

PHASE TRANSITIONS IN $(\text{CH}_3)_2\text{CHNH}_3\text{CdCl}_3$ CRYSTAL

U. KRZEWSKA, R. JAKUBAS

Institute of Chemistry, University of Wrocław
Joliot-Curie 14, 50-383 Wrocław, Poland

S. DACKO, Z. CZAPLA

Institute of Experimental Physics, University of Wrocław
Cybulskiego 36, 50-205 Wrocław, Poland

AND A. WAŚKOWSKA

Institute for Low Temperature and Structure Research, Polish Academy of Sciences
Okólna 2, 50-422 Wrocław, Poland

(Received December 30, 1991; in final form February 11, 1992)

The crystal of $(\text{CH}_3)_2\text{CHNH}_3\text{CdCl}_3$ was grown and its physical properties were investigated. On the ground of DSC, dilatometric and dielectric investigations the phase transition at 390 K on heating process was revealed. On cooling two phase transitions at 382 K and 352 K were found. Polarized microscope observations show appearance of ferroelastic domain structure and cracks at 390 K on heating. On cooling the observed domain structure vanishes at 352 K.

PACS numbers: 64.70.Kb, 05.70.Fh, 77.20.+y

1. Introduction

Number of crystals containing various kinds of methylammonium cations exhibit structural phase transitions and interesting properties, namely ferroelectric or ferroelastic [1-3]. Interesting phenomena related to the existence of incommensurate phases were also found in this big family of organic-inorganic crystals [4, 5]. The aim of our work was to grow the new, so far unknown crystal of this family, namely $(\text{CH}_3)_2\text{CHNH}_3\text{CdCl}_3$ and study its physical properties.

2. Experimental

The crystals of $(\text{CH}_3)_2\text{CHNH}_3\text{CdCl}_3$ were grown from water solutions containing stoichiometric quantities of $(\text{CH}_3)_2\text{CHNH}_3\text{Cl}$ and $\text{CdCl}_2 \cdot 4\text{H}_2\text{O}$ at the constant temperature of 295 K. The lattice constants and symmetry were found from X-ray investigations using Weissenberg method. Density was measured by means of floating method. Calorimetric measurements were done using DSC-7 Perkin Elmer apparatus. Dielectric permittivity was measured by means of the automatic capacitance bridge E-900 EUREKA. Polarized microscope was used to make optical observations.

3. Results

3.1. Symmetry, chemical formula and crystal description

X-ray measurements showed that $(\text{CH}_3)_2\text{CHNH}_3\text{CdCl}_3$ belongs to the monoclinic system at room temperature. The space group is $P2_1/c$ or P_c with the following lattice constants:

$$a = 9.677 \text{ \AA}, \quad b = 13.504 \text{ \AA}, \quad c = 6.632 \text{ \AA},$$

$$\beta = 95.1865^\circ, \quad d_m = 2.12 \text{ g/cm}^3, \quad d_x = 2.146 \text{ g/cm}^3,$$

$$Z = 4.$$

The chemical formula of the compound was found from chemical analysis and was confirmed from density measurements. The crystal exhibits a very distinct cleavage plane which is perpendicular to the b -axis.

3.2. DSC measurements

Temperature dependences of heat flow obtained for $(\text{CH}_3)_2\text{CHNH}_3\text{CdCl}_3$ are shown in Fig. 1a, b, c. As it can be seen in Fig. 1a in the first heating run the pronounced anomaly of heat flow is observed in the range 391–402 K. This anomaly is related to the phase transition of the first order. The temperature of the phase transition is assumed to be equal to 394 K and the enthalpy of the phase transition is equal to 2.8 kJ/mol. A cooling run is particularly interesting in which two anomalies of the heat flow are observed. Thus on cooling two phase transitions at 382 K and 347 K with the enthalpy being equal to -0.14 kJ/mol and -2.0 kJ/mol are found. The second heating process shows two anomalies at 348 K and 384 K which corresponds to the phase transitions observed on the cooling process of the sample. The enthalpy of the transitions equals 0.6 kJ/mol and 1.4 kJ/mol, respectively.

3.3. Microscopic observations

The microscopic observations were done on heating and cooling process in the temperature range 298–413 K along the a^* -, b - and c -axis. The results of observations are shown in Fig. 2. As it results from microscopic observations cracks of the samples appear at 390 K (the phase transition temperature). The cracks

