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# Dielectric properties in the vicinity of the ferroelectric phase transition in a mixed crystal of deuterated $\text{BP}_{0.01}\text{BPI}_{0.99}$

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## Abstract

The dielectric behaviour of ferroelectric hydrogen bonded deuterated betaine phosphate<sub>0.01</sub> betaine phosphite<sub>0.99</sub> is investigated in the region of the ferroelectric phase transition. Dielectric dispersion is investigated in the frequency range up to 12 GHz. The dielectric dynamics of a small admixture such as 1% BP is already able to change noticeably the character of the phase transition as well as the quasi-one-dimensional feature of deuterated betaine phosphite. The Debye type dispersion shows a critical slowing down. The frequency of the relaxational soft mode in the paraelectric phase varies according to the quasi-one-dimensional Ising model and decreases down to 0.55 GHz at the phase transition temperature ( $T_C = 299$  K). The activation energy for the deuteron flipping motion amounts to  $\Delta U = 3.6kT_C = 0.095$  eV. The obtained results show the order–disorder character of the proper ferroelectric phase transition. However, the small admixture of 1% betaine phosphate changes noticeably the character of the phase transition as well as the quasi-one-dimensional feature in comparison to pure deuterated betaine phosphite.

## 1. Introduction

Betaine phosphate (BP;  $(\text{CH}_3)_3\text{NCH}_2\text{COOH}_3\text{PO}_4$ ) and betaine phosphite (BPI;  $(\text{CH}_3)_3\text{NCH}_2\text{COOH}_3\text{PO}_3$ ) are molecular crystals consisting of the amino acid betaine and phosphoric and phosphorous acids as the organic and inorganic components, respectively. In both compounds, the inorganic components ( $\text{PO}_4$  or  $\text{PO}_3$  groups) are linked by hydrogen bonds to form quasi-one-dimensional chains [1–3]. Betaine phosphate shows three phase transitions. It undergoes the first phase transition from a paraelectric high-temperature phase (space group  $P2_1/m$ ;  $Z = 2$ ) at 365 K into an antiferrodistortive phase (space group  $P2_1/c$ ;  $Z = 4$ ) and the second one into an ferroelectric phase at 86 K (space group  $P2_1$ ;  $Z = 4$ ) [4–6]. In the high-temperature phase the  $\text{PO}_4$  groups and betaine molecules are disordered. They both order

in the antiferrodistortive phase, but the hydrogen atoms of the phosphate group linking  $\text{PO}_4$  groups remain disordered. Ordering of these hydrogen atoms at 86 K induces the second phase transition to the ferroelectric phase. The third transition into an antiferroelectric phase is induced by a doubling of the unit cell along the  $a$ -axis. This low-temperature phase has a  $P2_1/c$  symmetry with  $Z = 8$  [7].

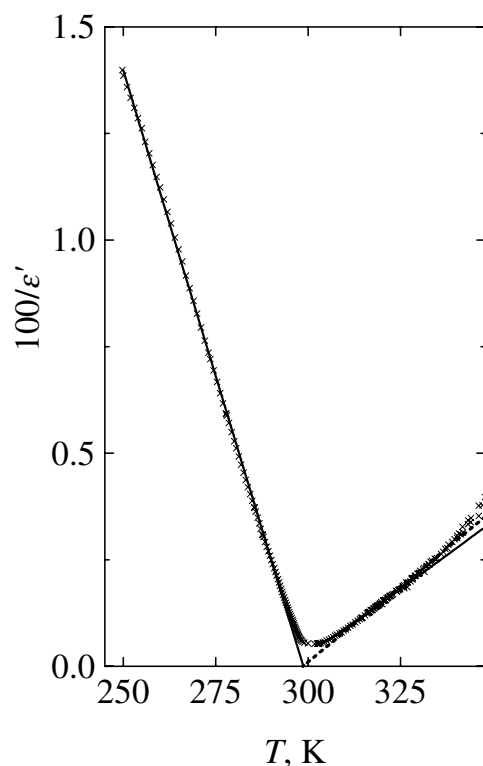
The structure of BPI was determined from x-ray and elastic neutron scattering experiments [1]. It was found that BPI is monoclinic (space group  $P2_1/c$ ) at room temperature. BPI crystals also show two phase transitions: from a paraelectric  $P2_1/m$  high-temperature phase into an antiferrodistortive  $P2_1/c$  phase at  $T_{C1} = 355$  K with a unit cell doubling along the  $c$ -axis and an order–disorder transition of the hydrogen bond system into the ferroelectric  $P2_1$  phase at  $T_{C2} = 216$  K [8]. The x-ray investigation confirmed the structural affinity to BP.

