THE INTERNAL BIAS FIELD
OF FERROELECTRIC $(CH_3NH_3)_5Bi_2Br_{11}$

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Spontaneous polarization of $(CH_3NH_3)_5Bi_2Br_{11}$ crystals has been measured and the ferroelectric hysteresis loop has been studied. The observed time changes in the polarization have been ascribed to the change in the internal bias field of the crystal. Measurement results have also been discussed for the lower phase transition ($T_{II} = 77$ K).
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1. Introduction

The alkylammonium halogenobismuthate, $(CH_3NH_3)_5Bi_2Br_{11}$, crystallizes at room temperature in orthorhombic symmetry space group, $Pca2_1$, and undergoes a second-order phase transition at $T_c = 312$ K to ferroelectric phase [1–2]. It is assumed that the phase transition is connected with the ordering of $CH_3NH_3^+$ cations. Dielectric anomaly [1], [3–6], differential scanning calorimeter (DSC) [7], birefringence [8], and dilatometric [9] studies confirm the continuous character of the ferro-paraelectric phase transition. The second much smaller dielectric anomaly along the c-direction at 77 K was interpreted as a phase transition [4], [10].

The published results show, however, some discrepances. The extremal values of the ratio C_p/C_f of the Curie constants in the para- and ferroelectric phases are equal to 3.6 [1] and 5.6 [4]. Spontaneous polarization in units of 10^{-2} C/m^2 below the phase transition temperature T_c ranges from 0.7 ($\Delta T = 27$ K) [1] to 1.75 ($\Delta T = 12$ K) [10]. Character of some phenomena observed in that crystal is not typical, namely high C_p/C_f, anomalous electric permittivity along the a- and b-directions [1] and discrepancy in the values of the spontaneous polarization for crystals biased with different electric fields [6]. The reasons of that can be

numerous; the one is due to crystal imperfections caused by the crystal defects. The aim of this work is to determine chemical defect impact (especially the presence of Br_2 in the lattice) on the dielectric response of $(CH_3NH_3)_5Bi_2Br_{11}$ in the vicinity of the phase transition. From the published papers it is known that the crystals were grown either from highly [5] or from slightly [1] HBr-rich solutions.

2. Experimental

The crystals were grown as described in Ref. [1] with a high excess of 40% HBr. A few crystals were grown from the same solution. The dielectric permittivity was measured at 1 kHz. The pyroelectric coefficient was measured by the short-circuit current method at the constant rate of 1.3×10^{-2} K/s on heating. Previously electrical poling was achieved by cooling a crystal from the para- into the ferroelectric phase in the applied electric field of 300 kV/m. The spontaneous polarization was measured with the Sawyer–Tower circuit at 50 Hz, by the pyroelectric charge method with an electrometer, and also was calculated by intergration of the pyroelecric coefficient.

3. Results

Electric permittivity was measured close to the phase transition temperature T_c. The constants determined from the Curie–Weiss law are as folows: $C_p = 2800$ K, $C_f = 560$ K, and $C_p/C_f = 5$. The phase-transition temperature determined from dielectric and pyroelectric measurements was 309 K, being lower by 3 K than that determined by Jakubas [1]. Observations of a ferroelectric hysteresis as a function of electric field and time rendered it possible to conclude certain rules. The hysteresis loop shape and the electric polarization were found to be determined by the rise time of the applied electric field. When the electric field increases with time very slowly, the hysteresis for fields below the threshold ($E < E_1$, cf. Fig. 1a) is not observed and the $P(E)$ relation is linear. The pyroelectric measurements for an as-grown sample indicate the non-zero unipolarity. For fields $E_1 < E < E_2$ there is a hysteresis loop and the polarization rapidly increases with field. The field E_1 being equal to the threshold is called the threshold field. At the field of E_2 the spontaneous polarization assumes to be constant and the saturation time lasts a few to several seconds.

When the electric field is decreasing back towards E_1 and below, the spontaneous polarization does not change at the beginning, but further on both the polarization and the coercive field E_c are decreasing upon decrease of the electric field and more rapidly upon approaching of E_3 (cf. Fig. 1a). At the field $E_3 > E_c$ the hysteresis disappears. The results were repeatable when breaks between the measurements lasted at least a few hundreds seconds. For shorter breaks the thresholds field was lower. A quite different picture of the hysteresis is achieved when the field is step-like. At the field of $E_1 + \Delta E$ there is a single (cf. Fig. 1b) or double (cf. Fig. 1c) hysteresis loop at the ends of the $P(E)$ relation with an internal bias field E_b depending upon the unipolarity. The E_b field decreases to zero within 8–10 seconds, and at last a single hysteresis remains (cf. Fig. 1c, dashed line). For

the repeated field rise the double hysteresis can occur again with the internal bias field of $E_{b2} > E_{b1}$ which decreases with time. The cycle can be repeated even a couple of times.
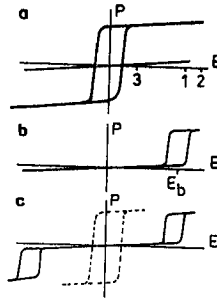

