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Effect of Hydrostatic Pressure on the Low Temperature Phase Transition in Ferroelectrics: $(CH_3NH_3)_5Bi_2Cl_{11}$ and $(CH_3NH_3)_5Bi_2Br_{11}$

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Results of hydrostatic pressure on the low temperature ferroelectric-ferroelectric phase transition in $(CH_3NH_3)_5Bi_2Cl_{11}$ at about 170 K and $(CH_3NH_3)_5Bi_2Br_{11}$ at 77 K are presented. The phase transition in both cases revealed a positive pressure coefficient. The pyroelectric coefficients in the vicinity of the low temperature transitions become more and more diffusive as pressure increases. A similar molecular mechanism of phase transitions in both methylammonium salts is postulated.

Key words: halogenobismuthates(III), ferroelectrics, phase transition, spontaneous polarization, pyroelectric coefficient, high pressure

The methylammonium halogenoantimonates(III) of the general formula $(CH_3NH_3)_5Bi_2X_{11}$ (X = Cl, Br) exhibit interesting polar properties, which have attracted considerable attention in recent years [1–5]. Both crystals display a similar sequence of phase transitions. The chlorine (MAPCB) and bromine (MAPBB) salts undergo paraelectric-ferroelectric phase transition from orthorhombic Pcab to $Pca2_1$ space group at 307 and 311 K, respectively. X-ray studies showed that the polarity of these crystals is connected with disordering of methylammonium cations [6]. The "order – disorder" character of ferroelectric phase transition was confirmed by the dielectric dispersion measurements [7,8] and numerous spectroscopic studies [9]. The isostructural anomaly at 170 K in MAPCB is visible as a relatively small change in the static electric permittivity and a continuous increase in the spontaneous polarization. The mechanism of this phase transition is related to the variation in the dynamics of two methylammonium cations. Contrary to a weak continuous phase transition at 170 K in MAPCB, the low temperature phase transition at 77 K in MAPBB exhibits a first order nature. The effect of hydrostatic pressure on the ferroelectric-paraelectric phase transition in MAPCB and MAPBB was reported by Gesi *et al.* [10].

In this paper the hydrostatic pressure studies on two ferroelectric crystals: $(CH_3NH_3)_5Bi_2Cl_{11}$ and $(CH_3NH_3)_5Bi_2Br_{11}$, in the vicinity of the low temperature ferroelectric-ferroelectric type phase transition are presented. The pressure effect will provide important information about the transition mechanism in these crystals.

EXPERIMENTAL

MAPCB and MAPBB single crystals were obtained using known procedure [3]. The samples of dimensions 5×5 ×1 mm^3 cut perpendicular to the polar c-axis were covered with a silver paste. The spontaneous polarization change was measured with an Unitra 219 electrometer. Hydrostatic pressure was generated by a three step oil gas Unipress compressor with helium as pressure transmitting medium. High pressure was measured with a manganine resistor with an accuracy of about 5 MPa. Temperature was stabilized by the PID regulator with PT-100 thermometer. The samples were poled with an electric field of about 1×10^5 V/m.

RESULTS AND DISCUSSION

The temperature dependence of the spontaneous polarization (ΔP) and pyroelectric coefficient (γ) for the $(CH_3NH_3)_5Bi_2Cl_{11}$ crystals in the vicinity of the low temperature isostructural anomaly at 0 MPa and 100 MPa is displayed in Fig. 1. One can observe both a diffusion of the pyroelectric coefficient and a distinct shift of the maximum of γ *versus* T curve towards higher temperature with the pressure increase. This effect is consistent with previous dielectric measurements for $(CH_3NH_3)_5Bi_2Cl_{11}$ [10]. The temperature dependence of the spontaneous polarization changes under various pressures for $(CH_3NH_3)_5Bi_2Cl_{11}$ in the low temperature region is shown in Fig. 2. An increase of the spontaneous polarization value measured at constant temperature with increasing pressures is clearly observed. The pressure dependence of the spontaneous polarization for $(CH_3NH_3)_5Bi_2Br_{11}$ crystal at various temperatures is shown in Fig. 3.

