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LETTER TO THE EDITOR

Proton glass behaviour in a solid solution of γ -irradiated deuterated betaine phosphate_{0.15} betaine phosphite_{0.85}

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Abstract. Measurements of the dielectric permittivity are reported for a deuterated solid solution of γ -irradiated antiferroelectric (betaine phosphate)_{0.15} ferroelectric (betaine phosphite)_{0.85} at frequencies $20 \text{ Hz} < \nu < 1 \text{ MHz}$. The freezing phenomena in DPB_{0.15}DBPI_{0.85} revealed the characteristics of a transition into a dipolar glass state. The activation energy was found to be $E_b = 311.6 \text{ K}$ (0.027 eV). The Kutnjak model showed a non-typical glass behaviour with an estimated glass temperature of 55.4 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 form 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 concentration [4]. It has been shown recently that at intermediate concentrations the long-range electric order is suppressed [4] and no spontaneous polarization occurs [5,6]. The mixed crystal BP_{0.4}BPI_{0.6} exhibits relaxational behaviour typical for an orientational glass state [7], with a hindering barrier $E_b = 252 \text{ K}$ (0.022 eV). 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]. The most probable relaxation rate follows an Arrhenius law $\tau = \tau_0 \exp(E_b/kT)$, with $\tau_0 = 2.4 \times 10^{-13} \text{ s}$ and $E_b = 518 \text{ K}$ (0.045 eV) [8]. The activation energy E_b is significantly higher than in BP_{0.4}BPI_{0.6} [7]. An external bias field $E = 0.57 \text{ kV cm}^{-1}$ significantly lowers the dielectric permittivity and changes the temperature behaviour of ϵ'' of BP_{0.15}BPI_{0.85} [8]. The relaxation time with bias field follows an Arrhenius law with parameters $\tau_0 = 7.1 \times 10^{-13} \text{ s}$ and $E_A = 488 \text{ K}$ (0.042 eV). 1 Mrad γ -irradiation increases the activation energy to 513 K (0.044 eV) [9].

Deuteration of hydrogen bonded ferroelectrics leads to significant changes of the dielectric properties and shifts the phase transition temperature to higher values [10–16]. This isotope effect has already been studied in deuterated crystals of the betaine family, namely betaine phosphate (DBP) and betaine phosphite (DBPI) [12–16]. The low-frequency dielectric measurements of DBPI showed [15,16] that the ferroelectric phase transition is

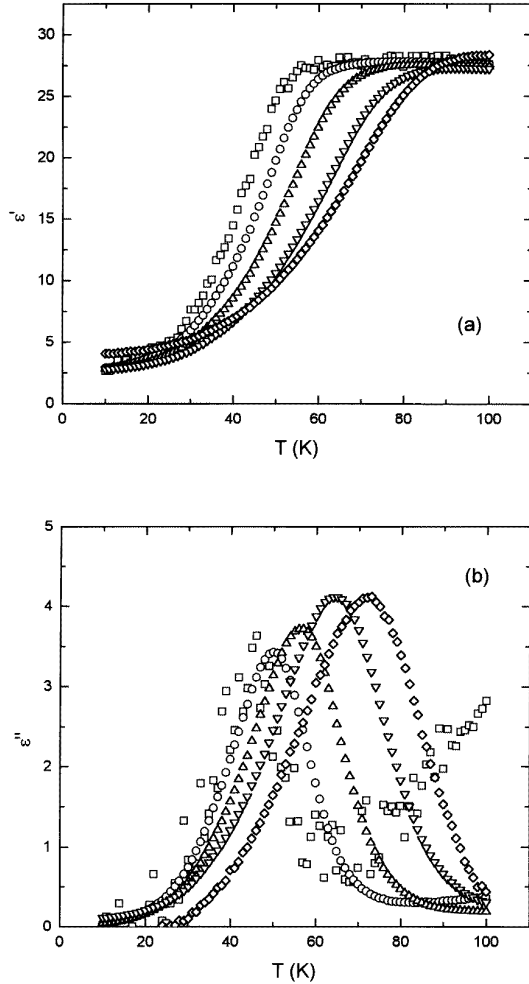


Figure 1. The temperature dependences of (a) ϵ' and (b) ϵ'' of $\text{DBP}_{0.15}\text{DBPI}_{0.85}$ at the following frequencies (kHz): \square , 0.2; \circ , 2; \triangle , 20; ∇ , 200; \diamond , 1000.

shifted up to 297 K. EPR studies revealed that the ferroelectric phase transition is related to the simultaneous ordering of deuterons in the O–D...O bonds [15].

