Proton glass behaviour in a solid solution of γ-irradiated betaine phosphate$_{0.15}$ betaine phosphite$_{0.85}$

LETTER TO THE EDITOR

Proton glass behaviour in a solid solution of γ-irradiated betaine phosphate$_{0.15}$ betaine phosphite$_{0.85}$

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Abstract. 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 Hz $< \nu < 1$ MHz. The freezing phenomena in PB$_{0.15}$BPI$_{0.85}$ reveal the characteristics of a transition into a dipolar glass state. The activation energy was found to be $E_b = 525$ K and an external bias field lowers this value to 513 K.

Betaine phosphate (BP, $(CH_3)NCH_2\ COOH_3PO_4$) and betaine phosphite (BPI, $(CH_3)NCH_2COOH_3PO_3$) 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 $T_c = 86$ K [2]. At this temperature the $O–H\cdots O$ 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 $T_c = 216$ 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 suppressed [4] and no spontaneous polarization occurs [5, 6]. The mixed crystal BP$_{0.4}$BPI$_{0.6}$ exhibits relaxational behaviour typical for a orientational glass state [7], with a hindering barrier $E_b = 252$ K. 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 $\tau_0 = 2.4 \times 10^{-13}$ s $E_b = 518$ K [8]. The activation energy E_b is significantly higher than in BP$_{0.4}$BPI$_{0.6}$ [7]. An external bias field $E = 0.57$ 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 follows an Arrhenius law with parameters $\tau_0 = 7.1 \times 10^{-13}$ s and $E_A = 488$ K.

In this paper we present the results of the dielectric investigations of γ-irradiated BP$_{0.15}$BPI$_{0.85}$ samples.

BP$_{0.15}$BPI$_{0.85}$ crystals were grown by controlled evaporation from aqueous solution. Crystals for measurements were irradiated by γ-rays with doses of 1 Mrad. For the dielectric spectroscopy gold-plated single crystals were oriented along the monoclinic b axis. The complex dielectric constant $\varepsilon^* = \varepsilon' - i\varepsilon''$ was measured by a capacitance bridge HP4284A

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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.
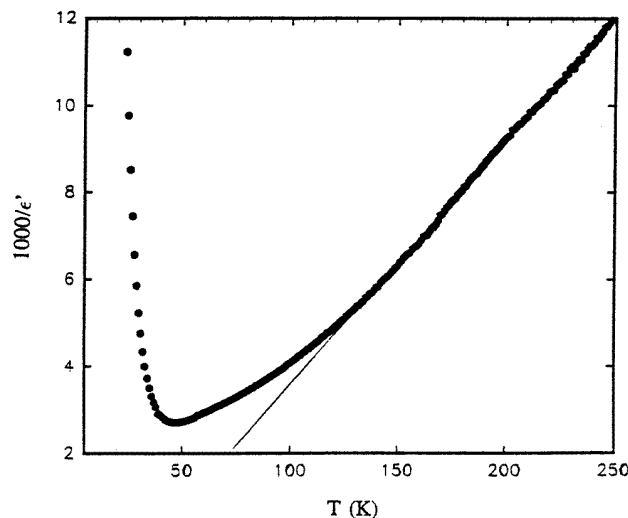
Figure 1. The temperature dependence of $1/\varepsilon'$ in a γ-irradiated crystal of BP$_{0.15}$BPI$_{0.85}$ at 200 kHz.

A Curie–Weiss law is valid for ε' in the temperature range 300–170 K. At lower temperatures the deviation from the Curie–Weiss law is very significant (figure 1). A similar behaviour observed in Rb$_{1-x}$(NH$_4$)$_x$H$_2$AsO$_4$ has been explained by random field freezing [9, 10]. This means that in BP$_{0.15}$BPI$_{0.85}$ random field freezing occurs at temperatures lower than 170 K. At temperatures lower than 60 K dispersion effects dominate the dielectric response (figure 2). γ-irradiation significantly changed the static dielectric permittivity in the phase transition region: in the γ-irradiated sample we observe $\varepsilon_{max} \approx 400$ whereas in the non-irradiated sample $\varepsilon_{max} \approx 250$ [8]. Such an effect has already been observed in NaNO$_2$ [11]. Such an effect most probably is caused by the existence of a bias field inside the crystal which can be caused by defects. The new defects created by γ-irradiation diminished the influence of the original defects and because the new defects most probably do not cause an internal electric field the dielectric constant increases. Without irradiation dielectric permittivity is suppressed by the internal electric field caused by defects.

