

DILATOMETRIC AND PYROELECTRIC STUDY OF PHASE TRANSITION IN $(\text{CH}_3)_2\text{NH}_2\text{Al}(\text{SO}_4)_2 \cdot 6\text{H}_2\text{O}$ FERROELECTRIC CRYSTAL

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The results of linear thermal expansion and pyroelectric coefficient are given for crystal of dimethylammoniumaluminium sulphate hexahydrate. Large anomalies of these quantities has been observed around the phase transition temperature at 151 K.

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1. Introduction

Dimethylammoniumaluminium sulphate hexahydrate (DMAAS) crystal $(\text{CH}_3)_2\text{NH}_2\text{Al}(\text{SO}_4)_2 \cdot 6\text{H}_2\text{O}$ undergoes phase transition at above $T_c = 150$ K accompanied by dielectric [1, 3], birefringence [1, 4], pyroelectric [3], electro- and piezooptic [4] anomalies. The phase transition is connected with the change of symmetry from $2/m$ at room temperature into m below T_c [1, 5]. Ferroelastic twinning observed in the crystals [5, 6] affects the measured properties of the DMAAS. Additional anomalies of electrooptic coefficient was found at 110.5 K and was stated that these anomalies probably are connected with the phase transition. The purpose of the work is to represent the dilatometric and pyroelectric properties of the crystal.

We have taken the choice of axes so as in [1] and [2]. In that system the y -axis is parallel to the twofold axis, which is crystallographic b -axis, while the x -axis which lies in the mirror plane is parallel to the spontaneous polarization direction and forms an angle 22.7° with the crystallographic a -axis [5]. The z -axis is perpendicular both to the x - and y -axis. The crystallographic c -axis forms an angle 45.8° with the x -axis and lies in the mirror plane.

2. Experimental

The crystal of DMAAS was grown at 310 K. A capacitive quartz dilatometer was used to measure the elongation of bars of 9.0 mm long. The capacitance was measured with an automatic C -bridge versus temperature (usually) with constant rate of heating. The samples with area of 25 mm² to 75 mm² and silver paste as electrode were used to measure the pyroelectric coefficient. The normal to the surface sample was along the x -axis. The pyroelectric coefficient measurement has been performed with a short-circuit current method on heating with constant rate of 13×10^{-3} K/s. Before the measurement the samples were poled with the constant electric field of 200 kV/m.

3. Results and discussion

The results of dilatometric measurements obtained on cooling run in the directions (x, z, c) axis which are in the symmetry plane m and in the direction y which is perpendicular to the symmetry plane are shown in Figs. 1–4, respectively. Relative expansions are expressed with respect to the room temperature lengths of the samples. The expansion along the spontaneous polarization direction x is shown in Fig. 1. On cooling run down to the phase transition temperature T_c the

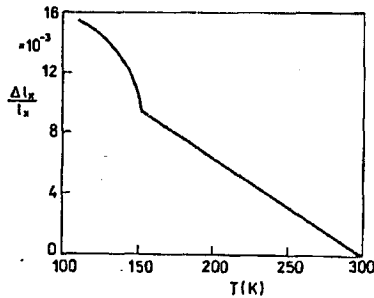


Fig. 1. Temperature dependence of the linear thermal expansion along the x -axis, that is polar direction in the ferroelectric phase.

linear thermal expansion coefficient changes monotonously. It seems that length of bar changes discontinuously at T_c . Below the phase transition temperature calculated the thermal expansion coefficient α_x has the same temperature dependence as the spontaneous polarization, $(T_c - T)^{-1/2}$. The maximum expansion is observed along the x direction. There was no anomalies in the measured temperature range 100–300 K besides that around T_c . Maximum contraction in this temperature range in the plane m is found along the z direction (Fig. 2). Anomaly along the z -axis is quite different from anomalies in other axes. Thermal expansion coefficient α_z on cooling is positive, goes to zero, changes its sign to negative at T_c and then again is positive. Thermal expansion along the c -axis (Fig. 3) is lower and similar in character to the expansion along the x -axis. The largest contraction is along the twofold b -axis as shown in Fig. 4. Thermal expansion coefficient is nearly constant above T_c and changes with temperature below T_c .

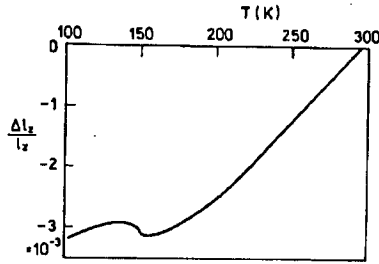


Fig. 2. Temperature dependence of the linear thermal expansion along the z -axis.

