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Dielectric anomalies in improper ferroelectric $Mn_3B_7O_{13}X$ boracites

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ABSTRACT. The temperature and frequency dependence of the permittivity in some halogen boracites has been measured in the polar and non polar phases. $Mn_3B_7O_{13}Cl$ showed the typical dielectric anomaly of most boracites whereas $Mn_3B_7O_{13}I$ and $Mn_3B_7O_{13}Br$ exhibited a different dielectric behavior. The results are discussed using a phenomenological theory of the improper ferroelectric phase transition in these compounds.

RESUMEN. Se han evaluado la dependencia en la frecuencia y la temperatura en algunas boracitas halógenas, tanto en la fase polar como en la no polar. $Mn_3B_7O_{13}Cl$ mostró la anomalía dieléctrica típica de la mayoría de las boracitas, en tanto que $Mn_3B_7O_{13}I$ y $Mn_3B_7O_{13}Br$ exhibieron un comportamiento dieléctrico diferente. Los resultados se discuten utilizando una teoría fenomenológica de la transición de fase ferroeléctrica impropia de estos compuestos.

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1. INTRODUCTION

Since the discovery of ferroelectricity in Rochelle Salt (sodium potassium tartrate) by Valasek [1], a vast number of compounds has shown to present the phenomenon of inversion, or reorientation, of its spontaneous polarization by means of an applied electric field. Once thought to be a great rarity in nature, the ferroelectric effect has been found to occur not only in inorganics [2,3] but as well in polymers and other organic materials [4,5]

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and speculations have merged whether it is present in living matter [6,7] and in high T_c superconductors [8,9].

Besides the existence of remanent polarization and hysteresis loops, a distinctive feature of ferroelectrics is to display a variety of phase transitions; generally, from a high temperature non polar phase to one, or more, low temperature ferroelectric phases [10]. Thus, for a ferroelectric crystal one of the most important characteristics to be evaluated is the temperature and frequency dependence of its electric permittivity since its hape enables one to draw preliminary conclusions as to the nature of the lattice instability causing the phase transition.

The first ferroelectrics to be discovered, Rochelle salt in 1921 [1], potassium dihydrogen phosphate in 1935 [11] and barium titanate in 1945 [12], shared in common: a high value of the dielectric constant (of the order of 10 000 near T_c in $BaTiO_3$), a pronounced dielectric anomaly at the phase transition without a change in volume of the primitive unit cell, and, above T_c where ferroelectricity disappears, the permittivity obeyed a Curie-Weiss law [13]. These are the characteristics of a so-called "proper" ferroelectric transition in which the primary order parameter is then the spontaneous polarization.

However, on the basis of group theory, Indembom [14] pointed out that the polarization need not be the primary order parameter at a ferroelectric phase transition. In such a case, the expected dielectric behaviour should be different from that of proper ferroelectrics, normally no Curie-Weiss law is obeyed and the primitive unit cell volume will change. Thus the term "improper" was proposed by Dvorak [15] to refer to ferroelectrics presenting these characteristics. Examples of improper ferroelectrics are gadolinium molybdate [$Gd_2(MoO_4)_3$] [16] and boracites ($Me_3B_7O_{13}X$) [17].

In this work we are interested in dielectric properties of boracites. The generic term "boracite" is given to a large number of compounds all with general formula $Me_3B_7O_{13}X$, where Me stands for a divalent metal such as Mg, Cr, Mn, Fe, Co, Ni, Cu, Zn, or Cd and X is generally a halogen Cl, Br, or I. The name is in allusion to the mineral $Mg_3B_7O_{13}Cl$ from which the family takes its name. Although there are substitutions for Me and X [18], we will restrict our attention to halogen boracites with Mn as a common metal. In what follows we will use the symbols of the metal and the halogen only to refer to boracites, *i.e.*, $Mg_3B_7O_{13}Cl$ = Mg-Cl etc.