In this letter we present the results of dielectric investigations of γ -irradiated $\text{DBP}_{0.15}\text{DBPI}_{0.85}$ samples.

$\text{DBP}_{0.15}\text{DBPI}_{0.85}$ crystals were grown by controlled evaporation from D_2O solution containing betaine and H_3PO_3 and H_3PO_4 . By analogy with DBPI [15] one expects that only the protons in the O–H...O bonds of the inorganic H_3PO_3 and H_3PO_4 groups should be replaced by deuterons. Crystals for measurements were irradiated by γ -rays with a dose of 1 Mrad. 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 Hz–1 MHz. For the temperature dependent measurements a Leybold VSK-4-320 cryostat was used. All measurements were performed on heating at a rate of about 0.1 K min^{-1} in the phase transition region. The sample was a thin plate of 0.25 mm thickness and 8.5 mm^2 area coated with gold electrodes.

A Curie–Weiss law is valid for ϵ' in the temperature range 300–200 K. At lower temperatures the deviation from the Curie–Weiss law is very significant. A similar behaviour

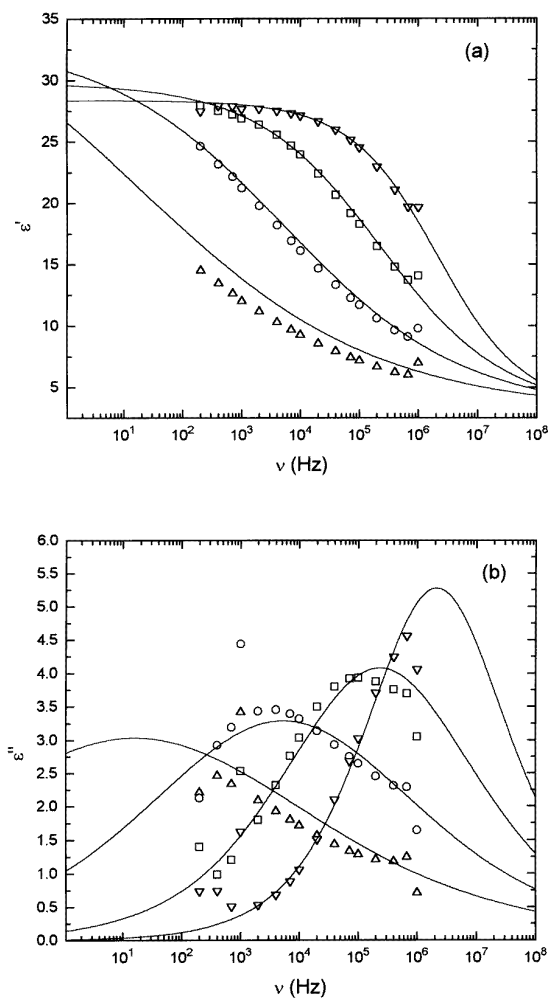


Figure 2. The frequency dependences of (a) ϵ' and (b) ϵ'' of $\text{DBP}_{0.15}\text{DBPI}_{0.85}$ at the following temperatures (K): Δ , 40; \circ , 50; \square , 60; ∇ , 70.

observed in $\text{Rb}_{1-x}(\text{NH}_4)_x\text{H}_2\text{AsO}_4$ has been explained by random field freezing [17, 18]. This means that in $\text{DBP}_{0.15}\text{DBPI}_{0.85}$ random field freezing occurs at temperatures lower than 200 K. At temperatures lower than 80 K dispersion effects dominate the dielectric response (figure 1). The maximum value of ϵ' is 28 and is much lower than in the non-deuterated sample [8, 9].

