59.50	Red purple	805 ± 8, decomp.
Zn	8.592	59.27	White	> 500
Cr[b]	12.131		Pale blue	

[a] $Mn_3B_7O_{13}F_{0.44}(OH)_{0.56}$

[b] Face centered cubic indexing at room temperature.

with that of $Co_3B_7O_{13}F$ and could be indexed in the same manner on the basis of a rhombohedral unit cell (Table IV). Analyses were in agreement with the formula $Fe_3B_7O_{13}F$.

Anal. Calcd: O, 44.23; F, 4.04. Found: O, 44.46, 44.58; F, 4.31.

Crushed fragments of this boracite were observed to be anisotropic under the optical microscope and a uniaxial symmetry figure was observed in confirmation of the rhombohedral indexing used for the X-ray powder pattern. No sharp transition to 475°C was detected by DSC.

$Mn_3B_7O_{13}F$. Reaction of $MnF_2/B_2O_3/2H_3BO_3$ at 3 kbars/700°C—4 hr/cool 20 hr to 200°C/quench gave transparent, light pink microcrystals of $Mn_3B_7O_{13}F$.

Anal. Calcd: Mn, 35.26; F, 4.06. Found: Mn, 35.31; F, 3.93.

The X-ray pattern of these crystals could be indexed as before on the basis of a rhombohedral unit cell (Table IV). The same Mn fluoroboracite could be prepared at pressures of 10–25 kbars.

The hydroxy boracite $Mn_3B_7O_{13}OH$ has been prepared by Joubert (*8*) using similar hydrothermal pressure techniques. Synthesis conditions must be controlled in order to obtain a completely fluorinated Mn boracite since variations in the amounts of water and fluoride present in the reactants lead to formation of a series of fluorohydroxy phases $Mn_3B_7O_{13}F_{1-x}(OH)_x$. Reaction of $MnF_2/5MnO/2OH_3BO_3$ at 10 kbars/1000°C—2 hr/cool 3 hr to 400°C/quench, for example, gave pale beige crystals of $Mn_3B_7O_{13}F_{0.44}(OH)_{0.56}$.

Anal. Calcd: F, 1.80. Found: F, 1.78.

These crystals gave a positive test for piezoelectricity and their X-ray pattern could be indexed on the basis of a rhombohedral unit cell (Table IV).

$Zn_3B_7O_{13}F$. Reaction of $ZnF_2 \cdot 4H_2O/2B_2O_3$ at 3 kbars/400° or 500°C—24 hr/quench gave a white microcrystalline powder that analyzed for the composition $Zn_3B_7O_{13}F$.

Anal. Calcd: Zn, 39.32; F, 3.81. Found: Zn, 38.03; F, 3.78, 3.98.

Temperature was critical to the formation of this Zn fluoroboracite since reaction at 600°C gave a mixture of the boracite plus the known (*14*) sodalite-type compound $Zn_4O(BO_2)_6$, while at 700°C only $Zn_4O(BO_2)_6$ was isolated. Reactions at 25 kbars pressure also required temperatures around 400°C to produce any $Zn_3B_7O_{13}F$. The X-ray powder pattern of this compound was indexed on the basis of a rhombohedral unit cell (Table IV). No boracite-like phase was isolated from reactions carried out at a pressure of 58 kbars.

$Mg_3B_7O_{13}F$. Reaction of $MgF_2/5MgO/$

$2OH_3BO_3$ at 25 kbars/600°C—8 hr/quench gave a low yield of opaque white polyhedral crystals whose X-ray pattern was isotypic with that of $Co_3B_7O_{13}F$ and could be indexed in the same manner on the basis of a rhombohedral unit cell (Table IV). Insufficient material was isolated for analysis but since the cell volume differs from that calculated from data by Joubert (*8*) for the iostypic compound $Mg_3B_7O_{13}OH$, formation of $Mg_3B_7O_{13}F$ is presumed.

