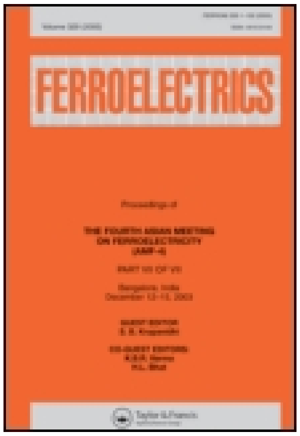

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DIELECTRIC ANOMALIES IN BORACITES

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Experimental results are reported on the dielectric behavior of $Fe_3B_7O_{13}I$, $Ni_3B_7O_{13}Br$, $Cu_3B_7O_{13}Cl$, and $Mn_3B_7O_{13}I$, near their cubic-orthorhombic phase transition. $Fe_3B_7O_{13}I$ and $Ni_3B_7O_{13}Br$ show the typical dielectric behavior of boracites, whereas $Cu_3B_7O_{13}Cl$ and $Mn_3B_7O_{13}I$ exhibit a different dielectric anomaly. Both types of behavior can be discussed on the basis of a Landau expansion of the thermodynamic potential.

INTRODUCTION

Crystals of halogen boracites (general formula $M_3B_7O_{13}X$, M = divalent metal, X = Cl, Br or I) possess peculiar dielectric behavior besides their unusual ferroelectric, magnetic, and structural properties.[1] Most boracites exhibit a first-order improper ferroelectric transition from a high temperature cubic phase $T_d^5(F\bar{4}3c)$ to an orthorhombic phase $C_{2v}^5(Pca2_1)$. The special character of this phase transition becomes apparent through the unusual dielectric behavior around the transition. The temperature dependence of the dielectric constant, ϵ, differs sharply from the usual Curie-Weiss dielectric anomaly in ordinary ferroelectrics like $BaTiO_3$ and TGS. Typically in boracites, ϵ, increases slightly as the transition temperature is approached from above, and jumps abruptly downward at the transition to the ferroelectric phase. This behavior has been reported for all the boracites studied so far[2–8] with the exception of Cu—Cl boracite in which ϵ jumps upward upon cooling through the transition from the paraelectric phase to ferroelectric phase.[9]

This paper reports the first measurement of the dielectric constant of a single domain Mn—I boracite. This material exhibits a similar behavior to that of Cu—Cl boracite, in that its dielectric constant jumps *upwards* on cooling through the transition from the paraelectric to ferroelectric phase. As a supplement to the data reported in the literature, we also present experimental results on the dielectric behavior of Cu—Cl, Fe—I, and Ni—Br boracites. The two types of dielectric behavior, represented by Mn—I and Cu—Cl boracite on the one hand and Fe—I and Ni—Br boracite on the other hand, can be discussed on the basis of a Landau expansion of the thermodynamic potential.

EXPERIMENTAL TECHNIQUE

The samples were $(100)_{cub}$ cut single crystal wafers; the sources and other pertinent data on the samples are listed in Table I. Poling of the samples was undertaken by cooling the sample through the phase transition while applying a dc electric field of the appropriate magnitude as shown in Table I. In Cu—Cl and Mn—I boracite the poling and the measurements were performed under optical control of the domain state of the samples. These samples were electroded with transparent gold and mounted freely in a heating stage of a Leitz polarizing microscope. The single domain state of the Cu—Cl and Mn—I samples was controlled throughout the entire temperature range of the measurements, by visual observation of the birefringence.[14]

Pyroelectric measurements were used to assess the state of poling of the Fe—I and Ni—Br sam-

TABLE 1

Data on the Samples Used in the Measurements

	$Fe_3B_7O_{13}I$	$Ni_3B_7O_{13}Br$	$Cu_3B_7O_{13}Cl$	$Mn_3B_7O_{13}I$
Source	Dupont	Plessey	Schmid	Schmid
Area (cm^2)	0.016	0.017	0.04	0.022
Thickness (μm)	150	240	60	55
Electrodes	Evaporated Antimony	Silver Paint	Evaporated gold on chromium	Evaporated gold on chromium
Poling Field (kV/cm)	10	10	20	2-4
Domain State	Unknown likely single domain	Unknown likely polydomain	Single domain	Single domain

ples. The Fe—I sample reversed its polarization readily under the application of a dc field of 10 kV/cm. Such behavior is indicative of a properly poled sample, however, it does not preclude the possibility that a multidomain structure exists which cannot be removed by application of an electric field as large as 10 kV/cm. Similar poling of the Ni—Br sample in the opposite direction resulted in a pyroelectric current whose magnitude differed from the initial measurement. This indicates a partial poling of this sample.

