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Proton-glass behavior in a solid solution of (betaine phosphate)_{0.15} (betaine phosphite)_{0.85}

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(Received 26 July 1994; revised manuscript received 11 October 1994)

Measurements of the dielectric permittivity are reported for a solid solution of antiferroelectric (betaine phosphate)_{0.15} and ferroelectric (betaine phosphite)_{0.85} at frequencies $20 \text{ Hz} < \nu < 1 \text{ MHz}$. The freezing phenomena in BP_{0.15}BPI_{0.85} reveal the characteristics of a transition into a dipolar glass state. The activation energy was found to be $E_b = 518 \text{ K}$ and the external bias field lowers this value up to 488 K .

Betaine phosphate [BP: $(\text{CH}_3\text{NCH}_2\text{COOH}_3\text{PO}_4)$] and betaine phosphite [BPI: $(\text{CH}_3\text{NCH}_2\text{COOH}_3\text{PO}_3)$] are molecular crystals of the amino acid betaine and phosphoric and phosphorous acids, respectively. In both compounds the inorganic components (PO_4 or PO_3 groups) are linked by hydrogen bonds to quasi-one-dimensional chains.¹ BP exhibits a ferroelastic phase transition at about 365 K followed by two phase transitions at 86 and 81 K .¹ Antiferroelectric order is established at $T_c = 86 \text{ K}$.² At this temperature the O-H...O bonds order along the one-dimensional chains and the chains are linked antiferroelectrically.³ At 355 K BPI transforms into an elastically ordered state and exhibits ferroelectric order below $T_c = 216 \text{ K}$.^{1,4} The two almost isostructural compounds form solid solutions at any concentrations.⁴ It has been shown recently that at intermediate concentrations the long-range electric order is suppressed⁴ and no spontaneous polarization occurs.^{5,6} The mixed crystal BP_{0.4}BPI_{0.6} exhibits relaxational behavior typical for an orientational glass state,⁷ with a hindering barrier $E_b = 252 \text{ K}$.

BP_{0.15}BPI_{0.85} crystals were grown by controlled evaporation from an aqueous solution. For the dielectric spectroscopy gold-plated single crystals were oriented along the monoclinic b axis. The complex dielectric constant $\epsilon^* = \epsilon' - i\epsilon''$ was measured by a capacitance bridge HP4284A in the frequency range $20 \text{ Hz} - 1 \text{ MHz}$. For the temperature-dependent measurements a Leybold VSK-4-320 cryostat was used. All measurements were performed in heating with a rate of about 0.1 K/min in the phase transition region.

For BP_{0.15}BPI_{0.85} no anomaly in ϵ' indicating the polar phase transition can be detected down to the lowest temperatures.^{5,6} A Curie-Weiss law is valid for ϵ' in the temperature range $300 - 170 \text{ K}$. At lower temperatures the deviation from the Curie-Weiss law is very significant. A similar behavior observed in $\text{Rb}_{1-x}(\text{NH}_4)_x\text{H}_2\text{AsO}_4$ has been explained by random field freezing.^{8,9} This means that in

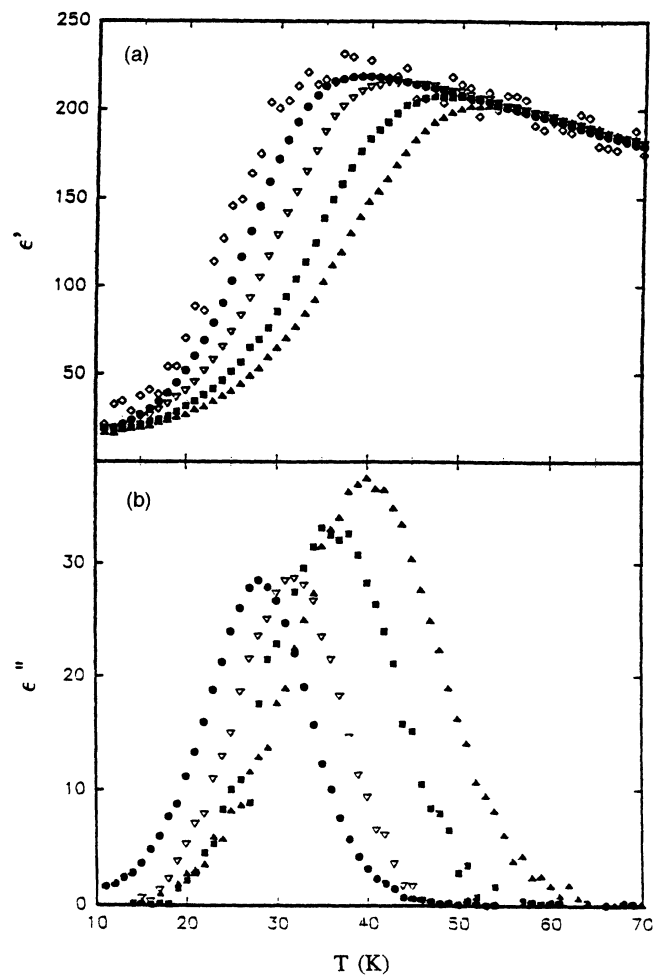


FIG. 1. Temperature dependence of ϵ' and ϵ'' of BP_{0.15}BPI_{0.85} at the following frequencies (kHz): (\diamond) 0.2; (\circ) 2; (∇) 20; (\blacksquare) 200; (\blacktriangledown) 1000.