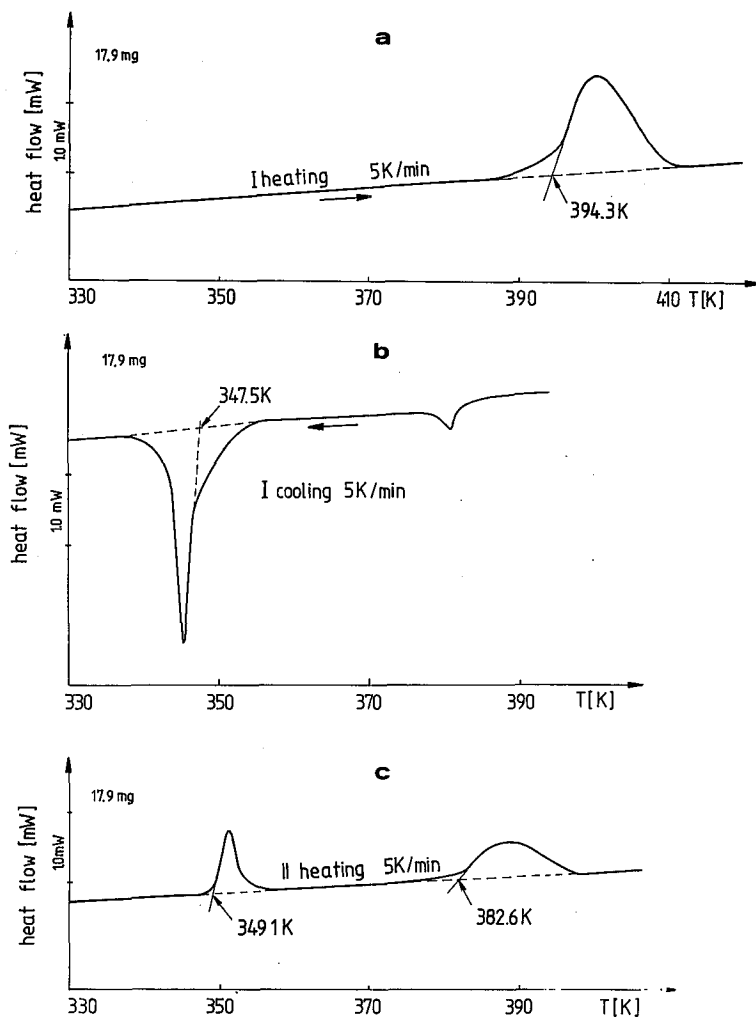


Fig. 1. Temperature dependences of the heat flow for $(\text{CH}_3)_2\text{CHNH}_3\text{CdCl}_3$ crystal: (a) the first heating run, (b) the first cooling run, (c) the second heating run.

are parallel to the cleavage plane. Sometimes the samples are splitted along the cleavage plane. Additionally, the observations along the c -axis (Fig. 2) revealed the appearance of the domain structure with the domain walls perpendicular to the cleavage plane and parallel to the b -axis of the room temperature phase. On cooling the observed domain structure is preserved down to 352 K and disappears at this temperature. No change of domain structure is observed at 382 K. One can expect that the observed domain is ferroelastic. Any additional cracks do not appear on cooling process.



Fig. 2. Optical evidence for the phase transitions in $(\text{CH}_3)_2\text{CHNH}_3\text{CdCl}_3$ crystal.

3.4. Dylatometric measurements

Dylatometric measurements were done along the c -axis (placed in the cleavage plane) and b -axis (perpendicular to the cleavage plane). In the first heating run nearly linear dependences of $\Delta l/l$ on temperature are found. At 394 K abrupt changes of $\Delta l/l$ are observed. The observed jump of $\Delta l/l$ related to the phase transition is probably influenced by cracks of the samples. Nevertheless the phase transition at 394 K can be seen. On cooling the anomalies at 383 K and 349 K are observed (it means in the range of phase transitions revealed in DSC experiments). The second heating process also gives evidences for the phase transitions at 350 K and 394 K although the difference between the cooling and the second heating run is clearly seen. Due to the cracks of the samples dylatometric measurements are regarded as qualitative ones.

3.5. Dielectric measurements

Results of dielectric permittivity measurements are presented in Fig. 3a, b, c, d. The dielectric measurements in the case of $(\text{CH}_3)_2\text{CHNH}_3\text{CdCl}_3$ are influenced very much by cracks at 390 K and therefore the dependences of ϵ' and $\text{tg}\delta$ may be unreproducible above this temperature. Especially the splitting of the sample gives the strange dependences of permittivity along the b -axis (direction perpendicular to the cleavage plane). Measurements along the a^* - and c -axis when the sample is covered with the thick electrodes which keep it together in spite of some cracks show smooth and reproducible dependences of permittivity although the $\text{tg}\delta$ values are not the same. Thus, we may consider the dependences along the