Two methods were used in the measurement of the dielectric constant. In the first method the electrical capacitance of the sample was measured directly, with accuracy better than 1%, using a Hewlett-Packard 4274 LCR meter. In the second method, we measured the ratio of the capacitance of the sample to that of a reference capacitor placed in series with it. A small ac signal was applied to the sample and reference and a lock-in amplifier (Ortholock-SC9505) was used to measure the in-phase voltage appearing across the reference capacitor. Both methods yielded similar results.

EXPERIMENTAL RESULTS

Figure 1 shows the temperature dependence of dielectric constant of Fe—I and Ni—Br boracite, as measured on heating in a field of ~7 V/cm at 8 kHz using the reference capacitor technique. Both materials exhibit the typical dielectric anomaly of boracites, i.e. the dielectric constant jumps upward in the transition to the paraelectric phase. Our data for Fe—I boracite are in good agreement with the previously reported measurement.[7] However, with Ni—Br boracite, our data give a distinctly different picture than is contained in the two previous reports in the literature.[2,10] We see a very large, sharp jump in ϵ at the transition.

Essentially the same abrupt jump was seen in some preliminary measurements made on another sample of Ni—Br boracite supplied by Plessey. These measurements were made at 1 MHz using a Boonton 72B capacitance meter with a test field of 400 V/cm and an external bias of 20 kV/cm.†

Measurement of ϵ in Cu—Cl boracite was made in a field of 2.5 V/cm at 100 kHz using the HP LCR meter. The results are shown in Figure 2. Upon heating ϵ increases from a value of 11.5 at room temperature to a peak value of 23 at the transition, temperature. The peak value corresponds to a single domain orthorhombic phase. In the transition to the paraelectric phase, ϵ jumps abruptly downward to a value of 14.5 and remains essentially constant up to 130°C. These results are in general agreement with the data reported by Schmid and Pétermann.[9] However, their data at 5 kHz show a slightly higher peak of ϵ at the transition and a significant temperature dependence of ϵ above the transition. These differences could be artifacts connected with the high dielectric loss (order of 10–100%) of the material at elevated temperatures. At higher frequencies the effect of the dielectric loss is reduced.

As was pointed out by Schmid and Pétermann[9] the dielectric behavior of Cu—Cl boracite is unusual. In most boracites (including Cu—Br[8]) ϵ exhibits an abrupt jump upward at the transition to the paraelectric phase.[2–8]

A second example of the unusual behavior of

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†These preliminary measurements were performed by Dr. J. P. Dougherty.

