Thermochimica Acta, 29 (1979) 165–169

THERMAL STABILITY OF SOME BORACITES

P. K. GALLAGHER
Bell Telephone Laboratories, Murray Hill, New Jersey 07974 (U.S.A.)
(Received 28 March 1978)

ABSTRACT

The thermal stability of some boracites, $CuB_7O_{13}Cl$, $NiB_7O_{13}Br$ and $FeB_7O_{13}I$, was investigated using thermogravimetry in air up to 1000°, DTA in air to 1200° and evolved gas analysis in vacuum to 1200°C. Only the Fe–I compound showed weight loss below 1000°C. The endothermic peaks associated with melting were Cu–Cl (1025°C), Ni–Br (1150°C) and Fe–I (965°C). Evolved gas analysis indicated major differences in the decomposition products of the three materials.

INTRODUCTION

There has been considerable interest in transition metal boracites because of their ferroelectric, magnetic, elastic and optical properties[1]. The general formula for boracites is $M_3B_7O_{13}X$, where M = divalent cation (Cu, Ni or Fe herein) and X = a halide ion.

Although the proposed uses of these materials do not demand a high degree of thermal stability, information concerning the behavior of these materials at elevated temperatures is of great value to those concerned with their crystal growth. For this reason three boracites, Cu–Cl, Ni–Br and Fe–I, were selected and their thermal decomposition studied in air and vacuum.

EXPERIMENTAL PROCEDURES AND RESULTS

Small single crystals of $Cu_3B_7O_{13}Cl$, $Ni_3B_7O_{13}Br$ and $Fe_3B_7O_{13}I$, grown from the vapor phase at around 700°C, were obtained from The Plessey Co. via Mr. G. M. Loiacono (North American Philips Laboratories, Briarcliff Manor, N.Y.).

A Perkin-Elmer TGS-1 thermobalance which had been modified for digital data collection[2] was used for the thermogravimetric (TG) studies. Chips, 4–8 mg, from the single crystals were heated to about 1000°C at 10° min^{-1} in 40 cm^3 min^{-1} of dry air. Figure 1 indicates the weight loss as a function of temperature for the three materials.

Differential thermal analysis (DTA) was performed using a Dupont Model 900 instrument in conjunction with its high temperature cell. Chips, 20–44 mg, of the

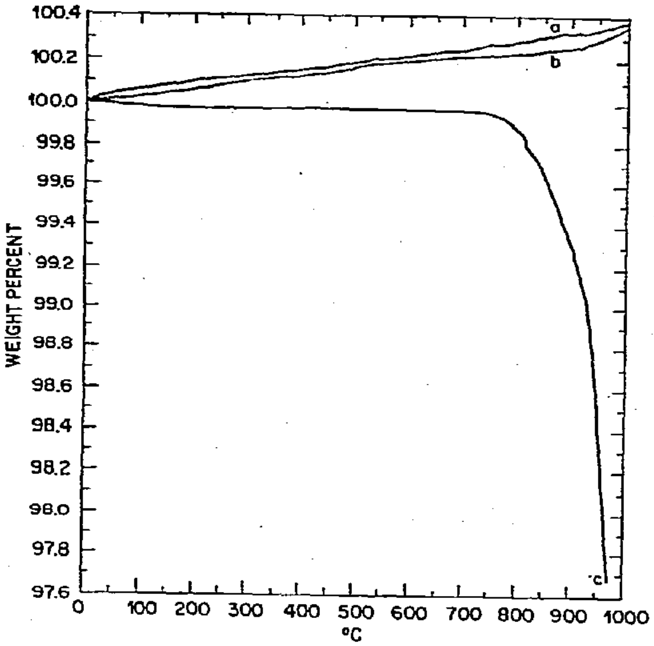

Fig. 1. TG curves for selected boracites (10° min^{-1}, flowing air). a, Cu–Cl, 5.98 mg; b, Ni–Br, 4.85 mg; c, Fe–I, 14.11 mg.

