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DILATOMETRIC STUDY OF THE PHASE TRANSITION IN $(CH_3NH_3)_5Bi_2Cl_{11}$

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The paper reports a dilatometric study on $(CH_3NH_3)_5Bi_2Cl_{11}$ single crystals. It is shown that elongation of the crystal is continuous but linear thermal expansion coefficients are discontinuous at phase transition temperature.

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Recently a new crystal was grown: namely $(CH_3NH_3)_5Bi_2Cl_{11}$ with promising dielectric properties [1]. This compound crystallizes at room temperature in orthorombic symmetry with space group $Pca2_1$. With increasing temperature crystals transform from the ferroelectric phase to the paraelectric phase at about $T_C = 308$ K. The phase transition is the second order with a peak of electric permittivity 5×10^3 [1]. The authors of Ref. [2] paid attention to similarity of the dielectric properties of this crystal and isomorphic $(CH_3NH_3)_5Bi_2Br_{11}$ crystal, for which dilatometric anomaly was shown in [3].

In this short note we report results of dilatometric measurements performed to study the ferroelectric phase transition in $(CH_3NH_3)_5Bi_2Cl_{11}$. Single crystals were prepared as described in [1]. A capacitive quartz dilatometer was used to measure the elongation of bars 9.2 mm long. The capacitance was measured with an automatic C-bridge versus temperature on heating with a constant rate of $4.35 \times 10^{-3}\,\mathrm{K\,s^{-1}}$ and also at constant temperatures. The thermal dilatations in the a, b and c directions and respective linear thermal expansion coefficients: α_a, α_b and α_c, are shown in Figs. 1–3. It was assumed that $\Delta l = 0$ at 295 K. Anomalous changes of these quantities are observed in the vicinity of $T_C = 308$ K. At the transition point continuous dilatations in all directions are seen on heating,

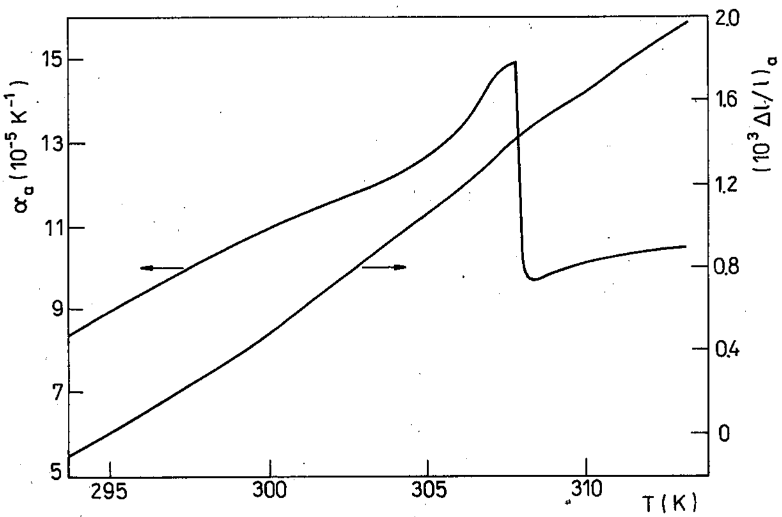

Fig. 1. Elongation of the crystal measured relative to the length at 295 K and linear thermal expansion coefficient along a-axis.