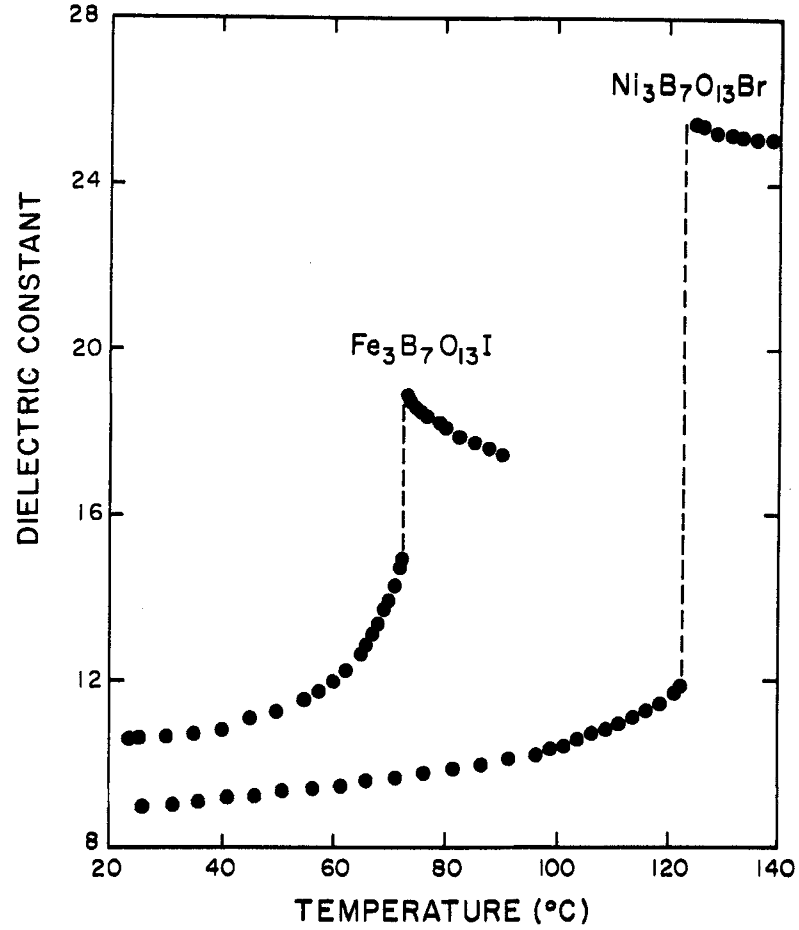

FIGURE 1 Dielectric constant of Fe—I and Ni—Br boracite measured in a field of 7 V/cm at 8 kHz.

Cu—Cl boracite is found in our measurements on Mn—I boracite (Figure 2). The dielectric constant of Mn—I boracite was measured in a field of 27 V/cm at 10 kHz using the HP LCR meter. Upon heating, ϵ rises from a value of 11 at room temperature to a peak value of 27 at 134°C. In contrast to Fe—I and similarly to Cu—Cl boracite, the dielectric constant of Mn—I boracite jumps abruptly downward in the transition to the paraelectric phase. The dielectric loss was less than 1.2% over the entire temperature range of this measurement.

DISCUSSION

The cubic-orthorhombic phase transition in boracites has been theoretically analyzed by several authors.[11-13] The present work discusses the experimental data on the basis of a thermodynamic model proposed by Dvorak and Petzelt[11] and Gufan and Sakhnenko.[12] In their analysis, the cubic-orthorhombic phase transition in boracites is caused by a primary structural phase transition which doubles the volume of the unit cell, while the polarization arises as a secondary effect driven by this primary distortion. The known space groups of both the paraelectric and ferroelectric phases, uniquely determine the form of the thermodynamic potential required to describe this phase transition. Describing the magnitude of the primary structural distortion by the order parameter η and the polarization by P, a simplified form of this potential is

$$F = F_0(T) + \tfrac{1}{2}\alpha\,(T - T_0)\eta^2 + \tfrac{1}{4}\beta\eta^4 + \tfrac{1}{6}\gamma\eta^6 + \tfrac{1}{2}\chi_0^{-1}P^2 + a_1\eta^2P + a_2\eta^2P^2 - EP, \quad (1)$$

where T and E are the temperature and electric field, and β, γ, δ, χ_0, a_1, and a_2 are assumed to be