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 (figure 3). The Cole–Cole diagram (figure 4) also shows that there is a wide distribution of relaxation times. The freezing phenomena in BP$_{0.15}$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 monodispersive Debye process [12, 13]. Dipolar glasses have been studied in detail: the most prominent examples are K$_{1-x}$Li$_x$TaO$_3$ [14], Rb$_{1-x}$(NH$_4$)$_x$H$_2$PO$_4$ [15], and Rb$_{1-x}$(NH$_4$)$_x$H$_2$AsO$_4$ [9, 10]. 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 transition which bears similarities with the spin-glass transitions in dilute magnetic systems
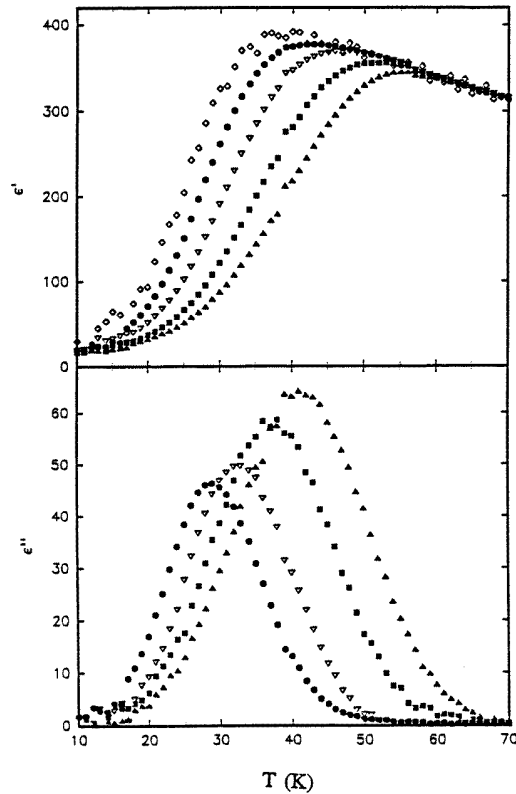
Figure 2. The temperature dependence of ε' and ε'' of $BP_{0.15}BPI_{0.85}$ at the following frequencies (kHz): $\Diamond$, 0.2; $\bullet$, 2; $\triangledown$, 20; $\blacksquare$, 200; $\blacktriangle$, 1000.

[16] and with relaxational dynamics in canonical glasses [17]. The experimental data were fitted with the Cole–Cole function [18]:

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

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 3 and 4. The temperature dependences of the fit parameters $\Delta\varepsilon$, α and τ are shown in figure 5. Comparing the Cole–Cole formula with the Kohlrausch–Williams–Watts function [19] one sees that $\alpha \sim 1 - \beta$, and therefore the here obtained value for α is very close to that observed in $BP_{0.4}BPI_{0.6}$ [7] and is approximately the same as in the non-γ-irradiated sample of $BP_{0.15}BPI_{0.85}$ [8]. The distribution function of the relaxation rate is given by [20]

$$F(\tau) = \sin(\alpha\pi)/(\cosh[(1 - \alpha)\ln(2\pi\tau_1/\tau)] - \cos(\alpha\pi))$$

where τ_1 is the most probable value of relaxation rate. When $\alpha > 0.5$ the relaxation rates are distributed over three decades (figure 6). 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 $KI:NH_4I$ [21]. The activation energy E_b is similar in pure BPI as shown by a ^1H ENDOR experiment [22] and dielectric measurements [23]
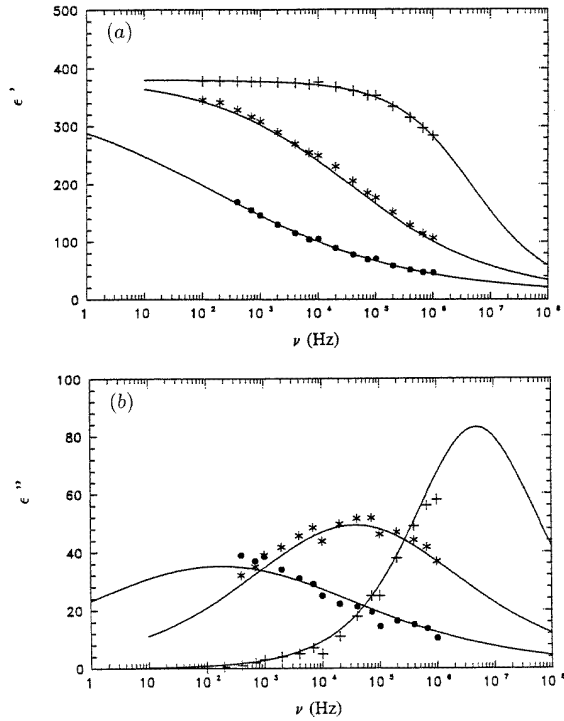
Figure 3. The frequency dependence of ε' and ε'' of $BP_{0.15}BPI_{0.85}$ at temperatures (K) of ● , 24, ∗, 32, and +, 45.
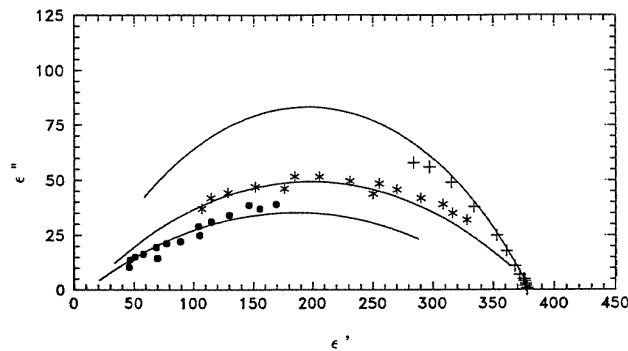

