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BORACITES: A STRUCTURAL FAMILY PRESENTING FERROIC PHASE TRANSITIONS

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Since the early demonstration of the ferroelectric effect in boracites, the physical properties of several of these materials have extensively been studied. The purpose of this contribution is to summarize recent results on structural and thermal properties in some members of this large family of ferroics.

Keywords: Boracites, ferroics, phase transitions, domains, specific heat, crystal structure.

INTRODUCTION

Halogen boracites form the core of a large family of compounds all with chemical formula $Me_3B_7O_{13}X$ where Me stands for a divalent metal cation and X is Cl, Br, I. Occasionally X can be OH, S, Se or Te and monovalent lithium has substituted the metal.

Although data on boracites are periodically published in the Landolt-Börnstein Numerical Data Series[1], the first comprehensive review on the properties and structures of boracites was published 36 years ago[2]. It is

not our intention here to recapitulate or improve on this excellent review due to R.J. Nelmes but only to report recent results as well as to stress the need to investigate the physical properties of more members of this interesting ferroic family.

Crystal growth

In a period of 120 years (1860-1980) synthetic boracites have been prepared by four basic techniques: sintering flux method[3], vapour transport method[4], hydrothermal method[5] and pressure reaction method[6]. With the aid of these methods all possible combination of halogen boracites have been synthesized, with the exception of Cu-I (In what follows we will use the symbols of the metal and the halogen only to refer to any boracite, i.e. Cu-I = $Cu_3B_7O_{13}I$), that was obtained until 1985 using high pressures applied to condensed phases[7]. With the present feverish search of new materials for thin film applications in ferroelectric-semiconductor devices[8], it is interesting to note that only one boracite has been epitaxially deposited on another boracite as a substrate[9]. This is a yet-unexplored field.

Single crystals of Mn-Br and Zn-X studied in this work were grown by the so-called "three-crucibles" method[4] that yielded crystals with masses up to 50 mg and dimensions up to 5 x 3 x 1 mm^3. For the synthesis work, the reactants were placed in three fused silica crucibles spatially separated by quartz rods (3 mm in diameter). The three crucibles contain boron oxide, metal oxide and metal chloride, boride or iodide. The crucibles are then inserted into a quartz ampoule which is sealed under a vacuum of approximately 0.02 mbar. Chemical transport reactions were carried out at about 1170 K in a vertical furnace, resistance-heated, over a period of 24 up to 72 hours, depending on the composition, and then cooling the ampoule freely down to room temperature.

Magnetic properties

Since the first report of Schmid et al.[10] on magnetic susceptibility measurements of several boracites, the magnetic order has been confirmed in more than fourteen compositions of this large family, and at least four different types of transitions from paramagnetic to ferro-or antiferromagnetic phases have been reported[1]. Recently an investigation of magnetic ordering in powders of the halogen Mn-X boracites appeared in the literature[11]. We have simultaneously been studying the magnetic properties in single crystals of Mn-Br boracite. We found that these compositions are rather sensitive to residual magnetic fields currently present in SQUID magnetometers which very often causes false negative

values of the magnetization. The only way to get rid of these effects is to perform a fluxgate operation to the magnetometer. On grounds of our own results we suspect that the magnetization values reported for Mn-I[11] could also be affected. Figure 1 shows the thermal behaviour of magnetization in Mn-Br single crystals under zero magnetic field. It is observed from this figure that the magnitude of magnetization depends on the rate of cooling. Precise results of this study and their interpretation will be published elsewhere.