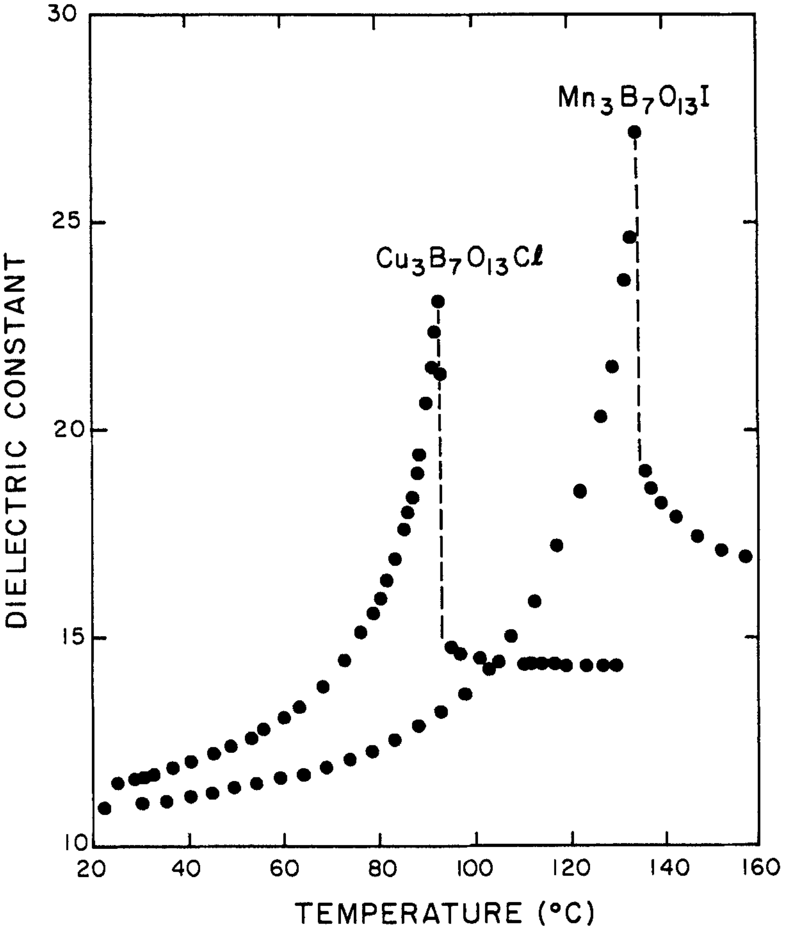

FIGURE 2 Dielectric constant ϵ_{33} of single domain Cu—Cl boracite (2.5 V/cm at 100 kHz) and Mn—I boracite (27 V/cm at 10 kHz) vs. temperature.

independent of temperature. It is significant to note that an interaction term in this thermodynamic potential must be included beyond the lowest order term allowed by symmetry. This term with the coefficient a_2 is required to describe the dielectric behavior in boracites.[11,12]

To determine the temperature dependences $P(T)$ and $\eta(T)$, we must find the minimum of the thermodynamic potential with $E = 0$ as a function of temperature. The equilibrium conditions $\partial F/\partial P = 0$, and $\partial F/\partial \eta = 0$, yield for the spontaneous polarization $P(T)$ and the inverse dielectric susceptibility $\chi(T)^{-1}$ in the ferroelectric phase,

$$P = -a_1\chi_0\eta^2/(1 + 2a_2\chi_0\eta^2) \qquad (2)$$

$$\chi^{-1} = \chi_0^{-1} + 2a_2\eta^2 - 2a_1^2/[(\beta + 2\gamma\eta^2)(1 + 2a_2\chi_0\eta^2)^2] \qquad (3)$$

where $\eta(T)$ is determined by the equation:

$$\alpha(T - T_0) + \beta\eta^2 + \gamma\eta^4 - 2a_1^2\chi_0\eta^2/(1 + 2a_2\chi_0\eta^2) + 2a_2a_1^2\chi_0^2\eta^4/(1 + 2a_2\chi_0\eta^2)^2 = 0. \qquad (4)$$

In the paraelectric phase, $P = 0$, $\eta = 0$ and $\chi = \chi_0$ is temperature independent. A general solution for $\eta(T)$ requires detailed numerical computations, and a careful least squares fitting of the measurements to determine the six† degrees of freedom in the thermodynamic potential. This work is still in progress. A good deal of insight, however, can be obtained from a preliminary dis-

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†Since no experimental result depends on the absolute scale of η, we are free to fix this scale by fixing any one of the parameters arbitrarily (say $\gamma = 1$). Conversely, no electrical measurements will suffice to determine the absolute scale of η.

cussion based on general considerations and reasonable approximations.

From the stability condition $\partial^2 F/\partial\eta^2 > 0$ it follows that $(\beta + 2\gamma\eta^2) > 0$, therefore, the last term on the right-hand side of Eq. (3) can only account for a decrease of χ in the transition to the paraelectric phase. However, when $a_2 > 0$ the term $2a_2\eta^2$ may lead to a reduction of this decrease or even to an increase of χ in that transition. Hence, the magnitude and the sign of the jump of χ at the transition is determined by the relative magnitudes of the two last terms in Eq. (3). As the transition is close to the second order type, the contribution of the third term on the right-hand side of Eq. (3) becomes more significant and the contribution of the second term becomes less significant. In this case a decease of χ in the transition to the paraelectric phase can be expected.