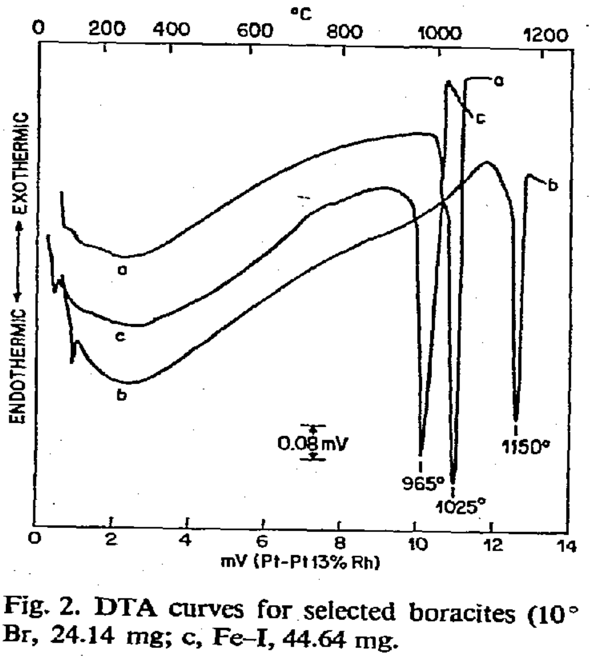

Fig. 2. DTA curves for selected boracites (10° min^{-1}, stagnant air). a, Cu–Cl, 20.87 mg; b, Ni–Br, 24.14 mg; c, Fe–I, 44.64 mg.

single crystals were heated somewhat above their melting points at 10° min^{-1} in stagnant air. The sample containers were Pt foil cups. Figure 2 presents the results of the experiments.

The mass spectrographic apparatus for the evolved gas analysis (EGA) has been described elsewhere[3]. Chips, 2–4 mg, of the single crystals were heated at 125°

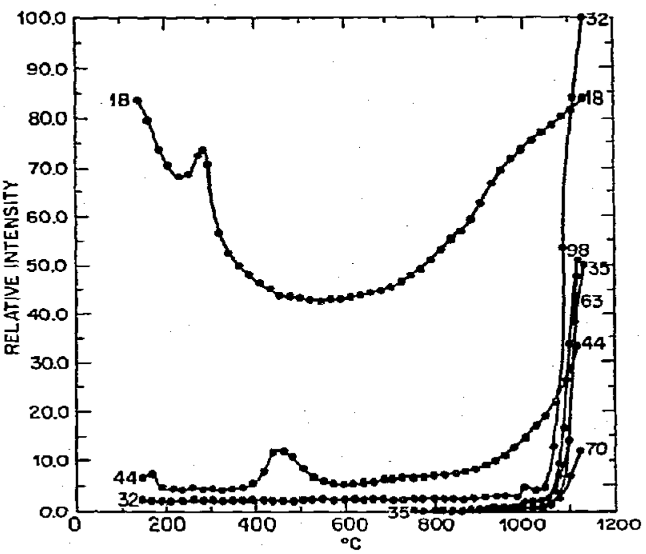

Fig. 3. EGA curves for Cu–Cl boracite (125° h^{-1}, vacuum, 4.36 mg). 18, H_2O^+; 32, O_2^+; 35, Cl^+; 44, CO_2^+; 63, Cu^+; 70, $B_2O_3^+$; 98, $CuCl^+$.