Evidence for ferroelectricity in Mg-Cl was first demonstrated by Le Corre [19]. However, there was a controversy on this matter for more than 25 years [20-22]. It was only until Ascher *et al.* [17] observed domain wall motion in Ni-Cl that the first undisputed demonstration of ferroelectricity in a boracite was given. Since then a large number of studies have been carried out on some of these compounds, not only because its improper ferroelectric character but also because Ni-I boracite displays mutually interacting ferroelectricity and ferromagnetism; so-called ferromagnetoelectricity [23], at low temperatures.

Physical characterization and structural studies have shown a diversity of structural transitions in halogen boracites: Most of these compounds have a piezoelectric-high temperature cubic phase (point group $\bar{4}3m$, space group $F\bar{4}3c$) which transforms to a low temperature orthorhombic phase which is ferroelectric, ferroelastic and pyroelectric (point group mm2, space group $Pca2_1$), or to a sequence of phases with point groups m and 3m. The $\bar{4}3m$-mm2 transformation involves a doubling of the primitive unit cell [24] confirming the improper character of the phase transition in boracites. There are three coumpounds

(Cr-Br, Cr-I, and Cu-I) which remain cubic down to 4 K [25]. Recently, a new tetragonal phase with point group $\bar{4}2m$ was found in Cr-Cl by Ye *et al.* [26] and evidences of a new transition (point group yet undefined) have also been observed in Mn-Br [27].

Besides this diversity of structural transitions, investigations of the dielectric constant behaviour as a function of temperature in halogen boracites have demonstrated serious differences in their transition anomalies.

In Fe-I [28], Co-Br [29], Co-I [30] and Mg-Cl [19] for example, as temperature is decreased from the high symmetry phase ($\bar{4}3m$), the dielectric constant, ϵ_r, increases slightly and at the transition to the orthorhombic phase (mm2) ϵ_r drops abruptly downwards. For long time this was thought to be the typical behaviour for boracites.

In the 70's, however, it was found that Cu-Cl [31] showed an unusual dielectric behaviour since ϵ_r increased abruptly upwards at the cubic-orthorhombic phase transition on cooling from the high temperature phase. Ni-I [32] and Mn-I [33] were later found to follow Cu-Cl dielectric behaviour.

In this work we present results of a comprehensive experimental study of dielectric properties of Mn-X boracites. The two types of dielectric anomaly observed in Fe-I and Cu-Cl boracites were found to occur in this triad of compounds which have Mn as common metal. Our results also show that Mn-Br is the fourth example of the unusual dielectric behaviour of Cu-Cl.

2. EXPERIMENTAL

The Mn-Cl, Mn-Br and Mn-I single crystals were grown by the chemical vapour transport method of Schmid [34]. All measurements were carried out with selected cubic (100) platelets having no defects visible in a polarizing microscope. Platelets were ground from as-grown crystals parallel to a naturally-formed cubic (100) facet and the opposite facet was polished to a 3 or 1 micron finish using diamond paste. Semitransparent gold-on chromium electrodes were evaporated on both sides of each sample with leads attached using silver paste from colloidal suspension. The purpose of the semitransparent electrodes is to allow us to observe, through the polarizing microscope, the domain state of the samples under physical characterization in the entire range of temperature, as well as to check the poling process applied to all samples previous to dielectric measurements. The starting point for the experimental study of a ferroelectric is the preparation of single crystals which are both single domain electrically and crystallographically [35]. Experimental procedures used for obtaining such a condition are generally known as "poling". If an electric field is used then the method is called "electrical poling", and "mechanical or elastic poling" if use is made of stress [36]. The single domain state in all samples was obtained by electric poling. This was undertaken by cooling the sample through the transition temperature under an applied electric field of the appropiate magnitude according to the sample under poling. Typical values for these fields as well as sample dimensions for the three compositions are described in Table I.

For dielectric characterization Mn-Br and Mn-I single crystals were lodged in an especially modified hot stage (Leitz 350, see Fig. 1) which was in turn mounted in the mechanical stage of an Orthoplan polarizing microscope, while Mn-Cl samples were mounted in a small over provided with quartz windows to allow optical observations.

TABLE I. Typical sample dimensions and poling fields for Mn-X boracites used in this study.

