

Ferroelectric Phase Transition in $(\text{NH}_4)_3\text{H}(\text{SeO}_4)_2$

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Dielectric properties of single crystal $(\text{NH}_4)_3\text{H}(\text{SeO}_4)_2$ were measured below room temperature. Two phase transitions were found at around $+2^\circ\text{C}$ and at -92°C . A λ -type peak of the dielectric constant along the c -direction is found at -92°C , and the crystal shows ferroelectricity below the transition. The temperature dependence of the spontaneous polarization was measured by a pyroelectric method. The Curie temperature linearly increases with increasing hydrostatic pressure up to 8.5 kbar with a slope of $2.3 \text{ deg kbar}^{-1}$.

§1. Introduction

Recently it was reported that triammonium hydrogen disulfate $(\text{NH}_4)_3\text{H}(\text{SO}_4)_2$ shows ferroelectric activity at high pressures.^{1,2)} At atmospheric pressure, however, the compound does not show ferroelectricity. Only a broad peak of dielectric constant along the c^* -direction is found at around -25°C .³⁾ The deuterated analogue $(\text{ND}_4)_3\text{D}(\text{SO}_4)_2$ shows ferroelectricity even at 1 atm.* A preliminary study on the pressure-temperature phase diagram indicated that the ferroelectric phases in $(\text{ND}_4)_3\text{D}(\text{SO}_4)_2$ are corresponding to the pressure-induced ferroelectric phases in $(\text{NH}_4)_3\text{H}(\text{SO}_4)_2$. That is, the deuterium-substitution has an equivalent effect to hydrostatic pressure to stabilize ferroelectric structures.

In order to see whether ferroelectric activity can be found in other $\text{X}_3\text{H}(\text{YO}_4)_2$ -type compounds, dielectric properties of $\text{K}_3\text{H}(\text{SO}_4)_2$, $(\text{NH}_4)_3\text{H}(\text{SeO}_4)_2$, and $\text{K}_3\text{H}(\text{SeO}_4)_2$ were measured. Ferroelectricity has not been observed so far in $\text{K}_3\text{H}(\text{SO}_4)_2$ and $\text{K}_3\text{H}(\text{SeO}_4)_2$ down to liquid nitrogen temperature at 1 atm. In $(\text{NH}_4)_3\text{H}(\text{SeO}_4)_2$, a peak of the dielectric constant along the c -direction was found at about -92°C . Below the temperature ferroelectric hysteresis loops were observed with a low frequency electric field. The results were preliminarily reported.⁴⁾ The present paper reports the dielectric properties of $(\text{NH}_4)_3\text{H}(\text{SeO}_4)_2$ in some detail. The effect

of hydrostatic pressure on phase transitions was studied. The pressure-temperature phase diagram of $(\text{NH}_4)_3\text{H}(\text{SeO}_4)_2$ is given. A comparison with the ferroelectricity in $(\text{NH}_4)_3\text{H}(\text{SO}_4)_2$ is made.

§2. Experimental

Single crystals of $(\text{NH}_4)_3\text{H}(\text{SeO}_4)_2$ were prepared by slow evaporation of an aqueous solution which contained 48 wt. % of $(\text{NH}_4)_2\text{SeO}_4$ and 20 wt. % of H_2SeO_4 at around 30°C . Figure 1 shows the solubility curve of the $(\text{NH}_4)_2\text{SeO}_4\text{-H}_2\text{SeO}_4\text{-H}_2\text{O}$ system at 30°C .⁵⁾ The as-grown crystals were of hexagonal plates belonging to the trigonal symmetry.⁶⁾ After polished with #1,200 mesh carborundum powder, gold foil or silver paste was attached to the c -surfaces as electrodes. The dielectric constant of the specimen was measured with a three terminal capacitance bridge at 100 kHz. Ferroelectric hysteresis loops were observed by means of a modified Sawyer-Tower circuit applying electric fields of 0.014 Hz triangular wave. The D - E hysteresis loops were recorded on an x-y recorder. The temperature dependence of the spontaneous polarization was measured with an electrometer and recorded on an x-y recorder. Effect of hydrostatic pressure on the phase transitions was observed by the measurements of temperature dependence of the dielectric constant at various pressures up to about 9 kbar. A detailed description of the experimental procedure of high pressure measurements was given elsewhere.²⁾

