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THERMAL DECOMPOSITION OF SOME BORACITES

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ABSTRACT

The thermal decomposition under argon of the boracites $M_3B_7O_{13}X$ (M = divalent metal ion, X = halogen ion or OH^-) has been studied by thermogravimetry (TG) and differential thermal analysis (DTA) for the compositions MgCl, MgOH, CrCl, CrBr, CrI, MnCl, MnBr, MnI, FeCl, FeBr, FeI, CoCl, CoBr, CoI, NiCl, NiBr, NiI, CuCl, CuBr, ZnCl, ZnBr, ZnI, CdCl, CdBr and CdI. The lithium boracites $Li_4B_7O_{12}X$, with X = Cl and Br, have also been studied. The stability of the boracites systematically decreases in the order MCl > MBr > MI. The most stable boracite is CrCl (1% weight loss at 1242°C) and the least stable one studied here is MgOH (1% weight loss at 717°C).

INTRODUCTION

Boracites are compounds with the general formula $M_3B_7O_{13}X$, hereafter designated by MX, where M is Mg, Cr, Mn, Fe, Co, Ni, Cu, Zn or Cd, and X is OH, F, Cl, Br, I or NO_3 [1–3]. Chalcogenide boracites with X = S, Se or Te and charge compensating oxygen vacancies [4,5], lithium boracites $Li_4B_7O_{12}X$ [6] with X = Cl, Br, I, and lithium sulfur boracite $Li_5B_7O_{12}S$ [7] are also known. Many boracites are of interest because of their ferroelectric/ferroelastic phases and most of the 3*d* transition element boracites because of simultaneous ferroelectricity, ferroelasticity and weak ferromagnetism [1,8]. Lithium boracites are of interest because of their ionic conductivity [7].

With a view to growing single crystals for physical characterizations, the knowledge of the stability limit is very important. Therefore a systematic study of the thermal decomposition of a series of 26 halogen boracites and of MgOH with simultaneous TG and DTA analysis has been undertaken and is described in this paper. It has to be stressed that such decompositions necessarily take place under non-equilibrium conditions and finally cannot

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TABLE I

Gaseous decomposition products of some boracites, detected as positively charged species in a mass spectrometer (data compiled from refs [12] and [14])

MX	Temp (K)	Total pressure (atm)	Components of gas phase, relative intensity sequence at T (K)	Ref.
FeI	~1403	[b]	$I > H_2O > HBO_2 > Fe > B_2O_3 > O_2$	12
NiBr	~1433	[b]	$H_2O > B_2O_3$(?)$> NiBr > HBO_2$('CO_2'? [a])$> Br > O_2 > Ni$	
CuCl	~1403	[b]	$O_2 > H_2O > CuCl > Cl > Cu > HBO_2$('$CO_2$'? [a])$> B_2O_3$	
FeCl	1310	1.8×10^{-5}	$BOCl > FeCl_2 > B_2O_3$	14
CoCl	1322	4.0×10^{-6}	$BOCl > CoCl_2 > B_2O_3$	
CoI	1452	5.6×10^{-6}	$B_2O_3 >> CoCl_2$ (I not measured)	
ZnCl	1223	6.7×10^{-5}	$Zn > O_2 > ZnCl_2 >> B_2O_3$	
ZnI	1326	1.3×10^{-4}	$Zn > O_2 >> B_2O_3$ (I not measured)	
ZnI	1249	?	$Zn > I > ZnI$	

[a] Remark: according to Delfino and Gentile [13] HBO_2^+, which has the same mass number as CO_2^+, is more probable.

[b] $P_{total} = 8 \times 10^{-8}$ (units omitted) at room temperature; no indication of decomposition temperature.

replace more detailed studies of the phase diagrams. However, they prove to be very useful in solving crystal growth problems.

