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A Thermodynamic Study of the Cubic ($\bar{4}3m$) → Orthorhombic ($mm2$) Ferroelectric Phase Transition of a Triad of Boracites with Mn as a Common Metal

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Results are presented for the first thermodynamic study of the cubic ($\bar{4}3m$) → orthorhombic ($mm2$) ferroelectric phase transition of a triad of boracites with Mn as the common metal; i.e., $Mn_3B_7O_{13}Cl$, $Mn_3B_7O_{13}Br$, and $Mn_3B_7O_{13}I$. This study shows that the transition is first order in the case of Mn–Cl and Mn–Br boracites, while in Mn–I it tends to a second-order transition. Multiple peaking of the specific heat at the transition has been observed in several samples of the three compositions. Thermal annealing of these samples was ineffective for removing the multiple peaks. The multiple peaking is thought to arise from growth sectors in these crystals.

Introduction

The family of compounds known as boracites has the general formula $Me_3B_7O_{13}X$ where *Me* stands for Mg, Cr, Mn, Fe, Co, Ni, Cu, Zn, Cd, and *X* for OH, F, Cl, Br, I, NO_3, S, Se, and Te. Occasionally Li has been used (*1*) and then the formula becomes $Li_4B_7O_{12}X$ with *X* being a halide, and $Li_5B_7O_{12}X$ with *X* being a chalcogenide. Most boracites are known to have a cubic $F\bar{4}3c$ (T_d^5) high temperature phase and an orthorhombic Pca (C_{2v}^5) low temperature phase.

The unusual dielectric (*2–5*) and optical (*6, 7*) properties exhibited by the boracites have attracted increasing attention in recent years. A literature search, however, showed a paucity of information about the thermodynamic nature of the cubic–orthorhombic phase transition of these compounds; this in spite of the fact that such a transition has been the subject of considerable interest (*2, 10*) as it is thought to be an improper ferroelectric phase transition (*2, 9*).

In order to test current phenomenological theories about the character of such a phase transition; which has previously been considered to be first order for most known boracites by Felix *et al.* (*8*), Dvorak (*9*), and by Delfino *et al.* (*10*), a study of thermal properties was undertaken in the vicinity of the $\bar{4}3m \rightarrow mm2$ structural transition of a triad of boracites with Mn as a common metal, i.e., $Mn_3B_7O_{13}Cl$, $Mn_3B_7O_{13}Br$, and $Mn_3B_7O_{13}I$. In what follows we will refer to these compounds by giving only the sym-

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bols of metal and halogen, i.e., Mn–Cl = $Mn_3B_7O_{13}Cl$, and so on.

To our knowledge, this is the first time that thermodynamic data have been available for a triad of boracites having a common metal. This is especially interesting because of Felix's (*8*) considerations about a possible relationship between the character of the transition and the mass and size of the halogen. On the basis of X-ray diffuse scattering studies Felix remarked "this first-order character of the phase transition decreases with decreasing mass and size of the halogen." Our results for this triad of boracites, however, does not support Felix's proposition.

Experimental

Crystal Growth and Sample Preparation

Single crystals of the three compositions studied in this work were grown by the vapor phase transport method of Schmid (*11*) in sealed quartz ampoules. However, it should be noted that in the case of Mn–I we had to use a modification of the technique suggested by Schmid (*12*) to successfully grow such crystals. This was due to a heavy attack of the quartz ampoule observed during the trials for growing Mn–I, which in some instances led to the explosion of the ampoule. The attack probably originated from reactions with metal oxides. The modification consisted basically of using polycrystalline Mn–I boracite prepared separately, thus eliminating the metal oxide and working under strict transport conditions.

Samples were cut from as-grown crystals, by means of a diamond saw, parallel to cubic (100) and (110). Thus we obtained platelets with a natural facet while the opposite was polished with a 1-μm diamond paste.

Mn–X boracite crystals vary from almost colorless to deep pink. Their high transparency allowed us to choose platelets with minimum visible defects. Several samples of each composition weighing from about 5 up to 47 mg were used. The weights of the samples were determined by the use of a H54 Mettler balance (accurate to within 5 decimal places). All measurements reported here were performed under open circuit electrical boundary conditions ($\mathbf{E} > 0$) (*13*) this applied to all samples of the three compositions.

