Proton-glass state in $\text{K}_{0.60}(\text{NH}_4)_{0.40}\text{H}_2\text{AsO}_4$ detected by dielectric measurements

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Dielectric permittivity measurements of ϵ'_a and ϵ''_a in a $\text{K}_{0.60}(\text{NH}_4)_{0.40}\text{H}_2\text{AsO}_4$ mixed crystal have been made in the temperature and frequency ranges 3–300 K and 1 Hz–30 kHz. We find proton-glass behavior in this material similar to that observed in the $\text{Rb}_{1-x}(\text{NH}_4)_x\text{H}_2\text{AsO}_4$ and $\text{Rb}_{1-x}(\text{NH}_4)_x\text{H}_2\text{PO}_4$ systems. Below T_g the dielectric dispersion characteristics of the freezing of the polarization are well described phenomenologically by the Vogel-Fulcher law. The best fit gives the Vogel-Fulcher temperature $T_0 = 5.4$ K, the attempt frequency $\nu_0 = 2.5 \times 10^{13}$ Hz, and the activation energy $E_c/k = 409$ K.

The proton-glass state in mixed crystals of the ferroelectric RbH_2PO_4 or RbH_2AsO_4 and antiferroelectric $\text{NH}_4\text{H}_2\text{PO}_4$ or $\text{NH}_4\text{H}_2\text{AsO}_4$ has received considerable attention, since the first publication in 1982.¹ Proton-glass behavior was detected in the phosphate systems $\text{Rb}_{1-x}(\text{NH}_4)_x\text{H}_2\text{PO}_4$ (Refs. 1 and 2) and $\text{Rb}_{1-x}(\text{ND}_4)_x\text{D}_2\text{PO}_4$ (Refs. 3 and 4) and in the arsenate systems $\text{Rb}_{1-x}(\text{NH}_4)_x\text{H}_2\text{AsO}_4$ (Refs. 5–9) and $\text{Rb}_{1-x}(\text{ND}_4)_x\text{D}_2\text{AsO}_4$ (Ref. 10). Recently, Ono, Hikita, and Ikeda,¹¹ and Kim and Sherman¹² have reported proton glass behavior in the $\text{K}_{1-x}(\text{NH}_4)_x\text{H}_2\text{PO}_4$ system. To contribute to better understanding of proton-glass behavior we present in this paper our dielectric investigation of

the new composition $\text{K}_{1-x}(\text{NH}_4)_x\text{H}_2\text{AsO}_4$ (KADA). The single crystal $\text{K}_{0.60}(\text{NH}_4)_{0.40}\text{H}_2\text{AsO}_4$ (KADA-40) was obtained by slow evaporation of an aqueous solution of KH_2AsO_4 and $\text{NH}_4\text{H}_2\text{AsO}_4$ crystals. The ammonium concentration x in the crystal was determined from the concentration of potassium ions by the atomic absorption spectroscopy method. A small plate of $1.55 \times 2.2 \times 0.78$ mm³ perpendicular to the a tetragonal direction was cut, and after polishing, conducting silver paint electrodes were applied.

The complex dielectric constant $\epsilon'_a(\omega, T)$ and $\epsilon''_a(\omega, T)$ was measured in the frequency range from 1 Hz to 30 kHz using a bridge that has been described elsewhere.⁷

FIG. 1. Temperature dependence of the dielectric constant ϵ'_a in KADA-40 at 10 kHz. The solid line shows Curie-Weiss fits.

FIG. 2. Dielectric dispersion in the proton-glass regime in KADA-40: (a) $\epsilon'_a(T)$ and (b) $\epsilon''_a(T)$.

Experiments were performed using an Oxford Instruments model ESR-900 continuous helium flow cryostat between 3 and 300 K. A calibrated Chromel-Alumel type-K thermocouple was used to determine the sample temperature. Figure 1 shows the temperature dependence of the real part of the dielectric constant ϵ'_a in the heating part of the temperature cycle for the measuring frequency 10 kHz. The solid line shows the Curie-Weiss fit, which is well obeyed down to the freezing onset temperature $T_f = 85$ K defined as an inflection point of ϵ' where the Edwards-Anderson order parameter q starts to increase upon cooling.¹³ The reciprocal of ϵ'_a located the Curie-Weiss temperature T_0 at -32 K. The Curie-Weiss constant is equal to 20 380 K. In the temperature range from 50 to 60 K we detected a rounded maximum of ϵ'_a

FIG. 3. Results of fits of ϵ''_a data using the Vogel-Fulcher law with fixed T_0 : activation energy $E_c(T_0)$ (left scale) and variance of scaling correlation coefficient against T_0 (right scale).

FIG. 4. Vogel-Fulcher plot of the cutoff frequency ν_c against inverse temperature $100/(T - T_0)$.

characteristic of proton-glass behavior. The maximum magnitude of ϵ'_a was 202. Below 50 K, ϵ'_a starts to decrease upon cooling. Figure 2 shows the dielectric dispersion detected for ϵ'_a and ϵ''_a . The temperature T_g at which ϵ'_a starts to decrease is a function of frequency and changes from 40 K at 30 kHz to 26 K at 1 Hz. The imaginary part of the dielectric constant [Figure 2(b)] starts to increase below T_g and reaches maximum value near $T_g - 10$ K. The low-temperature dispersion in ϵ'_a and ϵ''_a , characteristic of the freezing of the local configurations, is well described phenomenologically by the Vogel-Fulcher law:¹⁴

$$\nu_c = \nu_0 \exp[-E_c / (T - T_0)], \quad (1)$$

where $\nu_c(T)$ is the cutoff frequency (measurement frequency) for which $\epsilon''_a(\nu_c)$ is maximum at temperature T . The parameters chosen to give best fit over the whole range of measurement frequency ν_c are attempt frequency ν_0 , activation energy E_c , and Vogel-Fulcher temperature T_0 . Results of fits with fixed T_0 are shown in Fig. 3. Both E_c and ν_0 are strongly correlated with T_0 . The best fit was obtained for $T_0 = 5.4$ K, $\nu_0 = 2.5 \times 10^{13}$ Hz and $E_c = 409$ K. Figure 4 shows the Vogel-Fulcher plot of ν_c against inverse temperature $100/(T - T_0)$. The straight line corresponds to $T_0 = 5.4$ K, $\nu_0 = 2.5 \times 10^{13}$ Hz, and $E_c = 409$ K. The results presented here are similar to those for RADA.⁵⁻⁹ This implies that the type of metal cation is playing a rather small role in the nature of the appearance of the proton-glass behavior in ferroelectric-

antiferroelectric mixed crystals in the KH_2PO_4 family. Additional investigation of the KADA system will give a better understanding of the nature of the competing interactions in proton glass systems. Samples for future experiments are being prepared.

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