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Microscopic and Dielectric Studies of CH_3NH_3I Crystal

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Synopsis. Observation of CH_3NH_3I crystal under a polarizing microscope showed a rectangular domain structure in the δ phase. Dielectric measurement revealed an antiferroelectric behavior of the same phase. These results indicate that the δ phase has orthorhombic or monoclinic structure with C–N axes of $CH_3NH_3^+$ ions inclining along its a or b axis in an antiferroelectric way.

Methylammonium iodide CH_3NH_3I crystal has the tetragonal structure (α') at room temperature with their C–N axes arranged in the antiparallel way along the c axis of the unit cell (*P4/nmm, z*=2). The $CH_3NH_3^+$ ion is orientationally disordered[1–4] with locating its three-fold axis on the four-fold crystallographic axis. The crystal undergoes two different types of transition depending on cooling rate, either discontinuously to the stable β' phase at 220 K or continuously to the metastable δ phase at 166 K. The previous calorimetric study[5] revealed that the $CH_3NH_3^+$ ions were ordered at zero Kelvin in both of the low temperature phases and the higher-order α'-δ transition corresponded to the orientational order-disorder process of the $CH_3NH_3^+$ ions possibly without drastic structural change.

It is the purpose of this paper to report a polarizing microscopic observation of a single crystal and a dielectric measurement of a powdered crystal in order to clarify the nature of the α'-δ phase transition and to discuss a possible structure of the δ phase.

Experimental

A polarizing microscope, Olympus model POM with magnification of 4×10, was used with a home-made cold stage which was designed for the observation of single crystal at liquid N_2 temperature with a rapid cooling. The rapid cooling is important in realizing the full formation of the δ phase. Single crystal was grown by a slow recrystallization from the methanol solution at 5 °C in the dark. The obtained crystal was of a square plate whose side length was about 1 mm.

The complex dielectric permittivity was measured from 80 to 270 K at several frequencies ranging from 50 Hz to 100 kHz with a capacitance bridge, General Radio Co. type 1615A. Powdered crystal was pressed to form a disc, 10 mm in diameter and 1.158 mm in thickness. Circular gold leaves of the size of 60.1 mm^2 in area were stuck with N-Apiezon grease on both faces of the disc as the electrodes.

Results and Discussion

Figure 1(A) shows a room-temperature photograph of the single crystal with its face perpendicular to the c axis, the side lines being parallel to the [110] or its equivalent axis. The equivalent tetragonal axes are shown in the figure. This crystal habit was examined in advance by an X-ray diffraction method. The light passes through the crystal along its c axis. No anomaly was observed by the rotation of polarized light. The observation was obscured around the central part of the specimen owing to the coexistence of adhesively grown powdery crystals, but this did not disturb much the optical features of the following observations. Figure 1(B) and 1(C) show the photographs of the crystal in the δ phase obtained by a rapid cooling down to the liquid N_2 temperature. Dark and bright (green and yellow in the original photograph) bands appeared alternately with the boundaries in parallel to the a axis of the tetragonal phase. The directions of the polarization of light for (B) and (C) were just perpendicular to each other. The alternating colors of the domains were just reversed between (B) and (C), indicating the rectangular domain structure of the crystal. It follows that the two equivalent a axes of the tetragonal structure becomes nonequivalent ($a\neq b$) with keeping γ (the ∠ab angle) the same 90° in the δ phase. In other words, the crystal structure of the δ phase belongs to the orthorhombic or monoclinic system. In view of the necessary condition for the formation of rectangular domain structure, the directions of its a and b axes must be inclined by 45° from the original a axis of the tetragonal structure as shown in the figure.