Method

Thermal data for the three compositions were obtained with a Mettler DTA apparatus Model TA 2000 interfaced to a Tektronix computing system Model 4051. The Mettler system was calibrated relative to the melting point, T_M, and transition energy, ΔH_t, of indium metal (T_M = 429.75 K, ΔH_t = 3266.63 J mole^{-1}).

For the ΔH_t evaluations the reference substance used was Al_2O_3 powder, heat-treated at about 1000°C. The weight of this standard was made as close to that of the sample as possible, with a maximum error of about 0.1 mg. Aluminum pans with lids were used as crucibles for both sample and reference. To ensure good thermal contact between sample and crucible, the flattest and largest sample facet was in all cases put parallel to the bottom of the crucible. This facet happened to be that which had been previously polished.

Enthalpy and specific heat measurements were made on both heating and cooling modes but quantitative data reported in this paper corresponds to the heating mode.

Multiple-Peak DTA Curves

During the evolvement of these thermal studies, several samples of the three compositions were observed to exhibit multiple peaking of C_p and ΔH_t at the phase transition. This was especially true for Mn–I

crystals in which case only a couple of samples were found to present a single peak. Delfino *et al.* (*10*) are reported to have observed the very same phenomenon in Cr–Cl, Fe–I, Ni–Br, and Zn–Br boracites. According to these authors the effect was due to internal stresses in the crystals which could be eliminated by thermal annealing. They found that, after applying this treatment to their samples, multipeaks disappeared in a great number of cases though in others there were some residual effects.

In order to determine if this was the case for Mn–X boracites, we annealed a number of samples of the three compositions which displayed such peaks. Mn–Cl and Mn–Br crystals were annealed at about 700°C while Mn–I was annealed at about 400°C for a minimum soaking time of 24 hr, after which they were cooled at a rate of 15°C · hr^{-1} down to room temperature. This treatment was done in closed Pt crucibles which were heated in a small electrical furnace. The reason for not heating Mn–I samples above 400°C was that after the first thermal treatment (in which Mn–I was heated up to 700°C), an appreciable darkening of the sample was noticed which was attributed to the liberation of free iodine. It should be noted that the decomposition of Mn–X boracites has been found to start at about 800°C (*14*).

As a result of repeated annealing, samples of the three compositions showed internal fracture lines, probably an indication that stresses had disappeared, however, multipeaks in C_p and ΔH_t remained. We are led to the conclusion that either the annealing procedure was somehow incomplete or the effect in these boracites is due to different growth sectors having slightly different transition temperatures thereby causing such multiple peaks. In the latter case no thermal treatment would be fruitful.

For final thermal evaluation we chose samples of the three compositions showing a single DTA peak.

TABLE I

Boracite	T_c (K)	ΔT (K)	ΔH_t (J $mole^{-1}$)	ΔS_t (J $mole^{-1}K^{-1}$)
Mn–Cl	683.3	1.5	5527 ± 404	8.09 ± 0.60
Mn–Br	547.8	2.5	3196 ± 141	5.84 ± 0.25
Mn–I	404.3	4.2	1869 ± 103	4.63 ± 0.25

Results and Discussion

Enthalpy of the Transition $\bar{4}3m \rightarrow mm2$ in Mn–X Boracites

In the Mettler DTA 2000 system the enthalpy of transition, ΔH_t, is obtained in a given temperature range by integrating the basic DTA equation which gives the rate of heat flow, related to the sample in an endothermic/exothermic process. The entropy of transition, on the other hand, is obtained by dividing ΔH_t by T_c. For ΔH_t measurements use was made of the Tektronix 4051 system to integrate the peak area with integration intervals of 0.50 K and at heating rates of 1 and 2 K min^{-1}.

Thermodynamical data at the transition cubic–orthorhombic for Mn–Cl, Mn–Br, and Mn–I boracites are given in Table I. The thermal hysteresis, ΔT, mentioned in this table refers to the displacement of T_c to a lower temperature observed on cooling through the phase transition at cooling rates of 1 and 2 K min^{-1}.

In all cases, the transition $\bar{4}3m \rightarrow mm2$ was accompanied by an endothermic process. For Mn–Cl, Honea and Beck (*15*) has reported a sharp endothermic reaction at 680.15 K. This qualitative DTA study was made on a natural Chambersite crystal; the name of which relates to the locality in Chambers County, Texas, where that crystal was discovered. The agreement with our own result for a synthetic crystal (T_c = 683.3 K) is fairly good.