The frequency dependences of ϵ' and ϵ'' at fixed temperatures provide clear evidence that the ϵ'' frequency dependence is much broader than 1.14 decades as it should be for the Debye dispersion (figure 2). The Cole–Cole diagram (figure 3) also shows that there is a wide distribution of relaxation times. The freezing phenomena in $\text{DBP}_{0.15}\text{DBPI}_{0.85}$ reveal the characteristics of a transition into a dipolar glass state: the slowing down of the dipolar degrees of freedom exhibits a broad distribution of the relaxation rates, with the width of the distribution exceeding by orders of magnitude the width of a monodispersive Debye process [19, 20]. Dipolar glasses have been studied in detail: the most prominent examples are $\text{K}_{1-x}\text{Li}_x\text{TaO}_3$ [21], $\text{Rb}_{1-x}(\text{NH}_4)_x\text{H}_2\text{PO}_4$ [22], and $\text{Rb}_{1-x}(\text{NH}_4)_x\text{H}_2\text{AsO}_4$ [17, 18]. In orientational glasses (OGs) the reorienting moments freeze-in in random configurations. The interplay of site disorder and frustrated interactions is responsible for the freezing

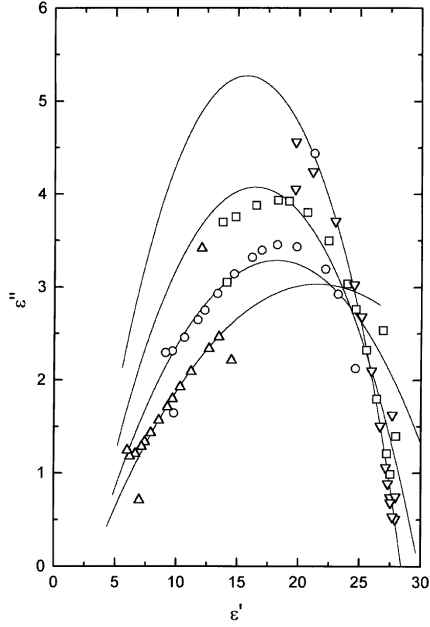


Figure 3. Cole–Cole diagrams of $\text{DBP}_{0.15}\text{DBPI}_{0.85}$ at the following temperatures (K): \triangle , 40; \circ , 50; \square , 60; ∇ , 70.

transition, which bears similarities to the spin-glass transitions in dilute magnetic systems [23] and to relaxational dynamics in canonical glasses [24]. The experimental data were fitted with the Cole–Cole function [25]:

$$\varepsilon^* = \varepsilon_\infty + \Delta\varepsilon/[1 + (i\omega\tau)^{1-\alpha}]$$

where $\Delta\varepsilon$ 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 data calculated using the Cole–Cole formula are shown as solid lines in figures 2 and 3. The temperature dependences of the fit parameters $\Delta\varepsilon$, α , and τ are shown in figure 4.

When $\alpha > 0.5$ the relaxation rates are distributed over three decades. Such a wide distribution of relaxation rates can mean that non-equilibrium effects or quantum fluctuations play a significant role at these temperatures where α reaches high values. Deviations from purely thermally activated processes at low temperatures might indicate the increasing importance of tunnelling transitions at low temperatures as in $\text{KI:NH}_4\text{I}$ [26]. The activation energy obtained, $E_b = 311$ K (0.027 eV), is similar to that in pure BPI as shown by ^1H ENDOR experiment [27] and dielectric measurements [28] and in $\text{BP}_{0.15}\text{BPI}_{0.85}$ [8, 9]. In the glassy state the protons are frozen-in at random in the double-minimum potentials, as in RADP [22], along the one-dimensional chains without any long-range order. The distributions of relaxation times are symmetrically shaped and can be explained in terms of a distribution of energy barriers [25, 26]. The cusp of the dispersion strength $\Delta\varepsilon$ indicates the temperature $T_a \approx 50$ K at which freezing of random bonds occurs (figure 4).

The observed experimental data were used for calculations with the model recently suggested by Kutnjak *et al* [29]. For this purpose the variable $\delta(\nu) = [\varepsilon'(\nu) - \varepsilon_\infty]/[\varepsilon_s - \varepsilon_\infty]$ is introduced with ε_s and ε_∞ denoting static and high-frequency permittivity. By determining the value of the frequency ν_δ for a given δ and for all accessible temperatures it is possible to construct an Arrhenius plot, the so called δ -plot shown in figure 5. Notable cases are $\delta \rightarrow 0$ and $\delta \rightarrow 1$ which correspond to the high- and low-frequency ends of the spectrum

