Pyroelectric and Dilatometric Studies on the Low Temperature Ferroelectric Phase Transition of $(CH_3NH_3)_5Bi_2Br_{11}$

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The results of the linear thermal expansion studies on $(CH_3NH_3)_5Bi_2Br_{11}$ single crystals in the temperature range 60–340 K are presented. The thermal anomaly in the vicinity of 77 K is assigned to the phase transition classified as close to first order type. The pyroelectric measurements of $(CH_3NH_3)_5Bi_2Br_{11}$ were carried out in the range of 45–320 K along the a- and c-axis. The step-like change in the spontaneous polarization along the a-axis at 77 K indicates a discontinuous character of ferroelectric transition.

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1. Introduction

Recently the alkylammonium halogenoantimonates(III) and halogenobismuthates(III) of the general formula $R_aM_bX_{3b+a}$ (where R denotes organic cations, M — Sb, Bi, and X — Cl, Br, I) evoke much interest. It was found that numerous compounds of this family underwent multiple structural phase transitions (PTs) [1–3]. The salts with the $R_3M_2X_9$ or $R_5M_2X_{11}$ compositions appeared to be specially interesting since they frequently demonstrate ferroelectric properties. The crystal structure of the $R_3M_2X_9$ subclass was characterized by three types of anionic form: (1) zigzag double chains [4], (2) two-dimensional layers of the MX_6 octahedra [5], and (3) by isolated $M_2X_9^{3-}$ units [6]. It was shown that polar

properties are observed only for the salts built up of the layer anionic sublattice and small-sized cations, like $CH_3NH_3^+$, $(CH_3)_2NH_2^+$, and $(CH_3)_3NH^+$ [7–10]. The second subclass — $R_5M_2X_{11}$ — was characterized exclusively by isolated $M_2X_{11}^{5-}$ units. There are only three known salts crystallizing with composition like this: $(CH_3NH_3)_5Bi_2Br_{11}$ [11], $(CH_3NH_3)_5Bi_2Cl_{11}$ [12], and $(C_5H_5NH)_5Bi_2Br_{11}$ [13]. All of them exhibited the ferroelectric properties. The origin of the ferroelectricity of both subclasses was attributed to dynamical ordering of dipolar organic cations.

$(CH_3NH_3)_5Bi_2Br_{11}$ (MAPBB) at 311.5 K undergoes a ferroelectric phase transition of the $mmmFmm2$ type (from $Pcab$ to $Pca2_1$ space group) [14]. The dielectric dispersion [15] and the Raman scattering [16] studies indicate the "order–disorder" mechanism of the phase transformation. Another phase transition is manifested by a nonlinear increase in spontaneous polarization and dielectric anomaly in the vicinity of 77 K [17]. The character of this phase transition is still unclear and the symmetry (space group) of the lowest temperature phase is unknown. Nevertheless, the dynamics of the methylammonium cations is expected to contribute both to the paraelectric-ferroelectric transition at 311 K and the phase transition at 77 K.

The linear thermal expansion studies on the MAPBB crystals have been limited to the high temperature ferroelectric transition [18, 19]. To throw more light on the character of the phase transition at 77 K and the linear thermal expansion in the wide temperature region of MAPBB we decided to perform the dilatometric studies of the compound in the temperature range 350–60 K. This paper also contains new pyroelectric measurements on MAPBB along three crystallographic directions (the *a*-, *b*-, and *c*-axis of the orthorhombic system) from 315 K to 30 K, with a special inspection of the lowest temperature phase transition at 77 K.

2. Experimental procedure

Single crystals of MAPBB were obtained in the reaction of $(BiO)_2CO_3$ with CH_3NH_3Br in concentrated HBr. The synthesized compound was purified by repeated crystallizations. Yellow and transparent single crystals were grown at room temperature and had the form of orthorhombic prism. Samples with three different orientations (plates perpendicular to the *a*-, *b*-, and *c*-axis) were prepared to study the pyroelectric and dilatometric properties.

The linear thermal expansion measurements in the temperature range 60–340 K were made with a capacitance dilatometer. Errors in $\Delta L/L_0$ values were generally smaller than 1%.

The temperature dependence of the spontaneous polarization and pyroelectric coefficient were carried out by using the method of an integration of the pyroelectric charge (with an electrometer UNITRA 219-type). A detailed description of this method is given by Dziedzic and Stolecki in Ref. [20]. The spontaneous polarization (P_s) and the pyroelectric coefficient (γ) measurements are accurate to within 15% and 10%, respectively.

