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PHASE TRANSITIONS IN $(CH_3NH_3)_5Bi_2X_{11}$ (X = Cl, Br) CRYSTALS

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Electric properties of $(CH_3NH_3)_5Bi_2Cl_{11}$ and $(CH_3NH_3)_5Bi_2Br_{11}$ single crystals in the direction of the crystallographic *b*-axis were studied. The samples tested were natural crystal seeds in the form of thin plates, whose crystallographic *b*-axis coincides with the normal to the plate. Measurements of the pyroelectric coefficient were performed near the high temperature phase transition and spontaneous polarization from the paraelectric phase down to helium temperature. The attempt of explanation of the anomalous electric properties of these crystals has been presented.

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1. Introduction

The alkylammonium halogenobismuthates (III) crystals, $(CH_3NH_3)_5Bi_2X_{11}$ (X = Cl, Br), crystallize at room temperature in orthorhombic symmetry, space group $Pca2_1$. With increasing temperature both crystals transform from the ferroelectric phase to the paraelectric phase, *Pcab*, at $T_c = 308$ K (X = Cl) and at $T_c = 312$ K (X = Br), respectively [1–3]. Dielectric [1, 2, 4, 5] and dilatometric [6, 7] studies confirm the continuous character of the ferro-paraelectric phase transitions. These phase transitions are accompanied by a large increase in the electric permittivity along the ferroelectric *c*-axis, of the order of 10^4, both for the bromide (MAPBB) and chloride (MAPCB) crystals [1, 2, 4, 5, 8]. Much lower dielectric anomaly, about two orders of magnitude, was also observed along the *b*-axis [1, 2]. Hysteresis phenomena and temporary changes of the spontaneous polarization below T_c [9] show non-typical behaviour of the $(CH_3NH_3)_5Bi_2Br_{11}$ crystals. In the low temperature region both analogues display the second-order phase transition with dielectric anomaly seen along the *c*-axis [10, 11]. The non-typical behaviour of spontaneous polarization [9] prompted us to examine electric properties along the *b*-axis in these crystals. Preliminary measurement results showed the existence of the spontaneous polarization along the *b*-axis at room temperature. These results seem to be in contradiction to structural investigations published up to the present. For this reason we have undertaken the examination of electric properties of $(CH_3NH_3)_5Bi_2X_{11}$ crystals along the *b*-axis for many samples, mainly on crystal seeds to eliminate the orientation error along the crystallographic axes during cutting of the crystals. We report the results of measurements along the *b*-axis, as well as the attempt at explaining the discrepancy of structural investigations with the physical properties observed.

2. Experimental

Natural seeds in the form of a rhombus with a surface of 20–50 mm^2 and thickness of about 1 mm with electrodes of silver paste, served as examination samples. The crystallographic *b*-axis coincides with the normal to the surface. In natural crystal seeds not polarized by an external electric field the pyroelectric current has been observed. The samples were additionally polarized by the electric field of 100 kV/m in the paraelectric phase and then cooled to room temperature and lower. After cooling the electrodes were short-circuited for 1 h, and for 15 h in control measurements. The pyroelectric coefficient was determined by short-circuit current method at constant heating rate of 13×10^{-3} K/s. Spontaneous polarization at temperatures above 295 K was calculated by the curve integration method. Also, changes of spontaneous polarization in a wide range of temperatures, up to helium temperatures, were determined with an electrometer by measuring the pyroelectric charge. The spontaneous polarization (P_s) and the pyroelectric coefficient (P) measurements are accurate to within 15% and 10%, respectively. Electric permittivity was measured with an automatic E315A meter at the frequency of 1 kHz.

3. Results

Figure 1 presents the temperature dependence of pyroelectric coefficient (P) and spontaneous polarization (P_s), for $(CH_3NH_3)_5Bi_2Cl_{11}$ crystals in the direction of the *b*-axis. The value of spontaneous polarization changes with temperature, and at the temperature of 295 K is about 15 times lower than in the direction of the *c*-axis. The results of measurements performed on some natural seeds and on samples cut out from large single crystals were repeatable. The phase transition at 308 K shows the continuous nature.

The results of measurements of pyroelectric coefficient and spontaneous polarization for the isomorphous $(CH_3NH_3)_5Bi_2Br_{11}$ crystal in the direction of the *b*-axis are presented in Fig. 2. Spontaneous polarization is higher for the bromide analogue in comparison with the chloride one. The value of spontaneous polarization is a dozen or so times lower than in the direction of the *c*-axis.

For $(CH_3NH_3)_5Bi_2Cl_{11}$ crystals in the direction of the *b*-axis electric permittivity measurements were performed (see Fig. 3). Temperature changes of electric

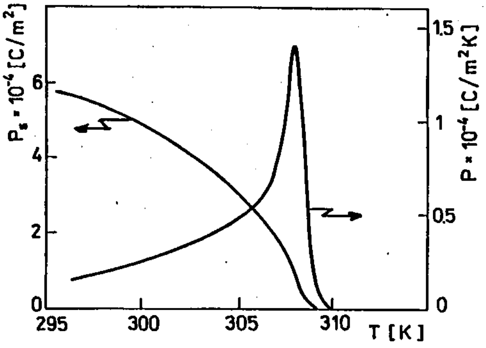

Fig. 1. Temperature dependence of the pyroelectric coefficient (P) and the spontaneous polarization (P_s) measured along the *b*-axis in the $(CH_3NH_3)_5Bi_2Cl_{11}$ crystal.