The complex dielectric permittivity of BPI has been investigated in a wide frequency range. At low frequencies [9], the best fit of the static dielectric permittivity with the quasi-one-dimensional Ising model gave the following parameters:  $J_{\parallel}/k = 270$  K,  $J_{\perp}/k = 21$  K. However, the best fit to the reciprocal permittivity data in the paraelectric phase is obtained for a second-order polynomial. It is necessary to note that the phase transition temperature of BPI is very sensitive to the crystal quality [9]: the values of  $T_{C2}$  vary from 216 to 224 K and the maximum values of  $\epsilon'$  vary from 14 000 to 20 000. Deuteration shifts the phase transition temperature up to 300 K [10]. For deuterated BPI (DBPI)  $J_{\parallel}/k = 187$  K and  $J_{\perp}/k = 80$  K were found [11, 12]. It seems that in contrast to BP the deuteration decreases the one-dimensionality in BPI [13].

The ferroelectric dispersion in the vicinity of  $T_{C2}$  begins at about 100 MHz and ranges up to short millimetre waves [14] in BPI. The characteristic minimum of  $\epsilon'$  appears at 9 GHz, indicating a critical slowing down in the microwave region. The ferroelectric dispersion around  $T_{C2}$  nearly vanishes at 77 GHz. This behaviour has been described with the Debye formalism. The obtained relaxation frequency  $\nu_s = 1/2\pi\tau$  on approaching  $T_{C2}$  varies according to  $\nu_s = 0.36(T[\text{K}] - 218)$  GHz in the paraelectric phase and decreases to 2.4 GHz at  $T_{C2} = 224$  K. It was found that there is an additional contribution to the static dielectric permittivity besides the contribution of the soft relaxational mode. Its origin is unknown so far [14]. High-frequency dielectric investigation of deuterated BPI [15] revealed a behaviour similar to the non-deuterated sample. The temperature dependence of the real part of the dielectric permittivity shows a minimum at 298 K at a frequency of 3.8 GHz indicating the critical slowing down in the DBPI crystal. A nearly monodispersive Debye type relaxation has been observed. The relaxation frequency on approaching  $T_{C2}$  varies according to  $\nu_s = 0.2(T[\text{K}] - 295.8)$  GHz in the paraelectric phase and decreases to 0.55 GHz at  $T_{C2}$ . In DBPI, the Curie–Weiss law follows from the critical slowing-down of the relaxation frequency  $\nu_s$ , but there exists an additional contribution to the static dielectric permittivity, as in BPI.

The phase diagram of  $\text{BP}_x\text{BPI}_{1-x}$  has been investigated [16, 17] by means of x-ray and pyroelectric methods. It is highly asymmetric. A very small amount of BP lowers the ferroelectric phase transition temperature significantly. The same effect has been observed in  $\text{DBP}_x\text{DBPI}_{1-x}$  [18]. Substituting only 15% of BPI by BP the ferroelectric phase transition is suppressed and a glasslike phase transition occurs. However, a glassy behaviour of the permittivity was already observed in  $\text{DBP}_{0.01}\text{DBPI}_{0.99}$  [19] in the form of an additional dielectric dispersion in the ferroelectric phase giving a freezing temperature  $T_f = 155.3$  K. Such dramatic changes in the phase transition temperature and phase transition type by a small amount of BP allow us to raise the question of how small amounts of BP influence the soft-relaxational-mode dynamics in BPI.

The aim of this paper is to investigate the influence of a small amount of BP on the dielectric dispersion in a DBPI crystal.



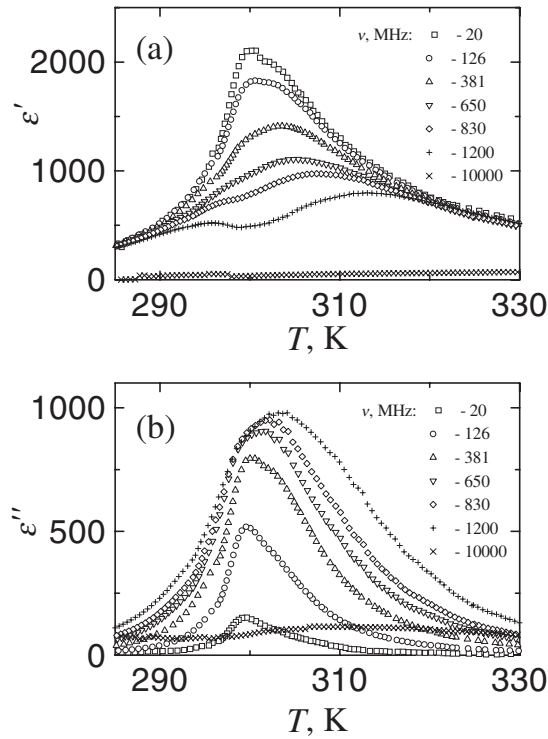
**Figure 1.** The temperature dependence of reciprocal static dielectric permittivity of  $\text{DBP}_{0.01}\text{DBPI}_{0.99}$ .

