

THERMAL EXPANSION OF  $(\text{CH}_3\text{NH}_3)_5\text{Bi}_2\text{X}_{11}$   
(X = Cl, Br) CRYSTALS IN THE TEMPERATURE  
RANGE FROM 80 TO 300 K

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(Received September 22, 1993)

Thermal expansion studies on  $(\text{CH}_3\text{NH}_3)_5\text{Bi}_2\text{Cl}_{11}$  and  $(\text{CH}_3\text{NH}_3)_5\text{Bi}_2\text{Br}_{11}$  in the temperature range 80–350 K are reported. The dilatometric measurements revealed a considerable similarity with respect to the anisotropy of dilatations of both isomorphous crystals. A diffused thermal anomaly was found around 170 K in  $(\text{CH}_3\text{NH}_3)_5\text{Bi}_2\text{Cl}_{11}$  crystal.

PACS numbers: 64.70.Kb, 65.70.+y

## 1. Introduction

$(\text{CH}_3\text{NH}_3)_5\text{Bi}_2\text{Cl}_{11}$  (MAPCB) and  $(\text{CH}_3\text{NH}_3)_5\text{Bi}_2\text{Br}_{11}$  (MAPBB) represent a new subfamily of alkylammonium halogenobismuthates (III) showing ferroelectric properties. Both compounds crystallize in the orthorhombic system (space group  $Pca2_1$ , phase II) at room temperature and display a continuous ferroelectric phase transition (PT) to the paraelectric phase (space group  $Pcab$ , phase I) at  $T_c = 307$  K for MAPCB and 311 K for MAPBB [1, 2]. The X-ray diffraction studies showed [3] that the loss of polarity is due to the motion of the methylammonium cations. For the chlorine analogue only one of the five methylammonium

cations is suggested to be involved in the mechanism of the ferro-paraelectric PT. The dielectric dispersion studies of MAPCB and MAPBB performed by Pawlaczyk et al. [4] and Iwata and Ishibashi [5] revealed critical slowing down in the vicinity of  $T_c$  (I  $\Rightarrow$  II) in the microwave region. Recent Raman studies on MAPCB and MAPBB [6–8] have reported that no soft mode was observed near the ferroelectric PT temperature. These results indicate that the ferro-paraelectric transition is of the order–disorder type. Dielectric and pyroelectric measurements of MAPBB have revealed [9] that the crystal undergoes a continuous PT at 77 K into a polar phase (III) visible as a distinct peak of  $\epsilon_c$  ( $\epsilon_{\max} = 60$ ). However, there are some divergences with respect to the nature of the low temperature anomaly found at 170 K in MAPCB. The pyroelectric measurements [10] recorded a diffused anomaly below 180 K interpreted as a structural PT between two polar phases. Numerous techniques: Raman [6], birefringence [11] and conduction calorimetry [12] have detected a diffused physical anomaly in the vicinity of 170 K. On the other hand, the polarizing-microscope observations of MAPCB around 170 K by Iwata and Ishibashi [13] did not confirm the existence of the PT. The dilatometric studies were performed on MAPCB [14] and MAPBB [15] only in the vicinity of the ferro-paraelectric PT (I  $\Rightarrow$  II). To obtain more information about the thermal properties of these two crystals and especially explain the nature of the diffused structural anomaly around 170 K in MAPCB, the dilatometric measurements were performed in a wide temperature range (80–350 K).

## 2. Experimental

$(\text{CH}_3\text{NH}_3)_5\text{Bi}_2\text{X}_{11}$  crystals were obtained in the reaction of  $(\text{BiO})_2\text{CO}_3$  and  $\text{CH}_3\text{NH}_2$  in a solution of HCl (or HBr). The single crystals were grown by slow evaporation of the aqueous solution at room temperature. The crystal rods ( $10 \times 3 \times 3$  mm<sup>3</sup>) were oriented along the three main crystallographic directions. To obtain partially deuterated analogue,  $(\text{CH}_3\text{ND}_3)_5\text{Bi}_2\text{Cl}_{11}$ , the powder material of  $(\text{CH}_3\text{NH}_3)_5\text{Bi}_2\text{Cl}_{11}$  was recrystallized three times from  $\text{D}_2\text{O}$  with an excess of DCl. The extent of deuteration was estimated to be more than 96%.

The linear thermal expansion was measured by a thermomechanical analyzer Perkin-Elmer TMS-2. The studies were made in the heating and cooling mode at rates of 0.1–0.4 K/min. The anomalies were reproducible within 5% for each sample. The accuracy of the thermal expansion determination is about 2%.

## 3. Results

The thermal dilation  $\Delta L/L$  along the  $a$ -axis for MAPCB (upper part) and MAPBB (lower part) on cooling is shown in Fig. 1. Starting from higher temperatures it is clear that the weak anomaly seen as a small deviation from the linear part of dilation versus temperature curve (within the paraelectric phase I) just below  $T_{cI}$  for both crystals corresponds to the ferro-paraelectric PT. In the low temperature region the chlorine compound reveals rather strange behaviour of dilatation in the vicinity of postulated continuous PT at about 170 K. One can observe a twofold change in the sign of the temperature expansion coefficient; at about 180 K and 140 K. Both thermal anomalies are rather diffused

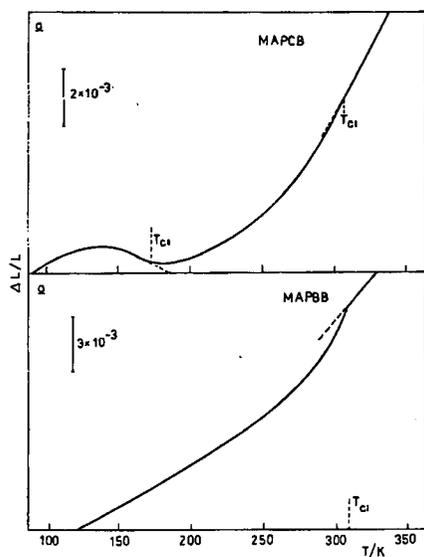


Fig. 1. Thermal expansion of  $(\text{CH}_3\text{NH}_3)_5\text{Bi}_2\text{Cl}_{11}$  and  $(\text{CH}_3\text{NH}_3)_5\text{Bi}_2\text{Br}_{11}$  crystals along the  $a$ -axis.