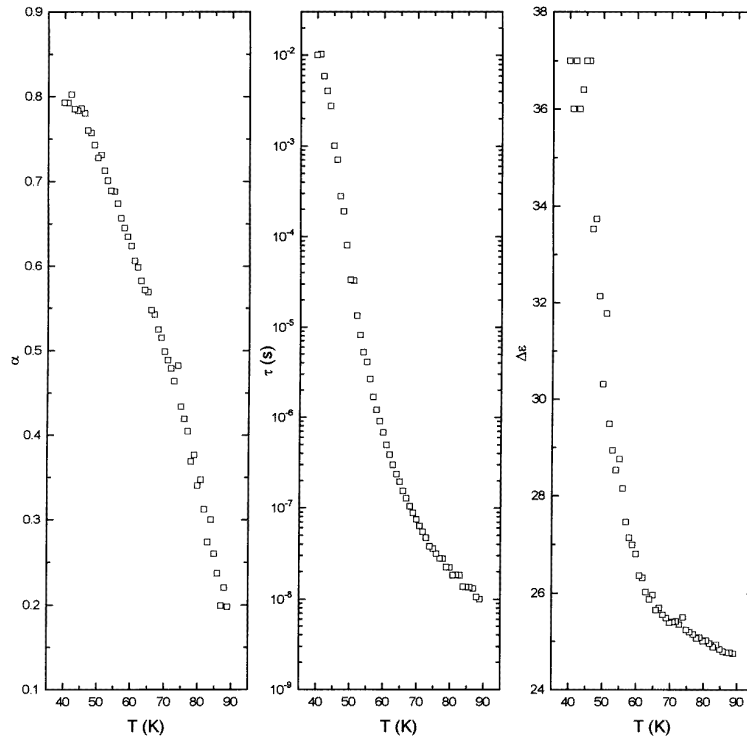


Figure 4. The temperature dependences of the fit parameters α , τ and $\Delta\epsilon$.

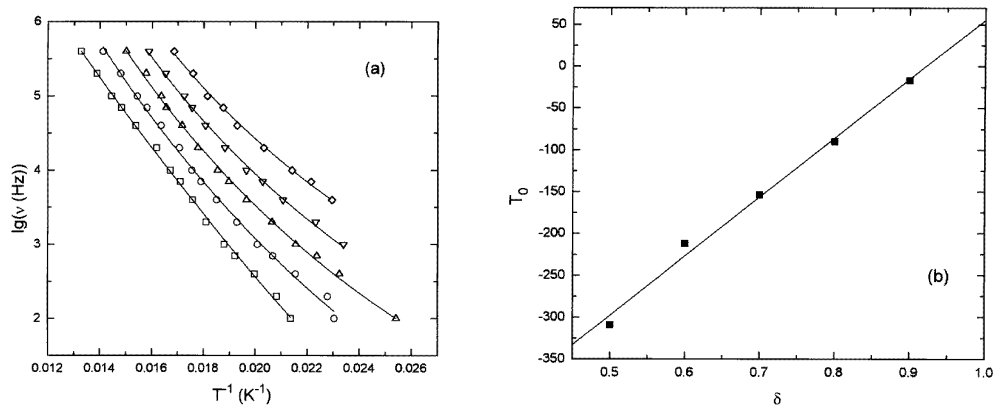


Figure 5. An Arrhenius representation (δ -plot) of data obtained from the reduced dielectric constant $\delta(\nu) = [\epsilon'(\nu) - \epsilon_\infty]/[\epsilon_s - \epsilon_\infty]$ at the following δ -values: (a) \square , 0.9; \circ , 0.8; \triangle , 0.7; ∇ , 0.6; \diamond , 0.5 and (b) the T_0 dependence on δ .

of relaxation times. Most interesting is of course the limit $\delta \rightarrow 1$ which reveals the temperature evolution of the slowest element in the spectrum. From figure 5 it is evident that for $\delta < 0.95$ the curves develop considerable curvature. The solid lines in this figure have been calculated using the Vogel-Fulcher expression $\nu_\delta = \nu_0 \exp(-B/(T - T_0))$ with

a δ -dependent Vogel temperature [29]. In figure 5(b) we show T_0 as a function of δ for $0.5 < \delta < 0.9$. It is clearly seen that for $\delta \rightarrow 1$ the Vogel temperature extrapolates to 55.4 K. It has to be noted that Vogel temperatures obtained from figure 5(a) are negative whereas in BP_{0.4}BPI_{0.6} it had a positive value [30]. This fact can be explained as follows: the case of BP_{0.4}BPI_{0.6} was an ergodic glass state, and in our case we observe a non-ergodic glass state.

Finally, one can conclude that DBP_{0.15}DBPI_{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 activation energy clearly manifests that the orientational glass state is related to the proton order.

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