Dielectric Study on the Effect of Hydrostatic Pressure on the Phase Transitions in the System of $\{(NH_4)_3H(SO_4)_2\}_{1-x}\{(ND_4)_3D(SO_4)_2\}_x$
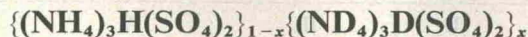
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The concentration-pressure-temperature three dimensional phase diagram of $\{(NH_4)_3H(SO_4)_2\}_{1-x}\{(ND_4)_3D(SO_4)_2\}_x$ system was studied by means of dielectric measurements in a pressure-temperature range of $p \lesssim 10$ kbar and $-100°C \lesssim T <$ room temperature. The two pressure-induced ferroelectric phases of VI and VII in the normal compound ($x=0$) are found in lower pressure region as the concentration x increases. Compounds with $x>0.90$ show the ferroelectric VI phase even at atmospheric pressure. A good correspondence between the effects of hydrostatic pressure and deuterium-substitution was established as regards the stability of the ferroelectric phases. Two pressure-induced phases (Phases VIII, IX) were newly observed in the normal-deuterated mixed crystal system.

§1. Introduction

At atmospheric pressure triammonium hydrogen disulfate $(NH_4)_3H(SO_4)_2$ has five polymorphic modifications above liquid nitrogen temperature.[1] Recently, one of the present authors (KG) found an additional phase transition at around $-210°C$.[2] Then, six phases have been known in $(NH_4)_3H(SO_4)_2$ at atmospheric pressure. They are conventionally denoted I, II, III, IV, V, and VII in the order of descending temperature. The transitions in $(NH_4)_3H(SO_4)_2$ are shown in Table I. The dielectric anomalies associated with the phase transitions in $(NH_4)_3H(SO_4)_2$ were described previously:[1,3] At atmospheric pressure, a slight break on the dielectric constant vs temperature curve is observed at the II-III and the III-IV transition temperatures. A discontinuous change in the dielectric constant accompanied with a thermal hysteresis is found at the IV-V and V-VII transitions. Besides the anomalies associated with the phase transitions, there is a broad peak of the dielectric constant along the c^*-direction at around $-25°C$ at atmospheric pressure. As hydrostatic pressure increases the broad peak becomes sharp and intense, finally it splits into two sharp λ-type maxima, and a ferroelectric phase (Phase VI) is stabilized between them. By further increase

in pressure another ferroelectric phase (Phase VII) appears in the lower temperature region. The phase transition between the two pressure-induced ferroelectric phases is of the first order. The first order nature, however, becomes more and more insignificant as pressure increases. The critical point at which the first order nature of the VI-VII transition completely disappears is estimated to be at about 11 kbar.[3]

The compound receives a marked isotope effect on the successive phase transitions. That is, the phase transitions in the deuterated compound $(NH_4)_3D(SO_4)_2$ at atmospheric pressure are quite different from those found in the normal compound; two ferroelectric phases are observed above liquid nitrogen temperature.[5] Our preliminary study on the pressure-temperature phase diagram of the deuterated compound[6] suggested that these ferroelectric phases are identical with the pressure-induced ferroelectric phases VI and VII in the normal compound. The phase transition sequence in the deuterated compound is also described in Table I. Recently, the present authors studied the phase diagram of the system $\{(NH_4)_3H(SO_4)_2\}_{1-x}\{(ND_4)_3D(SO_4)_2\}_x$.[4] The results showed that there is a marked similarity between the effects of the hydrostatic pressure and the deuterium-substitution as regards the stability of the

Table I. Phase transitions in $(NH_4)_3H(SO_4)_2$ and $(ND_4)_3D(SO_4)_2$ at atomspheric pressure. The deuterium concentration of the deuterated compound is estimated to be $x=0.97$.

$(NH_4)_3H(SO_4)_2$

Phase	I	II	III	IV	V	VII*
	trigonal	monoclinic A2/a[11]				(Ferroelectric)
Transition temperature (°C)		140[1]	−8[1]	−136[1]	−140[1]	−210[2]

$(ND_4)_3D(SO_4)_2$

Phase	I	II	III	VI	III′	VII
		monoclinic A2/a[12]		Ferroelectric		Ferroelectric
Transition temperature (°C)		122[4]	−9[5]	−24[5]	−64[5]	−92[5]

* Recent study of the low temperature phase diagram for normal-deuterated crystal system[2] showed that the lowest temperature phase of $(NH_4)_3H(SO_4)_2$ is identical with the ferroelectric VII phase of $(ND_4)_3D(SO_4)_2$.

ferroelectric phases.

It would be useful to complete the deuterium concentration (x)-pressure (p)-temperature (T) three dimensional phase diagram in order to understand the above peculiar isotope and pressure effects on the phase transitions in $(NH_4)_3H(SO_4)_2$. In the present study we intended to determine the x-p-T phase diagram of $\{(NH_4)_3H(SO_4)_2\}_{1-x}\{(ND_4)_3D(SO_4)_2\}_x$ system in a pressure and temperature range of $p \lesssim 10$ kbar, $-100°C \lesssim T <$ room temperature. The purposes of the study are (1) to confirm the identity relations between the pressure-induced ferroelectric VI and VII phases in the normal compound and the atmospheric pressure ferroelectric phases in the deuterated compound, (2) to detect the critical point of the ferroelectric-to-ferroelectric VI-VII phase transition (The critical point was expected to exist at a lower pressure in deuterated compound.[6]), and (3) to search for new pressure-induced phases in the mixed crystal system. Such a study will provide a useful piece of information about the complicated phase stability in the system of $\{(NH_4)_3H(SO_4)_4\}_{1-x}\{(ND_4)_3(SO_4)_2\}_x$.

§2. Experimental

Single crystals of $\{(NH_4)_3H(SO_4)_2\}_{1-x}$ $\{(ND_4)_3D(SO_4)_2\}_x$ with various concentration x were prepared by slow evaporation of water-heavy water solutions. Crystals with the highest deuterium concentration ($x=0.97$) were prepared by repeated recrystallizations from D_2O solution. The deuterium concentration in crystal was estimated from the molecular vibration spectrum intensity of ammonium ions by Raman scattering. Specimens of the pseudo-hexagonal c-plates were polished with 1,200 mesh carborundum powder. After attached with gold-foil electrodes, the specimen was set into a Cu–Be pressure vessel. The pressure-transmitting fluid used was 1:1 mixture of iso- and n-penthane. The details of the high pressure system used were described previously.[7,8] The pressure and temperature were respectively measured with a manganine gauge and a copper-constantan thermocouple. The dielectric constant of the specimen was measured with a three terminal capacitance bridge at 1 kHz, or with an LCR-meter at 100 kHz and recorded on an x-y recorder. Phase transitions at high pressures were detected by anomalies in the dielectric constant.

§3. Results

In the deuterated compound (the deuterium concentration x was estimated to be 0.97), new dielectric anomalies were observed other than those which were reported previously.[3,9] Figure 1 shows the temperature dependence of the dielectric constant ε and its reciprocal