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On the Phase Transitions in Cs_2CdBr_4: Dielectric, Dilatometric and Optical Studies

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Dielectric, dilatometric measurement and polarized microscopic observation were performed for single crystal of Cs_2CdBr_4. These investigations showed clearly the phase transitions at 252 K, 236 K and 153 K. The jump-like change of the crystal volume corresponding to the first-order phase transition was found at temperature of 236 K. Ferroelastic domain structure was observed along the a-axis below 236 K and it is preserved below the transition at 153 K. Observation along the c-axis revealed new domain structure below 153 K.

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1. Introduction

Caesium tetrabromocadmate (Cs_2CdBr_4) belongs to β-K_2SO_4 family of crystals where numerous phase transitions including transitions to incommensurate, ferroelectric, and ferroelastic phases were observed. The Cs_2CdBr_4 crystal exhibits successive phase transitions [1–10] and the phase transitions are supposed to appear at 252 K, 236 K, 208 K, 153 K, and 130 K. Nuclear quadrupole resonance (NQR) measurements [1–3] showed only three transitions at 252 K, 236 K, and 153 K. In dielectric measurement [4] phase transition at 208 K was observed. Recently, the sequence of phase transitions in this interesting crystal was studied with FIR spectroscopic method [11, 12]. The successive phases of the material can be numbered as I, II, III, III′, IV, and IV′ on descending temperature. The phases I, II, III, and IV were confirmed in various experiments. The symmetry of particular phases are proposed as: $Pnam$ (I) [3, 4], $P^{Pnam}_{\bar{1}ss}$ (II) [3, 4], $P2_1/n$ (III) [3, 4] and $P\bar{1}$ (III′) [4],$P\bar{1}$ (IV) [5] and $P\bar{1}$ (IV′) [6]. Particular phases in this crystal are regarded as paraelastic — I (above 252 K), incommensurate — II (252–236 K), ferroelastic — III (236–208 K), ferroelastic — III′ (below 208 K) [4]. So far, the character of phases below 156 K and 130 K is unknown. Taking into account discrepancies in the sequence of phase transitions and a lack of data about the character of low temperature phases we decided to perform dielectric, dilatometric measurements and optical polarized microscopic observation to get additional information about the number of phase transitions and properties of particular phases.

2. Experimental

Good optical quality single crystals of Cs_2CdBr_4 grown from the melt by the Czochralski method were used to prepare samples for investigations. Dielectric measurements were performed along three crystallographic directions. The sizes of the used samples were $1 \times 4 \times 4$ mm^3. The samples with the lengths about 7 mm along three crystallographic directions were prepared for crystal thermal expansion measurement. Thermal expansion was investigated using quartz capacitance dilatometer. Capacitance was measured using HP 4184 A RLC meter at the frequency of 1 kHz both for dielectric and thermal expansion measurement. The constant rate of temperature changes was equal to 0.5 K/min in dielectric and 0.1 K/min in dilatometric measurements. Both in dielectric and dilatometric measurement the rate of temperature change was sufficient to obtain repeatable results and temperature difference in the samples less than 0.01 K. Dielectric and dilatometric measurements were done in the temperature range 300–120 K. Microscopic observations were performed using polarized microscope along three crystallographic axes in the temperature range 300–110 K. Mechanical stress was applied to a-45° cut samples.

3. Results

Temperature dependences of dielectric permittivity along three crystallographic axes are shown in Fig. 1. As can be seen in Fig. 1, anomalies of permittivity are observed clearly at:

i) 252 K similar as at incommensurate transition in other crystals of β-K_2SO_4 type [13, 14] and 236 K characteristic of the first-order phase transition along the c-axis;

ii) 236 K small jump-like decrease along the a-axis;

iii) 236 K clear jump-like anomaly along the b-axis.

Thus, dielectric measurements confirmed the phase transitions at 252 K and 236 K. Temperature dependences of relative linear expansion along three crystallographic axes are shown in Fig. 2.

