Dielectric properties of orthorhombic Mn₃B₇O₁₃Cl, Mn₃B₇O₁₃Br, Mn₃B₇O₁₃I boracites


Abstract

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DIELECTRIC PROPERTIES OF ORTHORHOMBIC Mn$_3$B$_7$O$_{13}$Cl, Mn$_3$B$_7$O$_{13}$Br, 
AND Mn$_3$B$_7$O$_{13}$I BORACITES

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Abstract. Dielectric, pyroelectric, optical and thermal properties of Mn-Cl, Mn-Br and Mn-I boracites have been investigated in the ferroelectric orthorhombic phase (space-group Pca$_2$). These are the first such measurements made on a triad of closely related boracites. The peculiar and very different behaviour of dielectric constant, $\varepsilon$, in each compound seems to be consistent with the predictions of current $33$ phenomenological theories on improper phase transitions.

INTRODUCTION

Halogen boracites are compounds with the general formula Me$_3$B$_7$O$_{13}$X, where Me is a divalent metal and X stands for Cl, Br or I. A boracite is conventionally referred to by its metal and halogen only, with a hyphen, e.g. Mn-Cl is written for Mn$_3$B$_7$O$_{13}$Cl. Most halogen boracites have a high-temperature non-polar phase $3713$ (space-group F43c; point-group 43m) which transforms, on cooling through the transition temperature $T_c$, to a pyroelectric improper ferroelectric orthorhombic phase (space-group Pca$_2$; point-group mm2). Interest in these materials arose because their unusual dielectric, ferromagnetoelectric and optical properties make them potentially attractive for device applications, and also for testing phenomenological theories on improper phase transitions.

This paper presents measurements of the temperature dependence of dielectric constant, $\varepsilon_{33}$, pyroelectric coefficient $p$, spontaneous polarisation $P_s$, and spontaneous $33$ birefringence $\Delta n$ perpendicular to $P_s$, in the orthorhombic phase, as well as a DTA study, near $T_c$, of a triad of boracites which have Mn as the metal, i.e. Mn-Cl, Mn-Br, and Mn-OCl.

EXPERIMENTAL

We grew Mn-X single crystals by vapour transport reactions in closed quartz ampoules. Plates were ground parallel to cubic {100} natural faces and polished with one-micron diamond paste. Semitransparent gold on chromium electrodes were evaporated onto the principal faces. Sample thickness ranged usually from 60$\mu$m to 80$\mu$m, and area from 0.008 $cm^2$ to 0.025 $cm^2$. During dielectric and pyroelectric
measurements below T, the single-domain state of the samples was controlled by continuous observation of the birefringence under a polarizing microscope. Poling was typically by application of 10 kV cm\(^{-1}\) to 60 kV cm\(^{-1}\) just below T\(_c\) for ten hours.

**DIELECTRIC MEASUREMENTS**

The stress-free dielectric constant \(\varepsilon_{33}\) parallel to \(P\) was measured at 1 MHz, as a function of temperature, for the three compositions, with a test signal of 15 mV. The results are shown in figure 1. The dielectric anomaly in Mn-Cl is similar to that reported for some other boracites\(^3,4,5\), i.e. \(\varepsilon_{33}\) jumps downward on cooling through the transition. Mn-Br shows almost no anomaly.\(^6\) A prominent feature in this boracite is that \(\varepsilon_{33}\) is independent of the temperature above T\(_c\), thus fulfilling the predictions of the theories of Dvorak and Petzelt\(^6\) and of Gufan and Sakshenko\(^7\) on improper phase transitions. Our results for Mn-I are in agreement with an independent measurement made at 10 kHz\(^9\). These different anomalies can be explained by the theory\(^10\). However another theoretical model exists\(^11,12\) which can explain not only such behaviour but also the variation of \(\varepsilon_{33}\) with temperature above T\(_c\) as observed in Mn-Cl and Mn-I. As determined optically, T\(_c\) was 411±2°C in Mn-Cl, 276±2°C in Mn-Br, and 134±2°C in Mn-I.

