

Pressure-Induced Ferroelectricity in  $(\text{NH}_4)_3\text{H}(\text{SO}_4)_2$ 

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(Received July 12, 1976)

Dielectric properties of single crystals of  $(\text{NH}_4)_3\text{H}(\text{SO}_4)_2$  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  $-25^\circ\text{C}$  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  $(\text{NH}_4)_3\text{H}(\text{SO}_4)_2$  has five phases at atmospheric pressure.<sup>1)</sup> In order of descending temperature, they are denoted as I (stable above  $140^\circ\text{C}$ ; trigonal), II ( $140^\circ\text{C} \sim -8^\circ\text{C}$ ; monoclinic), III ( $-8^\circ\text{C} \sim -132^\circ\text{C}$ ), IV ( $-132^\circ\text{C} \sim -140^\circ\text{C}$ ) and V (below  $-140^\circ\text{C}$ ). Dielectric and thermal anomalies have been observed for the transitions between them.<sup>1,2)</sup> 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  $-25^\circ\text{C}$ .<sup>1)</sup> 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  $(\text{NH}_4)_3\text{H}(\text{SO}_4)_2$  were grown from an aqueous solution by slow evaporation at about  $30^\circ\text{C}$ . 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*-pentane. 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  $-25^\circ\text{C}$  at 1 atm becomes more and

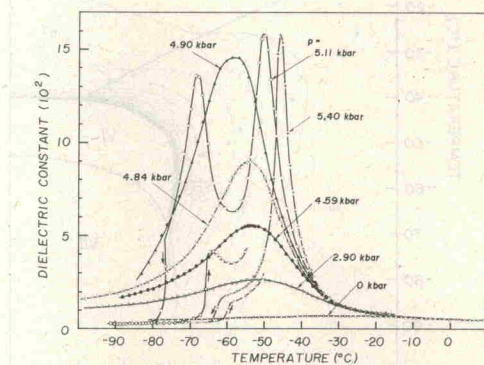


Fig. 1. Temperature dependence of the dielectric constant of  $(\text{NH}_4)_3\text{H}(\text{SO}_4)_2$  along the  $c^*$ -direction at various hydrostatic pressures. Frequency: 100 kHz.

more prominent as pressure increases. The reciprocal of the maximum dielectric constant linearly decreases with pressure as  $1/\epsilon_{\text{max}} = C(p_0 - p)$ , where the parameters  $C$  and  $p_0$  are estimated as  $C = (3.20 \pm 0.03) \times 10^{-3} \text{ kbar}^{-1}$  and  $p_0 = 5.1 \pm 0.1 \text{ kbar}$ . 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)

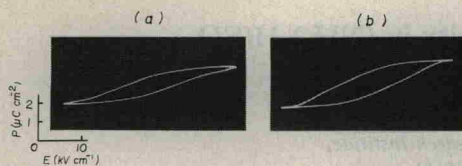


Fig. 2. Ferroelectric hysteresis loops of  $(\text{NH}_4)_3\text{H}(\text{SO}_4)_2$ . (a) in Phase VI ( $-51.4^\circ\text{C}$ , 5.7 kbar), (b) in Phase VII ( $-86.6^\circ\text{C}$ , 5.6 kbar). Frequency: 50 Hz.

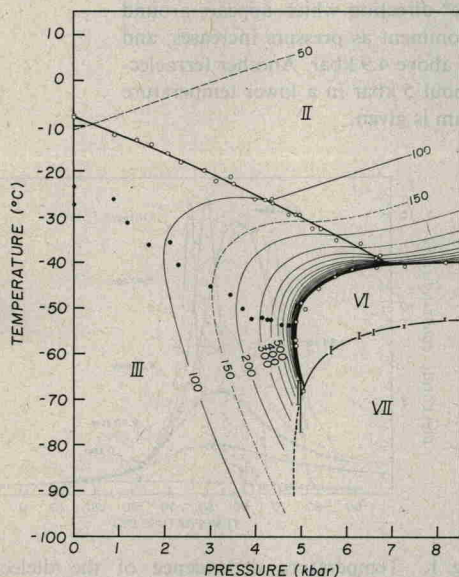


Fig. 3. Pressure-temperature phase diagram of  $(\text{NH}_4)_3\text{H}(\text{SO}_4)_2$ . Contour lines for equal dielectric constant are indicated by thin lines. The solid circles show the maximum position of dielectric constant in constant-pressure measurements.

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  $(\text{NH}_4)_3\text{H}(\text{SO}_4)_2$  given by the dielectric-constant measurements. In the figure, the contour lines of equal dielectric constant are indicated for non-ferroelectric phases 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  $-25^\circ\text{C}$  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.<sup>3)</sup> 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

The present author devotes his hearty thanks to Dr. K. Ozawa for his cooperation in high-pressure arrangements.

#### References

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