Composition	Area (cm^2)	Thickness (μm)	Poling field (KV/cm)
$Mn_3B_7O_{13}Cl$	0.019	110	50
$Mn_3B_7O_{13}Br$	0.025	80	30–50
$Mn_3B_7O_{13}I$	0.015	75	5–15

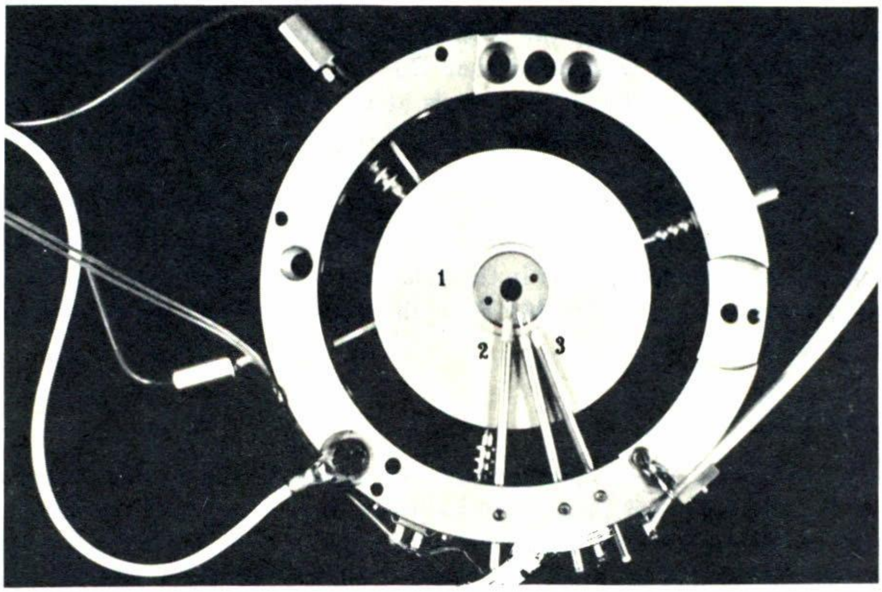

FIGURE 1. Modified hot-stage Leitz 350 used to lodge Mn-X boracites for dielectric measurements. 1. Chamber with fused quartz windows. 2. Chromel-Alumel Thermocouple. 3. Electric connections to sample electrodes.

Permittivity of the free crystal parallel to the spontaneous polarization, P_s, *i.e.*, ϵ_{33} of Mn-X boracites, was derived by measuring the electrical capacitance of the samples with either a HP4192 Impedance analyzer or a HP 4172 LCR meter. Temperature was measured by means of a Chromel-Alumel thermocouple placed as close to the sample as possible (Fig. 1). The absolute error in determining ϵ_r values, falls within 10%. This figure is a result of the rather small size of the samples as well as their thickness (*cf.* Table I), however, the curve of ϵ_r versus temperature for a given sample could be reproduced within about ± 0.1%.

3. RESULTS

The temperature dependence and results at 3 frequencies of the electric permittivity in single domain, single crystals of Mn-I boracite are shown in Figs. 2 and 3. ϵ_r has a room temperature value of about 8 (typical among halogen boracites) and it increases markedly as temperature is raised. It reaches a maximum value at the $\bar{4}3m$-mm2 phase transition (T_c = 400 K) and at that temperature the dielectric constant falls abruptly down to a value of about 15. Above the transition, in the non-polar (paraelectric) cubic phase the magnitude of the permittivity remains rather constant. Our results are in good agreement with an independent measurement made at 10 kHz [37]. However, our ϵ_r peak value is lower than that reported in a previous work on Mn-X boracite [33]. This difference could be due to the fact that at low frequencies the non-ferroelectric/ferroelectric phase boundary at a first order transition, as theoretically predicted for boracites, may oscillate in a small AC electric field and thus mimic a high intrinsic permittivity due to the alternative appearance and disappearence of a tiny fraction of the spontaneous polarization.

