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Coexistence of proton-glass and ferroelectric order in $Rb_{1-x}(NH_4)_xH_2AsO_4$

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The mixed crystal $Rb_{1-x}(NH_4)_xH_2AsO_4$ (RADA) has been investigated for several values of $x(x=0, 0.12, 0.15, \text{and } 0.20)$ by measuring the complex dielectric permittivity along the a tetragonal axis in the temperature range from 3 to 300 K and frequency range from 1 Hz to 30 kHz. We find coexistence of ferroelectric and proton-glass order in RADA for $x=0.12$ and probably at $x=0.15$. The long-range ferroelectric order is not destroyed by the onset of proton-glass ordering. This behavior is similar to that of other proton-glass systems and of the magnetic Ising glass systems reported by Wong *et al.* in $Fe_{0.55}Mg_{0.45}Cl_2$ and by Yoshizawa *et al.* in $Fe_xMn_{1-x}TiO_3$. The partial phase diagram for $Rb_{1-x}(NH_4)_xH_2AsO_4$ including the coexisting proton-glass and ferroelectric phases is presented.

Many experimental and theoretical studies have been made of mixed crystals of ferroelectric RbH_2PO_4 (RDP) and antiferroelectric $NH_4H_2PO_4$ (ADP). Courtens[1,2] discovered the proton-glass state in $Rb_{1-x}(NH_4)_xH_2PO_4$ (RADP) as an analog of the magnetic spin-glass system. Recently, a few results were found for the $Rb_{1-x}(NH_4)_xH_2AsO_4$ (RADA) system.[3-10] The phase diagrams for these two proton-glass systems, RADP and RADA, have received considerable attention. The first dielectric-susceptibility measurements in RADA made by Trybula *et al.*[3,5] at microwave frequencies show an asymmetric phase diagram, in contrast to the symmetric one for the RADP system.[10,11] Proton-glass behavior for RADA and RADP exists in the concentration ranges $0.1 \leq x \leq 0.5$ and $0.2 \leq x \leq 0.8$, respectively. In this paper, we present our dielectric investigations in RADA mixed crystals and show the coexistence of proton glass and ferroelectric order.

The mixed crystals RADA of various concentrations $x=0$, 0.12 ± 0.01, 0.15 ± 0.01, and 0.20 ± 0.01 were obtained by slow evaporation of aqueous solutions of RDA and ADA mixed in the proper molar ratios. The concentrations x were determined by rubidium analysis using flame atomic-absorption spectroscopy. Small platelets of approximate size $3.5\times3.5\times0.5$ mm^3 perpendicular to the a tetragonal direction were cut from single RADA crystals. After polishing, conducting silver paint electrodes were applied. The complex dielectric constant (ϵ_a' and ϵ_a'') was measured in the frequency range from 1 Hz to 30 kHz using a bridge described elsewhere.[8] Experiments were performed using an Oxford Instruments model ESR-900 continuous-helium-flow cryostat between 3 and 300 K. To determine the sample's temperature we used a calibrated Chromel-Alumel type-K thermocouple.

Figure 1 shows the temperature dependence of the real part of the dielectric constant ϵ_a' in the heating cycle for RADA with various ammonium concentrations x. The dielectric constant $\epsilon_a'(T)$ for the pure ferroelectric crystal RDP [$x=0$, Fig. 1(a)] shows the ferroelectric phase transition by the sharp peak of the ϵ_a' value at $T_c=110$ K. The temperature dependence of ϵ_a' near T_c for the a axis (which is perpendicular to the ferroelectric c axis) is similar to that for antiferroelectric transitions and is characteristic for the KH_2PO_4 (KDP) ferroelectric family.[12-14] In the whole temperature range for RDA, we did not detect dispersion of ϵ_a', and the value of the imaginary part of the dielectric constant ϵ_a'' was constant and very small in the whole temperature range.

