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Phase transitions in $(CH_3NH_3)_3Bi_2Cl_9$ studied by calorimetric, X-ray diffraction and dielectric methods

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Abstract

Differential scanning calorimetry studies revealed two phase transitions in $(CH_3NH_3)_3Bi_2Cl_9$ at $T_{c_1} = 349$ K and $T_{c_2} = 247$ K. X-ray diffraction and dielectric investigations showed only one anomaly at $T_{c_1} = 349$ K related, most probably, to the motion of methylammonium cations. The high temperature phase (above T_{c_1}) behaves as a plastic phase with disordered cations. This high temperature phase is orthorhombic with a contraction along the *a*-axis and an expansion along the *b* and *c* axes compared with the room temperature phase.

1. Introduction

Tris alkylammonium nonahalogenodiantimonates (III) and bismuthates (III) of general formula $[NH_{4-n}(CH_3)_n]_3M_2X_9$, where M ≡ Sb, Bi and X ≡ Cl, Br, I, represent an interesting family of crystals showing phase transitions with the mechanism related to the dynamics of alkylammonium cations [1, 2]. Of the various compounds of this family, the most characteristic seem to be the salts of general formula $(CH_3NH_3)_3M_2X_9$, where M ≡ Sb, Bi and X ≡ Cl, Br, I. The structure of the anions is affected by the type of halogen atom [2]. In the case of chlorine derivatives, the structure is characterized by the one-dimensional double-chain form of polyanions [2, 3]. The present communication is devoted to the $(CH_3NH_3)_3Bi_2Cl_9$ (MACB) crystal. Preliminary studies performed by Jakubas *et al.* [4] have shown that MACB is isomorphous with $(CH_3NH_3)_3Sb_2Cl_9$ [3] and β-$Cs_3Sb_2Cl_9$ [5] and undergoes one phase transition at high temperature detected by dielectric measurements. Our aim was to verify and complete the search for phase transitions in this crystal by means of differential scanning calorimetry (DSC), X-ray diffraction (XRD) and dielectric studies.

2. Experimental details

MACB was precipitated from stoichiometric aqueous solutions of $BiCl_3$ and CH_3NH_3Cl with high excess of HCl. The crystals were grown by slow evaporation at a constant temperature of 298 K. They were in the form of colourless transparent plates. Chemical analyses (Table 1) showed that the product obtained corresponded to the formula $(CH_3NH_3)_3Bi_2Cl_9$.

The XRD measurements were performed, at room temperature, on both single crystals (Weissenberg photographs) and powder using a Siemens diffractometer. Quartz was used as an internal standard to measure line positions. Cu Kα ($\lambda = 1.5406$ Å) monochromatized radiation was used. Least-squares refined unit cell parameters were obtained from powder data based on indexed lines only. In addition, powder XRD pattern photographs were taken at different temperatures using a Guinier–Lenne camera.

The DSC curves were registered on a Perkin–Elmer DSC-7 scanning calorimeter at a heating rate of 5 K min^{-1}.

The dielectric measurements were carried out on samples which were cut perpendicularly to the *a* axis and

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TABLE 1. Chemical analysis of $(CH_3NH_3)_3Bi_2Cl_9$

	C(%)	H(%)	N(%)	Cl(%)	Bi(%)
Theoretical	4.32	2.16	5.04	38.31	50.16
Experimental	4.35	2.10	4.85	37.47	51.24

covered with silver paste. The dimensions of the plates were approximately $7 \times 3 \times 1$ mm^3. The dielectric permittivity and losses were measured at 1 kHz by means of an automatic capacitance bridge meter (Wyne-Kerr type B905).

3. Results and discussion

3.1. X-ray diffraction

The Weissenberg photographs showed that MACB crystallizes in the orthorhombic system with space group *Pnma*, in agreement with the results obtained by Jakubas *et al.* [4]. The structural parameters are

$a = 20.426\,(2)$ Å $\quad b = 7.700\,(1)$ Å

$c = 13.249\,(2)$ Å $\quad Z = 4$

$V = 2084\,(1)$ Å^3 $\quad d_c = 2.66$ g cm^{-3}

$d_m = 2.67$ g cm^{-3}

The crystals of MACB are obviously isomorphous with $(CH_3NH_3)_3Sb_2Cl_9$ [3] and β-$Cs_3Sb_2Cl_9$ [5]. This means that MACB is built up of infinite polyanions of a one-dimensional zig-zag double-chain-stack structure directed along the *b* axis with three crystallographically inequivalent $CH_3NH_3^+$ cations.

