DILATOMETRIC STUDY OF THE PHASE TRANSITION IN (CH₃NH₃)₅Bi₂Cl₁₁

H. Pykacz
Institute of Physics, Technical University of Wrocław
Wybrzeże Wyspiańskiego 27, 50-370 Wrocław, Poland

AND R. Jakubas
Institute of Chemistry, University of Wrocław
F. Joliot-Curie 14, 50-383 Wrocław, Poland

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The paper reports a dilatometric study on (CH₃NH₃)₅Bi₂Cl₁₁ 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 (CH₃NH₃)₅Bi₂Cl₁₁ with promising dielectric properties [1]. This compound crystallizes at room temperature in orthorhombic symmetry with space group $Pc\alpha_2\gamma_1$. 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 $5 \times 10^3$ [1]. The authors of Ref. [2] paid attention to similarity of the dielectric properties of this crystal and isomorphic (CH₃NH₃)₅Bi₂Br₁₁ 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 (CH₃NH₃)₅Bi₂Cl₁₁. 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 $4.35 \times 10^{-3}$ K s⁻¹ and also at constant temperatures. The thermal dilatations in the $a$, $b$ and $c$ directions and respective linear thermal expansion coefficients: $\alpha_a$, $\alpha_b$ and $\alpha_c$, 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. $\bar{\alpha}$ 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 $\alpha_a$ (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 $\bar{\alpha}$ defined by $(l_T - l_{295})/l_{295}(T - 295\,\text{K})$ is also shown. It should be noticed that the $\alpha_C$ is relatively big, and about three times larger than the one for the a-axis (Fig. 3). (CH$_3$NH$_3$)$_2$Bi$_2$Cl$_{11}$ 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 $17 \times 10^{-5}\,\text{K}^{-1}$ at 295 K to $30 \times 10^{-5}\,\text{K}^{-1}$ 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$_3$NH$_3$)$_2$Bi$_2$Br$_{11}$ [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