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Abstract. Measurements of the dielectric permittivity are reported for a deuterated solid solution of antiferroelectric betaine phosphate$_{0.01}$ ferroelectric betaine phosphite$_{0.99}$ at frequencies 20 Hz $< \nu <$ 1 MHz. The freezing phenomena in the ferroelectric phase of DBP$_{0.01}$DBPI$_{0.99}$ shows a typical dielectric behaviour of a transition into a dipolar glass state. Using the Kutnjak model, a glass temperature of 155 K is estimated.

Betaine phosphate (BP; $(CH_3)_3NCH_2COOH_3PO_4$) and betaine phosphite (BPI; $(CH_3)_3NCH_2COOH_3PO_3$) 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 form quasi-one-dimensional chains [1, 2]. BP exhibits a ferroelastic phase transition at about 365 K followed by two phase transitions at 86 and 81 K [3, 4]. Antiferroelectric order is established at $T_c = 81$ K. At this temperature the O–H...O bonds order along the one-dimensional chains and the chains are linked antiferroelectrically [2]. The related compound BPI transforms into an elastically ordered state at 355 K and exhibits ferroelectric order below $T_c = 216$ K [1]. The two almost isostructural compounds form solid solutions at any concentrations. It has been shown that at intermediate concentrations no spontaneous polarization occurs. This was considered to be the experimental proof for the suppression of the long-range electric order [3]. However, by means of magnetic resonance techniques it was shown recently that at intermediate concentrations below about 150 K a long-range order in the protonic system does still exist but with remarkable local fluctuations of the order parameter [5]. The mixed crystals BP$_{1-x}$BPI$_x$ with x values between 0.4 and 0.15 exhibit a dielectric relaxational behaviour typical for systems undergoing a transition into an orientational glass state [6], whereas in the border ranges of the phase diagram with high phosphite and phosphate concentrations, respectively, the phase transitions into the ferroelectric or antiferroelectric phase still exist.

