Proton-glass state in $K_{0.60}(NH_4)_{0.40}H_2AsO_4$ detected by dielectric measurements

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Dielectric permittivity measurements of $\epsilon'_\omega$ and $\epsilon''_\omega$ in a $K_{0.60}(NH_4)_{0.40}H_2AsO_4$ mixed crystal have been made in the temperature and frequency ranges $3\text{–}300$ K and $1$ Hz–$30$ kHz. We find proton-glass behavior in this material similar to that observed in the $\text{Rb}_{1-x}(NH_4)_xH_2AsO_4$ and $\text{Rb}_{1-x}(NH_4)_xH_2PO_4$ 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 $v_0=2.5 \times 10^{13}$ Hz, and the activation energy $E_a/k=409$ K.

The proton-glass state in mixed crystals of the ferroelectric $\text{RbH}_2\text{PO}_4$ or $\text{RbH}_2\text{AsO}_4$ 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. 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, and Kim and Sherman have reported proton glass behavior in the $K_{1-x}(\text{NH}_4)_x\text{H}_2\text{PO}_4$ system. To contribute to better understanding of proton-glass behavior we present in this paper our dielectric investigation of the new composition $K_{1-x}(\text{NH}_4)_x\text{H}_2\text{AsO}_4$ (KADA). The single crystal $K_{0.60}(\text{NH}_4)_{0.40}H_2AsO_4$ (KADA-40) was obtained by slow evaporation of an aqueous solution of $\text{KH}_2\text{AsO}_4$ 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 $1.55\times2.2\times0.78$ mm$^3$ perpendicular to the $a$ tetragonal direction was cut, and after polishing, conducting silver paint electrodes were applied.

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

FIG. 1. Temperature dependence of the dielectric constant $\epsilon'_\omega$ in KADA-40 at $10$ kHz. The solid line shows Curie-Weiss fits.
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 $\varepsilon_r'$ 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 $\varepsilon_r'$ where the Edwards-Anderson order parameter $q$ starts to increase upon cooling. The reciprocal of $\varepsilon_r'$ located the Curie-Weiss temperature $T_\theta=20\,380$ K. The Curie-Weiss constant is equal to 20380 K. In the temperature range from 50 to 60 K we detected a rounded maximum of $\varepsilon_r'$ characteristic of proton-glass behavior. The maximum magnitude of $\varepsilon_r'$ was 202. Below 50 K, $\varepsilon_r'$ starts to decrease upon cooling. Figure 2 shows the dielectric dispersion detected for $\varepsilon_r'$ and $\varepsilon_r''$. The temperature $T_p$ at which $\varepsilon_r''$ 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 $\varepsilon_r''$ and $\varepsilon_r'$, characteristic of the freezing of the local configurations, is well described phenomenologically by the Vogel-Fulcher law:

$$
\nu_c=\nu_0 \exp\left[-\frac{E_c}{T-T_0}\right],
$$

where $\nu_c(T)$ is the cutoff frequency (measurement frequency) for which $\varepsilon_r''(\nu_c)$ is maximum at temperature $T$. The parameters chosen to give best fit over the whole range of measurement frequency $\nu_c$ are attempt frequency $\nu_0$, 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 $\nu_0$ 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 $\nu_c$ 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. 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-

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

FIG. 3. Results of fits of $\varepsilon_r''$ 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 $\nu_c$ against inverse temperature $100/(T-T_0)$. 

FIG. 1. Temperature dependence of the real part of the dielectric constant $\varepsilon_r'$ in the heating part of the temperature cycle for the measuring frequency 10 kHz.
antiferroelectric mixed crystals in the KH$_2$PO$_4$ 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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