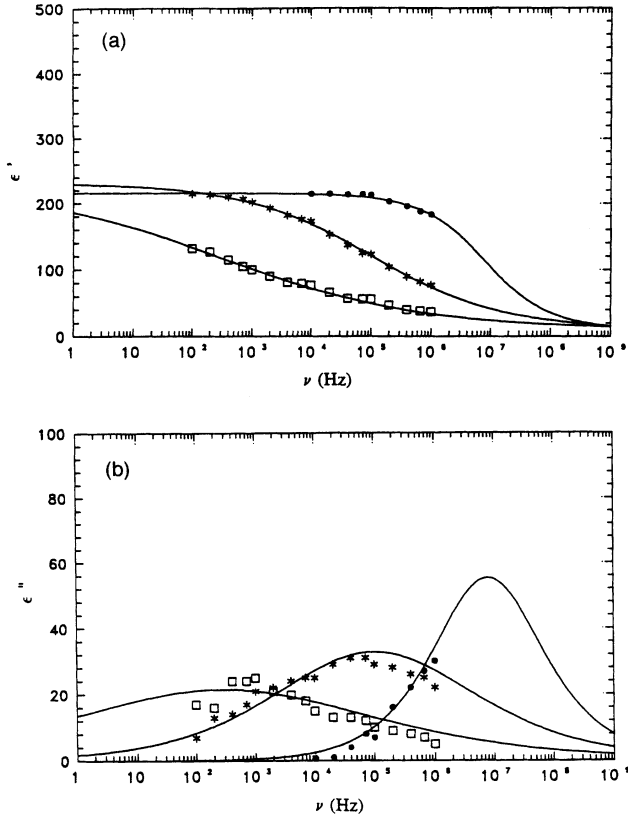


FIG. 2. Frequency dependence of ϵ' (a) and ϵ'' (b) of $\text{BP}_{0.15}\text{BPI}_{0.85}$ at the following temperatures (K): (\square) 24; ($*$) 32; (\bullet) 45.

$\text{BP}_{0.15}\text{BPI}_{0.85}$ random field freezing occurs at about $T_F \approx 170$ K. At temperatures lower than 60 K dispersion effects dominate the dielectric response [Figs. 1(a) and (b)]. The frequency dependence of ϵ' and ϵ'' at fixed temperatures provides clear evidence that the ϵ'' frequency dependence is much broader than 1.14 decades as it should be for the Debye dispersion [Figs. 2(a) and (b)]. The freezing phenomena in $\text{BP}_{0.15}\text{BPI}_{0.85}$ reveal the characteristics of a transition into a dipolar glass state: the slowing down of the dipolar degrees of freedom exhibits broad distribution of the relaxation rates, with a width of the distribution exceeding by orders of magnitude the width of a monodisperse Debye process.^{10,11} Dipolar glasses have been studied in detail: the most prominent examples are $\text{K}_{1-x}\text{Li}_x\text{TaO}_3$,¹² $\text{Rb}_{1-x}(\text{NH}_4)_x\text{H}_2\text{PO}_4$,¹³ and $\text{Rb}_{1-x}(\text{NY}_4)_x\text{H}_2\text{AsO}_4$.^{8,9} In orientational glasses (OG's) the reorienting moments freeze-in in random configurations.¹⁰ The interplay of site disorder and frustrated interactions is responsible for the freezing transition which bears similarities with the spin-glass transitions in dilute magnetic systems¹⁴ and with relaxational dynamics in canonical glasses.¹⁵

The experimental data were fitted with the Cole-Cole function:¹⁶ $\epsilon^* = \epsilon_\infty + \Delta\epsilon/[1 + (i\omega\tau)^{1-\alpha}]$, where $\Delta\epsilon$ is the relaxator strength, τ is the most probable relaxation time, α is the distribution coefficient, ϵ_∞ is the contribution of all higher-frequency modes to the dielectric permittivity, and $\omega = 2\pi\nu$ is the angular velocity. The calculated data using the Cole-Cole formula are shown as solid lines in Fig. 2. The

