

DIELECTRIC AND PYROELECTRIC STUDIES ON $[N(CH_3)_4]_3Bi_2X_9$ ($X = Cl, Br$)

R. JAKUBAS, G. BATOR

Institute of Chemistry, University of Wrocław, Joliot-Curie 14, 50-383 Wrocław, Poland

AND J. MRÓZ

Institute of Physics, Technical University of Wrocław
Wybrzeże Wyspiańskiego 27, 50-370 Wrocław, Poland

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Dielectric properties of $[N(CH_3)_4]_3Bi_2X_9$ ($X = Cl, Br$) single crystals were measured in the frequency range 1 kHz – 1 MHz in the vicinity of structural phase transitions of first-order type at 152 K (Cl) and 183 K (Br). The pyroelectric effect was observed in $[N(CH_3)_4]_3Bi_2Cl_9$ at structural phase transition ($T_c = 152$ K) with the ΔP_s of the order of 10^{-5} C m⁻². Polarized microscope observations show appearance of ferroelectric domain structure in $[N(CH_3)_4]_3Bi_2Br_9$ within the low temperature phase.

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1. Introduction

Alkylammonium salts with the general formula $[NH_{4-n}(CH_3)_n]_3M_2X_9$ ($M = Sb, Bi; X = Cl, Br, I$) undergo interesting phase transitions which are related to freezing of reorientational motion of cations [1–4].

Tetramethylammonium representatives of this family of crystals, namely $[N(CH_3)_4]_3Bi_2Cl_9$ (TEMACB) and $[N(CH_3)_4]_3Bi_2Br_9$ (TEMABB) undergo structural phase transitions at 155 and 183 K, respectively [5]. Differential scanning calorimetry (DSC) and dilatometric studies of these crystals corroborated the first-order nature and an “order–disorder” mechanism of these phase transitions [6]. Tetramethylammonium compounds are isomorphous at room temperature with $P6_3/mmc$ space group [7]. ¹H NMR studies showed that two inequivalent $N(CH_3)_4^+$ cations are present in the crystal lattice of TEMACB and TEMABB [8]. Nuclear quadrupole resonance (NQR) studies on $[N(CH_3)_4]_3Sb_2Br_9$ (TEMABA) by Ishihara et al. [5] suggested that the low temperature phase of this crystal ($T < T_c = 183$ K) has monoclinic symmetry with the Cm space group.

Since TEMACB and TEMABB are isomorphous at room temperature one could expect the same sequence of phase transition in both crystals. It was demonstrated by NQR studies that the TEMABB crystal transforms from nonpolar to polar symmetry [5]. Pyroelectric measurements were undertaken in the TEMACB material to verify whether it becomes polar as well.

Dielectric measurements in the frequency range (1 kHz – 1 MHz) were performed in TEMACB and TEMABB crystals to elucidate the nature of structural transitions in these materials.

2. Experimental

$[\text{N}(\text{CH}_3)_4]_3\text{Bi}_2\text{Cl}_9$ and $[\text{N}(\text{CH}_3)_4]_3\text{Bi}_2\text{Br}_9$ crystals were obtained in the reaction of $(\text{BiO})_2\text{CO}_3$ and $[\text{N}(\text{CH}_3)_4]\text{OH}$ in a solution of HCl (or HBr). Single crystals of TEMACB were grown by slow evaporation of aqueous solution with an excess of HCl at room temperature, whereas TEMABB — from HBr acid.

Dielectric measurements were performed in the frequency range 1 kHz – 1 MHz using a HP 4284A precision RLC meter in the temperature range 100–300 K with a constant cooling/heating rate of 0.1 K/min.

Pyroelectric properties of TEMACB crystals were performed using the continuous current method with a Keithley 617 type electrometer in the temperature range 120–250 K with the cooling/heating rate of 0.5 K/min. Repeatability of a pyroelectric current in TEMACB crystal was better than 10% for all samples with the experimental error smaller than $2 \times 10^{-7} \text{ C m}^{-2}$.