Deuteration of hydrogen-bonded ferroelectrics leads to significant changes of the dielectric properties and shifts the phase transition temperature to higher values [7]. This isotope effect has already been studied in deuterated crystals of the betaine family, namely betaine phosphate (DBP) and betaine phosphite (DBPI) [4, 8]. The low-frequency dielectric measurements of DBPI showed [8] that the ferroelectric phase transition is shifted up to 297 K.
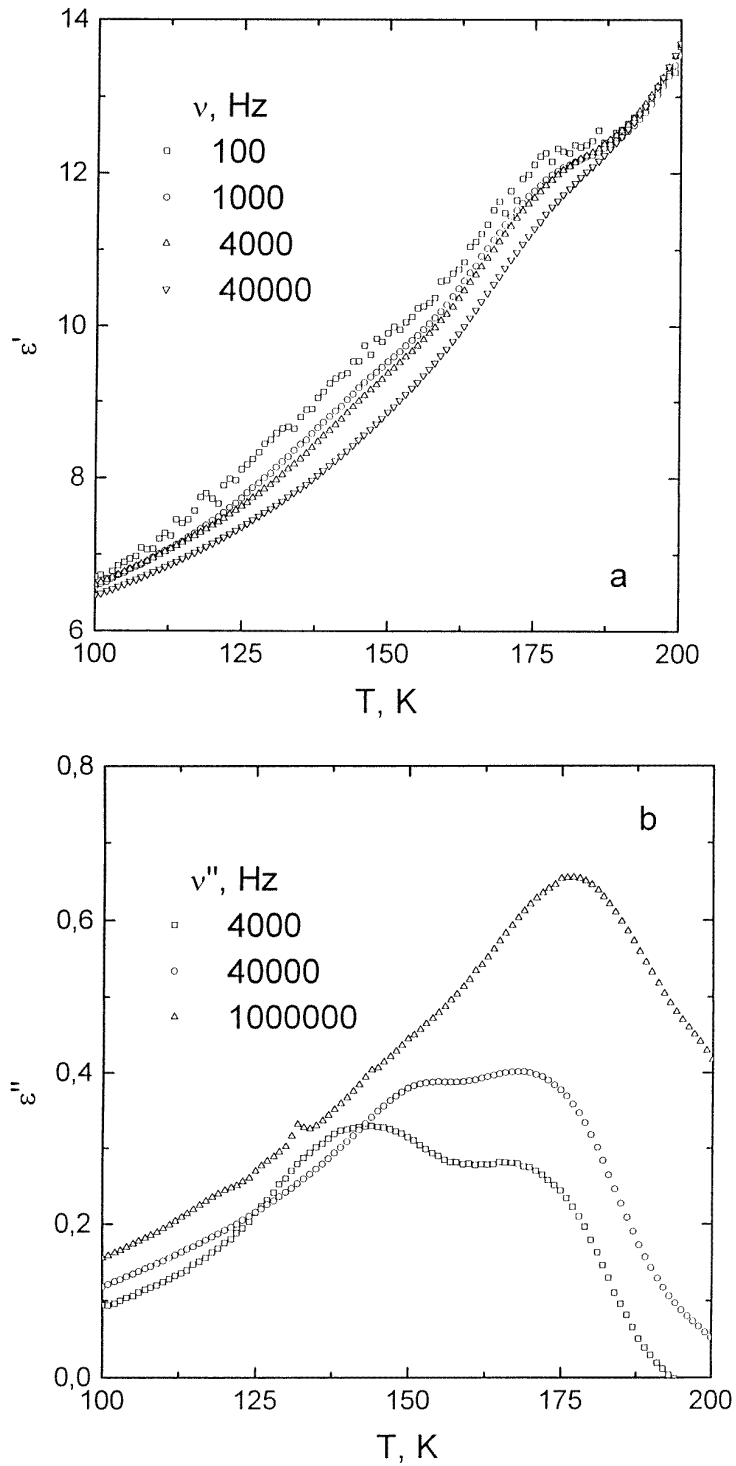
Figure 1. The temperature dependences of (a) ε' at the following frequencies (kHz): $\square$, 0.1; $\bigcirc$, 1; $\triangle$, 4; $\triangledown$, 40; and (b) ε'' of $DBP_{0.01}DBPI_{0.99}$ at the following frequencies (kHz): $\square$, 4; $\bigcirc$, 40; $\triangle$, 1000.
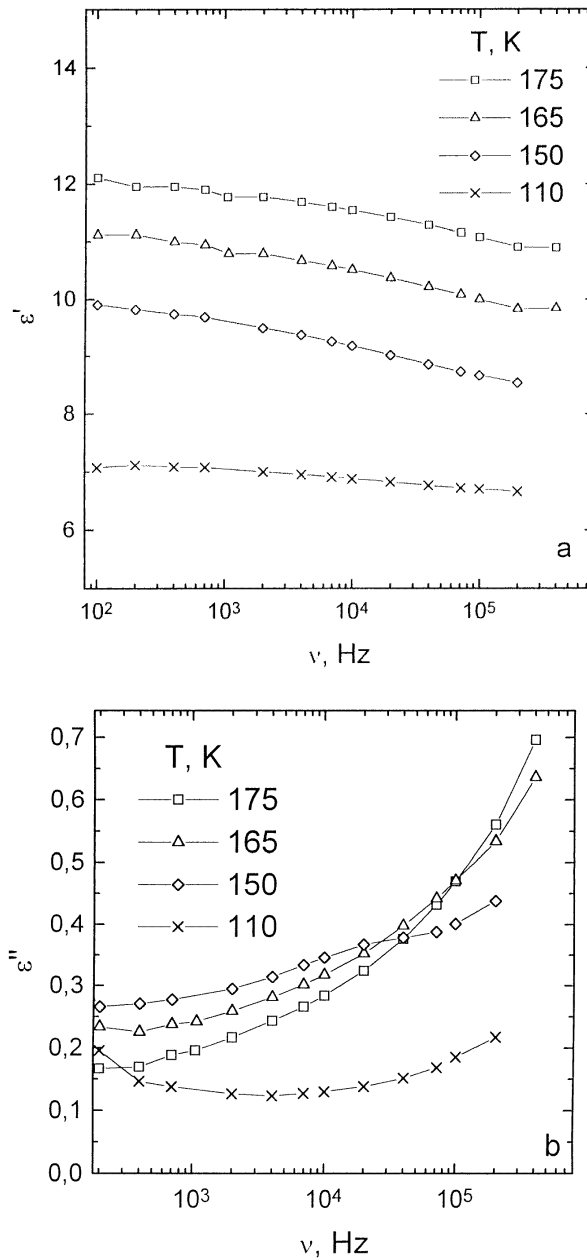
Figure 2. The frequency dependences of (a) ε' and (b) ε'' of $DBP_{0.4}DBPI_{0.6}$ at the following temperatures (K): $\square$, 175; $\triangle$, 165; $\Diamond$, 150; $\times$, 110. Lines are guides for eye.