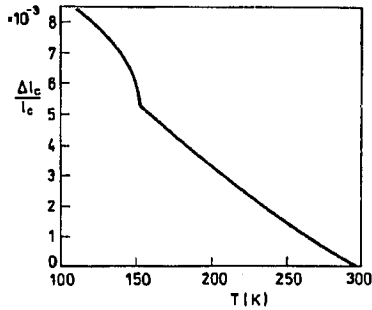


Fig. 3. Temperature dependence of the linear thermal expansion along the c -axis.

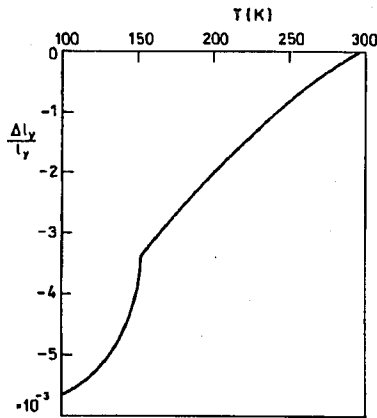


Fig. 4. Temperature dependence of the linear thermal expansion along the y -axis.

Temperature dependencies of the pyroelectric coefficient is shown in Fig. 5. It is seen that phase transition at 151 K is of the first order and close to the second order. Abrupt change of the pyroelectric coefficient shown on insertion and reduced $10\times$ (Fig. 5) testifies to it. "Tail" of the pyroelectric coefficient above T_c occurs rather frequently on heating. It represents disturbance caused by space charge, finite dielectric relaxation time, electric bias field. In contrary to [3] we

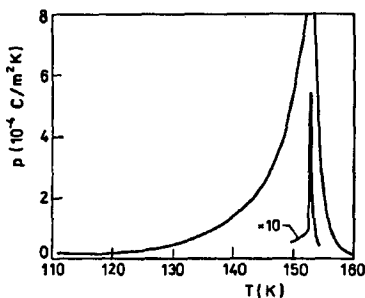


Fig. 5. Temperature dependence of the pyroelectric coefficient in the direction of polar x -axis.

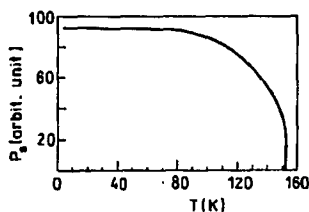


Fig. 6. Temperature dependence of the spontaneous polarization.

have not seen any anomalies at about 111 K and also the temperature dependence of the pyroelectric coefficient is different from that in [3].

We have performed the measurement of the spontaneous polarization in the range from liquid helium temperature up to 170 K by charge integration method, on cooling, and the result is shown in Fig. 6. Spontaneous polarization changes monotonically up to T_c . Below 80 K the change is very small. At phase transition temperature a small jump of spontaneous polarization is observed which is typical feature of the first-order phase transition.

Taking into account the temperature dependence of the thermal expansion, the pyroelectric coefficient and the spontaneous polarization there is no phase transition in the vicinity of 110 K, contrary to the suggestion given in the paper [4].

In the case when the phase transition is of the first order and closed to second order kind of the experimental method is important. Undoubtedly, measurement of the pyroelectric coefficient in a continuous manner (as in this paper) is better method than the static method, where the measurement is from point to point. In Sawyer-Tower method high electric field applied to the crystal develops induced polarization and it made it difficult to recognize the character of the phase transition. Electric field in the crystal during measurement is 100 kV/m to 250 kV/m [2] in the Sawyer-Tower method, 10 V/m to 100 V/m in the integration method and about 1 V/m in the pyroelectric short-circuit current method. Dependence of the polarization P on electric field E is by the formula

$$E = A(T - T_0)P + BP^3 + CP^5,$$

where A , B , C are constants. Coefficient B is positive for continuous and neg-

ative for discontinuous phase transition. When B is negative and close to zero high electric field may change the character of the phase transition. The second important problem is the occurrence of the temperature gradient in the crystal. High temperature gradient diffuses the phase transition. To minimize the gradient in the crystal the rate of the temperature change in our experiments was very low, equal to 13×10^{-3} K/s in the pyroelectric measurement and about 4×10^{-3} K/s in the dilatometric measurement.

On the ground of experimental results one can conclude:

1. Anomalies in thermal expansion around T_c are observed in all directions.
2. The phase transition at T_c is the first-order transition.
3. There is no phase transition besides that at T_c .
4. Below T_c spontaneous polarization occurs down to 4 K. In that respect this crystal differs from its analogue $(\text{CH}_3)_2\text{NH}_2\text{Ga}(\text{SO}_4)_2 \cdot 6\text{H}_2\text{O}$.

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