Pressure dependence of the coexistence of proton-glass and ferro-antiferroelectric order in Rb1-x(NH4)xH2AsO4

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PRESSURE DEPENDENCE OF THE COEXISTENCE OF PROTON-GLASS AND FERRO-/ANTIFERROELECTRIC ORDER IN $Rb_{1-x}(NH_4)_xH_2AsO_4$

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The effects of hydrostatic pressure, temperature and frequency on the dielectric properties and phase transitions of the material system $Rb_{1-x}(NH_4)_xH_2AsO_4$ (RADA) in the composition range $0.10 \leq x \leq 0.40$ have been investigated. This system exhibits coexistence of both ferroelectric/proton-glass and antiferroelectric/proton-glass behavior. Results on compositions in both regimes are presented and discussed, and the pressure-temperature phase diagrams are determined. By analogy with our earlier results on other hydrogen-bonded crystals, the present results indicate that all proton ordering will vanish below ~20 kbar, but the disordered O—H···O bond network which is responsible for the formation of the proton-glass phase will persist to higher pressures than does the long-range order which is responsible for either the ferroelectric or antiferroelectric phases. The temperature dependence of the dipolar relaxation process associated with the glass transition is represented by the Vogel-Fulcher equation, and the pressure dependences of the parameters of this equation are evaluated and discussed. All the results can be qualitatively understood in terms of a decrease in the potential barrier seen by the proton as it moves along the hydrogen bond.

Keywords: Ferroelectric, antiferroelectric, proton-glass, pressure.

INTRODUCTION

The study of the dynamic and static properties of systems in which randomly competing interactions cause the formation of a glassy state at low temperature has been an active research area. Examples of such systems include disordered ferroelectric (FE) or antiferroelectric (AFE) crystals in which the disorder can be due to impurities, compositional fluctuations or the competition between FE and AFE interactions. The KH_2PO_4 (KDP) family of crystals has provided some of the most interesting, and perhaps best understood, specific cases in this area. So-called proton glass behavior in this family was first discovered[1] in the mixed crystal $Rb_{1-x}(NH_4)_xH_2PO_4$ (RADP). The pure end members RbH_2PO_4 (RDP) and $NH_4H_2PO_4$ (ADP) are well understood FE and AFE crystals, respectively. For RADP, compositions with $0 \leq x \leq 0.2$ exhibit FE order, whereas for $0.8 \leq x \leq 1$, the crystals are antiferroelectric.[1] For in-between compositions, i.e., $0.2 \leq x \leq 0.8$, a proton glass state associated with the freezing of protonic motion in the

O—H···O hydrogen bonds and the development of short-range correlations is formed at low temperatures. The suppression of long-range order in this composition range is a consequence of the frustration of the system with respect to the proton ordering scheme (FE vs. AFE) and the random distribution of Rb^+ and NH_4^+ ions in the lattice. Specifically, Rb^+ ions favor FE order while NH_4^+ ions favor AFE order, but in the glass regime frustration inhibits the formation of either ordered state.

Subsequent to the discovery of a glassy state in RADP, glassy behavior has been found in other mixed crystals of the KDP family, namely in $Rb_{1-x}(NH_4)_xH_2AsO_4$ (RADA)[2–5] and in $K_{1-x}(NH_4)_xH_2AsO_4$ (KADA).[6] Of these two systems, RADA has been investigated in more detail, and, interestingly, it has been found that FE and proton glass states can coexist in this material over a substantial compositional range.[4,5]

An additional important feature of this system is the large asymmetry in the temperature (T)-composition (x) phase diagram. In RADP, the FE and AFE transition temperatures T_c and T_N of the end members are nearly equal, and the glassy state is symmetrically placed with respect to x in the T-x plane, whereas for RADA, T_N of ADA (216 K) is about twice T_c of RbH_2AsO_4 or RDA (110 K) resulting in a large asymmetry in x for the glassy state.

In earlier work,[7,8] we have demonstrated the important role of hydrostatic pressure as a variable in the study of the static and dynamic properties of the KDP family. Pressure results on FE and AFE members of this family as well as on RADP have provided much insight into the nature of the competing inter- and intramolecular interactions which are responsible for the establishment of long- and short-range order in these materials. This background has provided the motivation for our present study of the effects of pressure on the phase transitions and coexistence and relative stability of FE order and glassy behavior in RADA. In what follows, we shall present and discuss results on three samples of different compositions. The results on two of the samples also demonstrate the coexistence of AFE order and a glassy state in this system.