TEMACB sample dimensions for dielectric studies were about $6 \times 6 \text{ mm}^2$ (perpendicular both to the *a*- and *c*-axis) and $4 \times 3 \text{ mm}^2$ (perpendicular to the *c*-axis) for TEMABB crystals.

The size of TEMACB samples for pyroelectric studies was about $5 \times 5 \text{ mm}^2$ perpendicular to the *c*-axis. Conducting silver painted electrodes were used for dielectric and pyroelectric measurements.

The domain structure was observed using a polarizing microscope (AMPLIVAPOL) and a home-made low temperature sample stage. As-grown and not polished crystal plate ($3 \times 3 \times 0.3 \text{ mm}^3$) with the plane parallel to the cleavage plane (\perp to the *c*-axis) was used to observe the ferroelastic domain structure.

3. Results

3.1. Dielectric measurements

Figure 1 shows the temperature dependence of the real (ϵ') part of dielectric constant measured along the *c*-axis at 1 MHz for TEMABB. The structural phase transition (investigated by DSC and dilatometric methods [6]) at 180 K is accompanied by a very small dielectric anomaly. However, a slope variation of the $\epsilon'(T)$ curve in the vicinity of the phase transition temperature is clearly visible. No relaxation process was observed for TEMABB for frequencies between 1 kHz and 1 MHz. The background contribution increases with increasing temperature in agreement with the behaviour expected for ionic crystals.

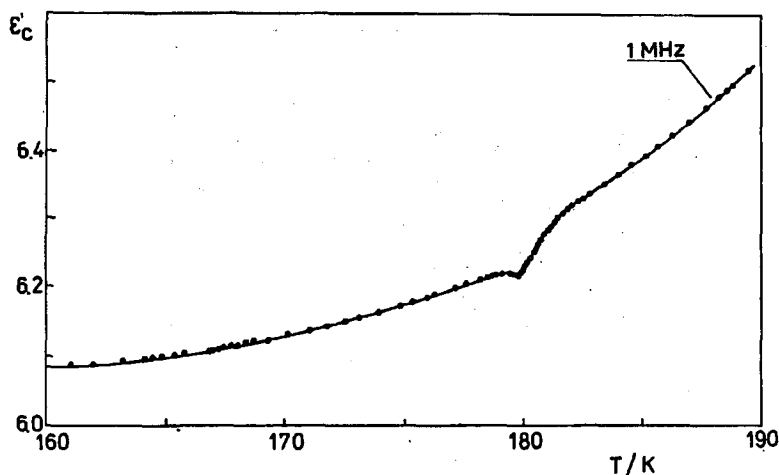


Fig. 1. Electric permittivity for the $[N(CH_3)_4]_3Bi_2Br_9$ crystals along the c -axis at the frequency 1 MHz on cooling.

Very interesting dielectric response for the low frequency region was found in the vicinity of the structural phase transition ($T_c = 150$ K) of TEMACB crystal. This phase transition was discovered by NQR method [5] and confirmed by DSC and dilatometric techniques as well [6]. Figure 2a shows the temperature dependence of ϵ' measured along the a -axis of TEMACB. The dielectric response $\epsilon_a^*(\omega)$ in the low frequency region indicates a residual relaxation process near the 150 K phase transition point. The strength of this relaxator is rather small ($\Delta\epsilon_a^* \approx 0.15-0.20$) and it appears above and below $T_c = 150$ K. For the direction placed perpendicular to the a -axis (see Fig. 2b) electric permittivity, ϵ_c , recorded at 1 MHz experiences an abrupt although small increase ($\Delta\epsilon_c = 0.04$). No dielectric losses were observed along the c -axis in the frequency range 1 kHz – 1 MHz. Taking into account the value of the electric permittivity along the c -axis (\perp to the cleavage plane) and a -axis (\parallel to the cleavage plane) the lack of the anisotropy of the electric properties is observed in TEMACB.