The dielectric response for the RADA $x=0.12$ [Fig. 1(b)] and RADA $x=0.15$ [Fig. 1(c)] crystals shows the phase transition to the ferroelectric phase (weak and diffuse for $x=0.15$) and the onset of proton-glass behavior. This behavior observed at low temperature is typical for proton glasses in that it shows dispersion in $\epsilon_a'(T)$ and $\epsilon_a''(T)$ (Fig. 2) and characteristic maxima of ϵ_a'' a few degrees below the proton-glass temperature $T_g(f)$ defined as the temperature at which ϵ_a' starts to drop for given frequency f. In the RADA $x=0.20$ crystal we detected no ferroelectric transition, but observed appearance of the proton-glass state with temperature T_g close to the temperature for the RADA $x=0.35$ crystal.[8] For the pure proton-glass state the temperature T_g is practically independent of x in the whole concentration range x, for both RADP (Refs. 10 and 11) and RADA.[5] The dielectric results for RADA $x=0.12$ and 0.15 crystals show that T_g for the mixed proton-glass–ferroelectric state is lower than for the pure proton-glass state. The differences are 14 and 3 K for RADA $x=0.12$ and 0.15, respectively.

The partial phase diagram of RADA, from our dielectric measurements, is shown in Fig. 3. The low-temperature phase for RADA $x=0.12$ and 0.15, below the F-P region where the ferroelectric and paraelectric phases coexist, is the mixed phase (F-G) when the ferroelectric and proton-glass state coexist. In our opinion its boundary is not a reentrant phase transition from a ferroelectric to a proton-glass state, as suggested by Takashige *et al.*[11] for phosphate glasses $Rb_{0.25}(NH_4)_{0.75}H_2PO_4$ close to the antiferroelectric-phase boundary, but coexistence of ferroelectric long-range and proton-glass short-range order. The long-range ferroelectric order is not destroyed by the proton-glass transition. Evidence for coexistence is the increase seen in Fig. 1 in the value of ϵ_a' at T_g with increasing ammonium concentration x, corresponding to the decreasing amount of the crystal existing

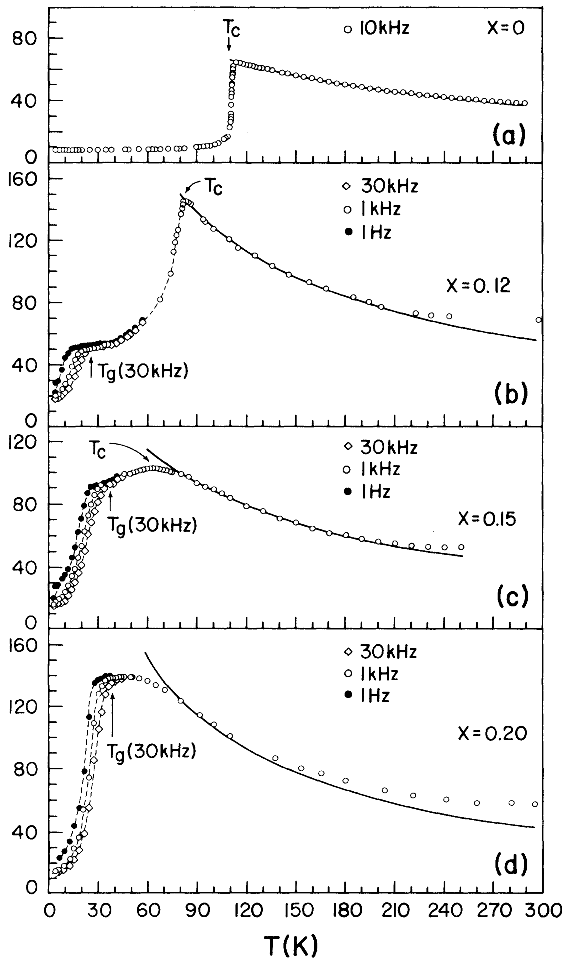

FIG. 1. Temperature dependence of the real part of the dielectric permittivity ϵ_a' in: (a) RDA; (b) RADA $x=0.12$; (c) RADA $x=0.15$; (d) RADA $x=0.20$.

