
Ferroelectric Phase Transition in DC Electric Field in $[\text{NH}_2(\text{CH}_3)_2]_3\text{Sb}_2\text{Cl}_9$ Crystals

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Dielectric investigations of ferro–paraelectric phase transition under influence of bias pooling DC electric field ranging from 0 to 500 kV/m were performed for $[\text{NH}_2(\text{CH}_3)_2]_3\text{Sb}_2\text{Cl}_9$. The linear shift of T_c towards higher temperatures was observed. The A_0 and B coefficients from the Landau state equation are determined.

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1. Introduction

Alkylammonium halogenoantimonates(III) with the general formula $\text{R}_3\text{Sb}_2\text{X}_9$ (where $\text{R} = (\text{CH}_3)_n\text{NH}_{4-n}$, $\text{X} = \text{Cl}, \text{Br}, \text{I}$) have been extensively investigated from the viewpoint of ferroelectricity. The reorientations of the alkylammonium cations are found to play a dominant role in the mechanism of numerous “order–disorder” phase transitions [1–3]. $[\text{NH}_2(\text{CH}_3)_2]_3\text{Sb}_2\text{Cl}_9$ (DMACA) crystallizes at room temperature (RT) in the monoclinic symmetry with the space group $P2_1/c$ [4]. The RT structure consists of two-dimensional layer structure of $(\text{Sb}_2\text{Cl}_9^{3-})_n$ anions and two sets of nonequivalent dimethylammonium cations (DMA). One type of DMA cations located inside the polyanionic cavities is disordered, whereas the second type of cations is placed between the layers. The former DMA cations are believed to contribute to the mechanism of phase transition. DMACA undergoes continuous ferroelectric phase transition from $P2_1/c$ to Pc at 242 K [5–7]. DMACA possesses also ferroelastic properties at RT and the hypothetical paraelastic phase $3m$ was proposed [8]. The dielectric dispersion studies in the microwave frequency region revealed the critical slowing down of the macroscopic relaxation characteristic of the second-order phase transition [9].

The purpose of the present work is to study both the influence of the pooling electric field on the dielectric permittivity and character of the phase transition.

2. Experimental

Single crystals of $[\text{NH}_2(\text{CH}_3)_2]_3[\text{Sb}_2\text{Cl}_9]$ was precipitated from the stoichiometric aqueous solution of Sb_2O_3 and $\text{NH}_2(\text{CH}_3)_2\text{Cl}$ at a high excess of HCl and purified by a recrystallization. A single crystal was grown by an evaporation of the solution at constant room temperature. The sample with dimensions $5 \times 5 \times 1 \text{ mm}^3$ of DMACA was investigated. The surfaces perpendicular to the ferroelectric a -axis were provided with silver paste electrodes. The real part (ε_a) of the complex electric permittivity, ε^* , was measured using an automatic RLC meter at 1 kHz frequency in AC field amplitude equal to 500 V/m. The temperature of the sample was changed with a cooling rate 0.1 K/min.

3. Results and discussion

The electric permittivity vs. temperature, $\varepsilon'_a(T)$, at various values of constant DC electric field is shown in Fig. 1. The electric field (E) lowers the maximum of the electric permittivity, ε_m , and it shifts the temperature T_m , at which that maximum occurs, according to the following relation:

$$T_c - T_m = \sqrt[3]{\frac{3B}{A_0}} E^{2/3}, \quad (1)$$

where $T_c - T_m = \Delta T$, T_c — Curie–Weiss temperature.

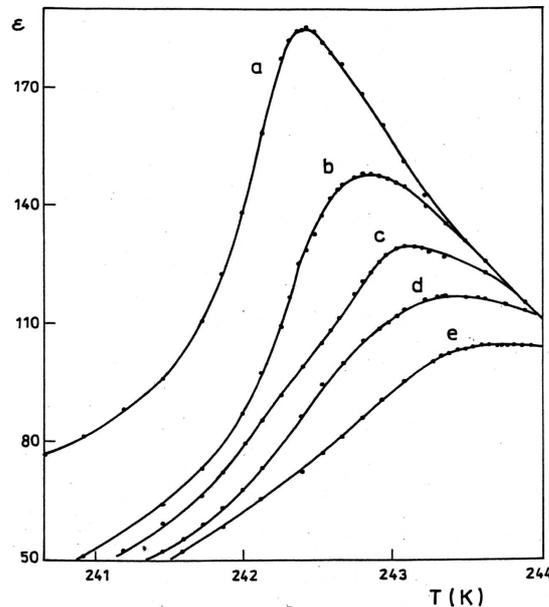


Fig. 1. Temperature dependences of the electric permittivity on cooling around the phase transition temperature at various external electric fields: a — 0 V/m, b — 100 kV/m, c — 200 kV/m, d — 300 kV/m, e — 500 kV/m.

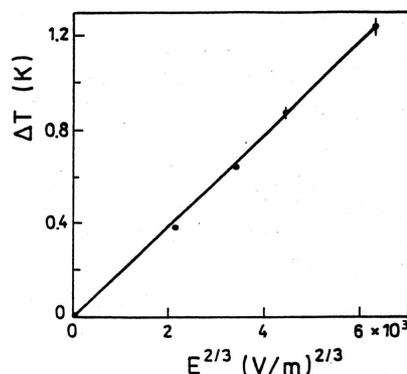


Fig. 2. The dependence of ΔT , at which maximum of ε occurs, as a function of $2/3$ power of DC electric field value.

In Fig. 2 the dependence of ΔT on $E^{2/3}$ is presented.

Using a simple relation between the Curie–Weiss constant ($C_{CW} = 400 \text{ K}$) and A_0 coefficient

$$C_{CW} = \frac{1}{\varepsilon A_0}, \quad (2)$$

the last coefficient was calculated to be $1.41 \times 10^8 \text{ V m}/(\text{C K})$. The B coefficient for the paraelectric phase calculated from Eq. (1) is equal to $7 \times 10^{12} \text{ V m}^5 \text{ C}^{-3}$.

It is interesting that the value of the B coefficient for DMACA crystals estimated for the paraelectric phase is comparable to those found for the closely related ferroelectric crystals like $(\text{CH}_3\text{NH}_3)_5\text{Bi}_2\text{Br}_{11}$ ($3.6 \times 10^{12} \text{ V m}^5 \text{ C}^{-3}$) [10] and $(\text{CH}_3\text{NH}_3)_5\text{Bi}_2\text{Cl}_{11}$ ($7.2 \times 10^{12} \text{ V m}^5 \text{ C}^{-3}$) [11].

It seems that these coefficients are frequently encountered for ferroelectric crystals which exhibit continuous “order–disorder” phase transition.

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