As it is seen in Figs. 2 and 3, the dielectric behaviour of Mn-I, independently of frequency, follows that of Cu-Cl boracite: ϵ_r increases abruptly upwards at the transition when cooling the crystal from the high temperature phase.

The temperature dependence of the stress-free permittivity, parallel to P_s, in single domain, single crystals of Mn-Br boracite at 3 MHz. and 5 MHz. frequencies is shown in Fig. 4. The electric permittivity in this boracite increases very slowly from a room temperature value of about 8 to a maximum peak value of about 15 at the cubic-orthorhombic phase transition. At such a temperature, T_c = 535 K, ϵ_r drops down to a value of about 12.5 and remains constant in the cubic paraelectric phase. This drop, however, is smoother than in Mn-I or Cu-Cl boracites. In spite that one could argue that there is no divergence of the permittivity in Mn-Br, it is clear from Fig. 4 that the permittivity increases upwards at the transition when the crystal is cooled from the high temperature cubic phase. Thus Mn-Br is the fourth example of the unusual dielectric anomaly of Cu-Cl boracite. The effect of the aforementioned oscillations of the phase boundary on the ϵ_r peak is clearly illustrated by this boracite, if one compares Fig. 4 in this work with Fig. 3 of Ref. [38] in which a much higher peak was observed, the origin of which was identified by the merging of a complicated domain structure a few degrees near the transition.

The temperature dependence of the permittivity in single domain, single crystals of Mn-Cl boracite at a frequency of 1 MHz, is shown in Fig. 5. The permittivity rises slowly from a room temperature value of 9 up to a 13 as the $\bar{4}3m$-mm2 phase transition is approached (T_c = 680 K), a temperature at which ϵ_r increases upwards to a maximum value of 16. Above T_c, in the paraelectric cubic phase, the permittivity in Mn-Cl varies slowly with temperature. The typical behaviour of most boracites is clearly observed in Mn-Cl, *i.e.*, ϵ_r decreases downwards at the phase transition on cooling the crystal from the high temperature phase.

It should be pointed out that the transition temperature of these compounds, as determined optically (as the temperature where the single domain structure disappears when entering the cubic phase) and dielectrically (as the temperature where the maximum of the permittivity occurs) resulted to be: 680 K (Mn-Cl), 535 K (Mn-Br) and 400 (Mn-I) within experimental uncertainty. Discrepancies in the transition temperature as determined by these two methods run from 4 K for Mn-Cl and Mn-I up to 13 K for Mn-Br. In Mn-Br, for example, Ascher *et al.* [17] had already found that T_c for this boracite could be within a range of temperature from 523 K to 569 K. The origin of these differences is thought to be the presence of growth sectors which shift the transition temperature to higher