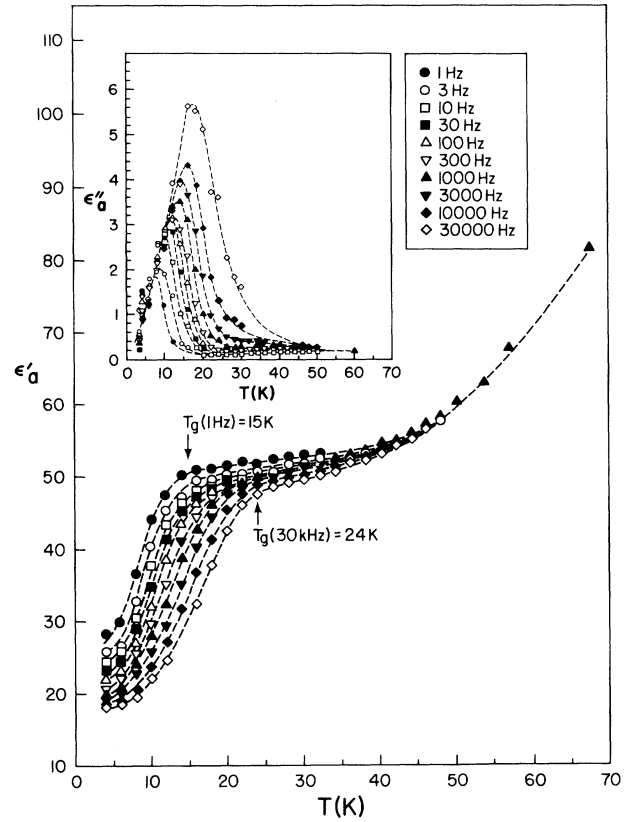

FIG. 2. Dielectric dispersion of ϵ_a' and ϵ_a'' in RADA $x=0.12$ in the proton-glass regime.

in the ferroelectric phase which cannot show proton-glass behavior. Phenomenologically similar coexistence of spin-glass and antiferromagnetic orders in the magnetic Ising systems $Fe_{0.55}Mg_{0.45}Cl_2$ (Ref. 15) and $Fe_xMn_{1-x}TiO_3$ (Ref. 16) has been discovered recently. Toulouse[17] and Nishimori[18,19] argued coexistence of ferromagnetic and spin-glass order below the Almeida-Thouless or Nishimori lines. The dashed line in our phase diagram for RADA in Fig. 3 is similar to the theoretical Nishimori line for magnetic Ising spin-glass systems.[18] The vertical phase boundary, which may be related to the Nishimori[18] geometry-induced phase transition, occurs where the pure proton-glass phase meets the mixed-phase region, near concentration $x=0.16$. This is lower than the value $x=0.2$ for which coexistence of ferroelectric and proton-glass phases was seen in x-ray studies of RADP.[20] The nature of the coexistence regions is an open question, but we believe there are interpenetrating ferroelectric and paraelectric (proton glass at low temperature) clusters with short correlation length, corresponding to regions of

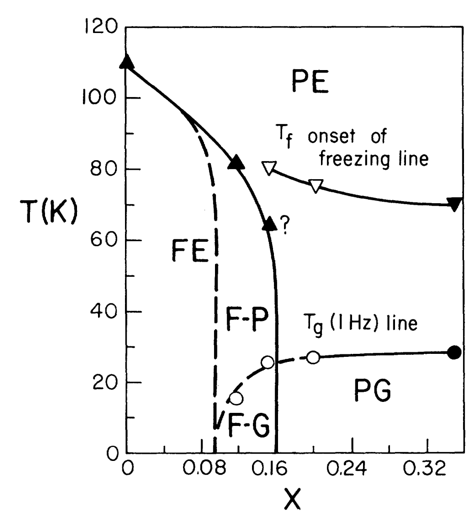

FIG. 3. The partial phase diagram of RADA as a function of fractional ammonium concentration x and temperature T. PE, FE, PG, F-P, and F-G denote paraelectric and ferroelectric phases, proton-glass regime, and mixed ferroelectric-paraelectric, and ferroelectric–proton-glass phases, respectively. The open circles, open triangles, and solid upright triangles are from this work; the solid circle and solid inverted triangle are from Trybula *et al.* (Ref. 8).

excess rubidium or ammonium density, respectively. The fact that T_g is lower in the mixed-phase crystals than in crystals having a pure proton-glass regime suggests that proton-glass clusters in the mixed-phase region especially for small x have shorter correlation length and hence have faster dynamics than seen in the pure proton-glass regime. These results show the need for additional investigation of the RADA system, especially in the mixed-phase region. We are currently conducting such investigations.

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