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Note

THERMAL DECOMPOSITION OF HALOGEN BORACITES

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Halogen 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 = Cl, Br, or I. These materials are of considerable interest because they are thought to be improper ferroelectrics [1,2], i.e. a ferroelectric where the spontaneous polarization is not the primary order parameter, although alternative interpretations have been offered [3,4]. For this reason, large single crystals are required, and thermal stability data are of importance for determining potential crystal growth methods.

A recent thermal study claiming that boracites melt [5] infers that melt techniques, e.g. Czochralski growth, may be viable. This work demonstrates that boracites do not melt, but decompose and that melt techniques are not feasible, at least under the conditions described.

EXPERIMENTAL

The boracite samples used in this work were obtained from a variety of sources: crystals of Ni—Br, Cu—Cl and Fe—I were generously supplied by F.W. Ainger and R. Whatmore (Plessey, England); crystals of Ni—Br and Fe-I were kindly furnished by T. Gier (DuPont, U.S.A.). These samples were synthesized by the vapor transport method of Schmid [6]. In addition, powder samples of Ni—Br, Mg—Cl, and Zn—Br synthesized by a low-temperature technique [7] were examined.

Thermogravimetric analyses at temperatures up to 950°C were performed with a Perkin-Elmer thermogravimetric system, model TGS-2, which includes a recording balance, model FDC-1. A Harrop thermogravimetric system, model TGA-716, interfaced to a model TA-700 control console, extended the upper temperature limit to above 1400°C.

The heating rate was 10°C min^{-1} and the boracite samples were typically

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of the order of 20 mg. Weight changes of the order of 0.01 mg, typically 0.05% were detected. Platinum sample cups were used and measurements were made both under static conditions in air and under a vacuum of 10^{-3} Torr.

Powder X-ray diffraction data were obtained with Cu*K*α radiation using a Norelco powder diffractometer.

RESULTS AND DISCUSSION

The thermogravimetric curves, measured in static air, of Mg—Cl, Cu—Cl, Ni—Br, Zn—Br and Fe—I are shown in Fig. 1. These samples exhibit no weight gain or loss (0.05%) up to 825° C reflecting no surface reactions with the atmosphere and relatively low vapor pressures up to that temperature. The first detectable weight loss of any halogen boracite occurs at 863° C in Fe—I. At the other extreme, Ni—Br begins to undergo a loss in weight at 1022° C. Thus the halogen boracites are thermally stable to relatively high temperatures.

The initial temperature corresponding to a weight change follows the trend, Ni—Br > Zn—Br > Mg—Cl > Cu—Cl > Fe—I. In addition, the general features of the thermogravimetric curves are markedly different for each halogen boracite, but the curves for a boracite type were nearly identical. The largest weight loss occurs in Cu—Cl (28.5% at 1127° C) and the smallest weight loss in Ni—Br (5.4% at 1127° C). In Mg—Cl and Fe—I, a strange weight gain occurs at 1077 and 1100° C, respectively. These observations, indicating different decomposition mechanisms for the various halogen boracites, suggest structural dissimilarities.

The thermogravimetric curves measured in vacuum of Mg—Cl, Ni—Br and

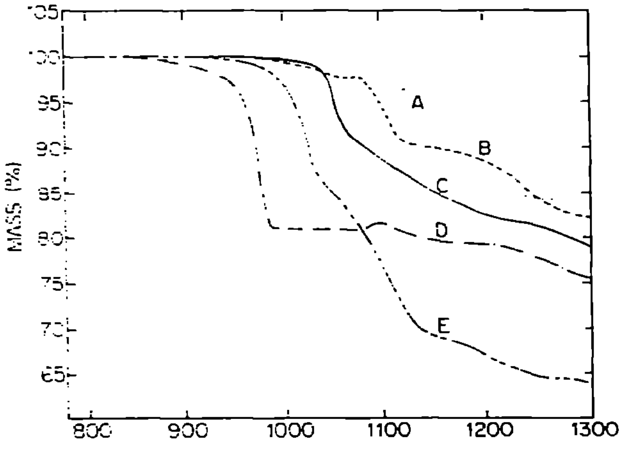

Fig. 1. Thermogravimetric curves for halogen boracites in static air. A, Ni—Br; B, Mg—Cl; C, Zn—Br; D, Fe—I; E, Cu—Cl.