Comparing dielectric properties of tetramethylammonium crystals belonging to the family of the general formula $[N(CH_3)_4]_3Me_2X_9$ (Me = Sb, Bi and X = Cl, Br) one should observe that all first-order phase transitions encountered in the low temperature region are usually accompanied by relatively small change in the electric permittivity. Moreover, in case of bismuth derivatives, these changes ($\Delta\epsilon$) are several times lower than those found in antimony crystals [9]. Numerous 1H proton magnetic resonance studies performed on crystals in this family showed that in general, dynamic state of tetramethylammonium cations is similar in all crystals in the high temperature phases [8, 10]. These cations perform practically isotropic motion and most likely contribute to an order-disorder mechanism of phase transitions. The dipole-dipole interaction between tetramethylammonium cations possessing small permanent dipole moment is rather weak. Thus, one could conclude that its contribution to the $\Delta\epsilon$ in the vicinity of T_c is negligible. The

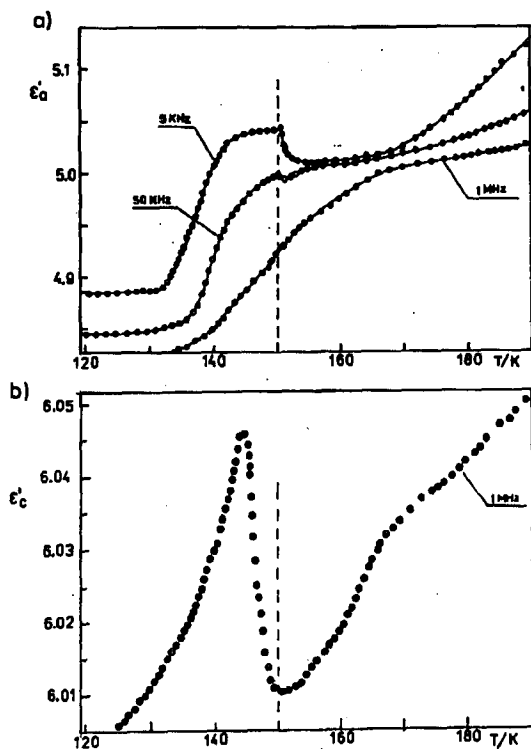


Fig. 2. Electric permittivity for the $[N(CH_3)_4]_3Bi_2Cl_9$ crystals measured at 5 kHz, 50 kHz and 1 MHz along the a -axis (a), along the c -axis at 1 MHz (b) (on cooling).

changes of the electric permittivity near the critical point are mainly due to the alterations of density of crystals. The lack of anisotropy of the dielectric properties for these crystals may be due to the absence of polymeric structure of the anionic form (there are discrete anions $Bi_2Cl_9^{3-}$ in the crystal lattice) and the presence of loosely packed $(TEMA)^+$ groups undergoing the same type of reorientations (isotropic). It should be stressed that a distinct dielectric anomaly was found in the crystals containing polymeric anionic structure (e.g. $[N(CH_3)_3H]_3Sb_2Cl_9$ [11], $[N(CH_3)_2H_2]_3Sb_2Cl_9$ [12], $[N(CH_3)_2H_2]_3Sb_2Br_9$ [13]).

3.2. Pyroelectric measurements

The behaviour of the current response of TEMACB samples cut in the perpendicular direction to the c -axis, namely, change of the sign of the current depending on the direction of temperature change, proved that we found a true pyroelectric current in the temperature range below 152 K. The temperature dependence of the spontaneous polarization measured along the hexagonal c -axis is presented in Fig. 3. At 152 K the polarization jumps suddenly up to about 3×10^{-6} C/m², and then it linearly increases down to about 120 K without any saturation. An attempt to reverse the direction of polarization in the low temperature phase was not successful. Application of DC electric field (500 V/cm)