Various experiments show that the ferroelectric transition in Cu—Cl boracite is close to being of the second order type, whereas the analogous transition of most other boracites is strongly first order.[14–16] Our pyroelectric measurements indicate that the phase transition in Mn—I boracite is similar to that of Cu—Cl boracite. Thus the special character of the phase transition in Cu—Cl and Mn—I boracite can account for their unusual dielectric anomaly.

A quantitative discussion becomes simple for the case where the term $2a_2\eta^2$ in Eq. (3) makes the principal contribution to the behavior of χ^{-1}. This approximation was found appropriate for MgCl boracite[17] and CoI boracite.[18] Assuming for η a temperature dependence which is typical for an order parameter in a first order transition:[11]

$$\eta^2 = \frac{2}{3}\Delta\eta^2\left[1 + \left(\frac{T_1 - T}{T_1 - T_0}\right)^{1/2}\right], \tag{5}$$

the dielectric stiffness becomes

$$\chi^{-1} = \chi_0^{-1} + \frac{2}{3}\Delta\chi^{-1}\left[1 + \left(\frac{T_1 - T}{T_1 - T_0}\right)^{1/2}\right], \tag{6}$$

where $\Delta\eta$ and $\Delta\chi^{-1}$ are respectively the jumps of η and χ^{-1} in the transition to the paraelectric phase, and $T_1 = (4T_c - T_0)/3$. This approximation seems to be very suitable for Ni—Br boracite where ϵ exhibits a very noticeable jump upward in the transition to the paraelectric phase. A fitting of the experimental data on Ni—Br boracite to the theoretical prediction is shown in Figure 3. The crosses in Figure 3 represent the measured inverse dielectric susceptibility and the solid line is a fit to Eq. (6) using the parameters given in Table II. It is seen that a good agreement exists over a wide temperature range below the transition point. However, above the transition the theory predicts a constant value of χ^{-1} while experimentally χ^{-1} slightly increases with temperature.

In the approximation made in Eq. (6), the spontaneous polarization (Eq. (2)) can be related to the dielectric susceptibility:

$$P = (\Delta P/\Delta\chi)(\chi - \chi_0), \tag{7}$$

where ΔP and $\Delta\chi$ are respectively the jumps of P and χ in the transition to the paraelectric phase. Thus a knowledge of the temperature dependence of χ enables one to characterize the behavior of the order parameter and spontaneous polarization. The calculated behavior of η^2 and P in Ni—Br boracite is shown in Figure 4. The weak temperature dependence of the spontaneous polarization is typical to many boracites and it is experimentally observed as a mild increase of the pyroelectric coefficient as the transition point is approached. It should be mentioned that the calculations presented in Figures 3 and 4 are not final since they are based on data obtained in a sample with unknown domain structure. A similar approach was used in Refs. 12, 18 and 17 in calculating the square of the order parameter in Co—I and Mg—Cl boracites.

The data on Fe—I boracite can be discussed in a fashion parallel to Ni—Br. It is apparent that the downward jumps observed in Cu—Cl and Mn—I boracite can be successfully encompassed within the more general case where the third term in Eq. (3) is not negligible. Such a discussion involves more degrees of freedom in the theory than can be determined from the dielectric data alone.

It is important to note that while the thermodynamic model of Dvorak and Petzelt and Gufan and Sakhnenko is capable of describing both types of dielectric anomalies observed in boracites, it does not explain the observed temperature dependence of the dielectric constant in the high temperature phase.