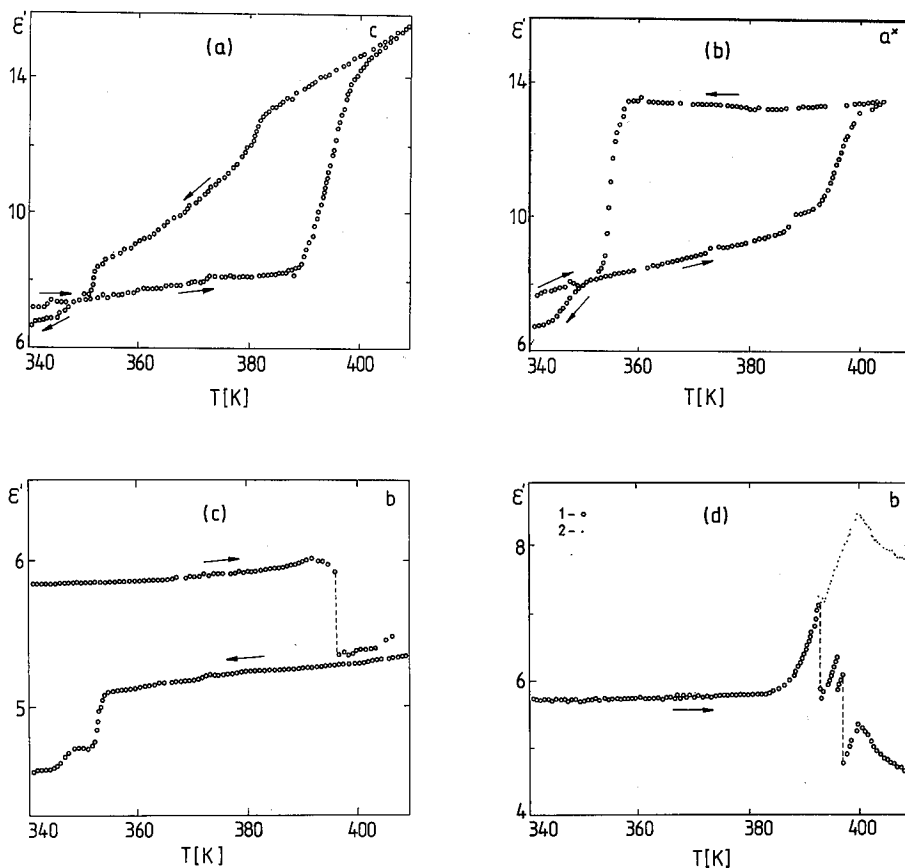
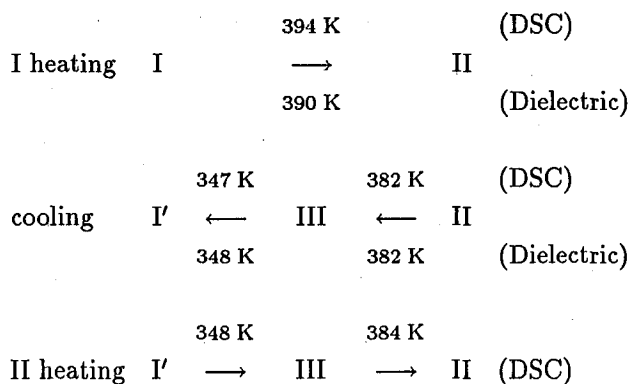


Fig. 3. Temperature dependences of dielectric permittivity for $(\text{CH}_3)_2\text{CHNH}_3\text{CdCl}_3$ crystal: (a) the c -axis, (b) the a^* -axis, (c, d) the b -axis.

c - and a^* -axis as characteristic properties of the crystal. Starting from room temperature the permittivity along the c -axis increases very slowly and at 390 K a sharp increase is observed up to 401 K where again the slow increase is observed. On cooling the permittivity shows two anomalies at 382 K and 352 K. The results of these measurements indicate one phase transition on heating and two phase transitions on cooling. The temperature dependence of permittivity along a^* -axis (Fig. 3) shows anomaly at 390 K on heating. On cooling decrease of permittivity is observed at about 352 K. The temperature dependence of permittivity along the b -axis shows irregular changes at 390 K (Fig. 3c, d) related to splitting of the sample. The cooling run along this direction shows one anomaly at 352 K. If there were no cracks one could expect that the permittivity along the b -axis would depend on temperature according to the curve 2 in Fig. 3d.

4. Summary and conclusions

On the ground of the presented above results obtained by means of various experimental methods one can state that $(\text{CH}_3)_2\text{CHNH}_3\text{CdCl}_3$ undergoes the sequence of phase transitions presented in the scheme:



Thus on cooling the new sequence of phase transitions in comparison to heating run was found. The differences in phase transitions temperatures observed in various methods may result from different rates of heating and cooling of the samples. The temperatures of phase transitions at the constant rate of heating or cooling are observed within ± 0.1 K for the same sample. The phases I and I' are not expected to be the same. Preliminary X-ray powder measurements confirmed our conclusion resulting from macroscopic investigations. The mechanism of phase transitions may be related to the freedom of various sorts of rotational or flipping motion in phase II (above 390 K) of isopropylammonium cations and the cooling process gives successive freezing of their rotational motions. Investigations of $(\text{CH}_3)_2\text{CHNH}_3\text{CdCl}_3$ crystal showed very interesting features but the crystal needs further studies which are now in progress.

References

- [1] Z. Czaplą, O. Czupiński, Z. Ciunik, *Solid State Commun.* **58**, 383 (1986).
- [2] R. Jakubas, Z. Czaplą, Z. Galewski, L. Sobczyk, *Ferroelectr. Lett.* **5**, 143 (1986).
- [3] K. Gesi, *Phase Transit.* **27**, 107 (1990).
- [4] H. Mashiyama, S. Tanisaki, *Phys. Lett. A* **76**, 347 (1980).
- [5] K. Gesi, M. Iizumi, *J. Phys. Soc. Jpn.* **48**, 337 (1980).