3.2. Differential scanning calorimetry and Guinier photographs

The DSC plot (Fig. 1), in the range 220–400 K, revealed two distinct endotherms perfectly reproducible with maxima at 349 K (T_{c_1}) and 247 K(T_{c_2}). The existence of two peaks confirms the possibility of two phase transitions for MACB and not a single transition as reported earlier [4].

The high temperature heat anomaly is characterized by a complex-shaped signal (Fig. 2). The fact that the thermal effect, which is responsible for this anomaly, is weak and the signal is very broad, between 273 and 400 K, shows that this phase transition is continuous and might be of second or slightly first order.

The smaller sharp peak at T_{c_2} (Fig. 3) presents features characteristic of a specific heat anomaly c_p; therefore, this is presumably a second-order phase transition. The enthalpy of this transition, obtained by integrating the area below the heat flow curve, amounts to 1.025 J g^{-1}, thus the entropy is 4.15×10^{-3} J g^{-1} K^{-1}.

The Guinier–Lenne photographs, taken between room temperature and 423 K, showed a sharp continuous shift of diffraction lines at a temperature coinciding with the high temperature phase transition (Fig. 4). Thus, an appreciable change of structural parameters at this temperature is expected. The continuous shift of diffraction lines, coupled with the DSC observations, agrees with a second-order transition. The part of the Guinier–Lenne photograph corresponding to the return to room temperature allowed us to conclude that the phase transition is reversible.

In contrast to the low temperature DSC results, the Guinier photograph, taken in the range 143–303 K,

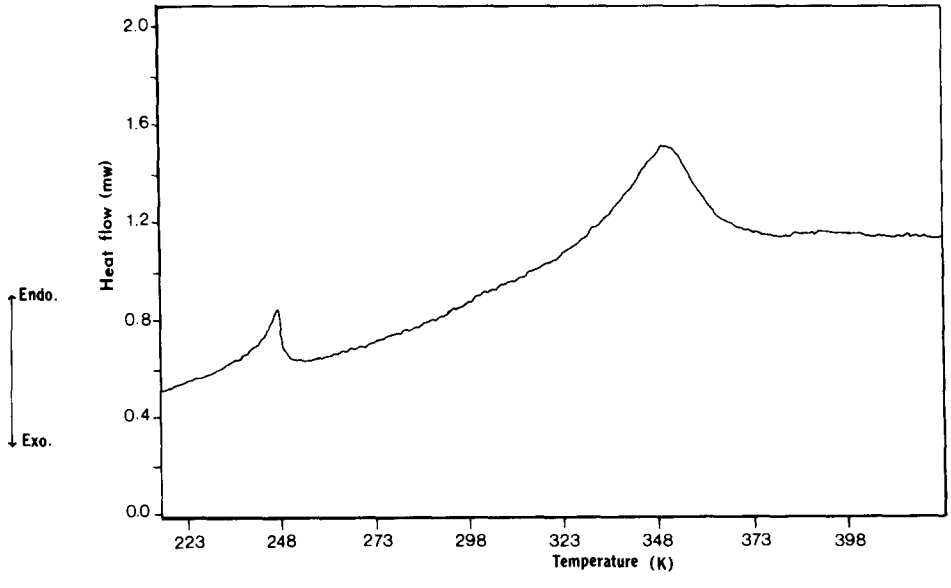

Fig. 1. Heat flow plotted *vs.* temperature on heating for $(CH_3NH_3)_3Bi_2Cl_9$ (MACB), scanning rate 5 K min^{-1}.