EXPERIMENTAL DETAILS

RADA crystals of nominal compositions $x = 0.10$, 0.22 and 0.40 were grown at Montana State University by slow evaporation of aqueous solutions of RDA and ADA mixed in the proper molar ratios. Small irregularly-shaped platelets ~0.1–0.2 cm^2 in area by ~0.1 cm thick were cut from grown single crystals with the a-axis perpendicular to the large faces. After polishing, conducting silver paint electrodes were applied. The real (ε_a') and imaginary (ε_a'') parts of the a-axis dielectric constant were measured as functions of frequency (10^2–10^6 Hz), temperature (4–300 K) and hydrostatic pressure (0–8 kbar). The measurements were made with the sample mounted inside a pressure cell which was in turn mounted in a conventional low-temperature cryostat. Helium was the pressure transmitting medium. The experimental details are similar to those described elsewhere.[9]

RESULTS AND DISCUSSION

RADA:x = 0.10

Figure 1 shows the temperature dependence of ε'_a measured at 10^6 Hz and different pressures. Several features in the response can be noted. Starting at the high-temperature end at 1 bar, ε'_a increases with decreasing temperature following a Curie-Weiss law of the form $\varepsilon'_a = \varepsilon'_0 + C/(T - T_0)$, as has been reported earlier.[5] Here ε'_0 is a background dielectric constant and C and T_0 are the Curie-Weiss constant and temperature, respectively. At 1 bar $\varepsilon'_0 = 11.9$, $C = 8{,}436$ K and $T_0 = -40.3$ K. C increases with pressure while T_0 decreases. A sharp cusp in $\varepsilon'_a(T)$ is observed at 110 K marked T_{c1} in the figure followed by a well-defined shoulder which defines another transition temperature marked T_{c2} (=90 K), then a sharp drop in ε'_a and finally a second shoulder which defines a third transition temperature marked T_g (=30 K).

Interestingly, T_{c1} matches exactly T_c of RDA, and, as will be shown below, the pressure dependence of T_{c1} is the same as that of T_c of RDA suggesting that this sample is inhomogeneous containing a sufficiently large region (estimated to be ~4% of the volume of the sample) that is essentially pure RDA. This observation is most likely due to the presence of a small RDA seed crystal in the sample. Unfortunately, the sample was destroyed after the pressure experiments, and con-

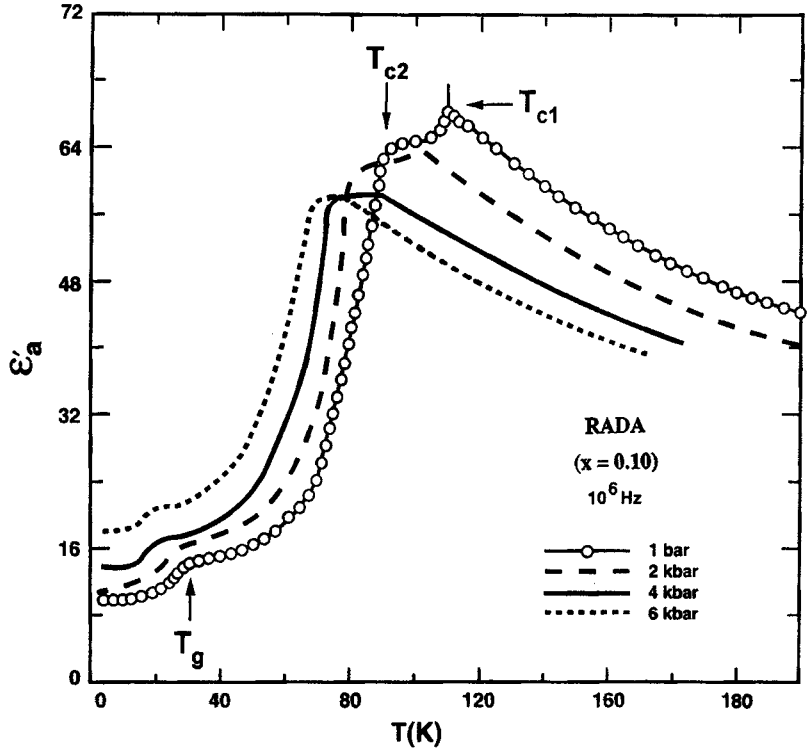

FIGURE 1 Temperature dependence of the *a*-axis dielectric constant of RADA:x = 0.10 at different pressures.

sequently it could not be analyzed. The value of T_{c2} (=90 K) matches the expected[4,5] transition temperature for a mixed crystal with $x = 0.10$, and we take it to represent such a transition. In support of this conclusion, the magnitude of the pressure dependence of T_{c2} is characteristic of a FE transition (see later discussion). Both T_{c1} and T_{c2} are frequency independent as expected for equilibrium FE transitions. Finally, strong frequency dispersion in both $\varepsilon'_a(T)$ and $\varepsilon''_a(T)$ around T_g are the hallmarks of relaxational phenomena associated with the freezing of local polar configurations. These features establish T_g as the dynamic glass transition temperature.