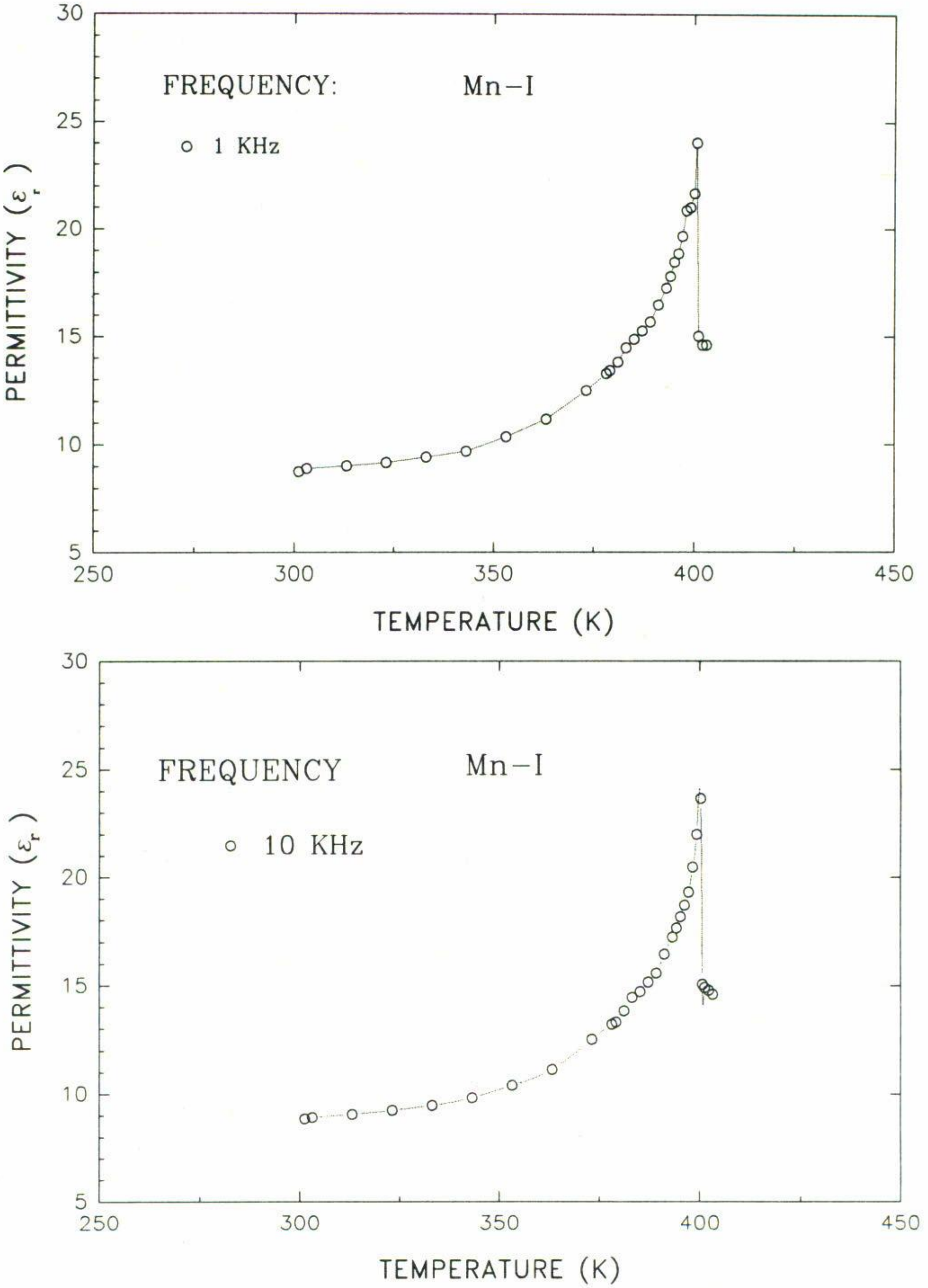

FIGURE 2. Stress-free permittivity of Mn-I as a function of temperature at 1 KHz and 10 KHz frequencies.