Some boracite compositions have already been studied by previous authors with respect to their stability. For MnOH Muller [9] and Levasseur [10] respectively find that strong decomposition starts at about 700°C and comes to an end at about 750°C. Kravchuk and Lazebnik [11] report that FeOH remains stable up to 650°C under hydrothermal conditions. Gallagher [12] finds endothermic peaks—interpreted by melting—for CuCl (1025°C), NiBr (1150°C) and FeI (965°C). Delfino and Gentile [13] report thermogravimetric curves measured in air for MgCl, CuCl, NiBr and FeI, and measured in vacuum for MgCl, NiBr and FeI. They contest the opinion [12] that CuCl, NiBr and FeI melt congruently. Vedenkina et al. [14] studied decomposition by mass spectrometry for FeCl, FeBr, CoCl, CoI, ZnCl and ZnI and find the formation of $MO \cdot B_2O_{3(s)}$, $B_2O_{3(l)}$, $MCl_{2(g)}$ or $M_{(g)} + I_{2(g)}$ in a first step and the final products to be B_2O_3 and MO for Co and Fe boracites, and B_2O_3 and free Zn for zinc boracites. The complete list of gaseous species detected during decomposition of some boracites by means of mass spectrometry [12,14] has been compiled in Table 1.

EXPERIMENTAL

All boracite compositions have been synthesized by chemical vapour transport [15–17] with the exception of MgOH which has been obtained by hydrothermal synthesis [9] and which was characterized by small amounts of manganese as impurity (i.e. MnOH served as seed for MgOH). Thermal analysis was carried out using a Mettler TA1 device, equipped for simultaneous TG and DTA. The samples weighed 15–20 mg (small crystals, <0.1 mm). Platinum crucibles were used. A heating rate of 4 deg min^{-1} and an argon flow of 5 l h^{-1} were chosen.

RESULTS AND DISCUSSION

Fig. 1 shows the TG and DTA curves obtained for all boracites studied. The weight loss and the peak height are normalized for unit weight, so that all the curves are directly comparable. Most of the compounds present a complex decomposition, usually with two endothermic peaks on heating and sometimes a multiple step weight loss. The DTA of the chromium boracites has also been performed in sealed crucibles, in order to prevent decomposition (results not presented here); the peaks observed are the same as the former ones obtained with an open crucible and were reversible on cooling. The nature of the double peaks is not yet understood.

Table 2 reports the temperature of the 'beginning of decomposition' (i.e. at

TABLE 2

Temperatures of ‘beginning of decomposition’ (1% weight loss, TG) and of DTA peak; comparison with literature [b] data (temperatures in °C)

M	X								Atmosphere
	Cl		Br		I		OH		
	TG	DTA	TG	DTA	TG	DTA	TG	DTA	
Li	864	870	823	830					Argon
	897[6]								?
Mg	948						717	715	Argon
	990[13]								Vacuum
	1002[13]								Air
Cr	1242	1250	1196	1200	1100	1150			Argon
Mn	1071	1070	983	1050	933	977			Argon
							700[9][a]		?
							700[10][b]		?

Fe	1014	985	999	1003	920	980	Argon
					908[13]	965[12]	Air
	985[14][a]				969[13]		Vacuum
Co	1073	1075	1049	1035	1013	1070	Argon
	1040[14][a]				643[14][a]		Vacuum
Ni	1005	1130	993	1125	940	975	Argon
			1075[13]	1150[12]			Air
			1033[13]				Vacuum
Cu	929	993	923	925			Argon
		1025[12]					Air
	978[13]						Vacuum
Zn	929	920	889	955	852	900	Argon
			1032[13]				Air
	516[14][a]				712[14][a]		Vacuum
Cd	958	960	951	955	852	915	Argon

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[a] Does not correspond to 1% weight loss.

[b] 700°C corresponds to a loss of 0.3 OH mole^{-1}; strong weight loss above 700°C.