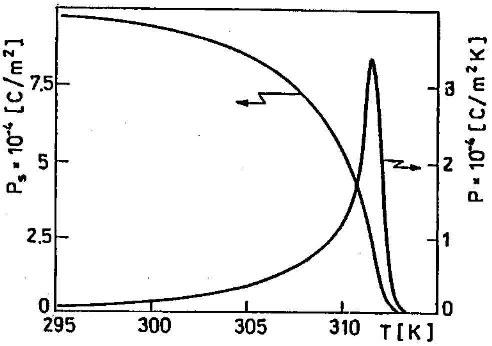

Fig. 2. Temperature dependence of the pyroelectric coefficient (P) and the spontaneous polarization measured along the *b*-axis in the $(CH_3NH_3)_5Bi_2Br_{11}$ crystal.

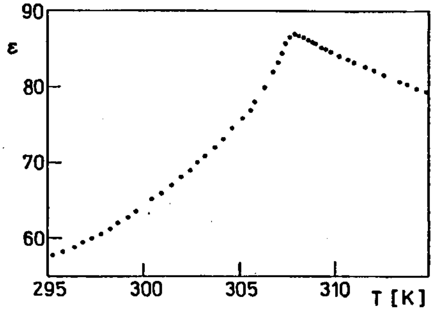

Fig. 3. Temperature dependence of the electric permittivity along the *b*-axis in the $(CH_3NH_3)_5Bi_2Cl_{11}$ crystal.

permittivity have a characteristic curve for ferroelectric crystals. Electric permittivity is much lower than that recorded for the *c*-direction. A similar temperature dependence is observed for bromide crystals.

Measurements of pyroelectric charge in the direction of the *b*-axis were performed both for MAPCB and MAPBB crystals. The results of measurements of spontaneous polarization changes for MAPBB are presented in Fig. 4. A discontinuous character of the polarization change around the temperature $T_{\rm II} = 77$ K was observed. Temperature hysteresis of phase transition averages about 1 K and depends on the rate of temperature changes. Repeating several times the measurements for different samples it was possible to observe a certain scattering of the spontaneous polarization changes at the temperature of 77 K. We presume that this is connected with the division of the single crystal into domains. Contrary to the *b*-direction the spontaneous polarization along the *c*-axis increases in a continuous manner during cooling, and its value is much greater than for the *b*-axis [10]. The temperature dependence of the spontaneous polarization for $(CH_3NH_3)_5Bi_2Cl_{11}$ crystal in the direction of the *b*-axis is presented in Fig. 5. The non-continuous anomaly is visible around the temperature of $T_{\rm II} = 170$ K. When the temperature is decreased further, jump changes of spontaneous polarization down to about 130 K are observed against a background of continuous changes. The observed anomalies (see Fig. 5) were recorded by two different experimental techniques: by charge integration with an electrometer and by pyroelectric short-circuit current method. Contrary the *b*-direction, the spontaneous polarization along the *c*-axis increases in a continuous way during cooling [12], and its value is much greater than for the *b*-axis.

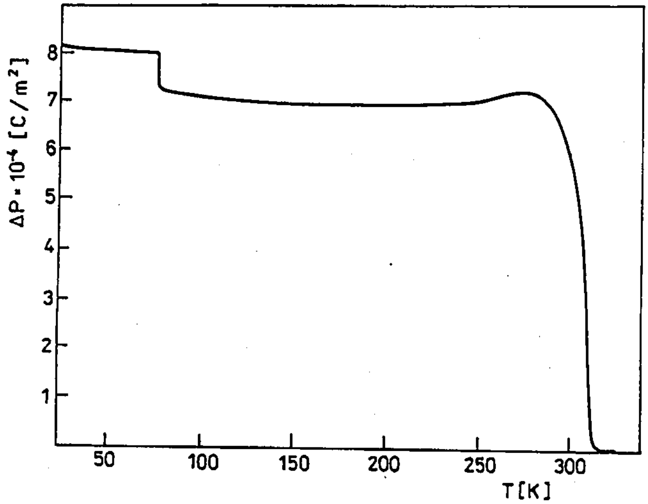

Fig. 4. Change of the spontaneous polarization as a function of temperature, $\Delta P_s^b(T)$, in the $(CH_3NH_3)_5Bi_2Br_{11}$ crystal.