$Cr_3B_7O_{13}F$. The known Cr boracites differ from the other cation members of the series $M_3B_7O_{13}X$ ($X = Cl$, Br, I) in that all three halogeno phases are reported (*2*) to be isotropic at room temperature. The same situation pertains for the new boracite $Cr_3B_7O_{13}F$. Reaction of $CrF_2/2B_2O_3$ at 3 kbars/700°C—24 hr/quench gave an intimate mixture of very small pale-blue plus deep-green crystals. An X-ray diffraction powder pattern showed the known calcite-type $CrBO_3$ (*15*) to be one of the two phases present (green crystals). The remaining lines in the pattern (Table V) could be indexed on the basis of a face centered cubic cell (Table IV) of dimension $a = 12.131$ Å. Although the blue boracite-type crystals could not be isolated as a single phase for analysis, the mixture contained fluorine indicating the presence of $Cr_3B_7O_{13}F$.

Anal. Calcd: F, 4.14. Found: F, 2.98.

TABLE V

X-RAY DIFFRACTION POWDER PATTERNS OF PSEUDO CUBIC AND CUBIC FLUOROBORACITES

	Co[a]		Cr[b]		Cr[c]	
h k l	I/I_0	*d*	I/I_0	*d*	I/I_0	*d*
2 0 0	10	6.173	10	6.198	—	—
2 1 0	2	5.498	—	—	—	—
2 2 0	30	4.352	10	4.359	20	4.284
2 2 2	75	3.551	55	3.557	50	3.494
3 2 0	10	3.409	—	—	—	—
4 0 0	100	3.075	100	3.079	100	3.027
4 1 0	5	2.984	—	—	—	—
3 3 0	5	2.895	—	—	—	—
4 2 0	55	2.751	50	2.753	70	2.708
4 2 1	10	2.687	—	—	—	—
4 2 2	65	2.510	60	2.514	10	2.474
5 0 0	10	2.463	—	—	—	—
5 2 0	5	2.285	—	—	—	—
4 4 0	80	2.174	75	2.177	80	2.141
5 3 1	85	2.079	75	2.081	75	2.048
6 0 0	20	2.049	20	2.053	10	2.022
6 1 0	10	2.024	—	—	—	—
6 2 0	20	1.945	15	1.946	—	—
5 4 0	5	1.923	—	—	—	—
6 2 2	90	1.854	95	1.856	60	1.827
4 4 4	50	1.775	50	1.778	50	1.749
6 4 0	10	1.705	10	1.707	20	1.681
7 2 0	5	1.690	—	—	—	—
6 4 2	5	1.644	5	1.649	—	—
7 3 1	15	1.601	5	1.604	10	1.579
6 5 0	5	1.575	—	—	—	—
8 0 0	5	1.537	2	1.538	20	1.516
8 2 0	20	1.492	10	1.494	25	1.470
8 2 1	5	1.480	—	—	—	—
6 6 0	20	1.450	10	1.452	5	1.430
6 6 2	25	1.411	15	1.413	20	1.391
8 4 0	40	1.375	35	1.377	40	1.356
6 6 4	10	1.311	10	1.313	2	1.293
9 3 1	5	1.291	5	1.289	2	1.271
8 4 4	40	1.255	30	1.257	40	1.237
10 2 2	5	1.184	10	1.187	2	1.168
10 4 0	—	—	—	—	2	1.126
10 4 2	10	1.123	5	1.124	—	—
11 2 0	5	1.102	—	—	—	—
8 8 0	10	1.087	10	1.089	10	1.072
11 3 1	—	—	2	1.075	—	—
8 8 2	—	—	—	—	5	1.056
10 6 2	5	1.040	4	1.041	10	1.025
12 0 0	20	1.025	20	1.026	25	1.011
10 7 0	5	1.008	—	—	—	—
12 4 0	15	.972	5	.973	20	.959
10 8 0	—	—	—	—	10	.948
12 4 4	5	.927	5	.928	15	.914
12 6 0	—	—	—	—	15	.904
14 2 2	—	—	—	—	10	.849
12 8 0	—	—	—	—	10	.841

[a] 58 kbar phase, primitive pseudocubic indexing, $a = 12.301$ Å.