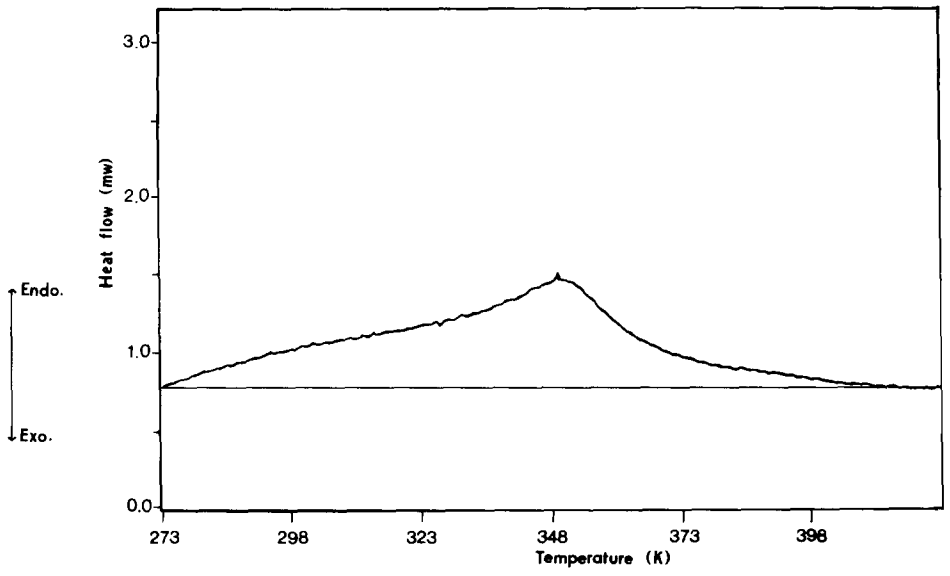

Fig. 2. DSC curve of the high temperature phase transition for MACB on heating.

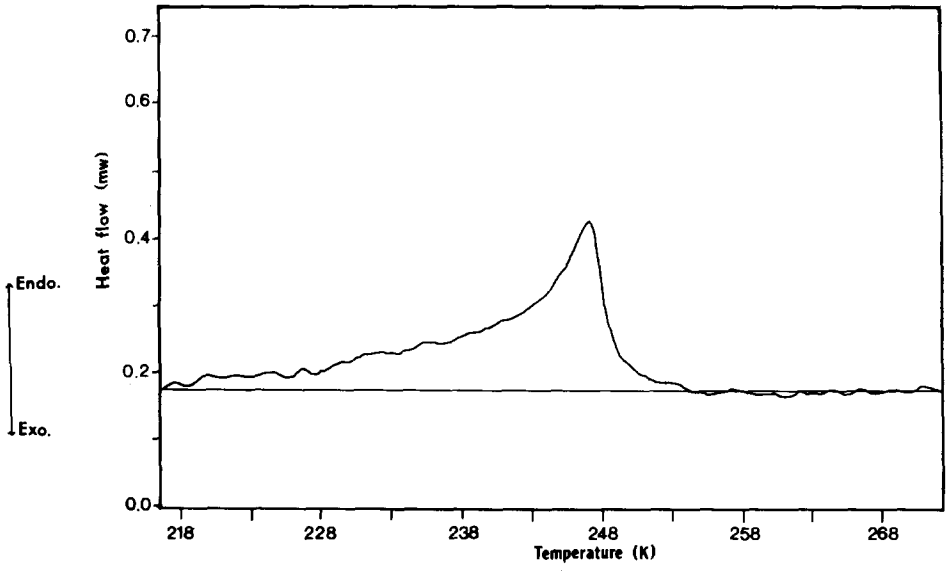

Fig. 3. DSC curve of the low temperature phase transition for MACB on heating.

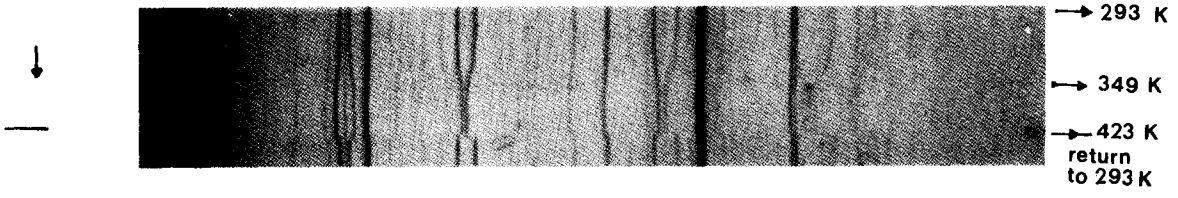

Fig. 4. High temperature Guinier–Lenne photograph of MACB.

does not show any anomaly. This might indicate, but does not necessarily mean, that the low temperature phase transition is not accompanied by a change in crystal symmetry. Further experiments with higher resolution are underway.