The aim of this paper is to investigate the dielectric properties of the $DBP_{0.01}DBPI_{0.99}$ crystal in the ferroelectric phase.

$DBP_{0.01}DBPI_{0.99}$ crystals were grown by controlled evaporation from D_2O solution containing betaine and H_3PO_3 and H_3PO_4. By analogy with DBPI [8], 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. For the dielectric spectroscopy, gold-plated single crystals were oriented along their monoclinic *b*-axis. The complex dielectric constant $\varepsilon^* = \varepsilon' - i\varepsilon''$ 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.
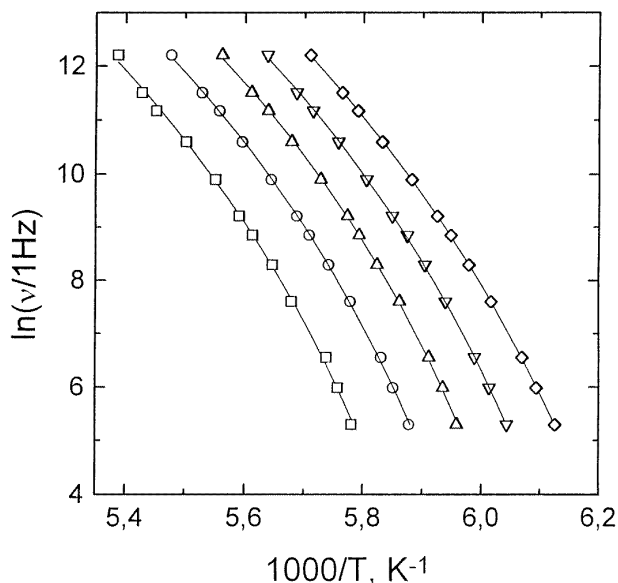

Figure 3. An Arrhenius representation (δ-plot) of data obtained from the reduced dielectric constant at the following δ-values (a): $\lozenge$, 0.85; $\triangle$, 0.875; $\triangledown$, 0.9; $\bigcirc$, 0.925; $\square$, 0.95.

At temperatures below 250 K, a decrease of the real part of the dielectric permittivity according to the Curie–Weiss law was observed. This behaviour is typical for the temperature range below the ferroelectric second-order phase transition. However, at temperatures lower than 190 K additional dielectric dispersion effects can be observed in the dielectric response (figure 1(a)), which are pronounced in the additional contribution to the dielectric permittivity. The same effect has been observed in pure BPI and DBPI [9]. The local maximum value of ε' in DBP$_{0.01}$DBPI$_{0.99}$ is 12.1 at 175 K and decreases with increasing frequency up to 10.8. The temperature dependence of dielectric losses ε'' (figure 1(b)) shows broad maxima which is shifted towards higher temperatures with increasing measurement frequency. The frequency dependences of ε' and ε'' provide clear evidence that the frequency dependence is much broader than 1.14 decades as it should be for a Debye type dispersion (figure 2). Due to the small changes of ε' and ε'' it was difficult to obtain reliable data for the relaxation time.