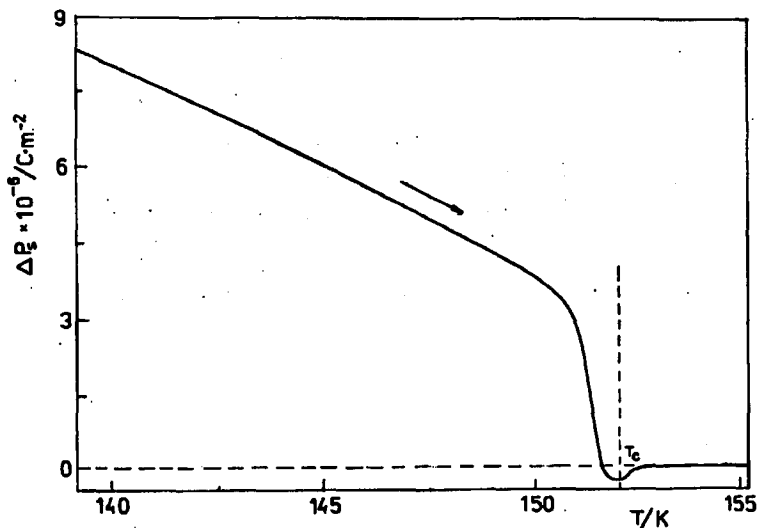


Fig. 3. Temperature dependence of the spontaneous polarization, ΔP_s , in the $[N(CH_3)_4]_3Bi_2Cl_9$ crystal measured along the c -axis.

produced conduction current through TEMACB samples which was much higher than the true pyroelectric current even when the electrodes were short-circuited for a long time. All experimental facts convinced us that TEMACB crystal is a pyroelectric below 152 K.

3.3. Observations of TEMABB crystal under the polarizing microscope

TEMABB crystals were observed under the polarizing microscope along the c -axis in the temperature range 100–200 K. These observations were performed on heating and cooling runs. It was impossible to make the same observation in TEMABB along the a -axis because single crystals of this compound are very fragile and rather small (only plates \perp to the c -axis 0.5 mm thick were available). Figure 4 shows microscopic photographs that were taken at 150 K (on cooling). All domains appear suddenly just below 183 K. Domain boundaries cross at the 120 degrees, are simultaneously parallel to the a -axis of the crystal (see Fig. 4). One can conclude that observed domains are ferroelastic. The appearance of the phase front proves that this is a first-order phase transition. The pyroelectric properties of TEMACB and ferroelastic domains of TEMABB should be discussed in view of possible sequence of phase transitions suggested by Ishihara et al. [5]. Their NQR results showed that $[Bi_2Br_9]^{3-}$ in the low temperature phase (below $T_c = 183$ K) has symmetry m in a monoclinic space group e.g. Cm , $Z = 2$. It means that a possible sequence of phase transition is $6/mmm \rightarrow m$. It is well known that such symmetry change permits the appearance of ferroelastic domains in a monoclinic phase. This is consistent with our microscopic observations. We should also remember that tetramethylammonium compounds, TEMACB and TEMABB, are isomorphous at room temperature. This is reasonable to assume that the structural



Fig. 4. Domain structure of the low temperature phase in $[N(CH_3)_4]_3Bi_2Br_9$ as observed along the c -axis (recorded at 150 K).

phase transition for chlorine analog at 152 K leads also to the monoclinic, polar symmetry m . This is in agreement with pyroelectric results that are presented in this paper.

4. Conclusions

1. All structural phase transitions of first-order type encountered in $[N(CH_3)_4]_3Me_2X_9$ ($Me = Sb, Bi$ and $X = Cl, Br$) crystals reveal subtle dielectric anomaly at the critical points.
2. The dielectric dispersion studies show that the relaxation process which is connected with the rotational motions of tetramethylammonium cations is expected to appear at least in the microwave frequency region.
3. The pyroelectric measurements on TEMACB reveal the existence of a polar phase below 152 K.
4. Polarizing microscope observations suggest that TEMABB crystal possesses ferroelastic domains below 183 K.

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