[b] 58 kbar phase, face centered cubic indexing, $a = 12.316$ Å.

[c] 3 kbar $Cr_3B_7O_{13}F$, face centered cubic indexing, $a = 12.131$ Å.

Results—58 kbar Boracite-like Phases

Co. Reaction of $CoF_2 \cdot 4H_2O/2B_2O_3$ at 58 kbars/1200°C—2 hr/cool 4 hr to 400°C/quench gave red, blocky crystals. Their powder pattern related to that of boracite and could be indexed on the basis of what appeared to be an anomalously large primitive pseudocubic cell (Tables V and VI). Analysis on this high-pressure boracite-like phase showed an oxygen content of 44.72%.

Fe. Reaction of $FeF_2/FeO/1.6B_2O_3$ or $FeF_2/2H_3BO_3$ at 58 kbars/1000°C—2 hr/cool 4 hr to 400°C/quench gave light-colored, irregularly shaped crystals. Their X-ray powder pattern was isotypic with that of the 58 kbar cobalt fluoroanalog and could be indexed in the same manner on the basis of an unusually large, primitive pseudocubic cell (Table VI). Untwinned single crystals could not be isolated for study but lower symmetry pertains since they were observed to be optically anisotropic.

Analyses and density determinations on this boracite-like phase suggested that a mixed oxy-hydroxy-fluoroborate anion might be incorporated in this high-pressure structure giving an approximate composition $Fe_3B_7O_{12}[BO_2F_{1.5}(OH)_{0.5}]$.

Anal. Calcd: O, 45.05; F, 5.53; density, 3.62 (based on 8 molecules per pseudocubic unit cell). Found: O, 44.37, 44.51, 44.67; F, 5.66; density, 3.60.

This high-pressure boracite-like phase proved to be metastable at room temperature and thermal analysis showed a large and irreversible endothermic reaction to occur on upheat over the temperature range 327–352°C. Following heating through the transition, the X-ray powder pattern of this material after cooling to room temperature was isotypic with that of the lower-pressure rhombohedral form of $Fe_3B_7O_{13}F$ with the exception of a few weak extra reflections.

Mn. Reaction of $MnF_2/3H_3BO_3$ at 58 kbars/1000°C—2 hr/cool 4 hr to 400°C/quench gave clear pink crystals 1–3 mm across. These crystals were optically anisotropic but their X-ray pattern was isotypic with those of the 58 kbar pressure Co and Fe boracite-like compounds and could be indexed on the basis of a similar large primitive pseudocubic cell (Table VI). Analyses and density determination again suggested a mixed oxy-hydroxy-fluoroborate anion species incorporated by high pressure into a boracite-like lattice of approximate composition $Mn_3B_7O_{12} \cdot [BO_2F_{1.6}(OH)_{0.4}]$.

Anal. Calcd: O, 44.96; F, 5.93; density, 3.50 (based on 8 molecules per pseudocubic unit cell). Found: O, 44.91, 46.02; F, 5.79, 5.80; density, 3.50, 3.52.

This high-pressure phase was piezoelectric and thermal analysis showed a large, irreversible endothermic reaction in the range 306–327°C. Following heating to 475°C and a cool to room temperature, the X-ray powder pattern was isotypic with that of the rhombohedral $Mn_3B_7O_{13}F$ phase.

Cr. Reaction of $Cr_2O_3/2CrF_3/2Cr/4B_2O_3$ at 58 kbars in the manner of the Co phase above gave a mixture of small blue plus green ($CrBO_3$) cystals. Lines in their X-ray diffraction powder pattern belonging to the blue phase (Table V) could again be indexed on the basis of a face centered cubic cell but with a slightly larger cell dimension $a = 12.316$ Å suggesting incorporation of a fluoroborate-type anion into this high-pressure boracite.