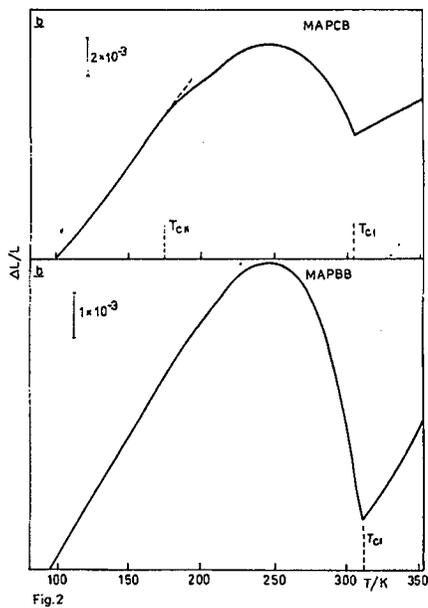


Fig. 2

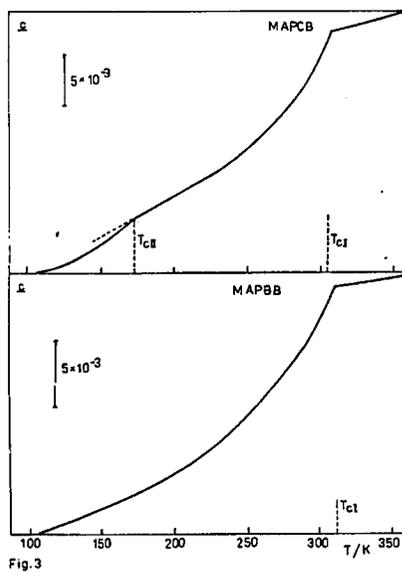


Fig. 3

Fig. 2. Thermal expansion of  $(\text{CH}_3\text{NH}_3)_5\text{Bi}_2\text{Cl}_{11}$  and  $(\text{CH}_3\text{NH}_3)_5\text{Bi}_2\text{Br}_{11}$  crystals along the  $b$ -axis.

Fig. 3 Thermal expansion of  $(\text{CH}_3\text{NH}_3)_5\text{Bi}_2\text{Cl}_{11}$  and  $(\text{CH}_3\text{NH}_3)_5\text{Bi}_2\text{Br}_{11}$  crystals along the  $c$ -axis.

and non-typical. The thermal expansion coefficient,  $\alpha_a$ , does not show a jump at these points. The thermal dilations  $\Delta L/L$  along the  $b$ - and  $c$ -axis for MAPCB and MAPBB are presented in Figs. 2 and 3, respectively. The ferroelectric PT at  $T_{CI}$  for both compounds is accompanied by a rapid change in the sign of the thermal expansion coefficient along the  $b$ -axis, and with further cooling the dilatation versus temperature curve exhibits a broad maximum at about 250 K. In the case of chlorine crystal we should notice a weak anomaly around 175 K. Along the  $c$ -axis the thermal expansion of MAPCB and MAPBB in the vicinity of  $T_{CI}$  exhibits a distinct change in the slope of  $\Delta L/L$  vs. temperature curve. The dilation along the  $c$ -axis of the chlorine compound shows relatively small anomaly near 170 K, similarly as for the  $b$ -axis. It should be noticed that both crystals, especially along the  $c$ -axis, are characterized by a very large thermal expansion within the ferroelectric phases.

A complete resolution of the question about the nature of structural anomaly at 170 K, however, must await further experimental evidence from X-ray studies at lower temperatures.

We also checked the isotope effect using the dilatometric technique on the  $(\text{CH}_3\text{ND}_3)_5\text{Bi}_2\text{Cl}_{11}$  crystals. It has turned out that deuteration (96%) shifts the ferroelectric PT point towards the higher temperature by only  $1.5 \pm 0.5$  K and does not influence the character of the PT (I  $\Rightarrow$  II). The values of the thermal expansion coefficients in the vicinity of  $T_{CI}$  of  $(\text{CH}_3\text{ND}_3)_5\text{Bi}_2\text{Cl}_{11}$  and  $(\text{CH}_3\text{NH}_3)_5\text{Bi}_2\text{Cl}_{11}$  crystals are practically the same.

#### 4. Conclusions

1. The structural isomorphism of  $(\text{CH}_3\text{NH}_3)_5\text{Bi}_2\text{X}_{11}$  crystals is well reflected in their thermal expansion for a wide temperature range (80–350 K).

2. The observed anomaly in the thermal expansion of MAPCB around 170 K corroborates the existence of physical anomaly visible by numerous techniques in the same temperature region. The question if this structural anomaly is connected with the phase transition is still open.

3. Very weak positive isotope shift of the ferroelectric PT in  $(\text{CH}_3\text{ND}_3)_5\text{Bi}_2\text{Cl}_{11}$  indicates the minor role of the N–H...Cl hydrogen bonds in the mechanism of ferro–paraelectric phase transition of  $(\text{CH}_3\text{NH}_3)_5\text{Bi}_2\text{X}_{11}$  crystals.

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