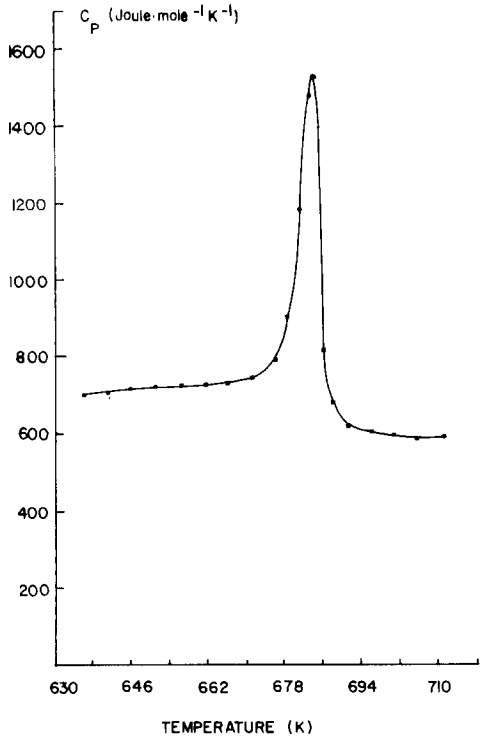

FIG. 1. Isobaric molar specific heat of Mn–Cl boracite in the vicinity of the cubic–orthorhombic phase transition.

Isobaric Molar Specific Heat versus Temperature for Mn–X Boracites

The temperature dependence of the isobaric molar specific heat, C_p, near the phase transition $\bar{4}3m \rightarrow mm2$ of Mn–Cl, Mn–Br, and Mn–I boracites is shown in Figs. 1, 2, and 3, respectively. These values represent the average of at least three sets of measurements on three different samples with the exception of Mn–I boracite of which only two samples were found free of the multiple peaks mentioned before. Samples used for C_p (at atmospheric pressure) vs temperature measurements were the same as those used for enthalpy determination. As in the latter case, we employed aluminum pans with lids as crucibles. After tracing the baseline with empty pans the sample was lodged in one of these crucibles always keeping its largest and flattest facet parallel to the bottom of the crucible in order to ensure good thermal contact. Data corresponds to the heating mode only, taken at heating rates of 1 to 2 K min^{-1}. Thermal hysteresis, ΔT, observed during the cooling cycle at these rates is given in Table I for each composition. In this C_p vs T evaluation use was made of a GA-11 Mettler strip chart recorder and an Allbrit Stanley Ltd. planimeter. Energy measurements can not be more accurate than the precision of the area measuring technique, thus a precision better than 1% in our specific heat results cannot be expected.

As before, the transition temperature has been taken as the peak in C_p. Our results are in excellent agreement with those of Honea and Beck (*15*) and Ascher *et al.* (*16*) for Mn–Cl and Mn–I boracites, respectively. In the case of Mn–Br boracite, how-

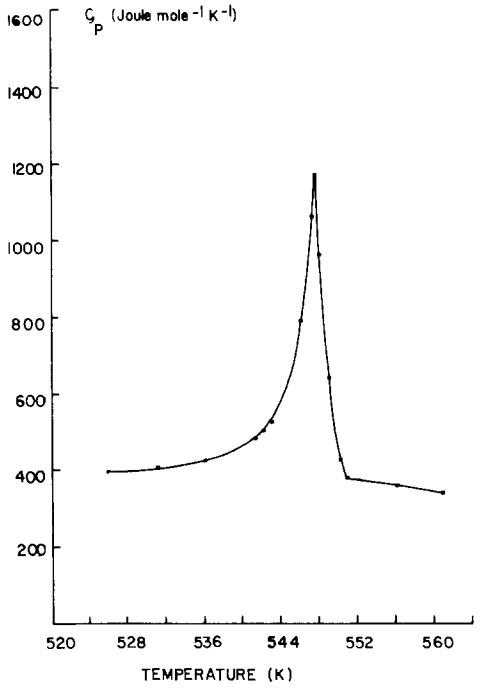

FIG. 2. Isobaric molar specific heat of Mn–Br boracite in the vicinity of the cubic–orthorhombic phase transition.