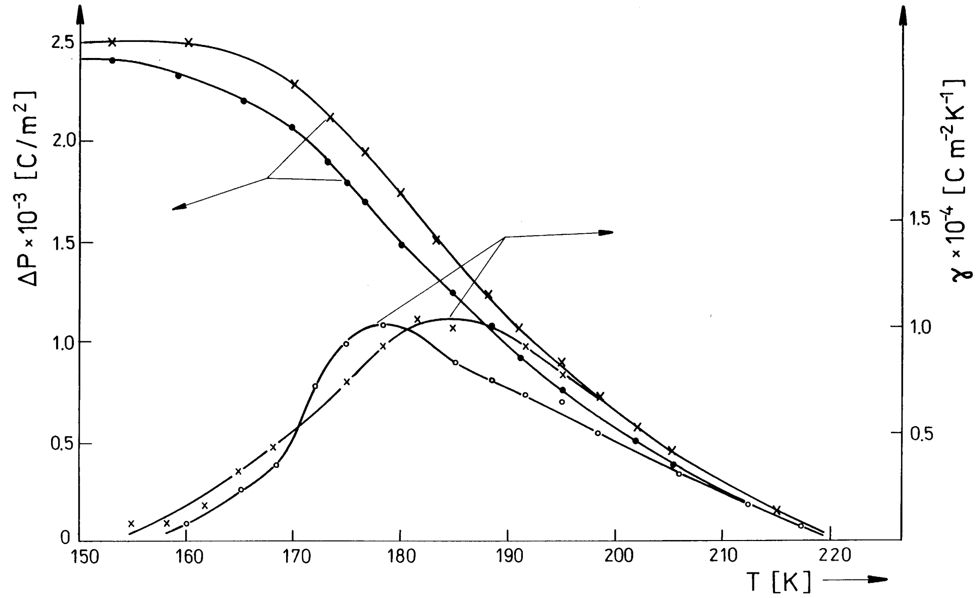

Figure 1. Temperature dependence of the spontaneous polarization (ΔP) and pyroelectric coefficient at p = 0 MPa (o) and p = 150 MPa (x) for the $(CH_3NH_3)_5Bi_2Cl_{11}$ crystals.

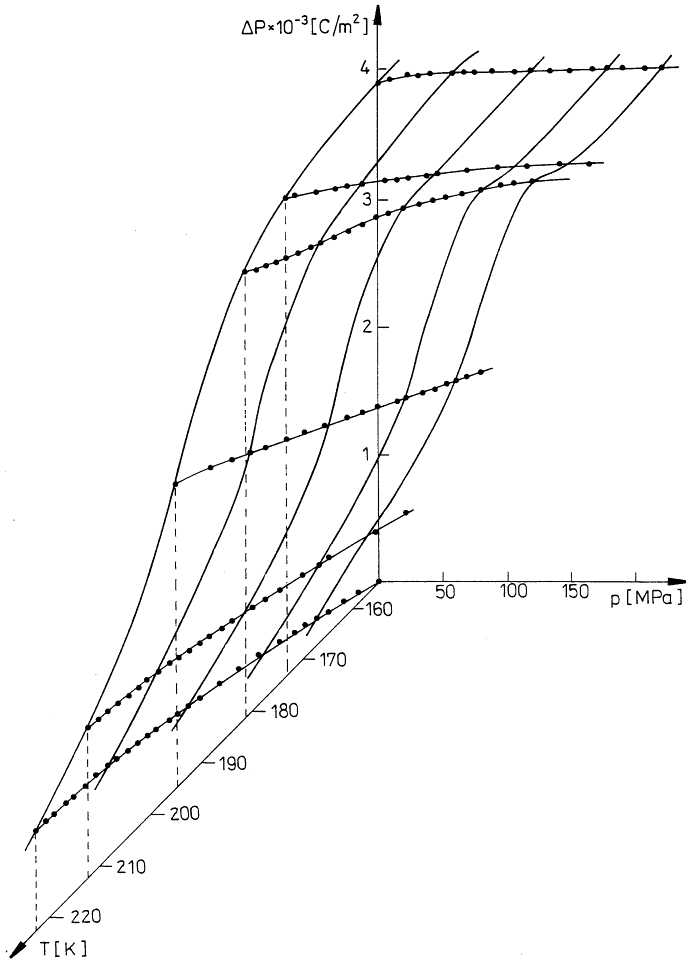

Figure 2. Pressure dependences of the spontaneous polarization (ΔP) for the $(CH_3NH_3)_5Bi_2Cl_{11}$ crystals at various temperatures.

The effects of hydrostatic pressure on ferroelectric crystals have been reported in numerous papers. Samara *et al.* [11] showed that the sign of pressure coefficient (dT_c/dp) depends on the mechanism of phase transition. For the proper displacive-type ferroelectrics the coefficient $dT_c/dp < 0$, whereas for an improper displacive-type ones $dT_c/dp > 0$. The order-disorder type ferroelectrics like TGS-family are characterized by $dT_c/dp > 0$. On the other hand for the KDP-family the dT_c/dp coefficient appears to be negative, in spite of the fact that these crystals are clearly order-disorder type. However, their ferroelectricity is coupled with the configuration of the hydrogen bonds linked with the PO_4 tetrahedra. The experimental studies showed that most of hydrogen bonds crystals are characterized by a negative coefficient dT_c/dp.