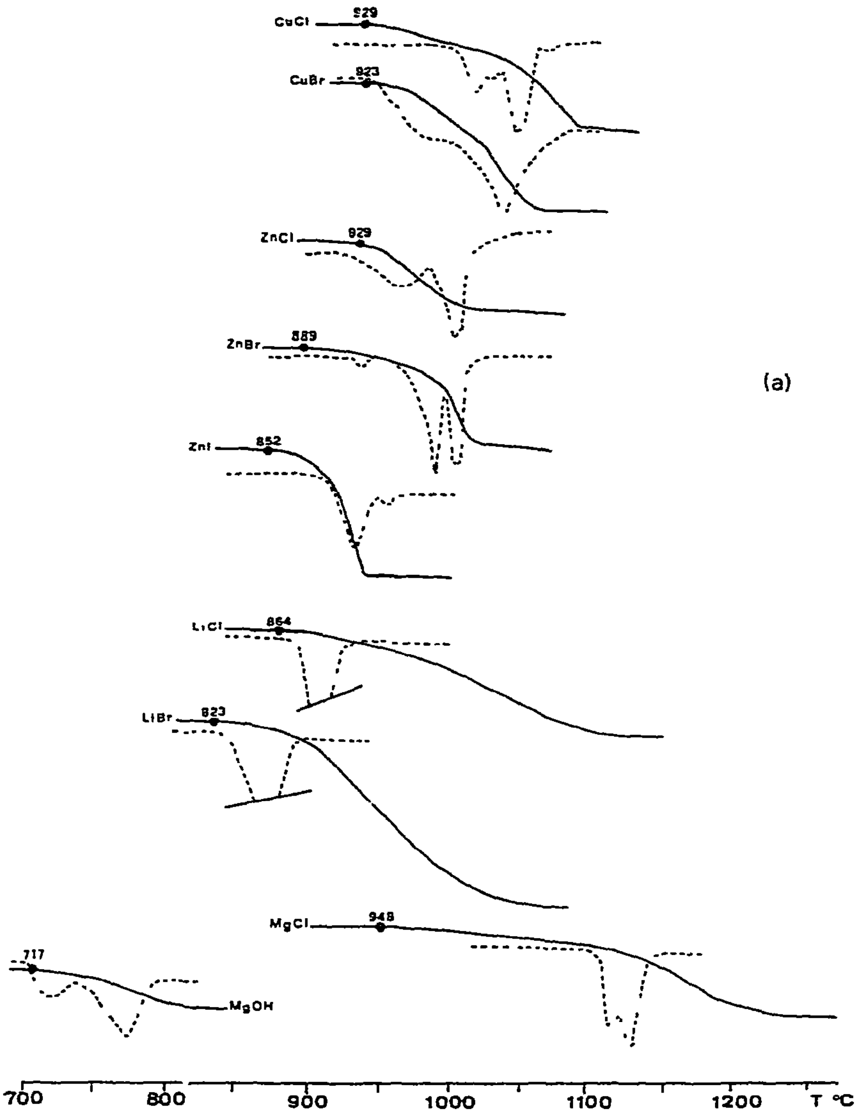


Fig 1(a)–(c). TG and DTA curves of the boracites studied. Heating rate, 4 deg min^{-1}, atmosphere, argon (5 l h^{-1}); sample weight, 15–20 mg

1% weight loss) and that of the first DTA peak. Generally these two temperatures are close to each other; however in the case of the boracites MgOH, MgCl, CrI, NiCl, NiBr, FeI, MnBr, MnI, NiI, CuCl, ZnBr, ZnI, CdI and CoI, the decomposition starts at a lower temperature than the first DTA peak. It is interesting to note that all MI boracites behave in this manner, probably because of the smaller bond strength caused by the large size of iodine.