The pressure dependences of T_{c1}, T_{c2} and T_g are shown in Figure 2, and compared in Table I with those for RDA, RDP, ADA, ADP, and RADP taken from earlier[7] work. Two features in the earlier results should be noted: (1) The pressure derivatives of T_c for the PE-FE transitions in RDA and RDP are about twice as large as those of T_N for the PE-AFE transitions in ADA and ADP; (2) The pressure derivative of T_g for the PE-PG transition in RADP ($x = 0.50$) is about the same as that of T_N of ADP suggesting that the compressibility of the ADP constituent of RADP is determining the response of the glass transition. Within experimental uncertainty, dT_{c1}/dP of the RADA ($x = 0.10$) sample is the same as dT_c/dP for RDA, strengthening the argument that this sample contains sufficiently large regions of essentially pure RDA. As already noted T_{c2} (=90 K) is the expected PE-

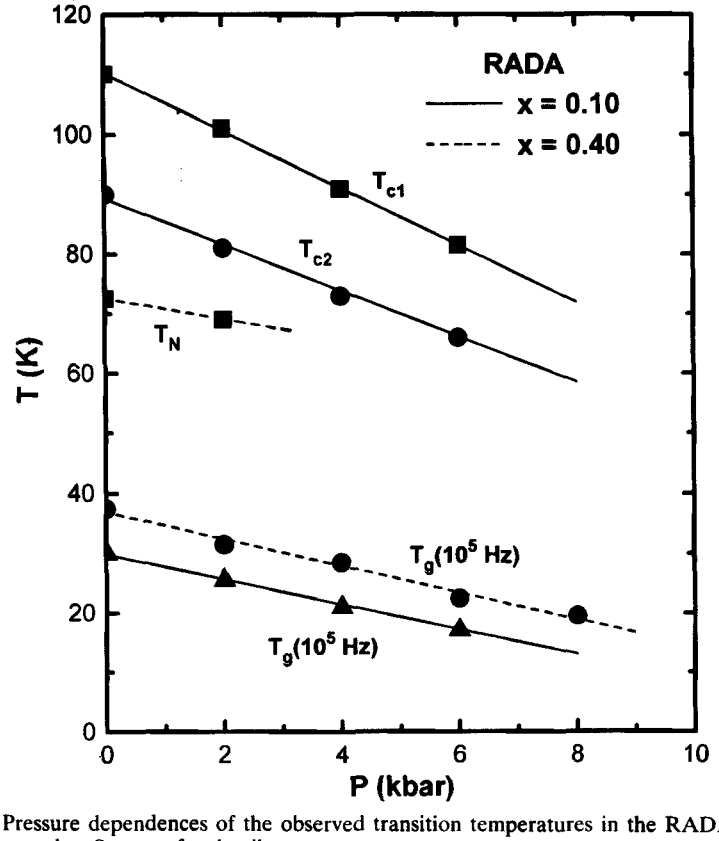

FIGURE 2 Pressure dependences of the observed transition temperatures in the RADA:$x = 0.10$ and $x = 0.40$ samples. See text for details.

TABLE I

Comparison of the pressure derivatives of the transition temperatures of the RADA samples with earlier results on FE, AFE and proton-glass (PG) transitions in other members of the KDP family: $T_x = T_c$, T_N or T_g

Crystal	Transition	T_x (K)	dT_x/dP (K/kbar)
RbH_2AsO_4	PE - FE	110.3	-4.59
RbH_2PO_4	PE - FE	146.0	-6.20
$NH_4H_2AsO_4$	PE - AFE	216.0	-1.97
$NH_4H_2PO_4$	PE - AFE	151.2	-3.39
$Rb_{1-x}(NH_4)_xH_2PO_4$: x = 0.50	PE - PG	17.3	-3.6
$Rb_{1-x}(NH_4)_xH_2AsO_4$: x = 0.10	PE - FE	110.0	-4.6
	PE - FE	90	-4.0
	PE - PG	24.5*	-2.2
$Rb_{1-x}(NH_4)_xH_2AsO_4$: x = 0.22	PE - AFE	78	-2.5
	PE - PG	29.5*	2.0
$Rb_{1-x}(NH_4)_xH_2AsO_4$: x = 0.40	PE - AFE	72.5	-2.0
	PE - PG	37.5*	-2.2

* The values of the dynamic glass transition temperatures correspond to the peaks in the ϵ_a'' (T) responses measured at 10^5 Hz.

