Pressure-Induced Ferroelectricity in $(NH_4)_3H(SO_4)_2$

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Dielectric properties of single crystals of $(NH_4)_3H(SO_4)_2$ were measured at various hydrostatic pressures up to about 8 kbar below room temperature. The broad peak of dielectric constant along the c^*-direction which appears around $-25°C$ at 1 atm becomes more and more prominent as pressure increases, and then a ferroelectric phase (Phase VI) develops above 4.9 kbar. Another ferroelectric phase (Phase VII) is also found above about 5 kbar in a lower temperature region. The pressure-temperature phase diagram is given.

Triammonium hydrogen disulfate $(NH_4)_3H$ $(SO_4)_2$ has five phases at atmospheric pressure.[1] In order of descending temperature, they are denoted as I (stable above 140°C; trigonal), II (140°C ~ −8°C; monoclinic), III (−8°C ~ −132°C), IV (−132°C ~ −140°C) and V (below −140°C). Dielectric and thermal anomalies have been observed for the transitions between them.[1,2] However, ferroelectric activity has not been observed for any of these atmospheric phases. In addition to these phase transitions, there is a broad peak of dielectric constant along the c^*-direction at around −25°C.[1] The maximum value of the dielectric constant is about 60 at 1 atm. The peak is too broad to be attributed to a phase transition. The present study deals with the effect of hydrostatic pressure on this anomalous dielectric-constant peak.

Single crystals of $(NH_4)_3H(SO_4)_2$ were grown from an aqueous solution by slow evaporation at about 30°C. Several c-plate specimens were polished with #1200 mesh carborundum powder, and then they were attached with silver-paste electrodes. A Cu–Be pressure bomb was served for the dielectric measurements at high pressures. The pressure-transmitting fluid used was 50–50 mixture of *iso*- and *n*-penthane. Dielectric constant was measured with a three-terminal capacitance bridge at a frequency of 100 kHz. Ferroelectric hysteresis loops were observed by using a conventional Sawyer-Tower circuit.

Figure 1 shows the temperature dependence of dielectric constant at various pressures. The broad dielectric-constant peak which is seen at about −25°C at 1 atm becomes more and
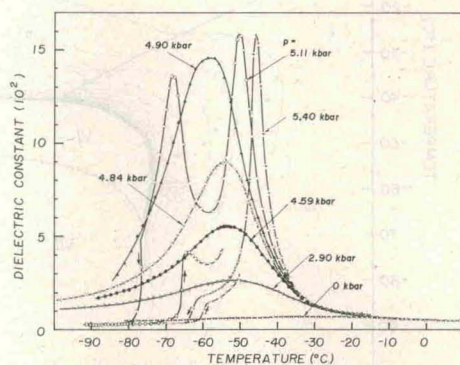

Fig. 1. Temperature dependence of the dielectric constant of $(NH_4)_3H(SO_4)_2$ along the c^*-direction at various hydrostatic pressures. Frequency: 100 kHz.

more prominent as pressure increases. The reciprocal of the maximum dielectric constant linearly decreases with pressure as $1/\varepsilon_{max} = C(p_0 - p)$, where the parameters C and p_0 are estimated as $C = (3.20 \pm 0.03) \times 10^{-3}$ kbar^{-1} and $p_0 = 5.1 \pm 0.1$ kbar. Slightly below the critical pressure of p_0, the peak splits into two rather sharp maxima indicating that a high pressure phase develops between them. The phase is denoted as phase VI. The lower-temperature peak, however, is masked by the appearance of another pressure-induced phase (Phase VII) at pressures higher than about 5 kbar in a lower temperature region. The transition from VI to VII is of the first order being accompanied with a discontinuous change in dielectric constant and thermal hysteresis. Both the pressure-induced phases of VI and VII are shown to be ferroelectric from dielectric hysteresis measurements. Figures 2(a) and (b)
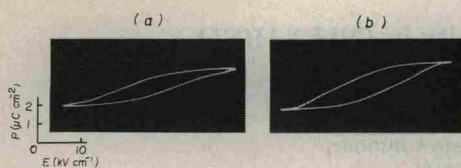
Fig. 2. Ferroelectric hysteresis loops of $(NH_4)_3$ $H(SO_4)_2$. (a) in Phase VI ($-51.4°C$, 5.7 kbar), (b) in Phase VII ($-86.6°C$, 5.6 kbar). Frequency: 50 Hz.
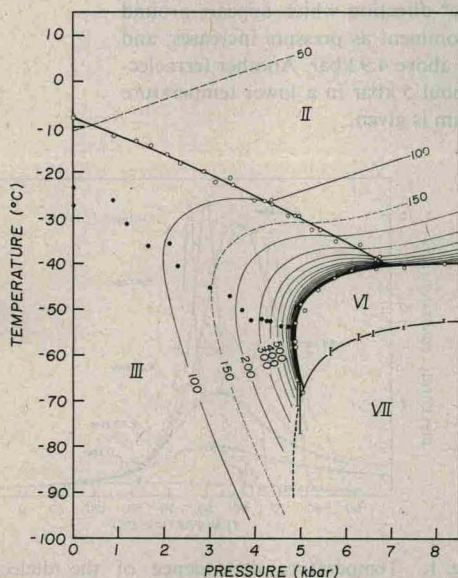

Fig. 3. Pressure-temperature phase diagram of $(NH_4)_3H(SO_4)_2$. Contour lines for equal dielectric constant are indicated by thin lines. The solid circles show the maximum position of dielectric constant in constant-pressure measurements.

show the ferroelectric hysteresis loops at 50 Hz in Phase VI and in Phase VII, respectively.

Figure 3 indicates the pressure-temperature phase diagram of $(NH_4)_3H(SO_4)_2$ given by the dielectric-constant measurements. In the figure, the contour lines of equal dielectric constant are indicated for non-ferroelectric phases of II and III. The maximum positions of the broad dielectric constant peak in constant-pressure measurements are indicated by solid circles. It is noted from Fig. 3 that a ridge of dielectric constant lies almost parallel to the II–III phase boundary.

The present results show that the broad dielectric peak around $-25°C$ at 1 atm corresponds to the polarization-fluctuation which brings about the ferroelectric structure of Phase VI at high pressures. The pressure-dependence of the dielectric constant vs temperature curves shown in Fig. 1 quite resembles to the content-dependence of them in the ammonium Rochelle salt-Rochelle salt system.[3] Although in the present compound the appearance of Phase VII makes the problem complicated, the ferroelectric process in Phase VI will be analogous to that in Rochelle salt.

Acknowledgement

References

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