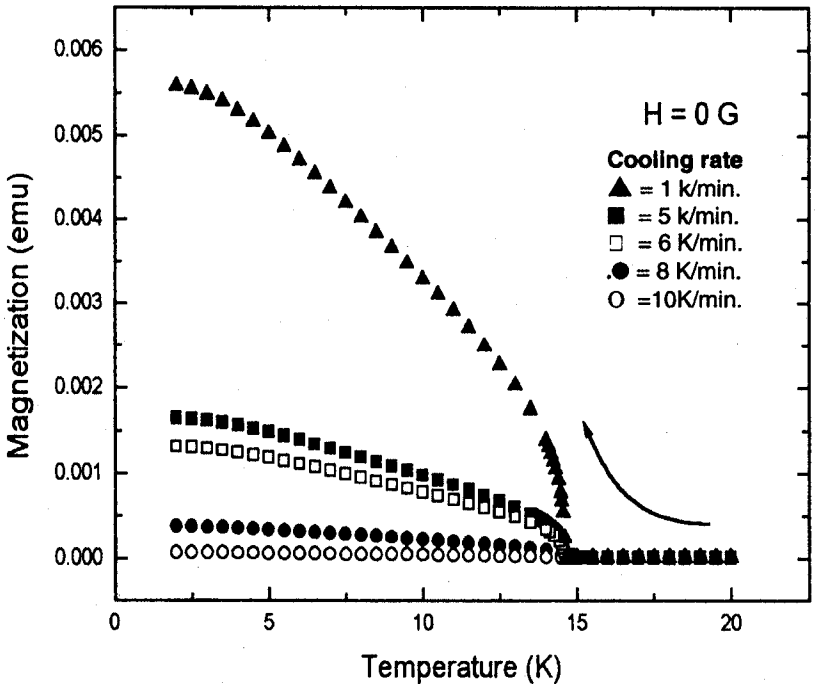

FIGURE 1. Magnetization versus temperature in Mn-Br boracite

Structural Phase Transitions

Most boracites undergo a first order ferroelectric/ferroelastic phase transition from a cubic (space group $F\bar{4}3c$) to an orthorhombic phase (space group $Pca2_1$). In six compositions (Fe-Cl, Fe.-Br, Fe-I, Co-Cl, Cu-Cl and Zn-Cl) the more complete sequence of phases was identified: $F\bar{4}3c \rightarrow Pca2_1 \rightarrow m \rightarrow R3c$ [1,2]. Recently a new additional tetragonal phase ($\bar{4}2m$) was found in Cr-Cl which is unique among boracites[12]. The room temperature crystal structure of Zn-Br, for which no structural

data were known, was investigated by the powder diffraction method (figure 2). Zn-Br is orthorhombic at 300 K with a = 8.5499(5)Å, b = 8.5590(7)Å, c= 12.1016(7)Å[13].

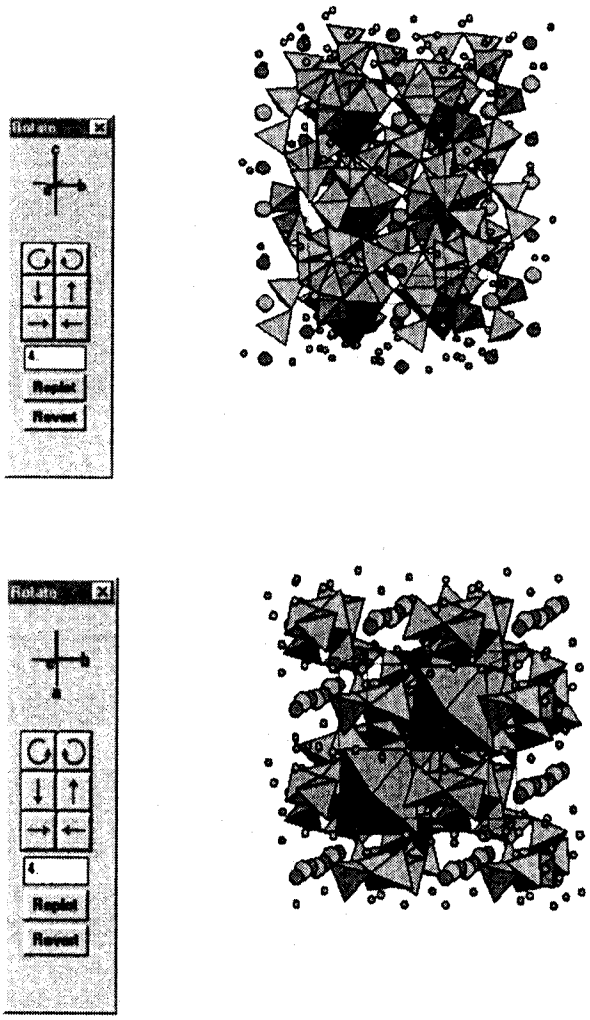

FIGURE 2. Crystal structure of Zn-Br boracite at room temperature
(See Color Plate I.)