FE transition temperature for a mixed RADA crystal with $x = 0.10$, and the relatively large magnitude of dT_{c2}/dP ($= -4.0$ K/kbar) is characteristic of a FE transition. As for T_g, dT_g/dP for this sample (-2.2 K/kbar) is of about the same magnitude as dT_N/dP for ADA, a situation akin to that observed in RADP.

There is always some vagueness in the determination of T_g. T_g is often taken as the temperature where ϵ_a' (T) first begins to show a rapid drop on cooling, i.e., the start of the dynamic glass transition, but this T is difficult to pin down accurately. A better defined temperature is T corresponding to the maximum in the ϵ_a'' (T) response. We have generally taken this T to represent T_g in the present work. A third alternative is to define T_g as the temperature at the midpoint in the ϵ_a' (T) anomaly at the glass transition. Although the values of these three definitions of T_g are different, we find that the magnitude of the slope dT_g/dP is to within experimental uncertainty independent of how we define T_g.

The coexistence of ferroelectric phases of two compositions and a glassy phase in this sample is quite remarkable, and, as noted, the pressure dependences of their transition temperatures provide considerable insight into the nature of these transitions.

RADA:x = 0.22

Figure 3 shows the temperature dependence of ε'_a measured at 10^5 Hz and different pressures. This response also shows the coexistence of long- and short-range order. Specifically, in the high temperature PE phase, ε'_a obeys a Curie-Weiss law. On cooling, $\varepsilon'_a(T)$ exhibits a broad but well-defined peak at 78 K (labeled T_N), which shifts to lower temperature with increasing pressure. There is no frequency dispersion in the vicinity of this peak. On further cooling, there is a relatively sharp decrease in ε'_a starting about 40 K (labeled T_g), and both the $\varepsilon'_a(T)$ and $\varepsilon''_a(T)$ responses below this temperature are characteristic of glassy behavior as shown in Figure 4.

Figure 5 shows the temperature-pressure phase diagram for this sample. The shift of the 78 K transition is nonlinear, the slope increasing with increasing pressure. Comparison of the initial slope −2.5 K/kbar of this phase boundary with the data in Table I shows that its magnitude is much closer to that of T_N of ADA (−1.97 K/kbar) than to that of T_c of RDA (−4.59 K/kbar) suggesting that the 78 K transition has AFE chai acter. We thus tentatively label the transition temperature in Figure 5 by T_N rather than by T_c. The amplitude of the $\varepsilon'_a(T)$ peak at the 78 K transition decreases, and this decrease becomes very rapid above 4 kbar as shown in Figure 3. This feature and the nonlinear decrease of T_N with pressure in Figure

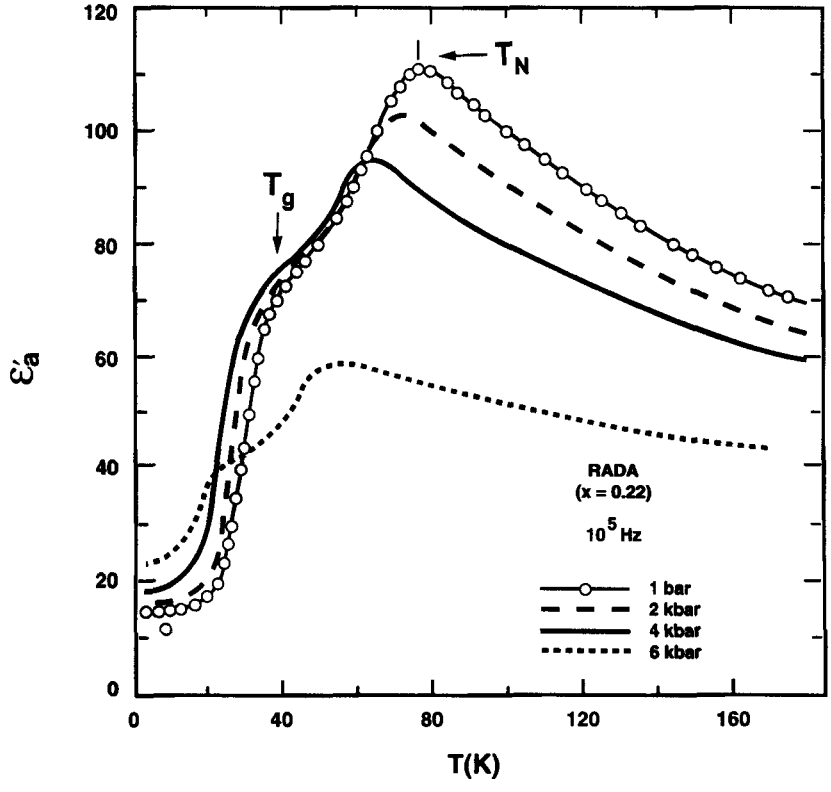

FIGURE 3 Temperature dependence of the *a*-axis dielectric constant of RADA:x = 0.22 at different pressures.