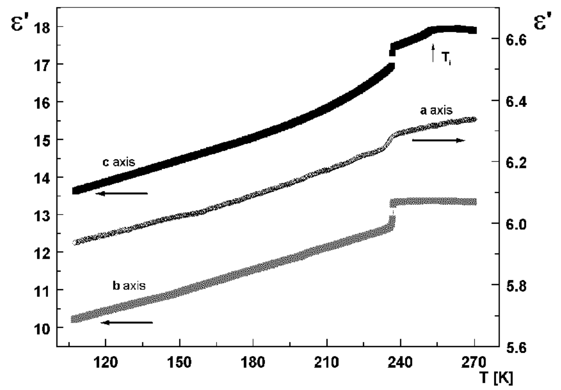

Fig. 1. Temperature dependences of electric permittivity along three crystallographic directions for Cs_2CdBr_4.

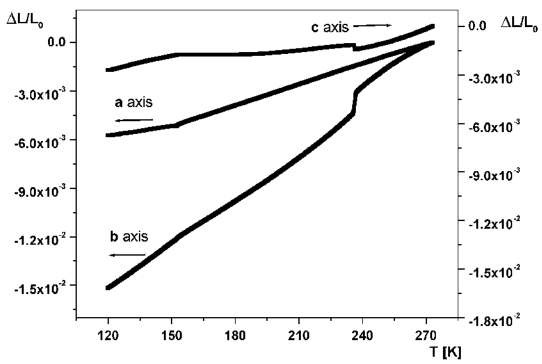

Fig. 2. Temperature dependences of linear thermal expansion ($\Delta L/L$): a — along the a-axis, b — along the b-axis, c — along the c-axis for Cs_2CdBr_4.

Anomalies of relative elongation of the samples $\Delta L/L$ were observed along three crystallographic directions at 236 K and 153 K. At 236 K a jump-like changes of relative sample lengths along the a-, b-, and c-axis were observed. The jump of relative sample length observed at this temperature along the a-axis is insignificant. At 153 K anomalies of relative sample lengths observed along three crystallographic directions are characteristic of continuous phase transition. Taking into account the changes of the sample lengths we could obtain the relative change of crystal volume as a function of temperature. Temperature dependences of relative volume expansion $\Delta V/V_0$ (V_0 — volume of the sample at 273 K) and volume expansion coefficient α_V as a function of temperature are illustrated in Fig. 3.

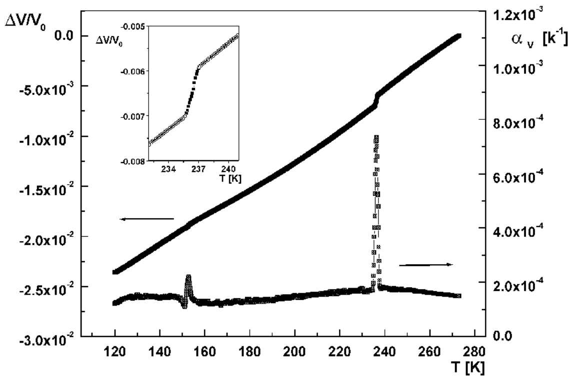

Fig. 3. Temperature dependence of relative volume expansion and linear volume expansion coefficient for Cs_2CdBr_4.

Anomalies of relative volume expansion and volume expansion coefficient are seen clearly at 236 K and 153 K. The changes of relative volume expansion at 236 K is characteristic of the first-order phase transition and at 153 K for continuous one. At the first-order phase transition (236 K) the jump of relative volume of the samples (on cooling run) is equal to about $-4.2\times10^{-5}\pm0.1\times10^{-5}$ (detailed change of $\Delta V/V_0$ is presented in the inset of Fig. 3). The decrease in the volume at this phase transition is in agreement with the results of the crystal investigation under pressure. The shift of the phase transition towards higher temperatures with increase in pressure [8] corresponds well to observed by us decrease in volume at 236 K. No anomalies of thermal expansion observed at 208 K and 130 K is in agreement with our dielectric measurement. The changes of dimensions are not observed at T_i in this crystal. Most probably the relative expansion at this temperature is too small to be measured with our dilatometer. It is worthy underlining that many