3.3. Dielectric properties

The plot of the static electric permittivity *vs.* temperature for MACB crystal, given in Fig. 5, was recorded along the crystallographic *a* axis only during heating. One single anomally was observed in all series of

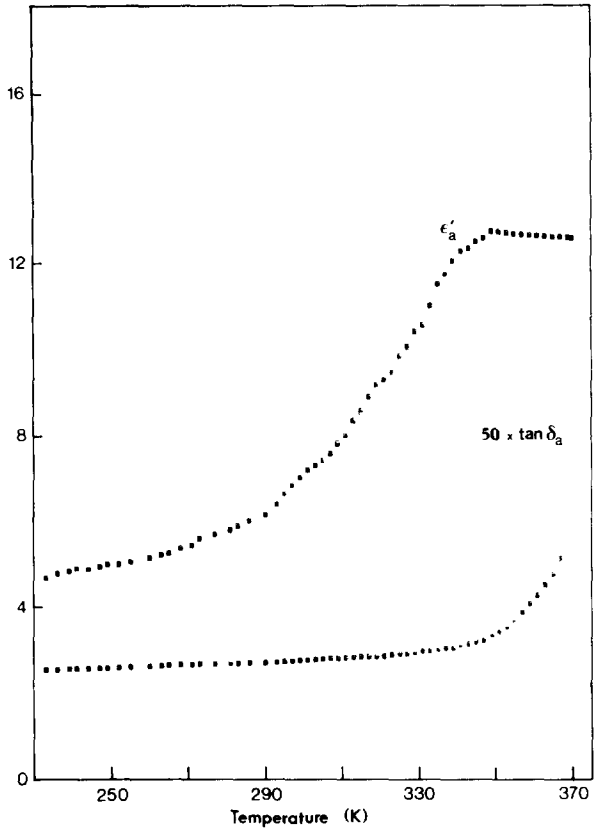

Fig. 5. Temperature dependence of static electric permittivity ε'_a and the dielectric loss tangent tan δ_a measured along the a axis in an MACB single crystal on heating at 1 kHZ.

measurements, which were performed on several samples. The phase transition temperature corresponding to this anomaly was found to depend on the quality of the sample, but did not exceed the value 349 ± 3 K. Similar results were obtained by Jakubas *et al.* [4]; however, the phase transition was found to occur at the higher temperature of 385 ± 2 K.

The phase transition temperature determined by dielectric measurements is in good agreement with that observed from DSC curves at high temperature. The values of the electric permittivity are very low ($\varepsilon'_{a\,max} = 13$). On heating from 200 K, $\varepsilon'_a(T)$ increases continuously up to T_{c_1}, where it remains relatively constant and diminishes slowly afterwards.

It should be emphasized that this phase transition is not accompanied by any anomaly of dielectric losses (tan $\delta_a(T)$, Fig. 5). In the direction of the a axis these losses are very small and do not change meaningfully for the whole temperature range below T_{c_1}, while after T_{c_1} they increase markedly.

The dielectric behaviour of the MACB crystal above 349 K is typical of plastic phases with unrestricted freedom of dipole reorientations, as were also observed for methylammonium salts of general formula $(CH_3NH_3)_3M_2X_9$ ($M \equiv$ Sb, Bi and $X \equiv$ Cl, Br, I) [2]. By analogy with $(CH_3NH_3)_3Sb_2Cl_9$ and other alkylammonium halogenometallates, and in agreement with the crystalline structure, one can suppose that the phase transition at T_{c_1} is connected with the continuous freezing of non-equivalent methylammonium cations on decreasing the temperature.

As is evident from Fig. 5, no anomaly of electric permittivity near T_{c_2} was observed. Thus the dielectric studies do not allow us to draw conclusions about the character of the low temperature phase transition.

4. Conclusions

The results of calorimetric studies show that MACB crystals undergo two phase transitions at 349 and 247 K on heating. However, XRD and dielectric studies show only the high temperature transition, which is most probably related to the motion of methylammonium cations. At present, the nature of the low temperature phase transition remains unclear. Indeed, the lack of auxiliary spectroscopic and crystallographic data for this crystal does not permit a deeper understanding and discussion of the mechanism of the observed phase transitions. Nevertheless, the preliminary XRD studies coupled with polarizing optical microscope observations, performed at high temperature (at exactly 393 K), show that the orthorhombic system is conserved. With respect to the room temperature phase, the high temperature phase is characterized by a contraction along the a axis and an expansion along the b and c directions. Further studies are underway to elucidate the mechanism of the observed phase transitions [6].

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