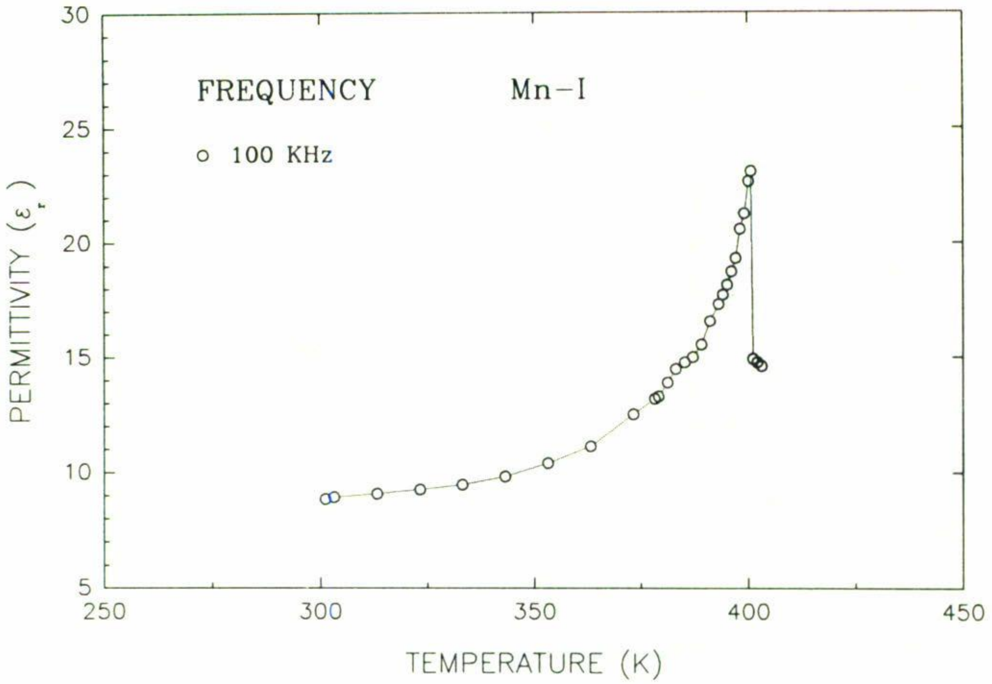

FIGURE 3. Stress-free permittivity of Mn-I as a function of temperture at a frequency of 100 KHz.

values. Growth sectors are common in synthetic crystals grown by methods such as that of Schmid [34] permitting the free development of growth facets.

4. PHENOMENOLOGY OF THE DIELECTRIC ANOMALY ON MN-X BORACITES

The free energy describing macroscopic properties of the cubic and orthorhombic phases of halogen boracites has been determined independently by Dvorak [15], Dvorak and Petzelt [39], Kobayashi *et al.* [40], Gufan and Sakhnenko [41], Sannikov [42], Levanyuk and Sannikov [43] and Toledano *et al.* [25]. None of these models has been able to explain the whole set of experimental data on boracites. However, it has been shown [44] that at least the temperature variation of permittivity in halogen boracites can be derived with a sufficient accuracy from a simplified Gibbs potential:

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

where η is the true order parameter, a primary structural distortion which double the volume of the primitive unit cell and it is associated with the normal coordinates at a zone boundary "soft" mode, while the polarization, P, merges as a secondary effect driven by such a primary distortion. T and E are the temperature and electric field, α, β, γ, χ_0, a_1 and a_2 are assumed to be independent of temperature.

