Preparation and Mechanistic Studies of Halogen Boracites

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A new synthesis for the preparation of multigram amounts of high purity halogen boracites is presented. The boracites Ni–Br, Mg–Cl, Zn–Cl, Co–Br and Mn–I among others are prepared in essentially 100% yields and at temperatures as low as 200 °C in less than six hours. Mechanistic studies prove that the metal oxide is not necessary for boracite formation, but demonstrates its utility in previous boracite syntheses. Water is found to be essential for the formation of boracite presumably in the form of HBO_2. An oxidizing atmosphere is shown to inhibit boracite formation by preferentially forming metal borates.

Introduction

Boracites are a large family of compounds of the empirical formula $M_3B_7O_{13}X$, hereafter designated as M–X, where M is a divalent metal and X is a monovalent anion. The prototype mineral Mg–Cl, from which the family receives its name, is found primarily in Stassfurt, Germany, and has been known for at least two centuries [1]. In nature, only Fe [2] and Mn [2–4] are known to replace the Mg isomorph. The essentially pure Fe–Cl is called ericaite [3] whereas the Mn–Cl analogue is named chambersite [4].

The halogen boracites of all possible combinations of M = Mg, Cr, Mn, Fe, Co, Ni, Cu, Zn or Cd and X = Cl, Br or I, with the single exception of Cu–I, have been synthesized [5, 6–23]. In many cases [6–13, 16–18, 23] the claim of a boracite product is far from substantiated due to inadequate chemical and physical characterization. Mixed crystals of the type $(M_{3-n} M'_n)$–X and $M–(X_{1-n}X'_n)$ were reported to form for some halogen boracites [5, 21], but here too the evidence is inconclusive at best. Attempts to prepare halogen boracites of Ti and V [5], and Ca, Sr, Ba and Pb [16] have been unsuccessful. Aside from Cd, no other 4d metal boracites are known and although Pt boracites have been suggested [5], no 5d metal boracites are known. In addition, the boracites, Fe–OH [24], Mg–F, Cr–F, Mn–F, Fe–F, Co–F and Zn–F [26] and the nitrate boracites Co–NO_3, Ni–NO_3, Cu–NO_3, Zn–NO_3 and Cd–NO_3 [26] have been reported.

The synthetic boracites have been prepared by three basic techniques which include: sintering-flux type methods [6, 15–16], vapor transport type methods [5, 10–14, 17–18, 21–23] and hydrothermal type methods [19–20, 24–26]. All these reported boracite syntheses, whether they are concerned with the preparation of a single boracite or a variety of different boracites, share at least two of the following disadvantages: *(i)* low boracite yields, typically on the order of 25%, and small quantities of boracite product which is never greater than a few grams, *(ii)* boracite contaminated with complex metal borates and metal oxides, *(iii)* impure boracites reflecting nonstoichiometry or substitutional impurities, *(iv)* and complex experimental techniques at elevated temperatures, typically on the order of 900 °C. In particular, the vapor transport methods are prone towards explosion, and the hydrothermal synthesis of fluorine and nitrate boracites required pressures exceeding 3 kbar and 58 kbar, respectively.

This paper extends the application of a new synthetic route [27] for the preparation of a variety of halogen boracites which eliminates all the aforementioned disadvantages. Wet chemical analyses help confirm the stoichiometric formula of the synthesized boracites. In addition, some insight into the mechanism of boracite formation is presented.

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TABLE I. Results of Boracite Synthesis.

| Boracite	T (K)	P (atm.)	t (h)	Atm.	MX_2	Reactants (g)		Yield (%)
						$LiBO_2$	H_2O	
Ni–Br	270	11	60	air	65.6	34.8	1.8	38
Ni–Br	270	11	60	argon	65.5	34.8	1.8	55
Ni–Br	270	11	60	oxygen	65.5	34.8	1.8	12
Ni–Br	270	26	60	air	65.5	34.8	21.8	87
Ni–Br	270	26	60	argon	65.5	34.8	21.8	95
Ni–Br	270	20	40	argon	65.5	34.8	21.8	95
Zn–Br	270	33	24	argon	135.2	69.6	16.0	98
Zn–Cl	270	18	24	argon	81.8	69.6	16.0	95
Cu–Cl	270	18	26	argon	80.6	69.6	16.0	91
Mn–Cl	270	5	24	argon	75.6	69.6	14.0	95
Co–Br	270	6	18	air	66.2	34.8	9.0	nm[a]
Mg–Cl	270	5	18	air	57.7	17.4	9.0	nm
Mn–I	270	5	18	air	45.0	17.4	9.0	nm

[a]nm = not measured.