TABLE VI

58 kbar FLUORO BORACITE-LIKE PHASES

Cation M	Cubic indexing of room temp. powder pattern a, Å	Color of crystals	Irreversible thermal decomp. range, °C, to rhombohedral form
Mn	12.487[a]	Pink	306–327
Fe	12.361[a]	White	327–352
Co	12.301[a]	Red	Not meas.
Cr	12.316[b]	Pale blue	Not meas.

[a] Primitive, pseudo cubic cell. Crystals optically anisotropic.

[b] Face centered cubic indexing.

Discussion

Five of the halogenoboracites are reported (*4*) to occur in a low-temperature rhombohedral form in addition to their normal higher temperature orthorhombic and cubic forms. These comprise the Fe–Cl, Fe–Br, Fe–I, Co–Cl, and Zn–Cl compounds with transitions to this form occurring around temperatures of 255, 132, −73, 195, and 207°C, respectively. Like the nitratoboracites, the new $M_3B_7O_{13}F$ fluoroboracites also show more distortion from cubic symmetry than do the reported rhombohedral halogenoboracites. This distortion, which is indicated by the amount of deviation of the rhombohedral angle α from 60°, runs from 59.27 to 59.59° for the fluoroboracites (Table IV) as compared to only 59.87 to 60.17° for the known boracites (*4*). In the boracite structure, the large iodide anion is the halide most easily accommodated in a symmetrical manner in the very large, cage-like lattice site occupied by the halogens. Least amounts of thermal energy are required to transform the iodo phases from their distorted, ferroelastic, rhombohedral or orthorhombic forms into their high-temperature cubic form, and transition temperatures are observed to increase progressively on going from the iodo to the bromo and chloro species. X-Ray and thermal data suggest that the small fluoride anion occupies an energetically very stable off-center position of lower coordination number at one side of this large anion cage, since the lattice shows both a higher degree of distortion than that of the other halides, as well as a thermal stability that precludes a transition to higher symmetry by retaining this network in the rhombohedral form up to a decomposition temperature of 800°C. In contrast, the Fe–Cl boracite transforms from the rhombohedral to orthorhombic form at 255°C (*4*) and the Cd–Cl compound, with the highest reported transition temperature of all the halogenoboracites, converts to the cubic form at a temperature of about 525°C (*2*).

The fluoro-containing boracite-like compounds prepared at a pressure of 58 kbars are presumed to be true high-pressure phases that are metastable at room temperature since they undergo an irreversible alteration to the appropriate lower-pressure $M_3B_7O_{13}F$ species upon heating in the range 300–400°C at atmospheric pressure. Although X-ray patterns of these compounds could be indexed on the basis of a primitive pseudocubic cell, optical anisotropy observed in crystals of the Co, Fe, and Mn species indicated lower symmetry to pertain. The pseudocubic unit cell volumes of these high-pressure compounds were some 5% *larger* than those of their corresponding lower-pressure form, also calculated on the basis of pseudocubic rather than rhombohedral geometry. These data thus indicate that the stoichiometry of the high-pressure boracite-like phases differs from that of the $M_3B_7O_{13}F$ compounds but that these phases basically contain the same chemical and structural elements since $M_3B_7O_{13}F$ compounds readily form from them upon heating. Occupation of the halogen site in the boracite lattice by a tetrahedrally coordinated borato- or fluoroborato-anion species of some sort is proposed. Chemical analyses coupled with density data suggest a mixed oxy-hydroxy-fluoroborate anion $BO_2F_{2-x}(OH)_x$ ($x \simeq 0.4$–0.6) as a possible candidate, leading to the overall stoichiometry $M_3B_7O_{12}\cdot[BO_2F_{2-x}(OH)_x]$. Decomposition of such a high-pressure boracite would readily lead to formation of the very stable $M_3B_7O_{13}F$ species by elimination of the elements [BO(F,OH)]. The absolute structural configuration remains unresolved, however, since extensive twinning has to date precluded single crystal studies on this novel high-pressure boracite series.

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