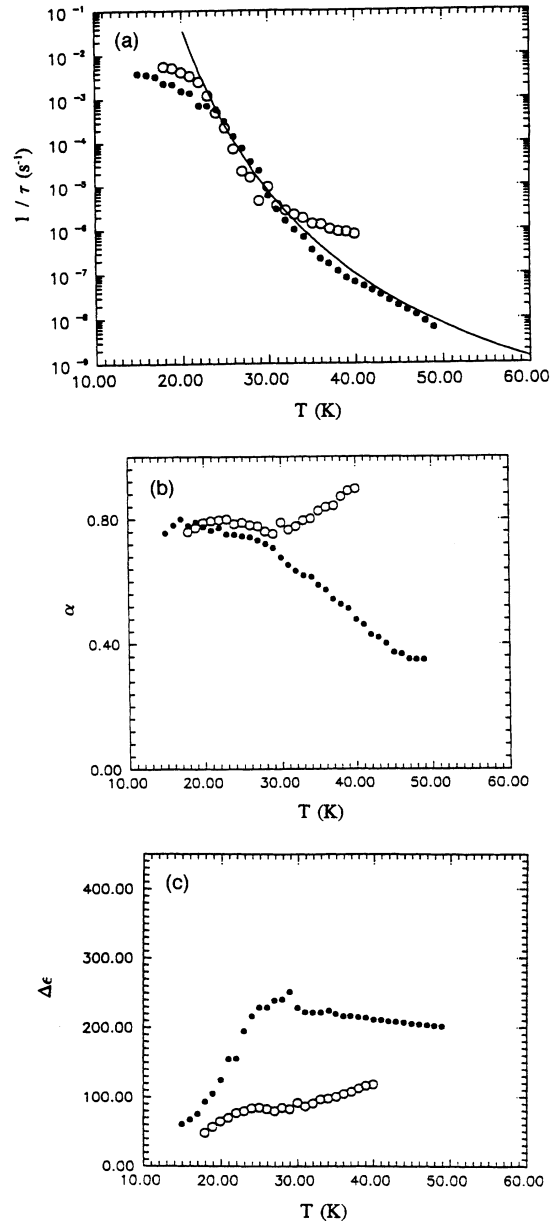


FIG. 3. Temperature dependence of the fit parameters τ (a), α (b), and $\Delta\epsilon$ (c) [(\bullet) 0 V/cm bias field, (\circ) 0.57 kV/cm bias field].

temperature dependence of the fit parameters $\Delta\epsilon$, α , and τ are shown in Fig. 3. Comparing the Cole-Cole formula with the Kohlrausch-Williams-Watts function¹⁷ one sees that $\alpha = 1 - \beta$, and therefore the here obtained value for α is very close to that observed in $\text{BP}_{0.4}\text{BPI}_{0.6}$.⁷ The distribution function of the relaxation rate is given¹⁸ by $F(\tau) = \sin(\alpha\pi) / \{\cosh[(1-\alpha)\ln(2\pi\tau_1/\tau)] - \cos(\alpha\pi)\}$, where τ_1 is the most probable value of the relaxation rate. When $\alpha > 0.5$ the relaxation rates are distributed over three decades. Such a wide distribution of relaxation rates can mean that nonequilibrium effects or quantum fluctuations play a significant role at these temperatures where α reaches high values. The most probable relaxation rate follows an Arrhenius law $\tau = \tau_0 \exp(E_b/kT)$, as indicated in Fig. 3(a) by the solid line with $\tau_0 = 2.4 \times 10^{-13}$ s and $E_b = 518$ K. The activation en-

ergy E_b is significantly higher than in $\text{BP}_{0.4}\text{BPI}_{0.6}$.⁷ Deviations from purely thermally activated processes at low temperatures might indicate the increasing importance of tunneling transitions at low temperatures as in $\text{KI}:\text{NH}_4\text{I}$.¹⁹ The activation energy E_b is similar as in pure BPI as shown by the H^1 electron-nuclear double resonance experiment²⁰ and dielectric measurements.²¹ In the glassy state the protons are frozen-in at random in the double minima potentials,¹³ along the one-dimensional chains without any long-range order. The distribution of relaxation times are symmetrically shaped and can be explained in terms of a distribution of energy barriers.^{10,13} The cusp of static dielectric permittivity $\Delta\epsilon$ indicates the temperature $T_a = 30$ K at which freezing of random bonds occurs [Fig. 3(c)].

An external bias field $E = 0.57$ kV/cm significantly lowers the dielectric permittivity and changes the temperature behavior of ϵ'' . This is shown in the temperature dependence of fit parameters α and $\Delta\epsilon$ (Fig. 3). The bias field causes a much

wider distribution of relaxation times, but at higher frequencies the temperature behavior should be similar to that without an external bias field. The relaxation times do not change in the low-temperature region up to 33 K, but at higher temperatures the deviation is quite significant. This deviation should remain till the random-field freezing temperature. The fit provided the parameters: $\tau_0 = 7.1 \times 10^{-13}$ s and $E_A = 488$ K.

Finally, one can conclude that $\text{BP}_{0.15}\text{BPI}_{0.85}$ exhibits an orientational glass state at low temperatures where the protons are frozen-in along the one-dimensional chains. The loss peaks are broad indicating a wide distribution of relaxation rates. The value of the activation energy clearly manifests that the orientational glass state is related with the proton order. Therefore, $\text{BP}_{0.15}\text{BPI}_{0.85}$ state is a proton glass.

This work was supported by Alexander von Humboldt Stiftung.

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