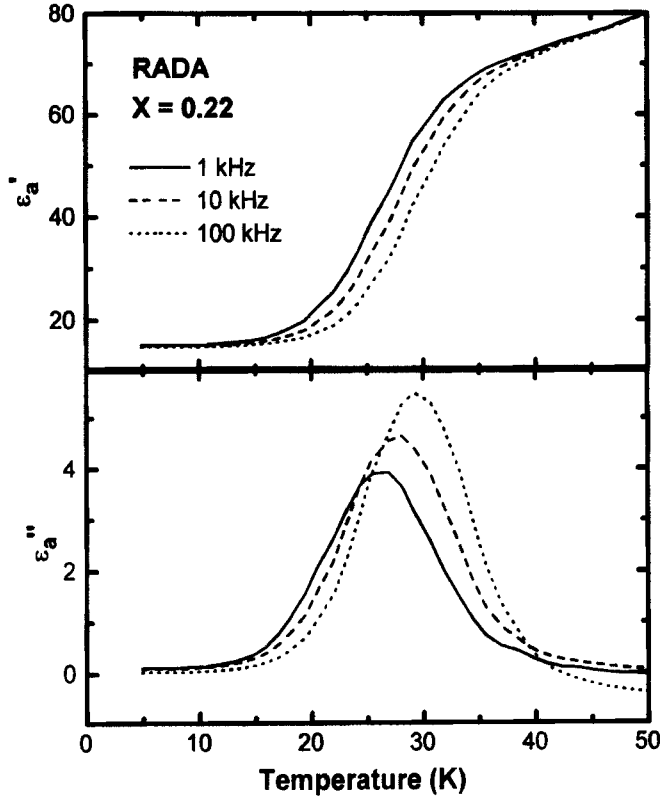

FIGURE 4 Frequency dispersion in the real and imaginary parts of the a-axis dielectric constant of RADA:x = 0.22 at 1 bar.

5 are the expected behavior for equilibrium FE and AFE phase transitions. In earlier work,[7,10] we demonstrated that $T_c(P)$ and $T_N(P)$ become nonlinear when T_c and T_N fall below ~80 K, and ultimately T_c and T_N vanish, i.e., $\rightarrow$0 K, with infinite slope, i.e. $dT_{c,N}/dP \rightarrow -\infty$. This is simply a requirement of thermodynamics for a first- or second-order equilibrium phase transition.[8] The $T_N(P)$ data in Figure 5 can be quite accurately represented by $T_N \propto [P(T_c = 0) - P]^{1/2}$, and extrapolation of this representation shows that $T_N \rightarrow 0$ K at 11 kbar. This extrapolation is depicted by the dashed line in the figure. Thus, the long-range ordered state (presumed to be AFE) in this sample should vanish for $P \geq 11$ kbar, a situation qualitatively analagous to what we have observed earlier for several members of the KDP family.[7,10] Figure 5 also shows the pressure dependence of T_g for the RADA:x = 0.22 sample. At 10^5 Hz the slope is -2.0 K/kbar and decreases slightly with decreasing frequency, a feature similar to that observed for RADP.[8] In RADP, we observed experimentally that $T_g \rightarrow 0$ K with a finite slope, specifically a linear $T_g(P)$ response, and in Figure 5 the dashed extrapolation of the $T_g(P)$ responses are intended to indicate that we expect the same behavior for RADA. For this x = 0.22 sample, the results suggest that the relaxational (glassy) response should vanish above ~16 kbar for frequencies $\leq 10^5$ Hz. We have earlier noted[8] that the vanishing of T_g with pressure with a finite slope is a unique manifestation of the non-equilibrium nature of the glassy state. This is a consequence of the existence