The complex dielectric permittivities of the δ and α' phases were measured in the following way. First, the complex dielectric permittivities were measured at eight frequencies (50, 100, 500, 1 k, 5 k, 10 k, 50 k, and 100 kHz) from 270 to 220 K at 5 K intervals in the cooling direction. After that, the sample was cooled rapidly to the liquid N_2 temperature from 260 K. The cooling rate 10 K min^{-1}, was rapid enough to prevent a possible transformation of the α' to β phase around 200 K. The dielectric constant ε' was then measured at the same frequencies from 77.5 K at 5 K intervals and especially in the δ-α' transition region at 1—2 K intervals in the heating direction. There was no considerable dielectric loss observed in the whole temperature and frequency regions, and the real part ε' was independent of the frequency. Figure 2 shows the temperature dependence of ε' measured at 1 kHz. The data between 190 and 220 K were omitted from the plots because they reflect partial transformation into the β' phase. From the high temperature side, ε' increases gradually and reaches a maximum at about 175 K. After that, it decreases steeply with decreasing temperature. This behavior is quite similar to those of the following antiferroelectric compounds; Pb_4SiO_6,[6] $CsH_3(SeO_3)_2$,[7] and $NH_4PF_6\cdot NH_4F$.[8] The α'-δ phase transition is thus concluded to be accompanied by the antiparallel arrangement of electric dipoles in the δ phase.

The $CH_3NH_3^+$ ions lie in the (100) plane in an antiparallel arrangement along the c axis in the tetragonal α' phase, and the orientations of the ions around the