3. Results and discussion

3.1. Dilatometric measurements

Figures 1–3 show results of the linear thermal expansion ($\Delta L/L_0$, where L_0 is the length of the sample at room temperature for the corresponding axes) and the linear thermal expansion coefficient ($\alpha = \partial(\Delta L/L_0)/\partial T$) as a function of temperature measured along the *a*-, *b*-, and *c*-axis (the directions presented correspond to those taken for the room temperature ferroelectric orthorhombic phase) during the cooling cycles. The linear thermal expansion for all axes of MAPBB in the vicinity of the paraelectric-ferroelectric phase transition is similar to that presented by Jakubas and Pykacz [18]. The α_a coefficient reveals a clear anomaly in the vicinity of the paraelectric-ferroelectric transition at 311.5 K and a small diffused anomaly in the vicinity of 220 K. It should be noted that the expected phase transition at 77 K is rather hardly visible along the *a*-axis. The α_a coefficient changes from 2×10^{-5} K^{-1} to about 4×10^{-5} K^{-1} in the range 70–220 K.

Quite unusual behaviour of the linear thermal expansion is found along the *b*-axis. Below 311 K the MAPBB is characterized by a negative coefficient α_b

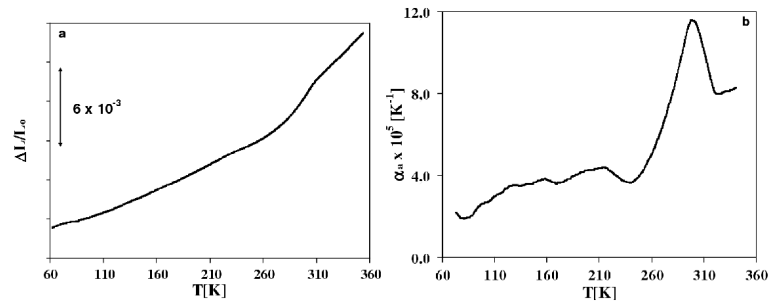

Fig. 1. (a) Temperature dependence of the linear thermal expansion and (b) the linear thermal expansion coefficient for MAPBB along the *a*-axis on cooling.
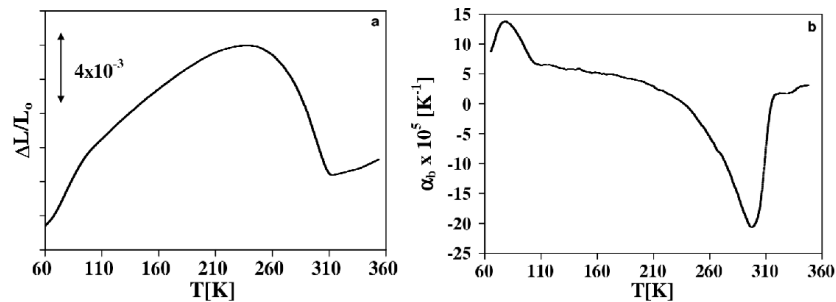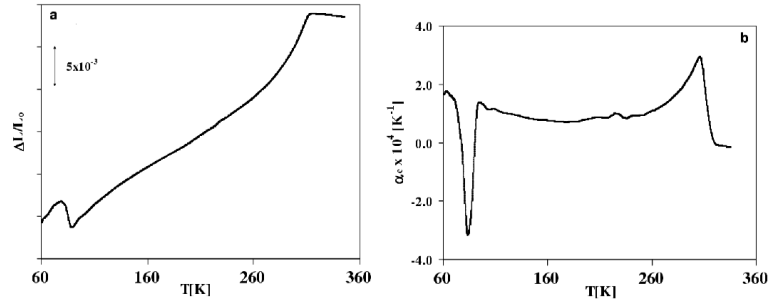

Fig. 2. The same as in Fig. 1 but along the *b*-axis.

Fig. 3.   The same as in Fig. 1 but along the *c*-axis.

with $\alpha_{b\,max} = 2 \times 10^{-4}$ K^{-1}. At 240 K the thermal expansion displays a change of sign of the α coefficient. On further cooling a visible anomaly in dilation of the crystal is observed close to 77 K accompanied by a clear peak on the α_b versus temperature curve.

The most interesting properties of the linear thermal expansion of MAPBB over the low temperature region were found along the polar *c*-axis. In the wide temperature region (100–260 K) the α_c coefficient maintains a constant value of about 1×10^{-4} K^{-1}. Close to 80 K a rapid expansion of the sample $(-\Delta L/L_0)$ of the order of 3×10^{-3} is observed due to the structural phase transitions between two polar phases. The transition is accompanied by an appearance of a significant α_c coefficient $(\approx 3 \times 10^{-4}$ K$^{-1})$. It should be underlined that the observed phase transition in MAPBB at 77 K has some features of the first order one. One can conclude that the 77 K phase transition reveals a mixed character and it is rather close to the first order type.