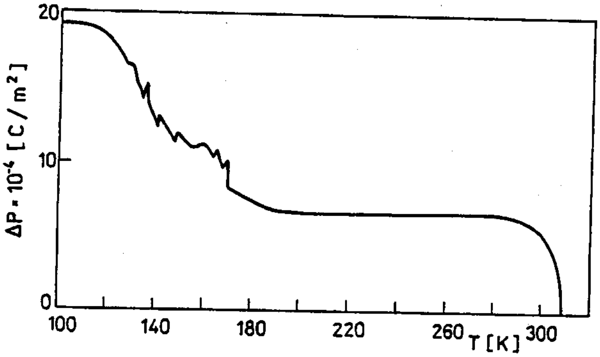

Fig. 5. Change of the spontaneous polarization as a function of temperature, $\Delta P_s^b(T)$, in the $(CH_3NH_3)_5Bi_2Cl_{11}$ crystal.

4. Discussion

First of all, we shall present the discussion about the high-temperature phase transition. From crystallographic investigations [3, 13] we know about the symmetry changes during the $Pcab \rightarrow Pca2_1$ phase transition. This indicates the possibility of appearance of spontaneous polarization along the *c*-axis being a double symmetry axis for the ferroelectric phase. The spontaneous polarization observed by us, both along the *c*-axis and *b*-axis, is not consistent with the symmetry given.

In the case when the normal to the surface plate forms with the *c*-axis the angle different from 90° the component of the spontaneous polarization (P_s^c) appears along the normal to the surface. We exclude this case because the measurements were performed on natural crystal seeds (without any polishing and cutting of the sample) whose normal to the surface of the sample coincides with the *b*-axis.

Besides, basing on polarizing microscope observations, we ascertain that the first bisectrix is perpendicular to the sample surface within the measurement limit of error. The angle between the optic axes is 20°.

A possible cause of spontaneous polarization increase observed along the *b*-axis near T_c is the coupled motion of dipole groups of C(12)–N(12) and C(22)–N(22) cations (designations from [13]). Though these cations are not ordered in the ferroelectric phase, the degree of their order clearly increases when temperature decreases. Since they are oriented in the lattice differently than methylammonium cations of type (3) inducing ferroelectric properties, they may give contribution to polarization both along the *c*-axis and along the *b*-axis. These cations are also crystallographically non-equivalent, and it is very probable that only one type of these cations subordinates to the long-range order along the *b*-axis near the low-temperature transformation (T_{II}) which is accompanied by a jump increase in P_s^b polarization. Therefore, we postulate that two methylammonium cations of type (2) give different contribution to P_s in the ferroelectric phase along the *c* and *b* axes. The results obtained also suggest that polar order along the *b*-axis is strongly susceptible to the influence of external electric field.

From the investigations of the low temperature phase transition at T_{II}, we conclude that the low temperature phase may be a ferroelastic one and concurrently polar (but not ferroelectric). Recently, Iwata and Ishibashi stated, on the basis of dielectric measurements and optic observations, that there are no signs of phase transition at temperature near 170 K in $(CH_3NH_3)_5Bi_2Cl_{11}$ crystals — no ferroelastic domains were observed in any plate by means of a polarizing microscope [14]. We declare for the occurrence of phase transition in this crystal for the following reasons:

1. Jump changes of DSC curve in the region of 160 K [2] have been observed.
2. Crystals of $(CH_3NH_3)_5Bi_2Cl_{11}$ and $(CH_3NH_3)_5Bi_2Br_{11}$ are isomorphic and show jump changes of spontaneous polarization along the *b*-axis. Changes of ΔP_s^b (Br) are large, and of ΔP_s^b (Cl) — small.

The thermodynamic potential proposed in [14] does not explain any of the given above and experimentally observed anomalies. From dilatometric measurements [6, 7] it is known that crystals expand in the direction of the *b*-axis during cooling in temperatures below T_c. This fact favours the occurrence of phase transition in the low-temperature region. From experience related to other crystals it is known that the lack of domains visible under the microscope in virgin crystal is no proof of the fact that the crystal is not ferroelastic. Sometimes in order to create domains it is necessary to impose a suitably large mechanical stress, larger than the coercive force field at the given temperature. In Refs. [5] and [13] the molecular mechanism of the phase transition at T_c has been presented. It has been assumed that in the temperature below 308 K the pair of C(i2)–N(i2) cations is not ordered. It is possible that around T_{II} the ordering of one or both methylammonium cations takes place. In temperatures below T_{II}, down to helium temperatures, we have not observed dielectric anomalies. Analyzing the lower phase transition it seems that the case of volume multiplication of the elementary cell may not be excluded. It is easy to notice that the temperature changes of ΔP_s^b for MAPCB are not typical. Jump changes of polarization take place in the temperature range of about 40 K below T_{II}. In this region a distinct lowering of electric permittivity is observed.

5. Conclusions

1. In $(CH_3NH_3)_5Bi_2X_{11}$ crystals in the ferroelectric phase spontaneous polarization appears along the crystallographic *b*-axis and *c*-axis.
2. In both compounds the low temperature phase transition takes place at T_{II}.
3. The character of temperature changes of spontaneous polarization along the *b*-axis in $(CH_3NH_3)_5Bi_2Cl_{11}$ crystal below T_{II} is non-typical.
4. The ordering of the methylammonium cations of type (2) most probably contributes to the P_s^b anomalies observed around T_{II}.

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