Experimental

Materials

For the synthesis work, the reactants were used as received, and obtained from the following sources: boron trioxide (99.9%), boric acid (99%), divalent metal halides, anhydrous (99%), lithium metaborate, anhydrous (99%), all from Apache, and argon (99.995%), from Matheson. Deionized water having a resistivity >7 MΩ cm^{-3} was used throughout the study.

For the mechanistic studies, boron trioxide 25 g, ingots ($>99.999\%$), and anhydrous nickel bromide, both from Apache were dried prior to use in quartz ampoules under a continuous vacuum of 10^{-3} torr at 160 °C for 48 h. These moisture sensitive reactants were handled under an argon atmosphere in a standard glove box.

Synthesis Method

The boracite synthesis can be described by the following stoichiometric reaction:

$$7LiBO_2 + 3MX_2 + H_2O \rightarrow$$

$$M_3B_7O_{13}X + 5LiX + 2LiOH \qquad (1)$$
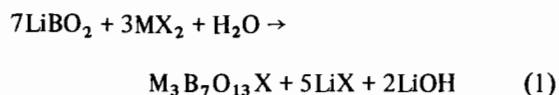
Additional water up to 15 mol in excess of that given by reaction (1) has been found to be beneficial. Consequently, the metal halide and the lithium metaborate may be used in hydrated forms with no effect upon the reaction. This is of considerable convenience since drying these reactants to the anhydrous state is difficult. The reaction is not limited to the use of $LiBO_2$ as we have used $NaBO_2$ and $CsBO_2$ as well with no apparent effect upon the reaction.

The reaction is carried out in a 250 cm^3 Parr pressure reaction vessel constructed of the metal Hastelloy C. The vessel is equipped with a thermocouple well, a pressure release valve and an interchangeable pressure gauge. The temperature was maintained to ±3 °C by a Parr temperature controller and the system is capable of continuous operation at temperatures and pressures up to 400 °C and 680 atm. The temperature was measured with a chromel–alumel thermocouple. The millivolt output from the thermocouple was read with a room temperature compensated digital temperature indicator and also displayed on a standard strip chart recorder. The accuracy of these instruments was periodically checked with a potentiometer. The accuracy of the pressure gauge was not verified.

In a typical synthesis applied to Ni–Br boracite, 34.8 g (0.7 mol) of $LiBO_2$, 65.6 g (0.3 mol) of $NiBr_2$, and 21.8 g (1.2 mol) of H_2O were placed in the reaction vessel under an argon atmosphere at one atm pressure. The contents were heated to a temperature of 270 °C which developed a pressure of 26 atm. After 60 h the vessel was rapidly cooled (~1 h) by quenching to room temperature. The product was treated with hot 10% HCl and then boiled in excess water for several hours to dissolve unreacted material as well as soluble by-products. Several hot water washings followed by filtration and air drying resulted in 51.4 g of Ni–Br (yield >95%).

Stoichiometric Analyses

Chemical analyses of the halogen boracites were performed by wet chemical methods using standard reagent grade chemicals.

For the determination of halogen, the boracite sample was digested in boiling 48% hydrofluoric

TABLE II. Chemical Analyses and Properties of Boracites.

Boracite	M.W.	Color[a]	B (wt.%)		X (wt.%)	
			Calcd	Found	Calcd	Found
$Mg_3B_7O_{13}Cl$	392.04	colorless	19.30	19.22	9.04	8.83
$Cr_3B_7O_{13}Cl$	475.12	deep blue	15.93	15.89	7.46	7.33
$Mn_3B_7O_{13}Cl$	483.93	pink	15.64	15.81	7.33	7.42
$Cu_3B_7O_{13}Cl$	509.76	blue green	14.84	14.75	6.96	7.09
$Co_3B_7O_{13}Br$	540.36	purple	14.00	13.78	14.79	14.07
$Ni_3B_7O_{13}Br$	539.70	yellow brown	14.02	14.13	14.80	14.68
$Zn_3B_7O_{13}Br$	559.71	colorless	13.52	13.36	14.28	14.25
$Fe_3B_7O_{13}I$	578.12	red violet	13.09	12.91	21.95	21.83

[a]Reflected light.

acid in a teflon reflux station and the silver halide precipitated with aqueous silver nitrate. The halogen was measured gravimetrically.