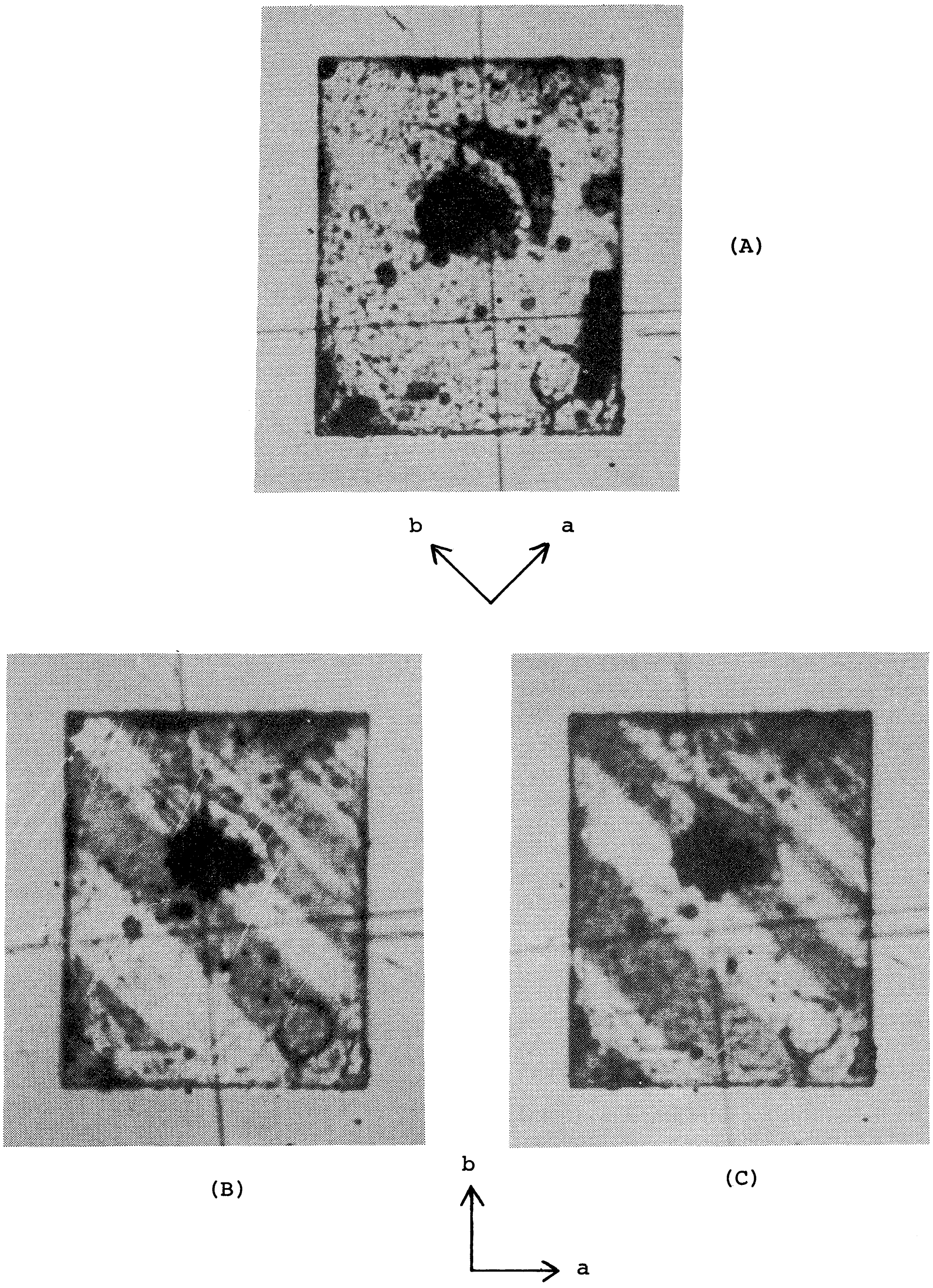

Fig. 1. Microphotographs of the domain structure in CH_3NH_3I single crystal; (A) at room temperature in the α' phase; (B),(C) at the liquid N_2 temperature in the δ phase. (B) and (C) were taken by using the polarized lights whose directions are perpendicular to each other. The crystallographic axes in each phase are shown in the figure.

C-N axes fall into the ordered state through the α'-δ phase transition.[5] The antiferroelectric fluctuation in the phase transition is therefore interpreted to originate from the motion coupled with the orientational ordering; that is, the tilt of the C-N axes from the c axis of the tetragonal structure probably resulting in the strengthening of some hydrogen bonds formed between I^- and $CH_3NH_3^+$ ions. Taking the above microscopic observation into consideration, the tilt would occur either in the (110) or $(1\bar{1}0)$ plane in an antiferroelectric way in the δ phase, leading to the loss of the tetragonal symmetry. There are many possible ways of antiferroelectric arrangement of the $CH_3NH_3^+$ ions in space, if we consider larger unit cells than the original one. None of them can be beyond a simple possibility. Direct determination of the low tempera-

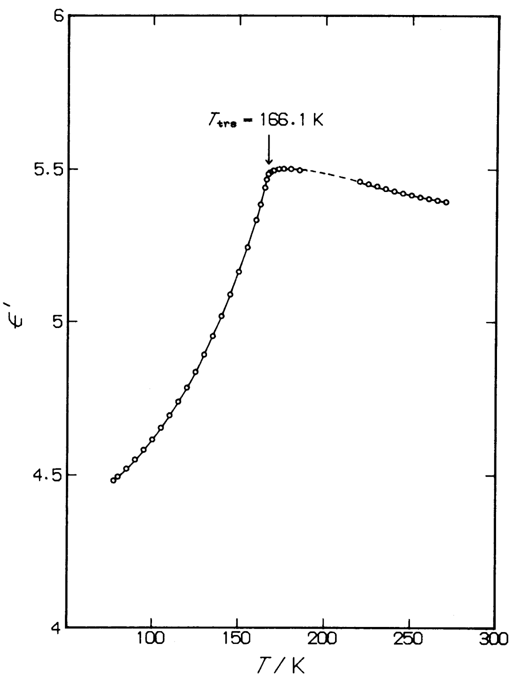

Fig. 2. Dielectric constant of CH_3NH_3I powder crystal measured at 1 kHz.

ture structure by neutron or X-ray diffraction method is highly desiderative.

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References

1) S. B. Hendricks, *Z. Kristallogr.*, **67**, 106 (1928).

2) M. Stammler, *J. Inorg. Nucl. Chem.*, **29**, 2203 (1967).

3) E. J. Gabe, *Acta Crystallogr.*, **14**, 1296 (1961).

4) O. Yamamuro, M. Oguni, T. Matsuo, and H. Suga, *Thermochim. Acta*, **98**, 327 (1986).

5) O. Yamamuro, M. Oguni, T. Matsuo, and H. Suga, *J. Chem. Thermodyn.*, **18**, 939 (1986).

6) V. A. Isupov, *Fiz. Tverd. Tela*, **7**, 2221 (1965); *Sov. Phys. Solid State*, **7**, 1789 (1966).

7) Y. Makita, *J. Phys. Soc. Jpn.*, **20**, 1567 (1965).

8) I. Todo and I. Tatsuzaki, *Phys. Status Solidi*, **32**, 263 (1969).