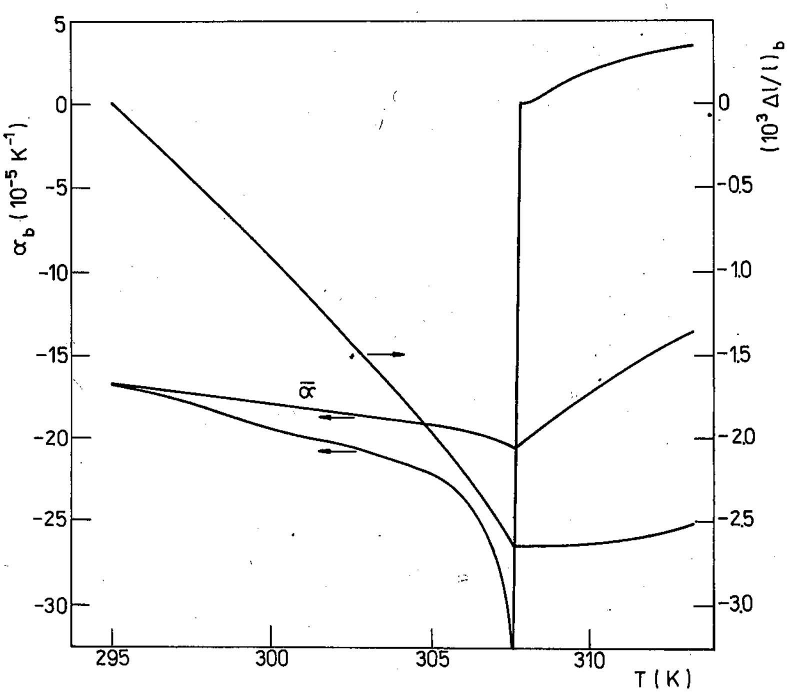

Fig. 2. Dilatation of the crystal along b-axis. $\overline{\alpha}$ is the mean value of the expansion coefficient between T and 295 K.

whereas the thermal expansion coefficients are changing discontinuously. These results speak in favour of the second order phase transition. The thermal expansion coefficient along the *a*-axis α_a (Fig. 1) is positive and increases with temperature in the ferroelectric phase, while the one along the *b*-axis having negative value in the polar phase, changes its sign exactly at T_C and becomes positive afterwards (Fig. 2). In Fig. 2 the mean value of the thermal expansion coefficient $\overline{\alpha}$ defined

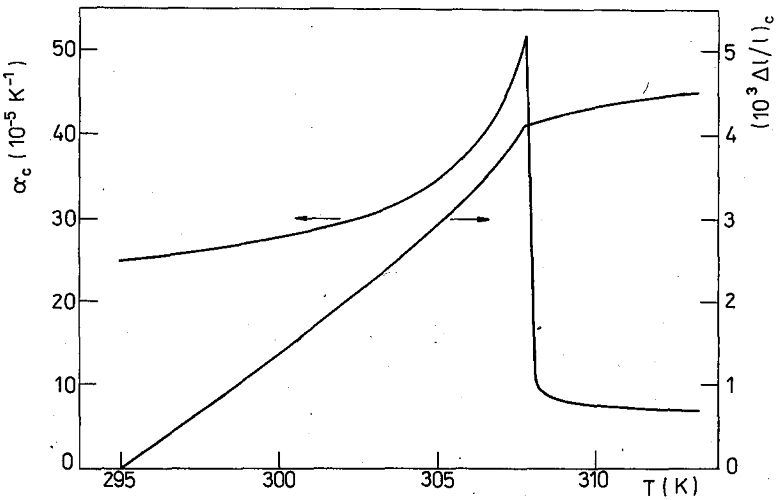

Fig. 3. Dilatation of the crystal along the *c*-axis.

by $(l_T - l_{295})/l_{295}(T - 295\,\mathrm{K})$ is also shown. It should be noticed that the α_C is relatively big, and about three times larger than the one for the *a*-axis (Fig. 3). $(CH_3NH_3)_5Bi_2Cl_{11}$ single crystals possess very large thermal expansion especially over the temperature range from room temperature up to the transition point. The volume thermal expansion coefficient increases with temperature from $17 \times 10^{-5}\,K^{-1}$ at 295 K to $30 \times 10^{-5}\,K^{-1}$ at T_C. The dilatometric measurements indicate that the symmetry of the crystal both in ferroelectric and paraelectric phases is not higher than orthorhombic. The phase transition then can be described by $mmmFmm2$. Comparing the obtained dilatometric results with those for $(CH_3NH_3)_5Bi_2Br_{11}$ [3] one can see large similarity of the dilatometric properties. Crystals containing Cl have slightly greater thermal expansion coefficients and their phase transition temperature is lower by 3 K.

References

[1] R. Jakubas, L. Sobczyk, J. Lefebvre, *Ferroelectrics* **100**, 143 (1980).

[2] J. Mróz, R. Jakubas, *Ferroelectr. Lett. Sect.* **11**, 53 (1990).

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