The observed experimental data were used for calculations with the model suggested by Kutnjak *et al* [10]. For this purpose the variable

$$\delta(\nu) = [\varepsilon'(\nu) - \varepsilon_\infty]/[\varepsilon_s - \varepsilon_\infty]$$

is introduced with ε_s and ε_∞ denoting the static and high-frequency permittivity. The observed low-frequency dielectric dispersion appears only in an additional contribution to the decreasing dielectric permittivity below the ferroelectric phase transition. Because
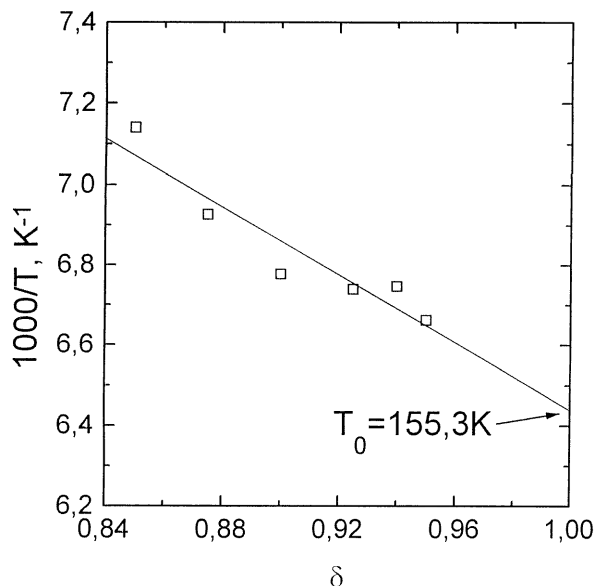
Figure 4. The T_0 dependence on δ.

the additional contribution of dielectric permittivity shows dielectric dispersion at much lower frequencies than the frequency of the soft relaxational mode [10] which gives the main contribution to the static dielectric permittivity, the whole value of the static dielectric permittivity is the sum of the additional contribution and the contribution of the soft relaxational mode. In this case the values of ε_∞ for the Kutnjak model will be the contribution of the soft relaxational mode. Because the contribution of the soft relaxational mode follows the Curie–Weiss law, the values of ε_∞ for the Kutnjak model have been evaluated from the Curie–Weiss law. The value of ε' at the frequency of 20 Hz represents the static dielectric permittivity ε_s as it is possible to see from figure 2(a) at temperatures higher than 130 K, because the value of ε' has already reached a plateau at the lowest measured frequencies and the imaginary part of the dielectric permittivity ε'' at low frequencies decreases nearly to zero (figure 2(b)).

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 3. Notable cases are $\delta \to 0$ and $\delta \to 1$ which correspond to the high- and low-frequency ends of the spectrum of the relaxation times. Of most interest is, of course, the limit $\delta \to 1$, which reveals the temperature evolution of the slowest element in the spectrum and which is most important for slow motions or glass freezing. From figure 1 it is possible to see that there are two maxima of ε'', and that one of them moves towards higher temperatures with increasing frequency, which is most probably caused by the glass behaviour.

From figure 3 it is evident that for δ values close to 1, the curves develop significant curvature. The full curves in this figure have been calculated using the Vogel–Fulcher expression with a δ-dependent Vogel–Fulcher temperature. Due to the high value of T_0, it is possible to observe the significant curvature of the δ curves even at low values of δ. In figure 4 we show T_0 as a function of δ for $0.8 < \delta < 0.95$. It is clearly seen that for $\delta \to 1$ the Vogel–Fulcher temperature extrapolates to 155 K.

The temperature behaviour of dielectric permittivity in the temperature range 100–200 K is very similar to the middle range concentrations of betaine phosphate–phosphite, only with the dispersion region shifted up to 150 K. A similar effect was observed in $Rb_x(NH_4)_{1-x}PO_4$ crystals [7] and in the antiferroelectric side of the phase diagram of BP_xBPI_{1-x} [12]. Finally, one can conclude that $DBP_{0.01}DBPI_{0.99}$ exhibits a coexistence of the orientational glass state with ferroelectric order at low temperatures where some of the deuterons are frozen-in along the one-dimensional chains.

Acknowledgment

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