Table 3 reports the weight loss, expressed in percent, measured between room temperature and the beginning of the steady state. (The boracites having an unsharp end of weight loss are not included in this Table.) Th

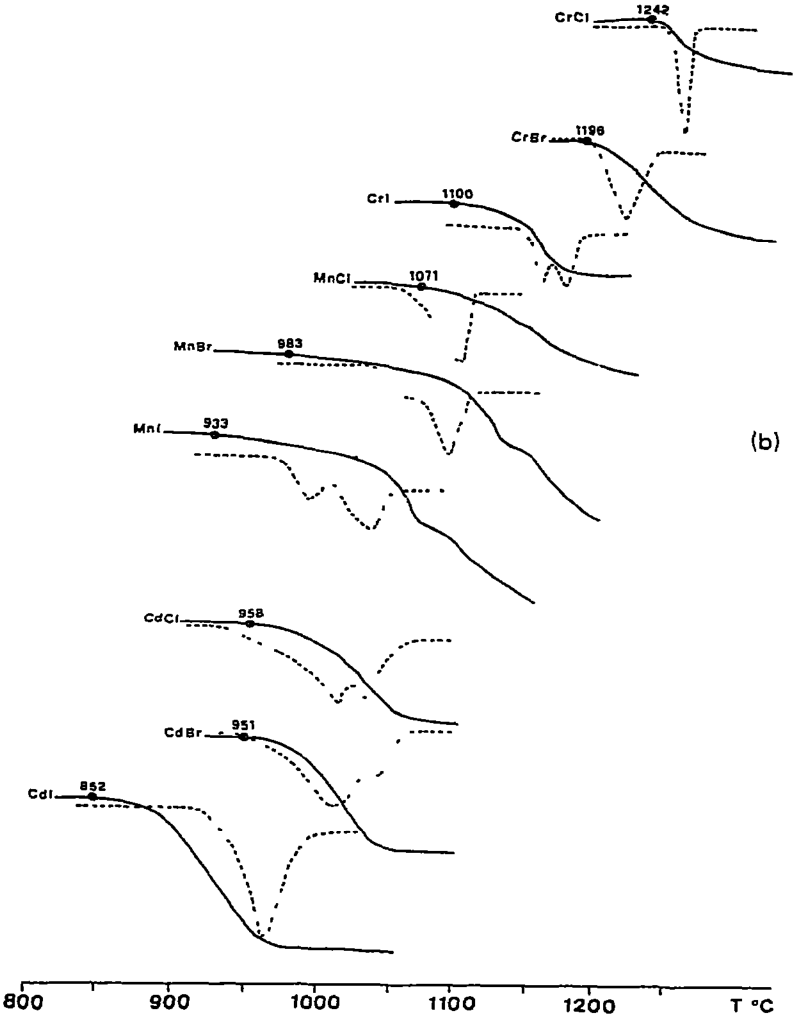
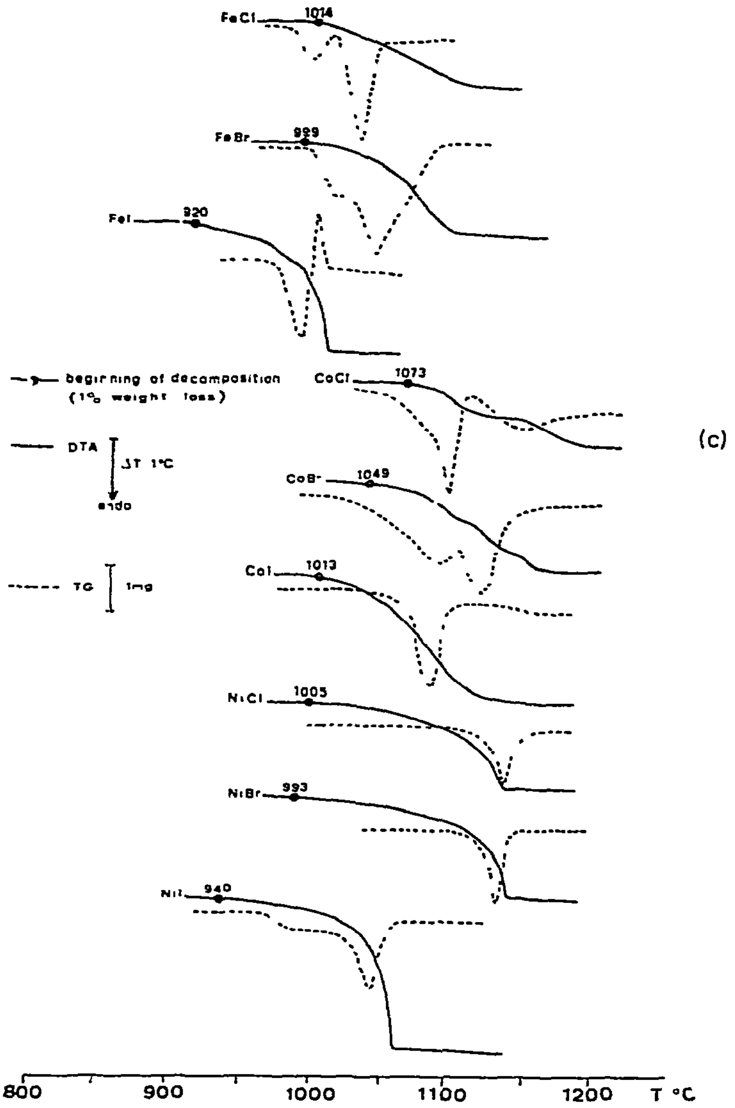