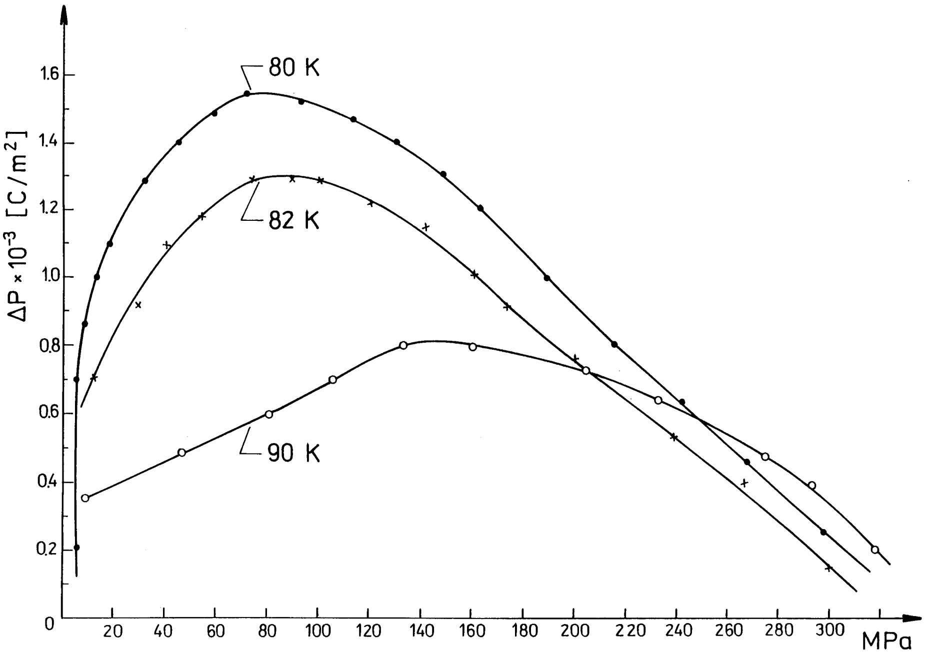

Figure 3. Pressure dependences of the spontaneous polarization (ΔP) for the $(CH_3NH_3)_5Bi_2Br_{11}$ at selected temperatures: 80, 82 and 90 K.

The effect of hydrostatic pressure on the ferroelectric phase transition has been studied up to now only for several halogenoantimonate(III) and halogenobismuthate(III) crystals, like $(CH_3NH_3)_5Bi_2X_{11}$ subgroup [12,13], $(CH_3NH_3)_3Sb_2Br_9$ (MABA) [14] and $(CH_3NH_3)_3Bi_2Br_9$ (MABB) [15]. All these crystals revealed the order-disorder mechanism of phase transitions; therefore, it seems to be interesting to compare their pressure-temperature diagrams. MABA undergoes two phase transitions: to the ferroelastic phase at 168 K and to the ferroelectric phase at 131 K. For these transitions, the positive pressure coefficients were found in accordance with an order-disorder mechanism. The second methylammonium analogue MABB, in spite of the fact that it is isomorphous to MABA, displayed a more complex sequence of phase transitions and quite different pressure-temperature phase relation in comparison to this found in MABA. MABB undergoes three phase transitions. The para-ferroelastic type at 188 K and ferroelastic – ferroelastic type at 140 K correspond to those found in MABA, but unexpectedly they are characterized by a negative pressure coefficient in contrast to positive ones found in MABA. It should be underlined, that the phase transitions at 188 and 140 K are clearly of order-disorder type and are expected to have a positive pressure coefficient. In turn, the lowest temperature transition of a displacive type at 104 K, leading to improper ferroelectric phase, is characterized by a distinct positive pressure coefficient. The atypical pressure-temperature behaviour for the discussed above two methylammonium crystals is probably connected with a strong influence of the pressure on the hydrogen-bond configuration and confirms the complexicity of the phase transitions.

The pressure-temperature phase diagram for the $(CH_3NH_3)_5Bi_2Cl_{11}$ and $(CH_3NH_3)_5Bi_2Br_{11}$ crystals are quite similar [12,13]. The high temperature paraelectric – ferroelectric phase transition in both crystals, being of an order – disorder type, revealed positive and comparable pressure coefficients (39 K/GPa and 58 K/GPa). In turn, the lower temperature phase transition, leading to consecutive ferroelectric phases at 77 K in bromine analogue and at about 170 K in chlorine one, is rather difficult to study. The first phase transition is quite close to the liquid nitrogen temperature, whereas the second one is diffused in nature without any visible maximum on ε' *versus* T curve. Present pressure studies showed that the low temperature isostructural phase transition in $(CH_3NH_3)_5Bi_2Cl_{11}$ at about 170 K and first order one in $(CH_3NH_3)_5Bi_2Br_{11}$ at 77 K are characterized by a positive dT_c/dp coefficient up to 320 MPa. Such a behaviour confirms an order – disorder mechanism of these transitions, that is in agreement with earlier X-ray studies [6] and observed critical slowing down of dielectric relaxation process in the microwave frequency region [7,8].

In statistical mechanics, the Ising model for an order-disorder type ferroelectrics gives the formula: $k \cdot T_c = \mu^2 \cdot J$, where k is the Boltzmann constant, μ the dipol moment and J the dipol – dipol interaction. The observed gradual increase of T_c with pressure for $(CH_3NH_3)_5Bi_2Cl_{11}$ and $(CH_3NH_3)_5Bi_2Br_{11}$ is ascribed to the increase of μ with pressure. For the pressure up to 320 MPa we probably deal with the increase of strength of N–H…Cl bonds. The X-ray studies suggest that dipole moments, which appear along the hydrogen bonds, are expected to contribute to the electric permittivity and the spontaneous polarization. As a result the higher pressure favours the configuration with stronger hydrogen bonds and larger dipole moments.

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