Pressure dependence of proton glass freezing in $Rb_{1-x}(NH_4)_xH_2PO_4$

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Studies of the frequency-dependent dielectric properties of a $Rb_{0.52}(ND_4)_{0.48}D_2PO_4$ (72% deuterated) crystal have shown that the deuteron glass-freezing temperature (T_g) is suppressed by hydrostatic pressure at a rate of -2.0 K/kbar. This is explained in terms of the influence of pressure on the hydrogen-bond potential. It is suggested that the glassy state should be completely suppressed (i.e., $T_g \rightarrow 0$ K) at a pressure of less than 10 kbar in undeuterated crystals of similar composition.

In this paper we report and discuss the effects of hydrostatic pressure on the dielectric properties and glass transition temperature of a crystal which is becoming a classic system for studying the freezing of dipolar motion in dielectrics. There has been much effort devoted to understanding the static and dynamic properties of the glassy state. A good deal of this work has been on the interesting phenomena associated with spin-glass states in disordered magnetic systems.[1] More recently, considerable attention has been given to dipolar and quadrupolar glasses (also referred to as molecular or structural glasses). Examples of these include $(KBr)_{1-x}(KCN)_x,$[2] $K_{1-x}Li_xTaO_3,$[3] $KTa_{1-x}Nb_xO_3$ at high pressure,[4] and mixtures of ortho- and parahydrogen.[5] On cooling, these systems exhibit a slowing down of the orientational relaxation of their multipoles, ultimately resulting (below the glass transition temperature) in a frozen-in frustrated multipole state with no long-range orientational order.

The KH_2PO_4 family provides us with another intriguing system for studying short-range ordering and freezing in a randomly mixed dielectric crystal. Specifically, the system that has attracted much recent attention[6-8] is $Rb_{1-x}(NH_4)_xH_2PO_4$ (RADP). As is well known, the pure end members RbH_2PO_4 and $NH_4H_2PO_4$ transform on cooling to ordered ferroelectric (FE) and antiferroelectric (AFE) phases, respectively. Both materials have the same crystal structure with nearly the same lattice parameters, and mixed crystals can be grown over the whole composition range. For compositions with $0 \le x \le 0.2$ ferroelectric order is obtained, whereas for $0.8 \le x \le 1.0$ the crystals are antiferroelectric.[6,7] For in-between composition, i.e., $0.2 \le x \le 0.8$, there is no evidence for long-range order, but convincing evidence exists for low-temperature short-range order and the formation of a proton glass state[6-8] associated with the freezing of protonic motion. The suppression of long-range order in this composition range is a consequence of the frustration of the system caused by the random substitutions of NH_4 ions for Rb ions (or vice versa) and the resulting competition between two kinds of order-disorder configurations of the protons in their bonds. Specifically, the Rb ion tries to achieve FE order while the NH_4 ion tries to achieve AFE order.

The development of the glassy state on cooling is accompanied by strong frequency dispersion in both the real (ε') and imaginary (ε'') parts of the dielectric constant.[6,7] There is no cusp in the $\varepsilon'(T)$ response, but there is a well-defined peak in the $\varepsilon''(T)$ response, and the peak temperature is taken as the frequency-dependent proton glass-freezing temperature.[6,7] There are also anomalous changes in the lattice parameters, but no macroscopic crystal symmetry change.[6,7] The crystals remain tetragonal down to helium temperatures. There is an expansion of the unit-cell volume on proton freezing.[6,7] It is known that in crystals of the KH_2PO_4 family, asymmetric H bonds are longer than symmetric ones, and there is lattice expansion on proton ordering.[9]

Pressure can be expected to have a significant influence on the glassy behavior of this system, primarily via the pressure dependence of the hydrogen-bond length. In this system, as in other members of the KH_2PO_4 family, we picture the proton moving in a double-well potential along the bond.[10] In the high-temperature phase the protons are disordered in the potential wells leading to an effectively symmetric H bond. On freezing into the glass state, the protons freeze in one or the other of the potential minima leading to elongated asymmetric H bonds. Pressure should oppose this tendency for elongation of the H bond and accompanying expansion of the unit-cell volume, and thereby should suppress proton freezing, i.e., lowering of the glass transition temperature. Alternatively, pressure reduces the H-bond length and thereby favors a more symmetric bond with a lower energy barrier, which in turn leads to a lower glass transition temperature. For sufficiently high pressure, we can anticipate that the H bond will become effectively symmetric, so that there will be no order; i.e., the glassy state will vanish as is true of the FE- and AFE-ordered states for the pure KH_2PO_4-type crystals.[10]

In order to test these predictions we have investigated the hydrostatic pressure dependence (to 6 kbar) of the dielectric properties of a partially (72%) deuterated RADP single-crystal sample with $x = 0.48$. Deuteration raises the ordering temperature, and this crystal has a proton freezing temperature near 50 K (see discussion below).

The sample, in the form of a thin plate ~ 5 mm^2 in area and 1.5-mm thick, was cut from a clear solution-grown[8] crystal with the large faces perpendicular to the tetragonal c axis. The large faces were coated with evaporated aluminum which served as electrodes.

The real (ε') and imaginary (ε'') parts of the dielectric constant were measured as functions of frequency $(10^2-5\times10^6$ Hz), temperature (20–80 K), and hydrostatic pressure (0–6 kbar). The pressure measurements were made in an apparatus using helium gas as the pressure fluid. The experimental details are similar to those described elsewhere.[11]

Some of our results are shown in Fig. 1 as plots of ε_c' and ε_c'' versus temperature at two frequencies and for different pressures. At atmospheric pressure the $\varepsilon_c'(T)$ response exhibits the characteristic[6] S-shaped curve shown, and the $\varepsilon_c''(T)$ response exhibits a well-defined, frequency-dependent peak. The peak shifts to higher temperature with increasing frequency. This shift is shown over a broad frequency range in Fig. 2, where it is seen that the peak temperature T_{max} varies essentially linearly with log frequency over the limited temperature range indicated.[12] In Fig. 2 the $P=1$ bar data were taken at Sandia for fre-

quencies $> 10^4$ Hz and at Montana State for frequencies $\leq 10^4$ Hz. The agreement between the two sets of data is very good.