For the determination of boron a modification of the volumetric determination of boric acid [28] was used. This method consisted of digesting the boracite sample in boiling 1 N hydrochloric acid under reflux with the addition of mannitol. The solution was then titrated with carbonate free 2.5 N sodium hydroxide and corrected for the acidity of the excess hydrochloric acid.

Analyses of the metals or oxygen were not performed.

Results and Discussion

The results of the syntheses of several different boracites are given in Table I. The pressure of the system is a function of temperature and the amount of reactant present in the vessel. This pressure represents the peak pressure attained at the beginning of the experiment. The column headed H_2O under reactants refers to the total amount of water in the system. In some cases this water was in the form of hydrated metal halide or hydrated metal borate. The boracite yields, which under optimum conditions are close to 100%, represent the highest yield of boracite ever reported.

Table II gives the calculated molecular weights, the color in reflected light, and the results of the chemical analyses for several boracites. The wt.% values of boron and the halogen support the empirical formula for boracite and show no appreciable deviations from stoichiometry.

From the data given in Table I several conclusions can be drawn. The yield of boracite is invariant with respect to temperature from 200 to 270 °C, pressure from 5 to 33 atm, and time from 12 to 60 h. The

boracite yield does however exhibit a strong dependence upon the atmosphere being very sensitive to oxidation. This can be explained by considering that the argon prevents the competing reaction

$$MX_2 + \tfrac{1}{2}O_2 \rightarrow MO + X_2 \qquad (2)$$
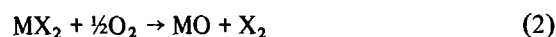
from occurring. This is supported by a thermodynamic study of the oxidation of $MgCl_2$ by Ball [29] who notes that at temperatures above 230 °C the equilibrium of reaction (2) lies appreciably to the right and at 425 °C and one atm pressure the ratio $P_{O_2}/P_{Cl_2} = 1.0$. The formed MO can then react with B_2O_3 to form metal borates. In the case of Ni–Br synthesized in oxygen and in air, a major product was identified as $Ni_3B_2O_6$ [30] which supports this argument. This result also indicates that the presence of metal oxide is not necessary for the formation of boracite as was previously assumed [5, 10–14, 21–23].

It was stated earlier that vapor transport methods of boracite synthesis are prone towards explosion and that most boracite reactions require a closed reactor system. The explosions are partially a result of the fact that all boracite synthesis result in the formation of the correspondingly hydrogen halide gas as a by product. This occurs by the reactions:

$$3MX_2 + B_2O_3 \rightarrow 2BX_3 + 3MO \qquad (3)$$

$$2BX_3 + 3H_2O \rightarrow 6HX + B_2O_3 \qquad (4)$$
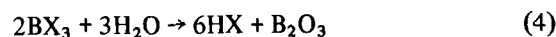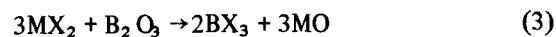
which were found to occur spontaneously at temperatures above 200 °C for $NiBr_2$, $NiCl_2$, $MgCl_2$ and $ZnBr_2$. Thus the role of metal oxide in previous synthesis can be understood by considering the reaction
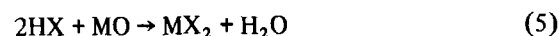
$$2HX + MO \rightarrow MX_2 + H_2O \qquad (5)$$

TABLE III. Effect of the B_2O_3:H_2O Mole Ratio on the Yield of Ni–Br.