Thermal properties

A part of the recent information on thermal data published on boracites appears here as table I. Our calorimetric data for Zn-X boracites were obtained with a METTLER Toledo Start System in closed aluminium crucibles. In Zn-Br boracite a single peak was detected (figure 3), the onset temperature occurred at 653 K. For Zn-Cl the $F\bar{4}3m/Pca2_1$, phase

transition occurred at about 723 K (figure 4), whilst for Zn-I the experiments resulted in a heat curve showing three peaks at three different temperatures: 375 K, 555 K and 610 K. (figure 5). This is a rather unusual result since no additional phase transitions was reported previously on this composition[1]

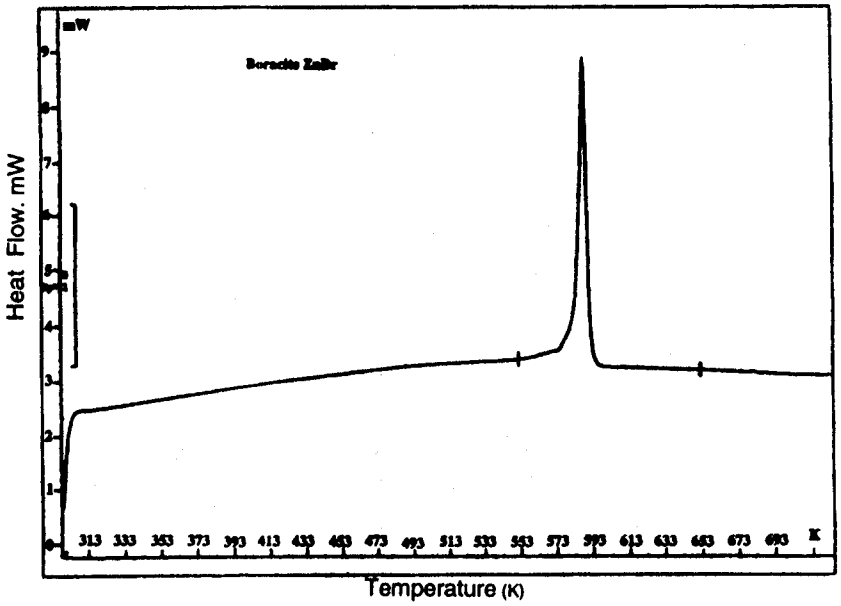

FIGURE 3. Calorimetric curve for Zn-Br boracite

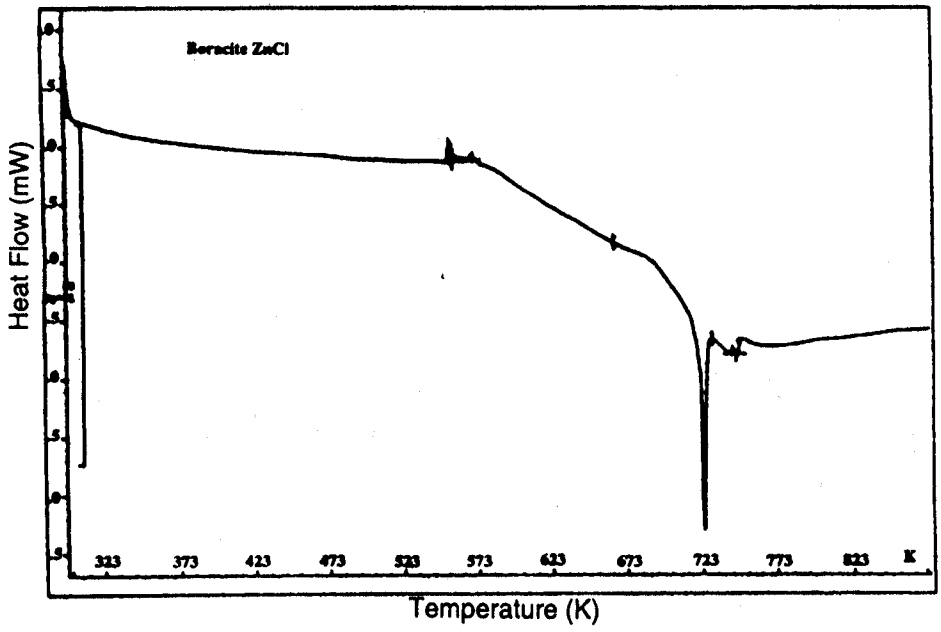

FIGURE 4. Calorimetric curve for Zn-Cl boracite.