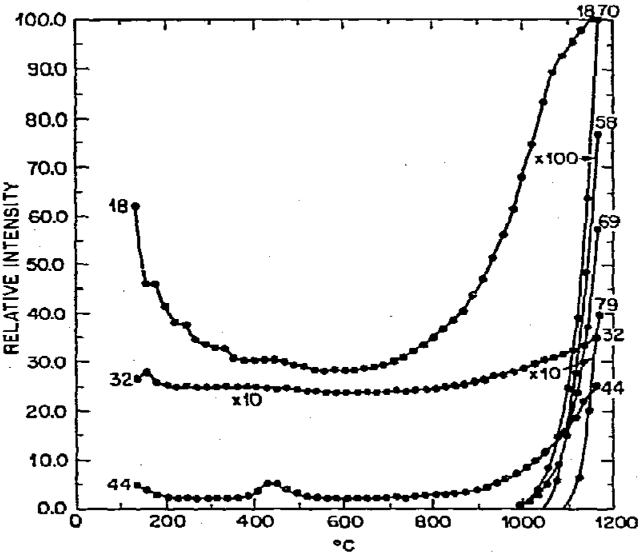

Fig. 4. EGA curves for Ni–Br boracite (125° h^{-1}, vacuum, 2.08 mg). 18, H_2O^+; 32, O_2^+; 44, CO_2^+; 58, Ni; 69 (broad), $NiBr^{2+}$; 70, $B_2O_3^+$; 79, Br^+.

h^{-1} in a Pt crucible. The vacuum was about 8×10^{-8} at room temperature in the absence of outgassing. For the Cu–Cl and Ni–Br samples, the mass range of 0–100 AMU was scanned repeatedly while for the Fe–I sample the range of 0–140 AMU was analysed. Each scan required 10 min. The peaks were integrated and computer plots of relative integrated intensity versus temperatures are shown in Figs. 3–5 for selected mass numbers. Each figure is normalized to the most intense peak during that experiment but they are not comparative from one figure to another. The weight losses associated with the EGA in vacuum were Cu–Cl (10%), Ni–Br (5%) and Fe–I (10%).

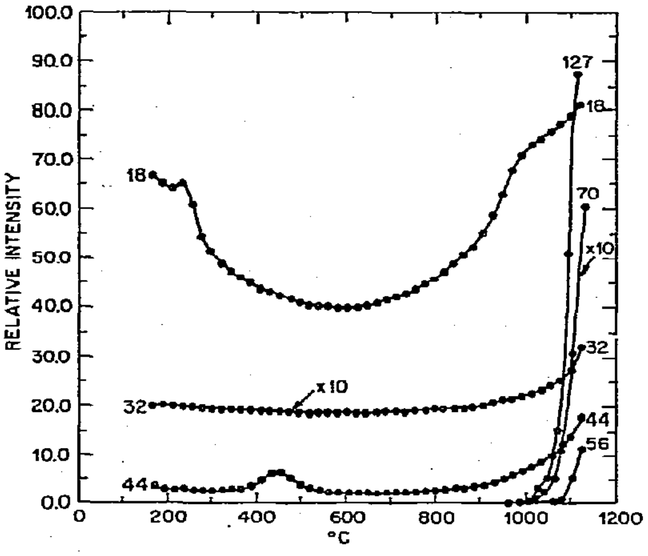

Fig. 5. EGA curves for Fe–I boracite (125° h^{-1}, vacuum, 3.35 mg). 18, H_2O^+; 32, O_2^+; 44, CO_2^+; 56, Fe^+; 70, $B_2O_3^+$; 127, I^+.

DISCUSSION

The results of the TG and DTA experiments in Figs. 1 and 2 are not very informative in terms of indicating the nature of the decomposition. Clearly the Fe–I boracite is the least stable in air since the TG curve shows the onset of weight loss at about 750°C. Both the Cu–Cl and Ni–Br boracites exhibit very small weight gains, slightly more than buoyancy effects on a Pt blank.

The DTA results in Fig. 2 serve to indicate the approximate melting points of the materials. There are low-temperature transitions but they are not relevant to this work and the experimental arrangement was far from optimum for investigating those phenomena. The peak temperatures associated with the melting endotherms are given in Fig. 1. However, some form of extrapolated onset or departure from the baseline would more accurately define the melting points.