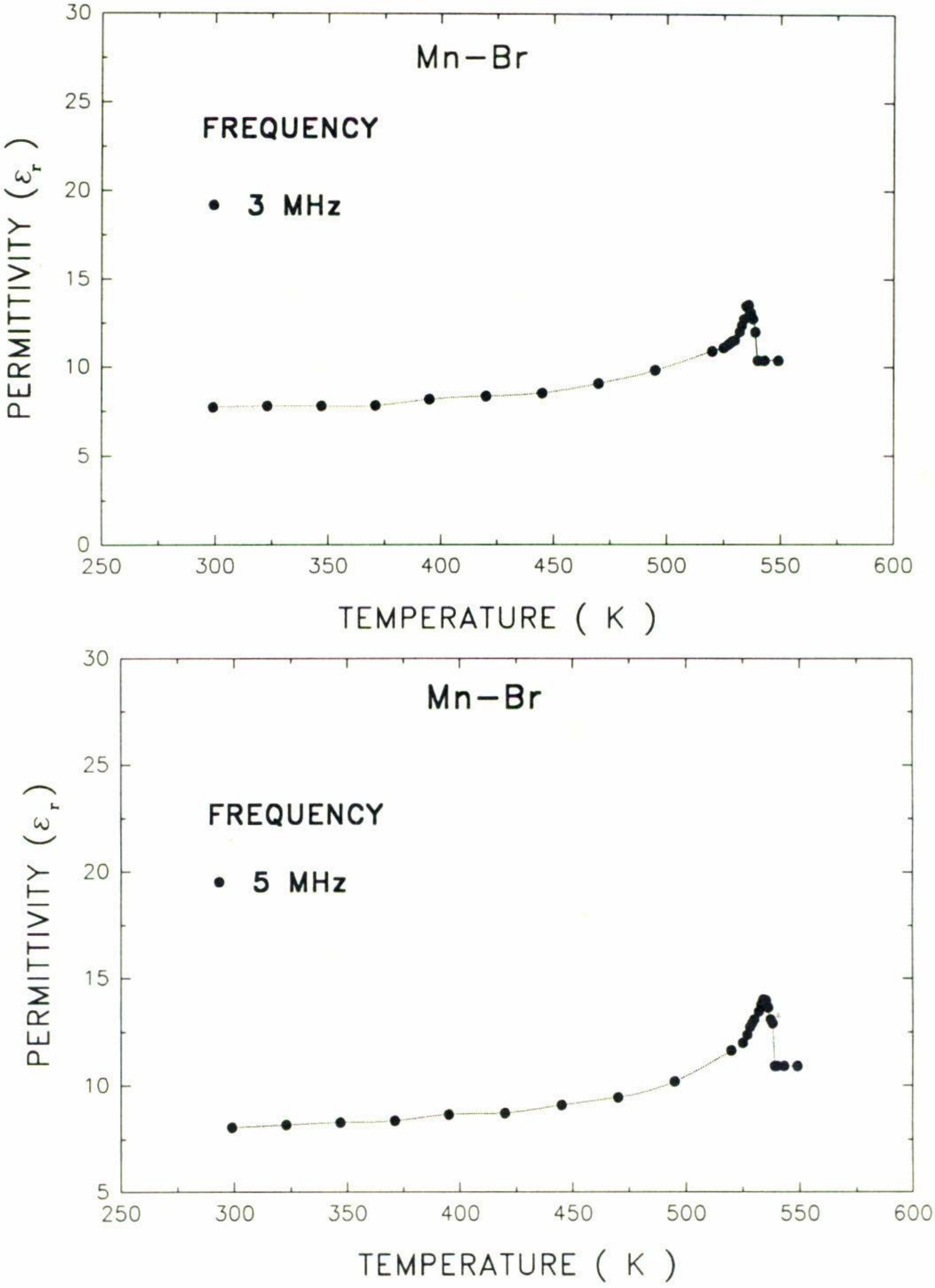

FIGURE 4. Stress-Free permittivity of Mn-Br as a function of temperature and frequency.

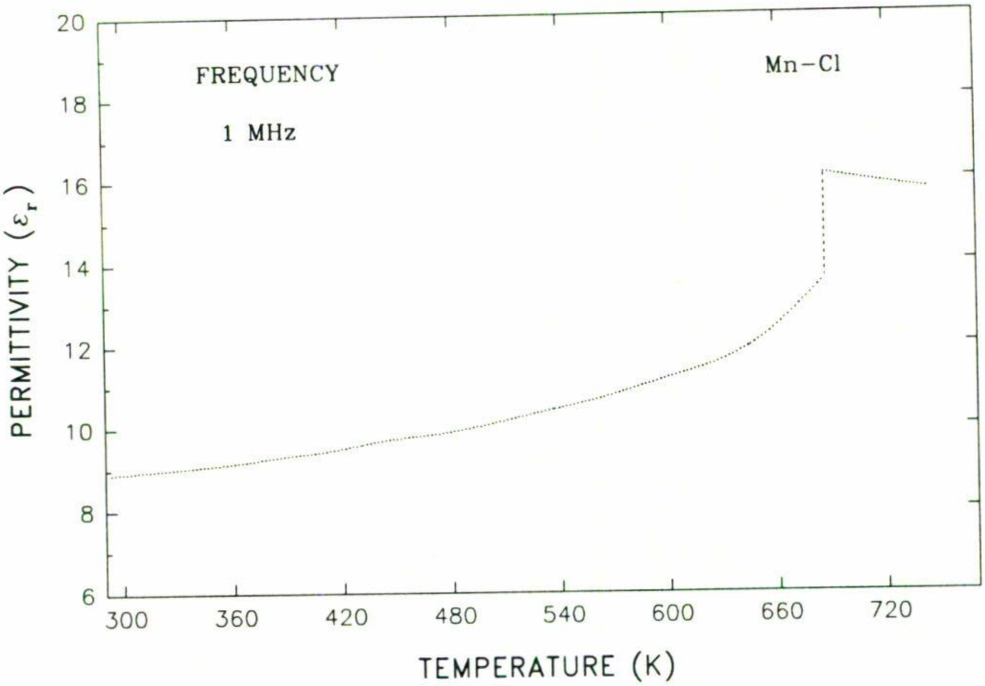

FIGURE 5. Temperature dependence of the stress-free permittivity of Mn-Cl Boracite.