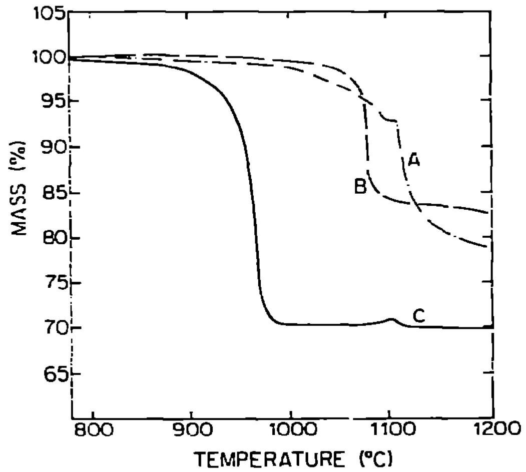

Fig. 2. Thermogravimetric curves for halogen boracites in vacuum. A, Mg—Cl; B, Ni—Br; C, Fe—I.

Fe—I are shown in Fig. 2. The general features observed for these samples in static air are preserved under vacuum conditions except that the magnitude of the weight loss is greater and that the temperature of the initial weight loss is lower. For example, in Mg—Cl, a 9.8% weight loss is observed at 1127°C in static air whereas a 16.5% weight loss is observed at 1127°C in vacuum. This behavior is typical of thermogravimetric curves in general when a comparison is made in vacuum and air. The weight gains in Mg—Cl and Fe—I are again observed at 1077 and 1100°C, respectively, in vacuum. This suggests that these small weight gains of the order of 0.7% are not due to oxidation. They may result from some decomposed gas product which reacts with the remaining boracite sample to form a new product which is momentarily stable and then rapidly decomposes. In Table 1, the decomposition temperatures corresponding to 1.0% weight loss recorded under static air and under vacuum are given. The 1.0% weight loss was selected over the initial weight loss since it is considered to be a more accurate reference point. The same trend for the initial temperature corresponding to a weight change is followed.

Gallagher [5] studied the thermal stability of Cu—Cl, Ni—Br and Fe—I in both flowing air (40 cm^3 min^{-1}) and vacuum. In general, there is considerable disagreement between his results and ours. He states that only Fe—I exhibits a weight loss below 997°C whereas we find that both Cu—Cl and Fe—I show appreciable loss of weight below 997°C. More importantly, Gallagher [5] claims that endothermic peaks, measured by differential thermal analysis in static air, are observed in the halogen boracites, which indicates melting. The melting points found were 1005°C for Cu—Cl, 1050°C for Ni—Br and 965°C for Fe—I. The melting points of Cu—Cl and Fe—I correspond to weight losses of 9.9 and 6.7% in our data. In Ni—Br, the results are less clear since we measure a 0.4% weight loss only. In order to resolve this fundamental discrepancy, single crystal samples of Ni—Br were heated in air at 1037°C for 24 h. When cooled down to room temperature at a rate of 5°C min^{-1}, the crystals had taken on an emerald green color, showed no signs of melting and had undergone a 6% weight loss. The same experiment was then performed at 1202°C for 24 h. The resulting crystals were a bright emerald green color and showed no signs of melting. In fact, the natural facet

TABLE 1

Decomposition temperatures corresponding to a 1.0 wt.% loss

Boracite	Decomposition temperature (°C)	
	Static air atmosphere	Vacuum
Mg—Cl	1002	990
Cu—Cl	978	nm *
Ni—Br	1075	1033
Zn—Br	1032	nm *
Fe—I	908	869

* nm = not measured.

morphology, although powdery, was still preserved. Similar results were obtained when done under vacuum or in flowing oxygen at 5 cm^3 min^{-1} proving that Ni—Br does not melt, but decomposes. The emerald green product obtained from these thermal treatments was identified as $Ni_3B_2O_6$ [8] by X-ray powder diffractometry. The overall decomposition of Ni—Br is represented as

$$Ni_3B_7O_{13}Br \rightarrow Ni_3B_2O_6 + [B_5O_7Br] \quad (1)$$

where the brackets refer to no specific compound, but suggest species such as $2\,B_2O_3 + 1/2\,O_2 + 1/2\,Br_2$. Evolved gas analysis of the decomposition of Ni—Br [5] did detect such species among others and is therefore consistent with our suggested decomposition mechanism.

A final point is that evolved gas analysis of Cu—Cl, Ni—Br and Fe—I detected a peak at a.m.u. = 44 which was attributed to CO_2^+ [5]. We suggest that the correct species is HBO_2^+, which recent mechanistic studies [9] have shown to be a dominant reactant in the formation of boracite.

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