The changes in the volume of the crystals $(\Delta V/V_0)$ and the volume thermal expansion coefficient (α_V) in the studied temperature range are illustrated in Fig. 4. The both phase transitions are evidently shown on the $\Delta V/V_0$ versus temperature curve. It is clearly seen that the α_V coefficient accompanying the transition at 77 K is distinctly larger than that for the paraelectric-ferroelectric
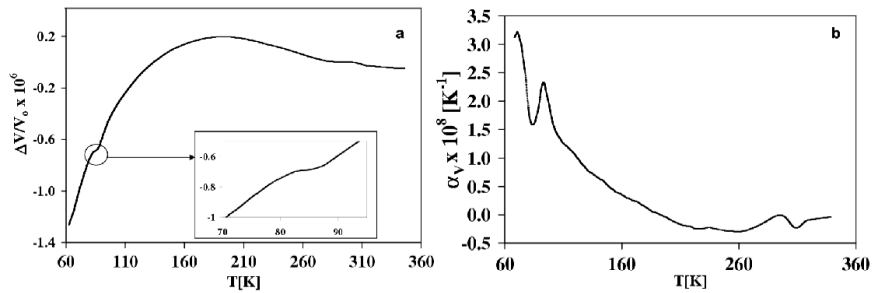

Fig. 4.   (a) Temperature dependence of the relative $\Delta V/V_0$ and (b) the volume thermal expansion coefficient for MAPBB in a wide temperature range. The inset in part (a) shows an anomaly of $\Delta V/V_0$ in the vicinity of 77 K.

transition (311.5 K). The dilatometric response of MAPBB shows that the phase transition at 77 K is featured as a discontinuous one in contrast to the clear second order transition at 311 K. It is interesting to notice that the $\Delta V/V_0$ versus temperature curve exhibits a maximum at about 200–190 K which corresponds to the minimum visible on the $P_s(T)$ curve (see also Fig. 5). Such a behaviour can be explained by interactions of dipolar units (methylammonium cations). An increase in the relative volume of the unit cell of the crystal leads to an increase in the distances between interacting dipoles contributing to the spontaneous polarization. As a result of this fact a continuous reduction of spontaneous polarization is observed below 250–260 K.

3.2. Pyroelectric measurements

The temperature dependence of the spontaneous polarization (P_s) along the polar c-axis in a wide temperature region is shown in Fig. 5. The pyroelectric response in the vicinity of the paraelectric-ferroelectric phase transition is similar to that reported in Ref. [17]. Nevertheless, a small but clearly visible anomaly as a jump in the ΔP_s value (see the inset of Fig. 5) is recorded. Besides, it turns out that the samples of virgin single crystals of MAPBB have a tendency to exist in a single domain state without any dc pooling. In our experiment before pyroelectric measurements the sample was pooled in a relatively small external dc electric field of the order of 10 V cm^{-1}. The dc electric field was switched in an opposite direction to the spontaneous polarization vector of a singledomain sample (not polarized before). It was shown that an increase in the pooling dc electric field led to a larger step-like anomaly on the P_s vs. temperature curve at 77 K. A detailed account of the electric field effect on the low temperature phase transition will be published elsewhere.

The most interesting behaviour of P_s is observed close to the phase transition at 77 K. A proper inspection of the pyroelectric coefficient ($\gamma(T)$) reveals two peaks situated closely to each other. It indicates the complex mechanism of this phase transition. The higher temperature peak on the $\gamma_c(T)$ curve nearly 77 K may be assigned to the onset of the structural phase transition being close to first
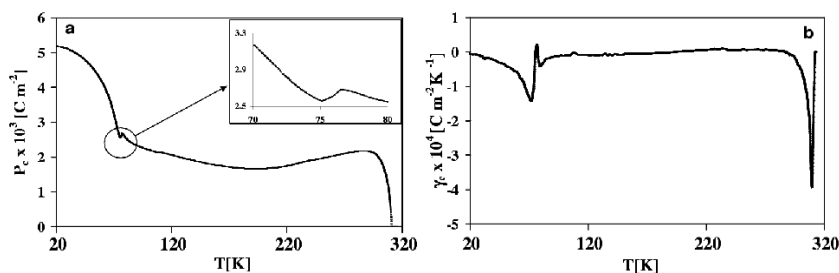

Fig. 5. (a) Spontaneous polarization (P_s) and (b) the pyroelectric coefficient (γ) as a function of temperature for MAPBB along the c-axis within 20 and 320 K. The inset in part (a) shows an anomaly of P_s in the vicinity of 77 K.

order. However, the lower temperature peak of $\gamma_c(T)$ curve justifies an important increase in P_s over the lowest temperature phase. It should be also added that quite similar increase in the P_s value is found in $(CH_3NH_3)_5Bi_2Cl_{11}$ (MAPCB) at 170 K, without any evident presence of the structural phase transition.