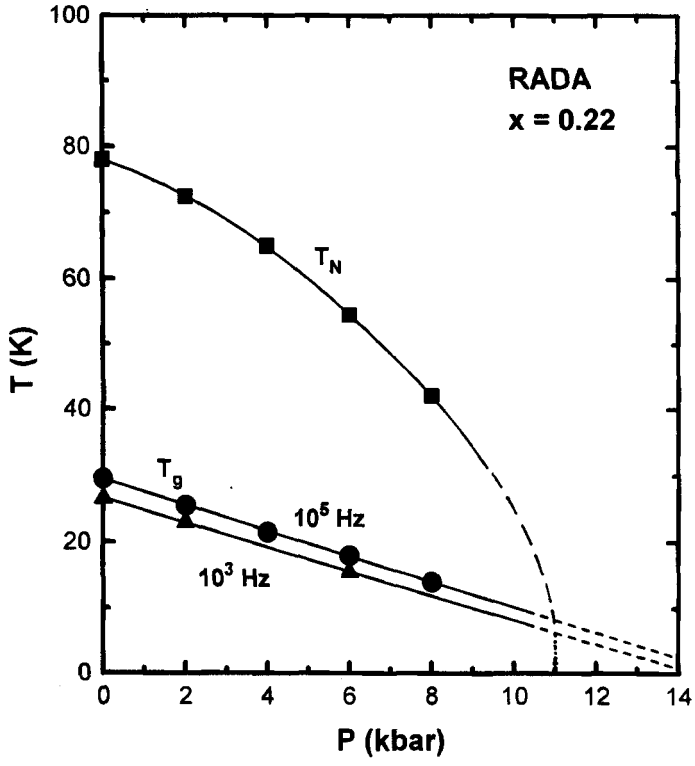

FIGURE 5 Temperature-pressure phase diagram for RADA:x = 0.22 showing the expected vanishing of the antiferroelectric (AFE) phase above ~11 kbar and of the proton glass (PG) phase above ~16 kbar.

at T = 0 K of residual configurational entropy in the glassy phase. Thus, for this sample there is coexistence of AFE and short-range (glassy) order between 0 and ~11 kbar, followed by the existence of only short-range order between ~11 and ~16 kbar and finally the vanishing of all proton ordering above ~16 kbar, leading to a paraelectric state.

RADA:x = 0.40

Figure 6 shows the ε_a' (T) response of the RADA:x = 0.40 sample at 1 bar and different frequencies. As for the other two compositions, this response demonstrates the coexistence of long- and short-range order. Again in the PE phase, ε_a' (T) obeys a Curie-Weiss law. At 1 bar, ε_a' (T) exhibits a broad dispersionless peak which we associate with the onset of AFE ordering. The pressure dependence of this peak and the relatively small magnitude of dT_N/dP (−2.0 K/kbar) are similar to the 78 K transition in the x = 0.22 sample and support the AFE character of the transition. On further cooling, the large decrease in ε_a' (T) and the frequency dispersion signify a glass transition beginning at ~50 K.

Figure 2 shows a partial P-T phase diagram for the x = 0.40 sample. When we performed the measurements on this sample, we were primarily interested in the pressure dependence of the glass transition, and we did not measure the pressure

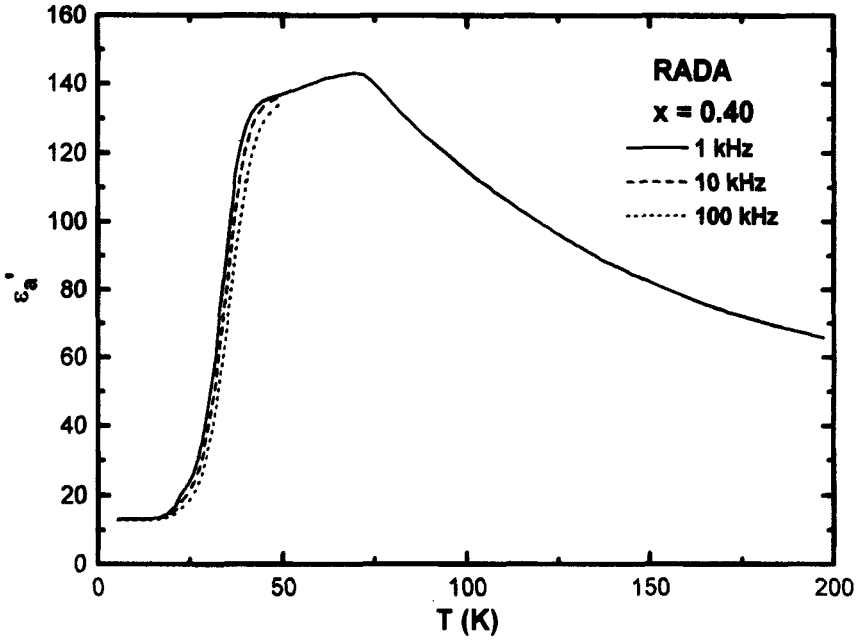

FIGURE 6 Temperature dependence of the a-axis dielectric constant of RADA:x = 0.40 at 1 bar showing the frequency dispersion in the vicinity of the proton glass transition.