Figure 4. The Cole–Cole diagram of $BP_{0.15}BPI_{0.85}$ at temperatures (K) of ● , 24, ∗, 32, and +, 45.

and in the non-γ-irradiated sample of $BP_{0.15}BPI_{0.85}$ [8]. In the glassy state the protons are frozen in at random in the double-minima potentials, as in RADP [15], 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 [12, 15]. The cusp of static dielectric permittivity $\Delta\varepsilon$ indicates the temperature $T_a = 30$ K at which freezing of random bonds occurs (figure 5(a)).

An external bias field $E = 0.44$ kV cm^{-1} significantly lowers dielectric permittivity
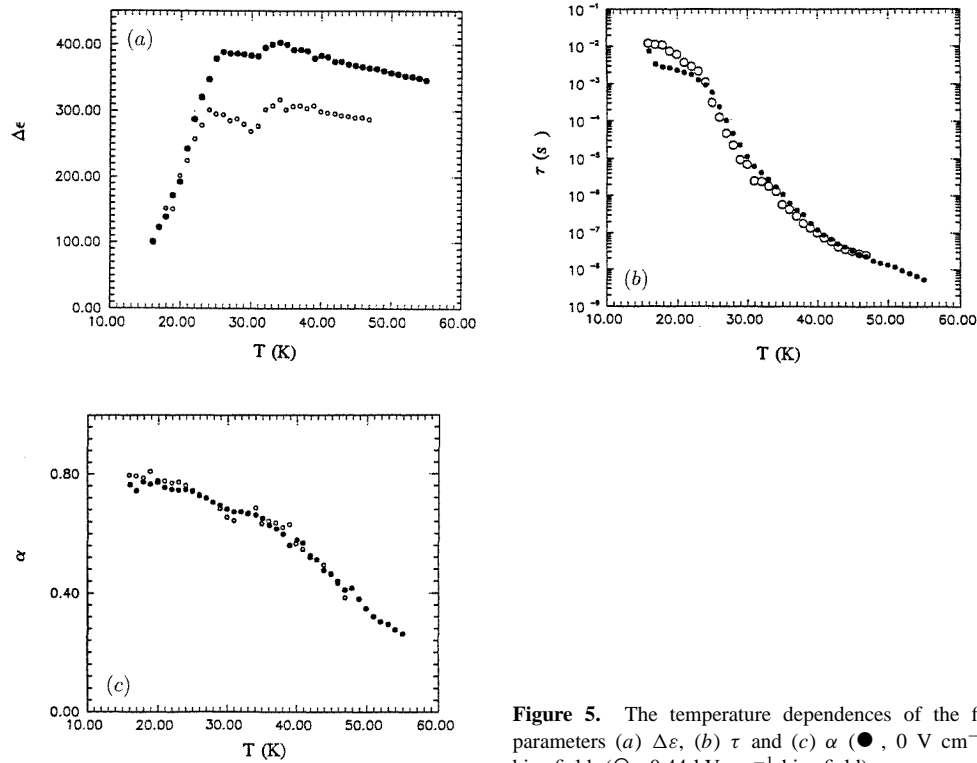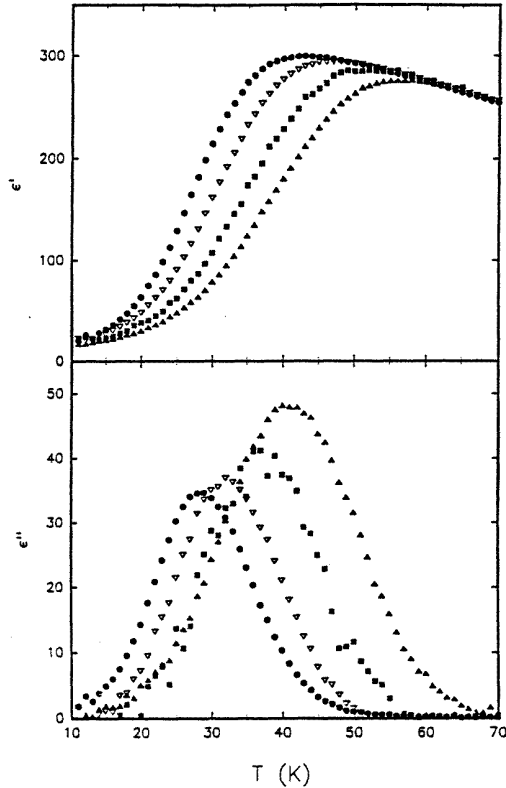
Figure 5. The temperature dependences of the fit parameters (*a*) $\Delta\varepsilon$, (*b*) τ and (*c*) α ($\bullet$, 0 V cm^{-1} bias field; ($\bigcirc$, 0.44 kV cm^{-1} bias field).
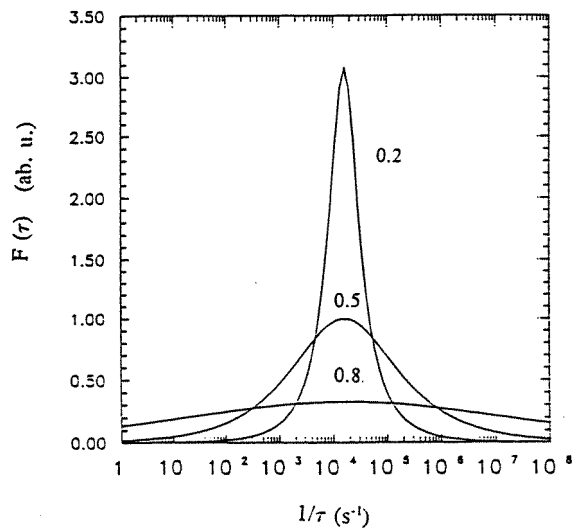
Figure 6. The distribution function $F(\tau)$ for $\alpha = 0.2$; 0.5; 0.8.