As can be seen from Figs. 1 and 2, the main effect of pressure is a simple displacement of the $\varepsilon_c'(T)$ and $\varepsilon_c''(T)$ responses to lower temperature. Figure 2 shows that the isobars of log frequency versus T_{max} are parallel. If we take T_{max} as a measure of the frequency-dependent glass transition (or proton-freezing) temperature T_g, then the results in Fig. 2 show that $dT_g/dP = -2.0\pm0.1$ K/kbar, and this slope is, to within experimental uncertainty, independent of frequency. The 6-kbar pressure range of the present experiments was not sufficient to completely suppress T_g to 0 K, but we expect to be able to effect this suppression in our 10 kbar apparatus in undeuterated RADP, where T_g at 1 bar will be lower, and the pressure derivative dT_g/dP can be expected to be larger due to tunneling. Pressure experiments on RADP are planned.

It is interesting to note here that the above value of dT_g/dP is of the same sign and comparable in magnitude to the pressure derivatives of the phase transition temperatures (T_c) of deuterated FE and AFE crystals of the KH_2PO_4 family.[10] This indicates that both (dT_c/dP) and (dT_g/dP) are more strongly influenced by the nature of the hydrogen-bond potential than by the range of the dipolar interaction, be it long or short.
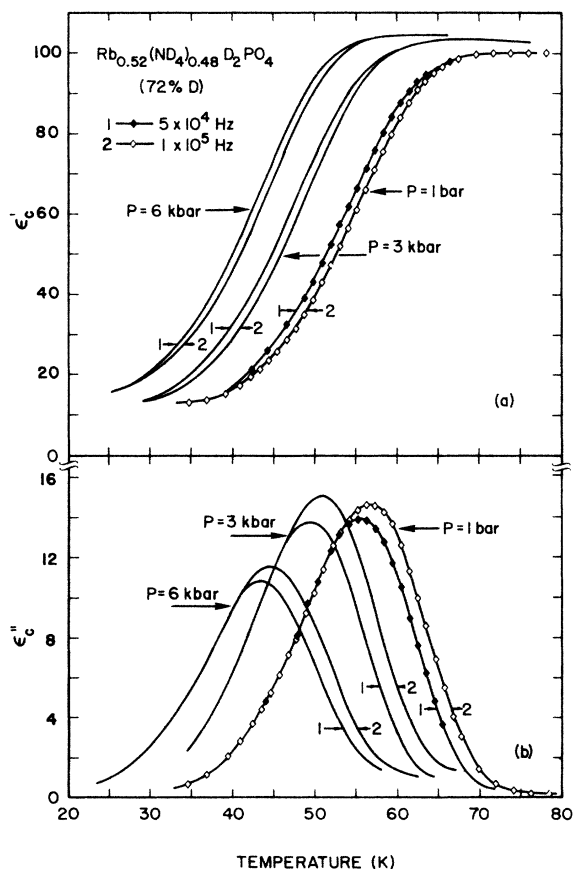

FIG. 1. Temperature dependences of the real (ε_c') and imaginary (ε_c'') parts of the dielectric constant of a 72% deuterated RADP crystal measured at different frequencies and hydrostatic pressures. The peak in the $\varepsilon_c''(T)$ response defines the frequency-dependent glass transition temperature.
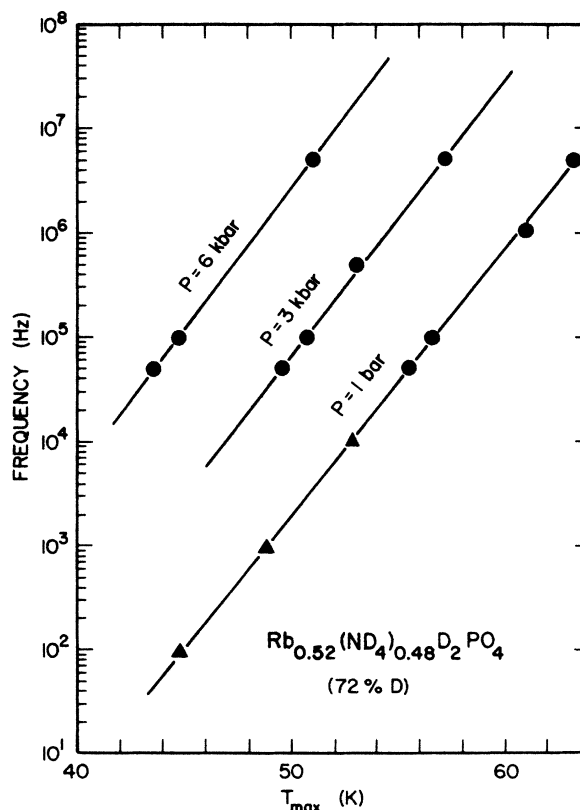

FIG. 2. A plot of the $\varepsilon_c''(T)$ peak temperature vs log measuring frequency at different pressures for the RADP crystal in Fig. 1. The displacement of the straight lines determines the shift of the glass transition temperature with pressure, which is shown to be independent of frequency.

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[12]A plot of $(T_{max})^{-1}$ vs log frequency is also linear over this temperature range.