**PYROELECTRIC MEASUREMENTS**

We used the charge-integration technique of Glass\(^13\) which measures the total pyroelectric coefficient, primary plus secondary. The specimen mounts were designed to be nearly as possible stress-free. We measured \(P\) from specimens selected to be visually free of defects and domain walls, and we measured from room temperature to a few degrees below T\(_c\). Our results are shown in figure 2. Values of \(P\) at 25°C were 0.761±0.014x10\(^{-2}\) C m\(^{-2}\) in Mn-Cl, -0.262±0.024x10\(^{-2}\) C m\(^{-2}\) in Mn-Br, and 0.924±0.015x10\(^{-2}\) C m\(^{-2}\) in Mn-I. In Mn-Br, \(P\) reverses its sign at about 140°C. This behaviour was observed in all samples studied. The origin of this effect is as yet unknown though several possible explanations have been given in the literature\(^14\). We believe that the region of negative values is not due to a metastable phase transition\(^14\) for we observed no dependence of \(P\) on dT/dt.

**BIREFRINGENCE MEASUREMENTS**

The behaviour of \(\Delta n\) versus temperature is well documented for most boracites\(^2\) so we concentrated our attention on \(\Delta n_s\) (perpendicular to \(P_s\)) in Mn-I. Birefringence, \(\Delta n_s\), was measured for Mn-I samples, ranging in thickness from 75 to 240μm, by means of a Leitz tilting compensator type M and compensating the path difference visually. Our measurements in white light gave indications of a highly dispersive crystal (figure 3). As a function of temperature, \(\Delta n\) increases as temperature is raised, and starts to decrease at about 110°C. In the cases of Mn-Cl and Mn-Br our measurements of \(\Delta n_s\) as a function of temperature are in agreement with those reported in the literature.\(^2\)
DIELECTRIC PROPERTIES OF ORTHORHOMBIC $\text{Mn}_3\text{B}_7\text{O}_{13}X$ BORACITES

Figure 1. Temperature Dependence of the Dielectric Constant in MN-X Boracites

Figure 2. Temperature Dependence of the Pyroelectric Coefficient in MN-X Boracites

Figure 3. Birefringence as Function of Wavelength in MN-I Boracite (Sample Thickness 240 μm)

Figure 4. Isobaric Molar Specific Heat, $C_p$, of MN-X Boracites in the Vicinity of the Cubic-Orthorhombic Phase-Transition
ORDER OF TRANSITION

Gufan and Sakhnenko's theory shows that the transition should be first order, but we have not been able to observe any displacement of $T_c$ larger than $\frac{1}{2}$ degree by applied fields up to 40 kV cm$^{-1}$; nor have we seen any hysteresis larger than $2^\circ$. A differential thermal analysis (DTA) near $T_c$ was made in a Mettler, type TA2000. Samples of Mn-Cl, Mn-Br, and Mn-I were as-grown single crystals weighing 7.32, 16.07, and 43.87 mg respectively. The reference substance used was Al$_2$O$_3$ powder heat-treated at 1000°C and we used the 429.75°C transition in indium metal for calibration. Measurements were made under open-circuit conditions. In all cases the transition was an endothermic process. Visual observation of the transition at the same scanning speed as in the DTA measurements (2 deg min$^{-1}$) showed it to occur over a small temperature range (4 K for Mn-Cl and Mn-Br, and 10 K for Mn-I). The specific heat, $C_p$, and entropy, $\Delta S$, of transition were found to be $5527\pm404$ J mole$^{-1}K^{-1}$ for Mn-Cl; $8.09\pm0.60$ J mole$^{-1}K^{-1}$ for Mn-Br; and $1869\pm103$ J mole$^{-1}K^{-1}$ for Mn-I. We observed that many samples showed multiple peaks in the measurements near $T_c$ similar to those reported for other boracites. It had been suggested that the multiple peaks might be caused by internal stresses in the crystals. In our case, however, annealing procedures tried for Mn-X boracites were ineffective; we discarded samples, showing multiple peaks, for DTA evaluation. Possibly this effect is due to different sector growths having slightly different transition temperature.

It has been suggested that the first-order character of this transition decreases with decreasing mass and size of the halogen, so that Mn-I would be more strongly first order. However our transition enthalpy values imply that the transition in Mn-Cl and Mn-Br is more strongly first-order whilst that of Mn-I is close to being second order; this is further supported by our pyroelectric measurements.

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