The EGA curves are much more informative regarding the nature of the thermal decomposition, at least in vacuum. All three materials give rise to slight evolutions of H_2O around 250°C and CO_2 around 450°C. These are only trace amounts and presumably arise from chemisorbed surface layers. There is evidence that hydroxide ions might partially substitute for the halide ions[4] in boracites; however, this is not likely in the present crystals which were grown at higher temperatures. Unfortunately, the water peak is by far the predominant one in the background and it is therefore difficult to unequivocally establish the evolution of minor amounts of water. The background in both H_2O and CO_2 increases at higher temperatures due to desorption from the walls of the vacuum chamber, power feed-throughs, etc., as the system is slightly warmed by radiation from the furnace. There does appear, however, to be a greater evolution of water at higher temperatures, > 1000°C, for the Ni–Br material than for the others. This may indicate greater OH content or substitution in that crystal.

Outside of the similarity in chemisorbed surface impurities, the decomposition of the three boracites is decidedly different. Figure 3 indicates that the predominant species evolved from Cu–Cl boracite during its thermal decomposition in vacuum is oxygen. Among the three divalent transition metals studied, Cu, Ni and Fe, the most easily reduced ion is Cu. It is therefore not unreasonable that major quantities of oxygen are lost at the initial stage of decomposition in vacuum. Substantially lesser amounts of CuCl, Cu and Cl are evolved. Only a minor amount of B_2O_3 is evolved. There may be a complete breakdown of the structure at this point or there may be a simple evolution of oxygen with the formation of the appropriate vacancies, since boracites are known with monovalent ions and reduced oxygen contents[5]. In air the reduction would be suppressed to somewhat higher temperatures and the decomposition scheme may be different.

The decomposition of Ni–Br boracite in vacuum, on the other hand, shows no evolution of oxygen or reduction. Figure 4 indicates that B_2O_3 and NiBr are the predominant species for masses lower than 100 AMU. Presumably the doubly charged NiBr and much smaller amounts of Ni and Br arise from the cracking pattern resulting during the ionization of gaseous $NiBr_2$. Both singly and doubly charged $NiBr_2$ would have been at higher mass to charge ratio than scanned.

Thermal decomposition of the Fe–I boracite in vacuum again involves oxidation–reduction mechanisms. Iodide ion is oxidized to free iodine which is readily evolved, as can be seen in Fig. 5. At higher temperatures B_2O_3 and smaller amounts of Fe are detected. To compensate for the oxidation of iodide ion, divalent iron is reduced.

The initial decomposition steps in vaccum, based upon the EGA results, can be summarized in the form of the following equations, where the brackets merely reflect a stoichiometric assemblage rather than any specific compound.

$$4\,Cu_3B_7O_{13}Cl \rightarrow [14\,B_2O_3 \cdot 4\,Cu_2O \cdot 4\,CuCl] + 3\,O_2 \quad (1)$$
$$2\,Ni_3B_7O_{13}Br \rightarrow 7\,B_2O_3 + NiBr_2 + 5\,NiO \quad (2)$$
$$2\,Fe_3B_7O_{13}I \rightarrow [7\,B_2O_3 \cdot 5\,FeO] + I_2 + Fe \quad (3)$$

ACKNOWLEDGEMENTS

The author is grateful to S. C. Abrahams and G. M. Loiacono for helpful discussions.

REFERENCES

1 H. Schmid, *J. Phys. Chem. Solids*, 26 (1965) 973.
2 P. K. Gallagher and D. W. Johnson, Jr., *Thermochim. Acta*, 4 (1972) 283.
3 P. K. Gallagher, *Thermochim. Acta*, 26 (1978) 175.
4 J. C. Joubert, J. Muller, C. Fouassier and A. Levasseur, *Krist. Tech.*, 6 (1971) 65.
5 A. Levasseur, C. Fouassier and P. Hagenmuller, *Mater. Res. Bull.*, 6 (1971) 15.