Mole Ratio B_2O_3:H_2O	B_2O_3–H_2O Species	Ni–Br Yield (%)
12:0	B_2O_3	0
11:1	$B_2O_3 + H_2O$	0
10:2	$B_2O_3 + H_2O$	5
9:3	$B_2O_3 + H_2O$	10
8:4	$B_2O_3 + H_2O$	40
7:5	$HBO_2 + B_2O_3$	50
6:6	HBO_2	55
5:7	HBO_2	55
4:8	HBO_2	55
3:9	H_3BO_3	50
2:10	$H_3BO_3 + H_2O$	45
1:11	$H_3BO_3 + H_2O$	5
0:12	H_2O	0

which shows that the metal oxide preferentially forms the metal halide under the conditions described. In addition, the halogen gas, when wet and at elevated temperatures, decomposes boracite. The same is true for the concentrated hydrohalogen acid. In reaction (1) $LiBO_2$ is utilized as a boron–oxygen source where the hydrolyzed Li base acts as an absorber for the hydrogen halide gas being evolved. Consequently, a lower operating pressure can be used than is normally required. The residual pressure is due to the presence of water at the initial stages of the reaction. In order to prove this important point, reaction (1) was performed in an evacuated (10^{-6} torr) quartz ampoule where the pressure of the system was not known precisely, but probably less than 3 atm (the pressure at which quartz tubes of 2 mm wall thickness typically explode). By this modification, Ni–Br and Co–Br were synthesized at 230 °C in 6 h in yields exceeding 90%. It should be noted, however, that the amount of boracite produced is restricted only by the volume of the quartz ampoule.

Mechanistic studies which examined the B_2O_3–H_2O phase equilibria were performed also. For this work the reaction

$$6MX_2 + 7B_2O_3 + 5H_2O \rightarrow$$

$$2M_3B_7O_{13}X + 10HX \qquad (6)$$
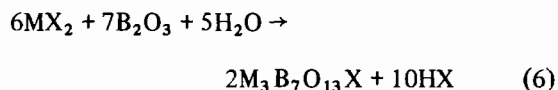
was employed with variations in the B_2O_3:H_2O mole ratio. The reaction was applied to Ni–Br and performed arbitrarily at 280 °C. The results of this set of experiments are summarized in Table III. The B_2-
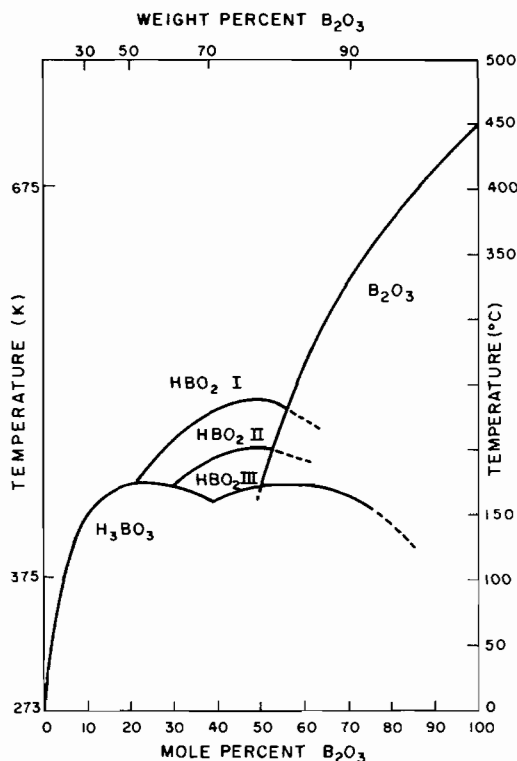
Fig. 1. B_2O_3–H_2O phase diagram (after Kracek, Morey and Merwin).

O_3–H_2O species, which are expected to be present in the reaction, are taken from the detailed B_2O_3–H_2O phase diagram of Kracek, Morey and Merwin [31] shown in Fig. 1. The highest yield of Ni–Br is obtained when the HBO_2 species is present. The observation that Ni–Br formed in high yields were H_3BO_3 and B_2O_3 are dominant species suggests the possibility that HBO_2 extends its stability range in the liquidus region of the phase diagram. The possibility of some other species, *e.g.* polymers of HBO_2, cannot be excluded.

These data prove that water is essential for the formation of boracite and that an appreciable amount of boracite will form over a relatively wide B_2O_3–H_2O composition. More importantly the data clearly show that HBO_2 is the major active species for the formation of boracite.

Acknowledgments

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