The model of Levanyuk and Sannikov is also able to subsume both upward and downward jumps in the dielectric constant.[19] This model does, in addition, predict a temperature dependence of the dielectric constant in the high temper-

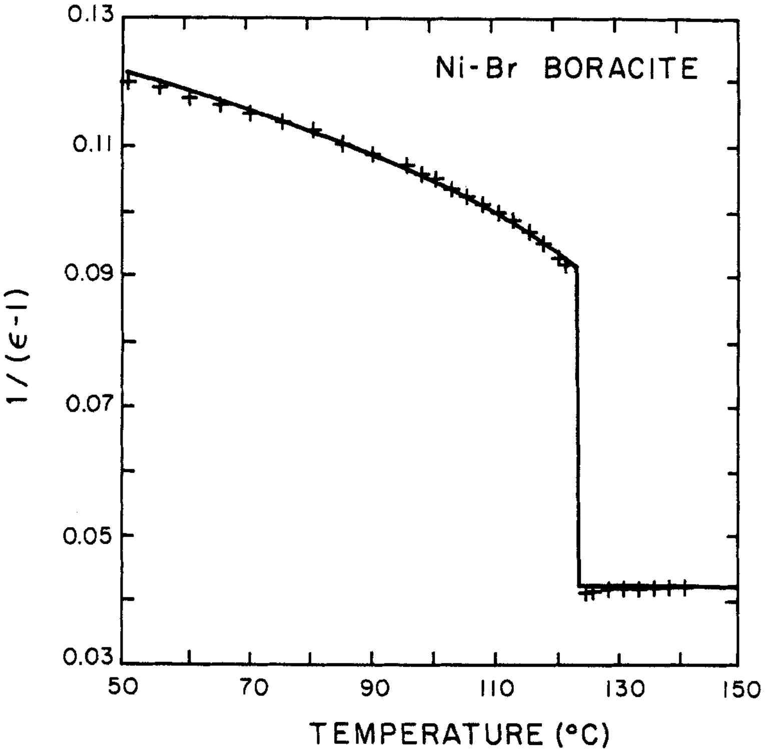

FIGURE 3 Temperature dependence of the inverse dielectric susceptibility of Ni—Br boracite. Crosses are experimental values; the solid line is a fit to Eq. (6) using the parameters given in Table II.

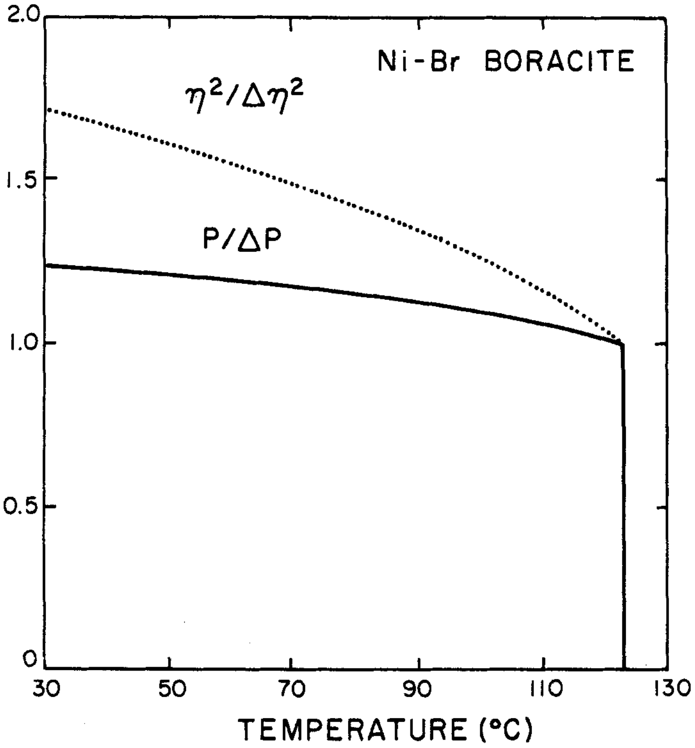

FIGURE 4 Calculated temperature dependence of the square of the order parameter and of the spontaneous polarization in Ni—Br boracite.

TABLE II

Parameters used in Calculating the inverse dielectric susceptibility of Ni—Br boracite

T_c (°C)	T_1 (°C)	T_0 (°C)	χ_0^{-1}	$\Delta\chi^{-1}$
123.5	134.0	92.0	0.042	0.0496

ature phase. Fits of our data to the expressions appropriate to the Levanyuk-Sannikov model suffer from the same problem of more degrees of freedom in the theory than can be determined by dielectric measurements alone.

It is interesting to reflect on how the difference in the dielectric behavior of Cu—Cl and Mn—I boracites might correlate with other properties of these materials and with the crystal chemistry of these compounds.

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