One can conclude that the 77 K phase transition may be explained in terms of the coupling of the order parameter assigned to the structural phase transition with the spontaneous polarization (the P_s value in the lower temperature phase is probably not the order parameter). The type of the transition is classified as an improper ferroelectric phase transition. The suggested coupling of the order parameter with P_s in MAPBB seems to be stronger than that for the chlorine analogue (MAPCB).

The presence of these two possible effects is better visible taking into account the spontaneous polarization evolution with temperature changing along the a-axis (see Fig. 6a,b). Since over the intermediate polar phase (from 311.5 K

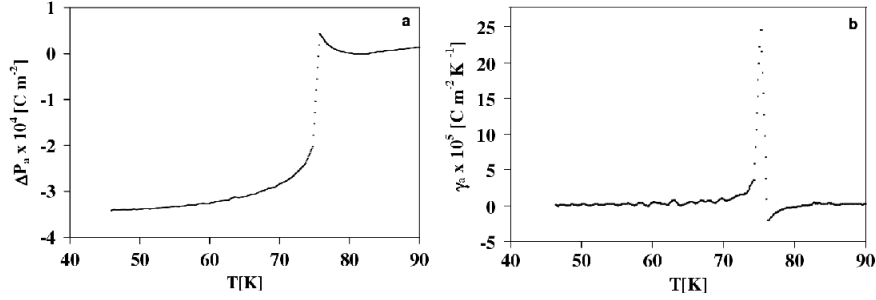
Fig. 6. The same as in Fig. 5 but along the a-axis in the vicinity of phase transition at 77 K.

to 77 K) the spontaneous polarization component P_s along the a-axis should be zero, the observed stepwise change in the P_s value ($\Delta P_{s(a)}$) below 77 K is strictly connected with the structural phase transition and appearance of a new component of the P_s vector. This phase transition is accompanied by a significant pyroelectric coefficient ($\gamma_{a\,max} = 2.5 \times 10^{-4}$ C m^{-2} K^{-1}).

4. Conclusions

1. The dilatometric measurements indicate that the $(CH_3NH_3)_5Bi_2Br_{11}$ crystals undergo a low temperature ferroelectric transition at 77 K close to the first order type.

2. The pyroelectric measurements reveal the complex mechanism of the phase transition at 77 K. The low temperature ferroelectric phase transition is believed to be classified as an "improper" one.

References

[1] R. Jakubas, L. Sobczyk, *Phase Transit.* **20**, 163 (1990).

[2] V. Varma, R. Bhattacharjee, H.N. Vasan, C.N.R. Rao, *Spectrochim. Acta A* **48**, 1631 (1992).

[3] L. Sobczyk, R. Jakubas, J. Zaleski, *Polish J. Chem.* **71**, 265 (1997) (and references cited therein).

[4] R. Jakubas, Z. Czapla, Z. Galewski, L. Sobczyk, O.J. Żogał, T. Lis, *Phys. Status Solidi A* **93**, 449 (1986).

[5] A. Kallel, J.W. Bats, *Acta Crystallogr. C* **41**, 1022 (1985).

[6] B. Chabot, E. Parthe, *Acta Crystallogr. B* **34**, 645 (1978).

[7] R. Jakubas, U. Krzewska, G. Bator, L. Sobczyk, *Ferroelectrics* **77**, 129 (1988).

[8] R. Jakubas, *Solid State Commun.* **69**, 267 (1989).

[9] R. Jakubas, Z. Czapla Z. Galewski, L. Sobczyk, *Ferroelectrics Lett.* **5**, 143 (1986).

[10] J. Zaleski, A. Pietraszko, *Acta Crystallogr. B* **52**, 287 (1996).

[11] J. Matuszewski, R. Jakubas, T. Głowiak, L. Sobczyk, *Acta Crystallogr. C* **46**, 1385 (1990).

[12] J. Lefebvre, P. Carpentier, R. Jakubas, *Acta Crystallogr. B* **51**, 167 (1995).

[13] J. Jóźków, G. Bator, R. Jakubas, A. Pietraszko, *J. Chem. Phys.* **114**, 7239 (2001).

[14] R. Jakubas, *Solid State Commun.* **69**, 267 (1989).

[15] R. Jakubas, J. Lefebvre, *Ferroelectrics* **108**, 115 (1990).

[16] Cz. Pawlaczyk, H. Motsch, R. Jakubas, H.G. Unruh, *Ferroelectrics* **108**, 127 (1990).

[17] J. Mróz, R. Jakubas, *Solid State Commun.* **72**, 813 (1989).

[18] R. Jakubas, H. Pykacz, *Phys. Status Solidi A* **115**, K17 (1989).

[19] R. Jakubas, P. Francois, J. Lefebvre, *Acta Phys. Pol. A* **85**, 579 (1994).

[20] J. Dziedzic, B. Stolecki, *Acta Phys. Pol. A* **98**, 55 (2000).