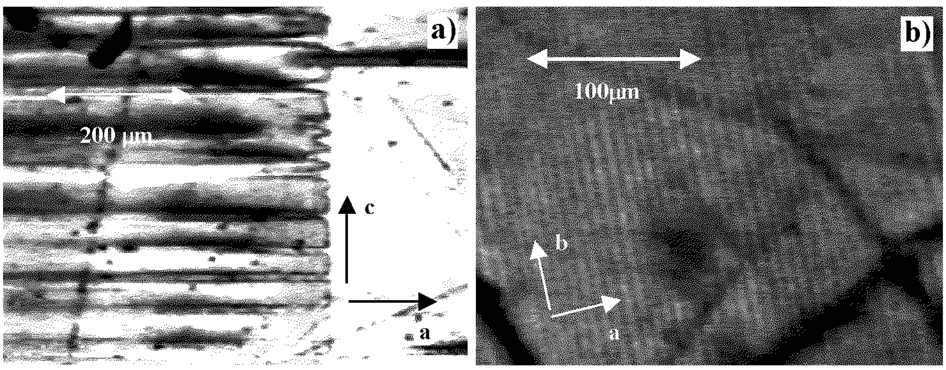

Fig. 4. Domain structure observed in particular phases of the Cs_2CdBr_4: (a) along the a-axis, (b) along the c-axis.

precise measurements of permittivity and dilatation in the vicinity of 208 K and 130 K were done and we did not observe any traces of phase transitions at these temperatures. Microscopic observation along the *a*-axis showed an appearance of a phase front at 236 K and, below 236 K, an appearance of ferroelastic domain structure usually with domain walls in a plane (010). Occasionally, for the first time we observed domain walls in the plane (001). Two kind of domain walls are expected at the phase transition from orthorhombic to monoclinic system as predicted by Sapriel [15]. Mechanical stress applied to the *a*-45° cut samples caused easy change of domain structure. No changes of domain structure was observed on cooling down to 110 K and it means that domain structure is preserved below the phase transition at 153 K and below this temperature the crystal is still ferroelastic. An interesting observation was done along the *c*-axis. In some cases we observed along this direction an appearance of new domain structure below 153 K. This observation supports the phase transition at this temperature and it may be connected with triclinic symmetry of phase IV [5]. The domain walls are placed in the plane (100). These domains are rather narrow and with poor contrast. The observed domain structure is shown in Fig. 4a, b.

4. Discussion and summary

To discuss the number of phase transitions we should take into account our results and to look at the discrepancies in the previous investigations. No dielectric anomaly observed at 208 K in our measurement is in contradiction to the results by Maeda et al. [4].

It is worthy mentioning that even the change of domain structure pattern can give unexpected anomalies of permittivity. No anomalies of thermal expansion at 208 K is consistent with our dielectric measurement. Thus, the phase transition is not confirmed at this temperature. Observation of rotation angle of optical indicatrix by Maeda et al. [4] showed very smooth temperature dependence both in the vicinity of 208 K and 130 K. These results did not confirm any phase transitions at mentioned temperatures. No traces of the phase transition at 208 K and 130 K were observed in NQR [2, 3], ultrasonic and optical birefringence studies [8]; these methods are particularly sensitive for the changes of crystal symmetry. Far-infrared spectra [11] did not confirm any change of symmetry at the transition from phase III to III′. Thus, on the ground of literature data and our measurements three successive transitions at 252 K, 236 K, and 153 K and existence of the phase I, II, III, and IV are well documented.

One can summarize the result of the paper as follows:

1. Anomalies of permittivity were observed at 252 K, 236 K, and 153 K.
2. Anomalies of thermal expansion were found at 236 K and 153 K.
3. Dielectric and dilatometric measurement proved the continuous phase transitions at 252 K and 153 K and the first-order phase transition at 236 K.

4. Ferroelastic domain structure with domain walls in (001) and (010) below 236 K were observed along the *a*-axis; observation along the *c*-axis revealed new domain structure below 153 K with domain walls in a plane (100).

5. According to our dielectric, dilatometric studies, domain structure observation and some literature data three successive phase transitions occur in the Cs_2CdBr_4 crystal.

Acknowledgments

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