The equilibrium conditions $\partial G/\partial P = 0$ and $\partial G/\partial \eta$, yield for the spontaneous polarization $P(T)$ in the ferroelectric phase (below T_c):

$$P = -\frac{a_1 \chi_0 \eta^2}{1 + 2\chi a_2 \chi_0 \eta^2}, \tag{2}$$

and for the inverse dielectric susceptibility, $\chi(T)^{-1}$ in the ferroelectric phase:

$$\chi^{-1} = \chi_0^{-1} + 2a_2\eta^2 - \frac{2a_1^2}{(\beta + 2\gamma\eta^2)(1 + 2a_2\chi_0\eta^2)}, \tag{3}$$

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

$$\alpha(T - T_0) + \beta\eta^2 + \gamma\eta^4 - \frac{2a_1^2\chi\eta^2}{(1 + 2a_2\chi_0\eta^2)} + \frac{2a_2a_1^2\chi^2\eta^4}{(1 + 2a_2\chi_0\eta^2)^2} = 0. \tag{4}$$

In the paraelectric phase, $P = 0$, $\eta = 0$ and $\chi = \chi_0$ is temperature independent. A general solution for Eq. (4) is not simple and a quantitative comparison of our experimental results with the predictions of this free energy is still in progress. However a good deal of insight has been obtained [44] for halogen boracites based on approximations.

From the stability condition $\partial^2 G/\partial \eta^2 > 0$ 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 non polar 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 last two 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 decrease of χ in the transition to the non polar phase can be expected.

The form of the free energy requires that the cubic-orthorhombic transition be first order, and in a large number of boracites it has such a pronounced first order character. However, the spontaneous polarization behaviour versus temperature in Mn-Br [38] seems to indicate a second-order type transition, this also would explain the magnitude decrease of the permittivity observed in this boracite. It also has been shown that the cubic-orthorhombic phase transition in Mn-I and Cu-Cl [45-46] seems to be closer to second order, but then this contradicts theoretical expectations of this model concerning the magnitude of the ϵ_r at the transition in these compounds.

It is interesting to mention that the model of Sannikov [42] based on considerations of double phase transitions, can also explain the two types of dielectric anomalies observed in this family of compounds. It also predicts the absence of dielectric divergence at the phase transition, a point that should be further explored due to the large number of boracites which have not yet been characterized.

5. CONCLUSIONS

Our experimental results have shown that Mn-X exhibit the two types of dielectric anomalies reported previously for crystals of this large family of compounds: Mn-Cl followed the typical dielectric behaviour of most boracites in which the permittivity drops downwards at the phase transition when cooling from the high temperature phase, while in Mn-Br and Mn-I the permittivity increases upwards, an unusual dielectric behaviour among these compounds firstly observed in Cu-Cl boracite [31].

An attempt was made to describe these dielectric anomalies by a simplified thermodynamic potential which can explain both types of dielectric behaviour observed in boracites. However, fits of our data to the free energy expressions of such a model involve more degrees of freedom in the theory than can be determined from the dielectric data alone. The theoretical model used to analyze qualitatively our experimental results explains both types of dielectric anomalies, but it fails to account successfully for the magnitude of the jumps in ϵ_r in Mn-X boracites when taking in consideration the order of the phase transition in these compounds. The order of the transition itself is yet unclear for Mn-X boracites. Taking Mn-Br as example, from pyroelectrics measurements [38] the $\bar{4}3$m-mm2 transition seems to be close to second order, but this is in opposition to results from thermal measurements [46] that shows a typical first order behaviour. This situation reflects the striking differences in physical properties of boracites which are awaiting for a satisfactory theoretical description.

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