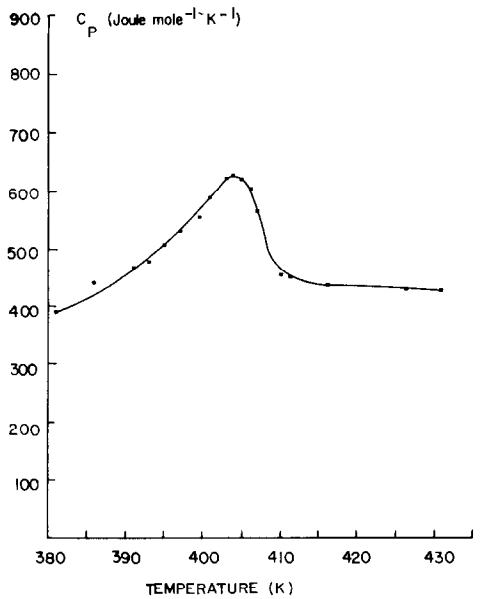

FIG. 3. Isobaric molar specific heat of Mn–I boracite in the vicinity of the cubic–orthorhombic phase transition.

ever, there is a discrepancy as high as 22 K with the T_c value given by Schmid (*11*) and of 20 K with that found by Ascher (*16*). On the basis of some other experimental evidence (dielectric and optical) (*17*) we believe that our results reflect the true transition of this boracite. Furthermore, recently we have been able to reexamine our specific heat measurements for Mn–I and Mn–Br boracites with the aid of a Mettler DSC-Thermomicroscopy system Model FP-800 which allows visual observation of the sample, under the polarizing microscope between cross-polars, throughout the entire range of measurement (*18*) (because of the working temperature range of the DSC-FP800; T_{max} = 573 K, we were unable to repeat thermal measurement for Mn–Cl boracite). Under these conditions it was easy to check the temperature at which all ferroelectric domains in the sample vanished; an indication that the crystal was then in the $\bar{4}3m$ phase, and to compare such temperature with that of the C_p peak. The difference between these two values was less than 0.4 K for both compositions. Visual observation of the sample showed the transition to occur in a small temperature interval (within 3 K). This small interval validates the approximation usually made when determining the entropy of the transition, i.e., that such an interval be less than 8 K (*10*).

On the basis of these specific heat measurements, under simultaneous visual observation of the sample, we found a value of 547.0 ± 2 K for the transition temperature of Mn–Br boracite. This is in excellent agreement with that determined previously with the Mettler TA 2000 system.

For specific heat measurements with the Mettler DSC-FP800 system, samples are lodged in a small sapphire crucible, i.e., a birefringent material. The hot stage windows are also made of the same material. Thus, in order to be able to observe the ferroelectric domains of the sample one has to employ certain time and patience to put the crystal in the right orientation. Quantitative specific heat data for Mn–Br and Mn–I were obtained with the DSC-FP800 in the heating mode only. These data agreed well with those obtained with the TA 2000 system.

For a long time boracites have been considered to belong to the class of improper ferroelectrics (*9*), so called because the phase transition involves more than one order parameter (*2*). On the basis of the thermodynamic theory, the form of the free energy for improper ferroelectrics requires that the cubic ($\bar{4}3m$)–orthorhombic ($mm2$) phase transition be first order (*19, 7*). Indeed, our thermodynamic data for Mn–Cl and Mn–Br boracites (Figs. 1 and 2) show the typical behavior of a first-order phase transition; large values of ΔH_t, ΔS_t, relatively small values of the thermal hysteresis, ΔT, and a sharp peak in the temperature dependence of the specific heat. In the case of Mn–I, however, the broad peak of C_p, and the somewhat smaller values of en-

TABLE II

Boracite	Atomic wt. of halogen[a]	Halogen ionic radii[b] (Å)	ΔH_t (J mole^{-1})	ΔS_t (J mole^{-1}K^{-1})
Mn–Cl	35.453	1.81	5527	8.09 ± 0.60
Mn–Br	79.909	1.96	3196	5.84 ± 0.25
Mn–I	126.904	2.20	1869	4.63 ± 0.25

[a] Based upon carbon-12.
[b] Based upon Ahren ionic radii.

thalpy and entropy of the transition together with higher value of the thermal hysteresis seem to be an indication that this composition is closer to a second-order transition.

With respect to Felix's remarks (*8*) concerning a decrease of the first-order character of the phase transition with decreasing mass and size of the halogen, we have abridged pertinent data about Mn–X boracites in Table II. Our results do not support Felix's expectations for these compositions. Such a situation reflects the complex microscopic mechanisms involved in boracites phase transitions whose correct interpretation requires not only a very accurate structure determination but a dynamical treatment of the phase transition.

Acknowledgments

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