dependence of T_N beyond 2 kbar. Nevertheless, the data points at 0 and 2 kbar fairly accurately establish the initial slope of T_N (−2.0 K/kbar). As for the x = 0.22 sample, we expect the magnitude of this slope to increase with increasing pressure and ultimately T_N should vanish with $dT_N/dP \rightarrow -\infty$. The pressure dependence of T_g (−2.2 K/kbar) is quite comparable to that for the other two RADA samples (Table I).

DIPOLAR RELAXATION IN THE PROTON GLASS PHASE

The dipolar relaxation process associated with the glass transition is thermally activated for the three RADA compositions studied. Over the relatively narrow range of frequencies of our measurements, the temperature dependence of the dipolar relaxation time, τ, can be fairly well fit by a simple Arrhenius expression. However, it is known from earlier work,[8] and we also find for RADA, that such a fit yields an unphysically large value for the pre-exponential term (= the attempt frequency ν_0). It is now well established that when relaxation measurements on dipolar glasses are carried out over a broad range of frequencies, it is necessary to resort to the Vogel-Fulcher (V-F) equation

$$\tau^{-1} = \nu = \nu_0 \exp[-E/(T - T_f)] \tag{1}$$

to accurately represent $\tau(T)$. In this equation ν ($=2\pi f$) is the cut-off (or lowest) frequency of the distribution of relaxation times, ν_0 is an attempt frequency, E is an activation energy in units of temperature, and T_f is a reference temperature

where all relaxation times diverge and where the distribution of τ's becomes infinitely broad. T_f can thus be viewed as the "static" dipolar freezing temperature of the relaxation process. It is not an experimentally accessibly quantity because it requires an infinite equilibration time to be reached.

We have fit the present data to Equation (1). An example is shown in Figure 7 for RADA:x = 0.22. At 1 bar a very good fit is obtained with T_f = 15 K which yields E = 246 K and $\nu_0 = 1.44 \times 10^{13}$ Hz, values comparable to those obtained for RADP.[1,8] We should note, however, that the quality of the fit was not very sensitive to the choice of T_f around 15 K. Data over a broader frequency range are needed to refine the fitting parameters. Figure 7 also shows results at 6 kbar. In this case the data are fit with T_f = 6 K which yield E = 199 K and $\nu_0 = 1.06 \times 10^{13}$ Hz. The other two RADA compositions yielded similar results.

Our results clearly show that pressure lowers both E and T_f. The formation of the proton glass state is associated with the freezing of protonic motion in the O—H···O hydrogen bonds. The activation energy E relates to the average energy barrier between different orientations of the dipoles. Pressure is known to lower this barrier,[7,8] and the consequences are lower E and T_g, or T_f. For sufficiently high pressure, E becomes sufficiently small (or vanishes) allowing the dipoles to reorient or tunnel freely between different orientations even at the lowest tem-

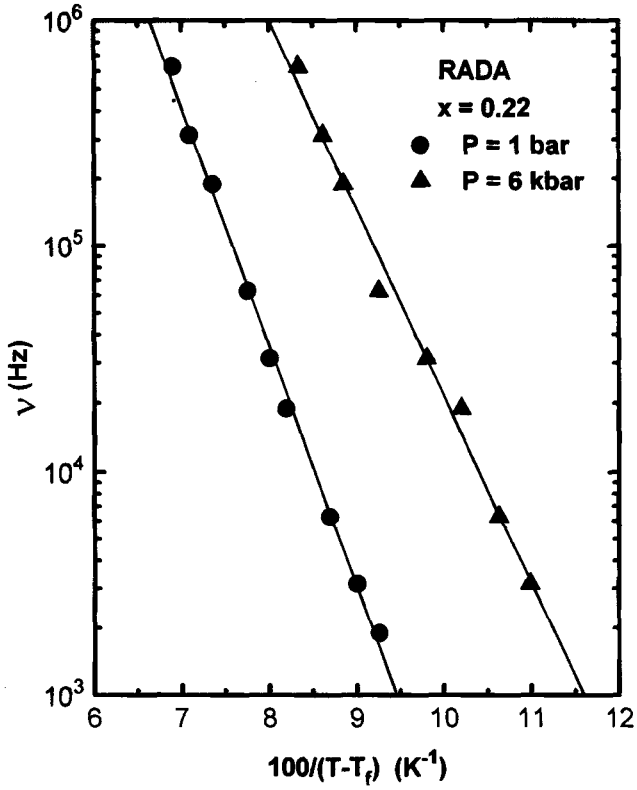

FIGURE 7 Fit of the temperature dependence of the cut-off, or lowest frequency of the distribution of dipolar relaxation times ($\nu = 1/\tau$, where τ is the relaxation time) to the Vogel-Fulcher equation at 1 bar (T_f = 15 K) and 6 kbar (T_f = 6 K).