$\Delta\varepsilon$ (figure 7), but the temperature dependence of the relaxation time τ and α does not change significantly (figure 5). The bias field does not cause a much wider distribution of relaxation times as in the non-irradiated sample. In the non-irradiated sample at higher

Figure 7. The temperature dependence of ε' and ε'' of $BP_{0.15}BPI_{0.85}$ with bias field $E = 0.44$ kV cm^{-1} at the following frequencies (kHz): ●, 2; ▽, 20; ■, 200; ▲, 1000.

temperatures than 30 K the external bias field increases α until the random field freezing temperature [8]. As mentioned above this is possible to explain in terms of defects which exist in the non-irradiated sample and cause the internal electric field. The internal electric field acting together with the external bias field causes a wider distribution of relaxation times at $T > 30$ K in the non-irradiated sample due to the influence of defects. Due to the γ-irradiation defects the original defects' influence disappears: ε' increases; the relaxation time distribution does not change with applied external bias field significantly at $T > 30$ K and is only slightly increased at $T < 26$ K. The relaxation times do not change in the high-temperature region up to 25 K, but at lower temperatures the deviation is quite significant. The fit parameters τ_0 and E_A are presented in table 1.

Table 1. The fit parameters of the relaxation rate calculated according to an Arrhenius law for the $BP_{0.15}BPI_{0.85}$ crystals.

E (kV cm^{-1})	$\tau_0 \times 10^{-13}$ (s)	E_A (K)
0	2.4	518
0.57	7.1	488
0 (γ)	3.03	525
0.44 (γ)	2.76	513

Finally, one can conclude that $BP_{0.15}BPI_{0.85}$ 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 activation energy clearly manifests that the orientational glass state is related to the proton order. Therefore, $BP_{0.15}BPI_{0.85}$ is a proton glass and γ-irradiation does not change significantly the glass transition properties.

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