TABLE 3

Weight loss (%) of some boracites (characterized by sharp decomposition points) between room temperature and the steady state

	Weight loss %	
	Exptl.	Calcd. [eqn. (1)]
FeI	17.5	26.8
NiCl	12.3	13.1
NiBr	15.2	20.1
NiI	20.8	26.6
CuCl	15.8	13.2
CuBr	19.7	20.2
ZnCl	7.0	13.2
ZnBr	14.6	20.0
ZnI	17.9	26.3
CdCl	14.3	14.0
CdBr	17.1	19.4
CdI	18.7	24.5



results are compared with the weight loss calculated according to the hypothetical decomposition reaction

$$2\,M_3B_7O_{13}X \rightarrow \text{residue} + MX_{2(g)} \qquad (1)$$

This comparison shows that the decomposition is generally incomplete, with the exception of CuCl, CuBr and CdCl. Examination of the residue shows that it is covered by B_2O_3 on the bottom of the Pt crucible. This oxide may hinder the diffusion of gaseous MX_2 and prevent total decomposition of the boracite.

Another reason for the difference between the experimental and the calculated weight loss may be the decomposition of MX_2 at elevated temperature; we have not detected metals in the residue, but we often

TABLE 4

Experimental conditions of decomposition applied by different authors

Author	Method	Weight of sample (mg)	Heating rate (deg min^{-1})	Atmosphere	Flow rate (cm^3 min^{-1})
Gallagher [12]	TG	4–8 (single crystal chips)	10	Dry air	40
	DTA	20–44 (single crystal chips)	10	Dry air	Static
	Evolved gas analysis by mass spectrometry (EGA)	2–4	2	Vacuum (8×10^{-10} torr?, units omitted) at room temperature	
Delfino and Gentile [13]	TG	20	10	Air	Static
	TG	20	10	Vacuum (10^{-3} torr)	
Vedenkina et al. [14]	Knudsen cell + mass spectrometry				
Muller [9]	TG			Air (1 atm)	
Levasseur [10]	TG		1.25	Air	
This work	TG–DTA	15–20	4	Pure argon	83

observed an attack of the crucible which may have resulted from the formation of an alloy with platinum. This would be consistent with the fact that metal vapour was detected by mass spectrometry (Table 1) [12,14] during decomposition of certain boracites. The experimental conditions used by different authors to study the decomposition of boracites are indicated in Table 4.

CONCLUSION

The results of the TG and DTA study of the decomposition of boracites, in conjunction with the results obtained by other workers by means of different methods (EGA, X-ray analysis), allow the conditions of synthesis of these compounds to be chosen more judiciously. No boracite was found to be stable in the molten state in an open crucible, but the exact temperature corresponding to 1% weight loss ('beginning of decomposition') was found to be a very useful parameter for the upper temperature limit of crystal growth. Further detailed studies with a view to elucidating the nature of the double peaks are in progress.

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