peratures. In such a circumstance, there is no possibility for (short-range) dipolar order, and the glassy state is expected to vanish. We have observed this behavior in RADP[8] and the present results suggest that it should obtain for the RADA samples as well, but at a higher pressure than was possible with the apparatus used.

CONCLUDING REMARKS

The coexistence of *ferroelectric* order and proton glass in RADA was first observed by Trybula *et al.*[4] and has been further investigated by Howell *et al.*[5] Those studies showed that the coexistence region extends from $x \cong 0.05$ to $x \cong 0.16$. As discussed above, the present results suggest that *antiferroelectric* order and proton glass also coexist in both the $x = 0.22$ and $x = 0.40$ samples. Our $x = 0.10$ sample exhibited coexistence of FE order and proton glass as expected, but, additionally, there was evidence that this sample apparently contained a small pure RDA seed in it. The $\varepsilon_a'(T)$ response of our $x = 0.22$ sample differs from earlier results in that this sample shows coexistence between an ordered (AFE) phase and proton glass at low temperature, whereas the earlier work[3,4] indicates that composition in the $0.20 \leq x \leq 0.4$ range exhibit only a single PE-PG transition on cooling. The reason for this difference is not known at present, but it could be due to uncertainties in composition in the various samples or to a lack of detailed knowledge of the phase diagram.

More research needs to be done to establish the details of the phase diagram and the nature of the coexistence regions. This coexistence is undoubtedly due to the presence of interpenetrating ordered and paraelectric clusters with short correlation lengths, corresponding to regions of compositional inhomogeneities, as has been suggested earlier.[4]

It can be seen from Figures 1 and 3 that the low-temperature limiting value of ε_a' (i.e., in the low temperature phase at 4 K) increases considerably with pressure. A similar effect was observed earlier in studies on KDP, RDP and ADP.[10,11] A physical explanation is that as the double-minimum "average" well goes toward a single minimum with pressure, the curvature at the bottom has to decrease because it goes to zero just at the pressure where the minimum becomes single. Lower curvature implies greater response to an external (electric) driving field, hence higher permittivity (or ε_a').

It has been observed[4-6] that T_g is weakly dependent on composition over most of the range of stability of the PG phase. We find that dT_g/dP is also essentially independent of composition (see Table I).

The temperature dependence of the dipolar relaxation time associated with the glass transition in the RADA samples can be well represented by the Vogel-Fulcher equation. The resulting attempt frequencies, (ν_0), activation energies (E), and limiting "static" freezing temperatures (T_f) are comparable in magnitude to those obtained for RADP. Both E and T_f decrease with pressure, effects that can be understood in terms of changes in the potential for protonic motion along the O—H···O hydrogen bonds.

One of the most intriguing properties of crystals of the KDP family is the large hydrogen isotope effect on the FE and AFE properties. Even larger isotope effects

are also evident in the PG transition temperatures of both the RADP[8] and RADA[5] systems. Specifically, T_g's nearly triple on deuteration. A large isotope effect is also seen in the magnitude of dT_g/dP of RADP[8] which decreases from -3.6 K/kbar for RADP to -2.0 for a 72% deuterated RADP. We have not investigated any deuterated RADA samples as yet, but we expect these materials to exhibit large isotope effects in their dT_g/dP values as well.

These pressure and isotope effects can be qualitatively understood in terms of the physics of the tunneling model for KDP-type crystals. Specifically, the decreases of T_c, T_N and T_g with pressure result from an increase in tunneling frequency and a decrease in the dipolar interaction which is long-range in the case of the FE and AFE phases and short-range in the proton glass.[8] Both effects are expected and are observed for this class of hydrogen-bonded crystals.[7] In this model, at sufficiently high pressure, the tunneling field becomes larger than the dipolar field, and the FE, AFE and PG states vanish. The effects of deuteration on the transition temperatures and their pressure dependences relate to the fact that the deuterons sit deeper in their potential wells than do the protons (lower zero-point energies) and have much lower probability for tunneling between the two potential wells along the hydrogen bonds.

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