Fig. 1. Sketch of ferroelectric hysteresis loops with marked electric field. (a) $E_1 = E_p$ is the threshold which is necessary to form the hysteresis loop. In the field E_2 and higher a rise of the loop to a constant hight proceeds quickly. In the field E_3 the hysteresis loop disappears. After switching the field E_2 on one observes a single or double loop ((b) and (c)) which at last passes to a single one. Such pictures on a screen were observed at temperatures a few degree below the phase transition temperature T_c.
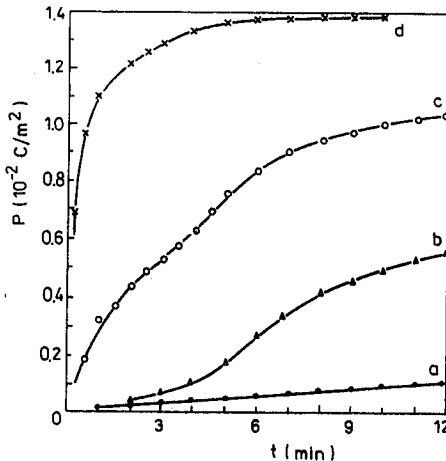

Fig. 2. Temporary changes of the electric polarizations at the temperature 8 K below T_c obtained from the hysteresis loop. The loop appears at the threshold field $E_p = 1150$ kV/m. The amplitude of the applied field E and the coercive field E_c in units of kV/m are the following : a) 1190, 115; b) 1220, 250; c) 1250, 270; d) 1300, 280. The loop disappears at $E_0 = 480$ kV/m.

Figure 2 shows the time dependence of the electric polarization for various electric bias fields at $(T_c - T) = 8$ K. At the threshold field $E_p = 1150$ kV/m and lower, there is no hysteresis ($E_p \equiv E_1$). At the field of 1190 kV/m the electric

polarization increases linearly with time (cf. curve a). Ten minutes after the biasing the coercive field assumes the value of 115 kV/m. The polarization increases rapidly with time at higher fields (cf. curve b, c and d). The polarization becomes constant at 1300 kV/m within a few minutes and at 1350 kV/m as soon as several seconds. Decreasing the field down to 600–500 kV/m casuses a clear lowering of the hysteresis loop height, and at $E_0 = 480$ kV/m the loop disappears despite the field is much higher than the coercive field ($E_0 \equiv E_3$ in Fig. 1a).
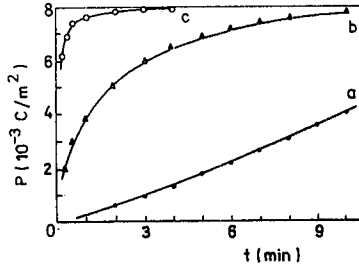

Fig. 3. Temporary changes of the electric polarization at the temperature 3 K below T_c. The threshold field $E_p = 670$ kV/m. The amplitude of E and the coercive field E_c are the following: a) 720, 158; b) 770, 170; c) 815, 180.
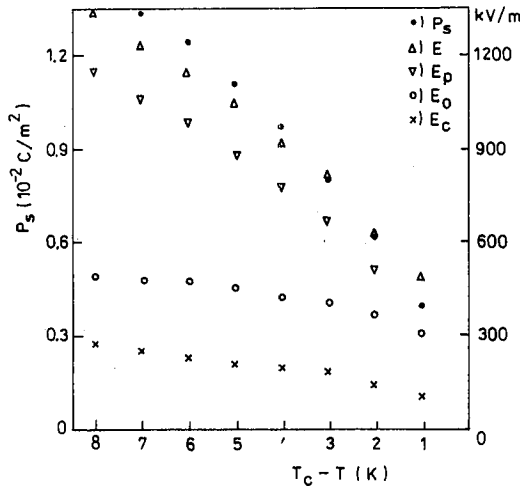

Fig. 4. Temperature dependence of the spontaneous polarization P_s, the applied electric field E ($E \geq E_2$), the threshold field E_p, the coercive field E_c, and the field E_0 at which the hysteresis loop disappears.

The time dependence of the electric polarization at 6 K below T_c is similar to that of Fig. 2 with the constant value of the spontaneous polarization being equal to 1.23×10^{-2} C/m^2. Figure 3 shows the analogous dependence for 3 K below T_c. Figure 4 shows the temperature dependence of the spontaneous polarization P_s

along the c-axis (with applied fields E at which a constant polarization is acheved within ca. 10 seconds), the applied field E, the threshold field E_p required for the hysteresis occurrence and with the field of E_0 at which the hysteresis disappears. E_c is the coercive field. One may notice that $E_0 > E_c$. The threshold field depends to some extend upon time lasting from the latest bias process. In order to obtain repeatable results the breaks between the subsequent biases lasted at least two minutes. The hysteresis loop height depends slightly upon the electric bias field. Based on the described observations a slight difference in the spontaneous polarization determined with the Sawyer–Tower circuit and that determined by the pyroelectric method may be expected. The temperature dependence of the pyroelectric coefficient and the spontaneous polarization obtained from the integration are show in Fig. 5. The results of the spontaneous polarization and the electric
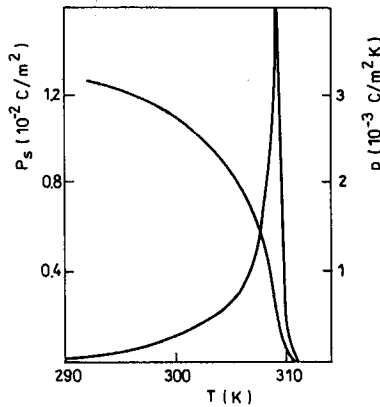