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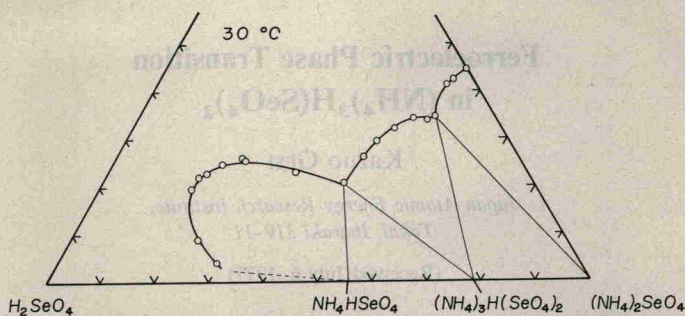


Fig. 1. Solubility curve of $(\text{NH}_4)_2\text{SeO}_4\text{-H}_2\text{SeO}_4\text{-H}_2\text{O}$ system at 30°C .⁵⁾

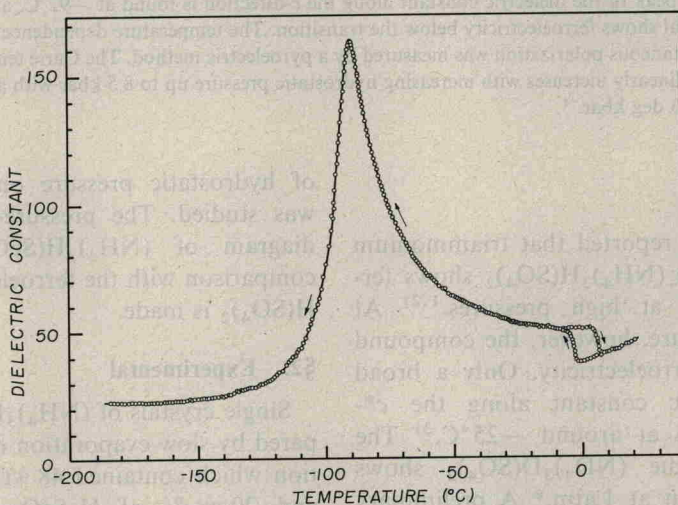


Fig. 2. Temperature dependence of the dielectric constant along the c -direction of $(\text{NH}_4)_3\text{H}(\text{SeO}_4)_2$. Frequency: 100 kHz.

§3. Results

Figure 2 shows the temperature dependence of the dielectric constant along the c -direction. A discontinuous change in the dielectric constant is seen just below room temperature corresponding to a first order phase transition. Because of a large thermal hysteresis of $10\sim 15^\circ\text{C}$ during cooling and heating processes, it was difficult to determine the transition temperature at equilibrium. If one assumes the equilibrium transition temperature to be the middle point of the observed thermal hysteresis, one gets about $+2^\circ\text{C}$ as the transition temperature. Below the transition, the dielectric constant increases with decreasing temperature and shows a λ -type peak at about -92°C . The maximum value at the peak is about $170\sim 200$. The peak is somewhat rounding.

It was difficult to observe ferroelectric hysteresis loops at 50 Hz because of high

coercive field and increase in loss factor as temperature approaches the Curie point from below. At very low frequencies, one may observe ferroelectric hysteresis loops. Figure 3 shows the D - E hysteresis loops at -105°C for various amplitudes of 0.014 Hz triangular waves. Figure 4 shows the corresponding switching current vs applied electric field curves. Due to an increase in the coercive field the ferroelectric hysteresis loop collapses below -140°C even with low frequencies of ~ 0.01 Hz. Figure 3 and 4 indicate that the spontaneous polarization of $(\text{NH}_4)_3\text{H}(\text{SeO}_4)_2$ can be reversed by the application of an electric field; namely the compound is ferroelectric. Figure 5 shows the temperature dependence of the spontaneous polarization. The specimen was poled by the application of 24 kV cm^{-1} electric field at -100°C along the $+c$ or $-c$ -direction, then it was cooled to about -185°C . The pyroelectric charge was recorded