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New and Improved Syntheses of Boracites

M. DELFINO*

Philips Laboratories, Briarcliff Manor, N.Y. 10510, U.S.A.

and P. S. GENTILE

Department of Chemistry, Fordham University, Bronx, New York, N.Y. 10458, U.S.A.

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Boracites are complex-cage compounds of the general formula $M_3B_7O_{13}X$, where M is a divalent metal and X is a monovalent anion. Structurally, boracite is a cubic borate cage composed of BO_4 and BO_3 groups with the halogen in the center of the cube and the metal occupying face centered sites.

To date, the most general method of synthesizing boracites, particularly the halogen type exclusive of fluorine, has been the vapor transport method of Schmid [1] and its various modifications [2–4]. From a synthetic point of view, this method of preparation has the following disadvantages; a sophisticated experimental arrangement which is often susceptible to explosion, a relatively low yield of boracite, high reaction temperatures, and boracite contaminated with the often difficult-to-separate metal borates. In this preliminary communication, we report a new synthesis of boracites by a low-temperature method which eliminates all of these problems.

The boracite syntheses reported are 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 for this reaction. Consequently, the metal halide and the lithium metaborate may be used in hydrated forms with little or no effect upon the reaction. This is of considerable convenience since drying the metal halide and lithium metaborate to the anhydrous state is difficult. The reaction is carried out in a 250 cm^3 Paar pressure reaction vessel constructed of hastelloy C. The vessel is equipped with a thermocouple well and a pressure gauge. The temperature of the reaction vessel is recorded by a chromelalumel thermocouple and read with a d.v.m. A temperature stability of ±3 °C is maintained by a Paar temperature controller.

In a typical synthesis applied to $Ni_3B_7O_{13}Br$, 34.8 g (0.7 mol) of $LiBO_2$ (99% Apache Chemicals), 65.6 g (0.3 mol) of $NiBr_2$ (99.99% Apache Chemicals) and 21.8 g (1.2 mol) of deionized–deoxygenated H_2O were placed in the reaction vessel under an argon atmosphere at atmospheric pressure. The inert atmosphere prevents the competing reaction,

$$MX_2 + \tfrac{1}{2}O_2 \rightarrow MO + X_2 \qquad (2)$$

from occurring which leads to the formation of unwanted metal borate. The contents were heated to a temperature of 270 °C and a pressure of 26 atm in approximately 3 h. After 60 h the vessel was rapidly cooled (~1 h) 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 water solutle by-products. A repeated water rinsing followed by filtration and air drying resulted in 51.4 g of $Ni_3B_7O_{13}Br$ (a yield of >95%). The chemical integrity of the boracite was verified by wet chemical analysis, X-ray powder diffraction and infrared absorption spectra. Under similar conditions, the boracites $Ni_3B_7O_{13}I$, $Zn_3B_7O_{13}Br$ and $Mg_3B_7O_{13}Cl$ were synthesized in yields exceeding 95%. These results represent the highest yields of boracites reported to date by any method. Additional work in progress has demonstrated the feasibility of the synthesis of $Ni_3B_7O_{13}Br$ in yields exceeding 90% at pressures under 3 atm. Consequently, the synthesis can be carried out in sealed quartz ampoules at 225 °C.

Further details establishing experimental minima will be reported separately.

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*Present address: Fairchild Research and Development Laboratory, Palo Alto, Ca. 94304, U.S.A.