Fig. 5. Temperature dependence of the pyroelectric coefficient and the spontaneous polarization measured on heating. The electrical poling was achieved by cooling a crystal from the paraelectric phase in the field of 300 kV/m.
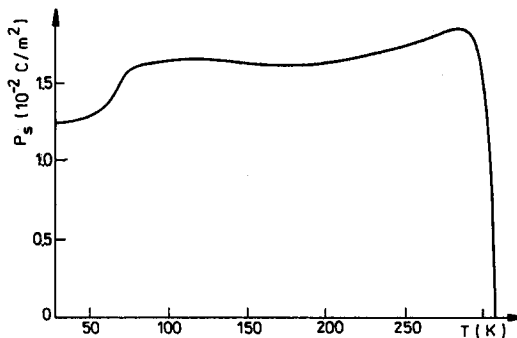

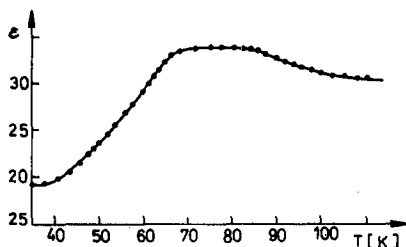Fig. 6. Temperature dependence of the spontaneous polarization.

Fig. 7.   Temperature dependence of the electric permittivity along the polar c-axis in the vicinity of the phase transition temperature T_{II}.

permittivity in the vicinity of the lower phase transition for the crystal grown in subsequent cycles from the same solution are shown in Figs. 6 and 7, respectively, and they clearly differ from those reported in Ref. [10].

The observed difference in the spontaneous polarization shown in Figs. 5 and 6 may have two reasons. The measurements were performed with two different samples of different history and with different electric fields 10^{-3} V and 1 V, respectively, applied to the samples during the measurement (the measurement methods were different).

4. Discussion

For convenience the experimental results for the studied crystals are listed below:

1. Freshly-grown crystals show a non-zero unipolarity.
2. They exhibit a strong internal bias much higher than the coercive fields.
3. Strong alternating electric field can make the crystal younger; the internal field decreases with time and at last a single hysteresis loop occurs.
4. When the electric field applied to the crystal made younger is switched off, the internal field is formed again within a few minutes.
5. Alternating electric field of 50 Hz frequency and intensity slightly greater than the coercive field cannot depolarize the crystal.

The field needed to create a single-domain state must be greater than the threshold field.

Hysteresis phenomena similar to those above-mentioned have been observed for $[(CH_3)_3NH]_3Sb_2Cl_9$ [11]. In many works it is assumed that the internal field is caused by intentional dopants or defects. In our case the crystals were grown under high excess of HBr and it is likely that Br_2 molecules may form defects. Polar properties of the crystal depend upon $(CH_3NH_3)^+$ cation ordering [7]. The hysteresis phenomena should then be ascribed to the cations movement due to their free reorientation ability and to their move limitations due to Br_2 defects. The cations surrounded by the defects create an internal field. In a weak external one the hysteresis loop does not occur. Whereas a sufficiently strong field causes

releasing of the cations. Consequences of that are the following: the spontaneous polarization increases and the internal field decreases to zero.

The internal field in the crystal also manifested itself in the electric permittivity measurements. When an external electric field opposite to the internal one was applied to the crystal the electric permittivity was increased with the DC external field up to the moment when the internal field was compensated by the external one. Further bias caused a rapid decrease of the electric permittivity. The crystal cooled down to below 285 K shows an anomalous decrease in the spontaneous polarization (cf. Fig. 6). The effect is observed both on heating and cooling for all the grown crystals.

At the temperature of $T_{II} = 77$ K the second phase transition is observed. The transition shows an interesting peculiarity since in crystals grown under small excess of HBr the spontaneous polarization increased on cooling [10] whereas for crystals grown with an additional amount of HBr in the same solution the polarization and the electric permittivity decreased (cf. Figs. 6 and 7). The reason of that can be ascribed to freezing of a part of cations due to defects after the transition.

Above the temperature of T_{II} the crystal symmetry is of $Pca2_1$ while a symmetry of the low-temperature phase is unknown. Below T_{II} spontaneous polarization occurs along the b-axis. Taking into account experimental results confirming a continuous character of the phase transition at T_{II} and basing on the group theory we can conclude that the point group m is the only possible sub-group. Two occurred orientation states in the low-temperature phase refer to a spontaneous deformation. When during this phase transition ferroelastic domains occur, they are expected to decrease both the electric permittivity and the spontaneous polarization in the c-axis.

A study of the lower phase transition at T_{II} along the b- and a-axes are in progress and will be published.

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