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Pressure-Temperature Phase Diagram
of $(ND_4)_3D(SO_4)_2$

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The pressure-temperature phase diagram of $(ND_4)_3D(SO_4)_2$ was determined in a pressure and temperature region of $p < 9$ kbar and RT $> T > -110°C$. Comparison with the phase diagram of $(NH_4)_3H(SO_4)_2$ shows that two ferroelectric phases in $(ND_4)_3D(SO_4)_2$ correspond to the pressure-induced phases VI and VII in $(NH_4)_3H(SO_4)_2$.

It has been reported that the polymorphic transitions at 1 atm in $(ND_4)_3D(SO_4)_2$ are quite different from those in $(NH_4)_3H(SO_4)_2$. In $(NH_4)_3H(SO_4)_2$ four successive phase transitions take place at 1 atm; I $\overline{140°C}$ II $\overline{-8°C}$ III $\overline{136°C}$ IV $\overline{140°C}$ V.[1] Phase I belongs to the trigonal system while Phase II and III are monoclinic. None of these phases are ferroelectric at 1 atm. On the other hand, the deuterated compound $(ND_4)_3D(SO_4)_2$ shows four phase transitions below room temperature; II $\overline{-9°C}$ III $\overline{-24°C}$ VI $\overline{-64°C}$ III' $\overline{-92°C}$ VII.[2] The transition temperatures are dependent on completeness of deuteration. Phase II and III of deuterated compound are monoclinic, and dielectric constant measurements showed that these phases respectively correspond to Phase II and III in the normal compound.[1,2] However Phase VI and VII in the deuterated compound were known to be ferroelectric.[2] That is, there are no corresponding phases in the normal compound at 1 atm. In this work we studied the pressure-temperature phase diagram of $(ND_4)_3D(SO_4)_2$ in order to explain the marked isotope effect on the phase transitions.

Single crystals of $(ND_4)_3D(SO_4)_2$ were prepared by repeated recrystallizations from D_2O-solutions containing slight excess of D_2SO_4. Several c-plates were cut from a single crystal. After attached with gold-foil electrodes, the specimen was set in a Cu–Be pressure bomb which had seven electrical terminal plugs. The dielectric constant of the specimen was measured with two types of

three-terminal capacitance bridges at frequencies of 100 kHz or 1 kHz as functions of temperature at various hydrostatic pressures. The pressure-transmitting fluid used was 1:1 mixture of *iso-* and *n*-penthane. The deuterium contents of the specimen were estimated to be 97% from a Raman spectroscopic measurement of vibrational bands of ammonium ions.

The transition temperatures at high pressures can be determined from anomalies in the dielectric constant; at the II–III, III–VI, VI–III', and III'–VII transitions there are a change in the temperature coefficient, a pronounced λ-type peak, a rather broad maximum, and a discontinuous change in the dielectric constant, respectively.[2] The pressure-temperature phase diagram of $(ND_4)_3D(SO_4)_2$ obtained in this work is shown in Fig. 1. As pressure increases the II–III transition temperature decreases and the III–VI transition temperature increases. As the result of this, Phase III disappears at about 2.1 kbar, and above this pressure Phase II directly transforms to Phase VI. The pressure derivative of the II–VI phase boundary increases with increasing pressure. The VI–III' transition temperature decreases and the III'–VII transition temperature increases with large pressure coefficients of ~ -60 deg kbar^{-1} and ~ 70 deg kbar,$^{-1}$ respectively, as pressure increases. Hence Phase III' is restricted in a very narrow area in the pressure-temperature plane. It may disappear in the fully deuterated compound. The direct transition from Phase VI to VII takes place above about 0.2 kbar. The
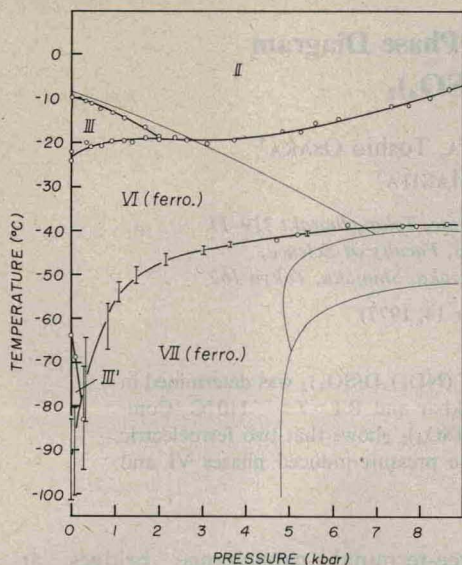
Fig. 1. Pressure-temperature phase diagram of $(ND_4)_3D(SO_4)_2$. The vertical bars indicate thermal hysteresis of the transition temperatures. Phase boundaries of $(NH_4)_3H(SO_4)_2$ are shown by thin solid curves.

VI–VII transition is of the first order, but the first order nature becomes more and more insignificant as pressure increases. The thermal hysteresis of the VI–VII transition is hardly recognized above about 7 kbar. Above 8 kbar no discontinuous change in the dielectric constant is observed, instead an inflection point is seen on the dielectric constant vs temperature curve.

In Fig. 1, the phase diagram of $(NH_4)_3H(SO_4)_2$ is shown by thin solid curves. In the normal compound two pressure-induced phases are seen above 5 kbar. The present authors previously denoted them as Phase VI and VII.[3] Phase VI is the higher temperature phase. Both the phases have been known to be ferroelectric.[4] By comparing the pressure-temperature phase diagrams of the deuterated

and normal compounds, it is evident that the ferroelectric phases of the normal compound which are stable above 5 kbar are stabilized at 1 atm by deuterium-substitution. Namely, Phase VI and VII of $(ND_4)_3D(SO_4)_2$ respectively correspond to the pressure-induced ferroelectric phases of VI and VII in $(NH_4)_3H(SO_4)_2$. Then, it is concluded that Phase III and III' in the deuterated compound are isostructural.

It would be interesting to see what is the type of the critical point at which the first order nature of the VI–VII transition disappears: Is it a tricritical point or a vapor-liquid type critical point? The problem can be solved by determination of the crystal structures of Phase VI and VII. If they are isostructural the critical point should be a vapor-liquid type one. A simple two-sublattice model of $(NH_4)_3H(SO_4)_2$ suggests that the VI–VII transition is an isomorphous one, and the critical point would be a vapor-liquid type one.[5] Detailed study on the critical point of the VI–VII transition can be easily done for $(ND_4)_3D(SO_4)_2$ since the critical point exists at a relatively low pressure.

The present compound provides a beautiful example in which the effects of hydrostatic pressure and deuterium-substitution are closely correlating each other. Study of the x-p-T three dimentional phase diagram of the $[(NH_4)_3H(SO_4)_2]_{1-x}[(ND_4)_3D(SO_4)_2]_x$ system is in progress.

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