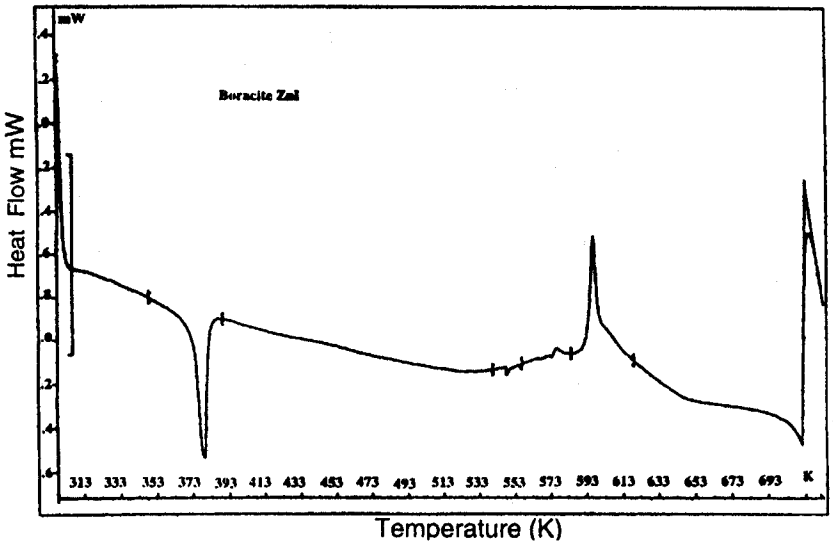

FIGURE 5. Calorimetric curve for Zn-I boracite

Table I. Data obtained from heat capacity measurements on botacites at the structural and phase transitions.
(After reference 1)

Boracite	$\Delta H \left[kJ/mol \right]$	$\Delta S \left[kJ/mol\,K \right]$	T_c [K]
Cr-Cl	2.145 (110)	8.07 (45)	265.8
Cr-Cl	1.98 (2)	7.50 (8)	264
Cr-Cl	0.030 (5)	0.18 (3)	164
Mn-Cl	5.527 (404)	8.09 (60)	684 (2)
Mn-Br	3.196 (141)	5.84 (25)	549 (2)
Mn-I	1.869 (103)	4.63 (25)	407 (2)
Fe-I	3.1 (3)	8.9 (5)	344
Fe-I	1.005 (50)	2.90 (15)	346.2 (2)
Co-Cl	----------	12.7	11.5
Co-Br	----------	13.12	17.5
Co-I	1.5 (2)	7.5 (2)	196
Co-I	----------	9.76	37.5
Ni-Cl	4.9 (4)	8.1 (6)	608
Ni-Br	2.845(150)	7.14 (40)	398.4 (2)
Cu-Cl	1.220 (60)	3.30 (20)	369.7 (2)
Zn-Br	4.275 (200)	7.31 (35)	584.6 (2)

Domain structure

The static domain structure of boracites has traditionally been studied by polarised-light microscopy[14]. Three different types of domains are currently observed in these materials: 180° domains, i.e. domains with $\mathbf{P}_s$ vectors mutually anti-parallel, and 90° domains, for which two types are noticed; head-tail domains and head-head domains. The domain structure of Zn-X boracites as observed at room temperature in the diagonal position between crossed polars of an Olympus BH50 optical microscope, is shown in figure 6. It basically consists of a complicated lamellar configuration that makes difficult a clear identification of composition planes.

FIGURE 6.- Domain structure in Zn-X boracites as observed by Polarised-light microscopy. (See Color Plate II.)

CONCLUSIONS

Though at present a great amount of information about boracites is available, a relative paucity of accurate physical and structural studies is

noted for several members of this large ferroic family, and there is quite a number of debatable and non-solved experimental and theoretical problems. For example, DSC studies showed two additional phase transitions at 375K and 555 K in Zn-I boracite but those reported to occur in Zn-Cl were not detected. These results require further investigations.

Acknowledgments

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