## 2. Experiment

Deuterated  $\text{DBP}_{0.01}\text{DBPI}_{0.99}$  crystals were grown by controlled evaporation from  $\text{D}_2\text{O}$  solution containing betaine and phosphoric acid  $\text{H}_3\text{PO}_3$ . In such a way, only the  $\text{O}-\text{H} \cdots \text{O}$  bonds were deuterated. The deuteration level was about 95% as follows from ENDOR measurements. For the dielectric spectroscopy, gold-plated single crystals oriented along the monoclinic  $b$ -axis were used. The complex dielectric permittivity  $\varepsilon^* = \varepsilon' - i\varepsilon''$  was measured using an HP4284A capacitance bridge in the frequency range 20 Hz to 1 MHz. In the frequency region 10 MHz to 2 GHz measurements were performed by a coaxial dielectric spectrometer set-up [20]. The samples were cylindrically shaped with  $2 \text{ mm}^2$  area and 3 mm height. In the cm wave region a waveguide dielectric spectrometer was used [21]. The radius of the sample in the cm wave region was 0.37 mm. All measurements were performed on cooling.

## 3. Results and discussion

The low-frequency dielectric measurements revealed that there is no dielectric dispersion in the kHz region. Due to that  $\varepsilon'$  at 1 kHz is considered as the static dielectric permittivity. The inverse static dielectric permittivity of  $\text{DBP}_{0.01}\text{DBPI}_{0.99}$  is presented in figure 1. In the high-temperature phase, the reciprocal dielectric permittivity reveals significant curvature.



**Figure 2.** The temperature dependences of (a)  $\epsilon'$  and (b)  $\epsilon''$  of  $\text{DBP}_{0.01}\text{DBPI}_{0.99}$  at different frequencies.

The quasi-one-dimensional Ising model was used to fit the static dielectric permittivity [13]:

$$\epsilon(0) = \epsilon_{\infty} + \frac{A}{T} \left[ \exp\left(-\frac{2J_{\parallel}}{kT}\right) - \frac{J_{\perp}}{kT} \right]^{-1} \quad (1)$$

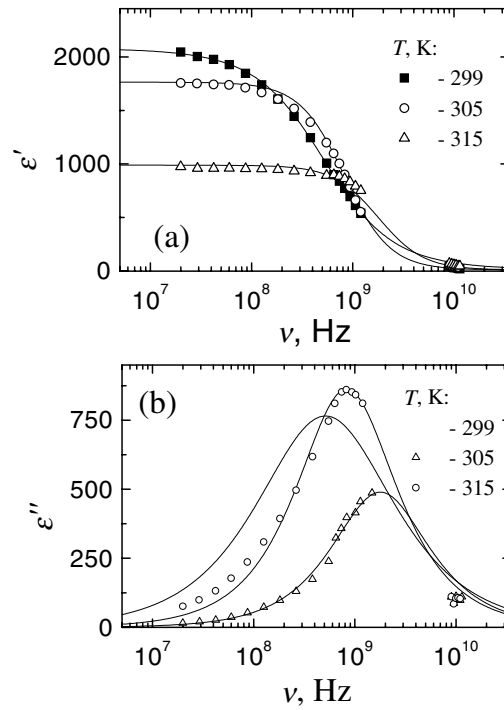
where  $J_{\parallel}$  and  $J_{\perp}$  are the nearest-neighbour intrachain and the effective mean field interchain coupling constants;  $k$  is the Boltzmann constant. From the best fit the following parameters have been obtained:  $J_{\parallel}/k = 230$  K and  $J_{\perp}/k = 61$  K,  $A = 9692$  K,  $\epsilon_{\infty} = 5$ . In figure 1 the Curie–Weiss fit is shown for comparison in the high-temperature phase. It is possible to see that the quasi-one-dimensional Ising model gives better agreement with experimental results than the Curie–Weiss law (solid line) with the same  $\epsilon_{\infty} = 5$ .

In the ferroelectric phase, the reciprocal dielectric permittivity follows the Curie–Weiss law:

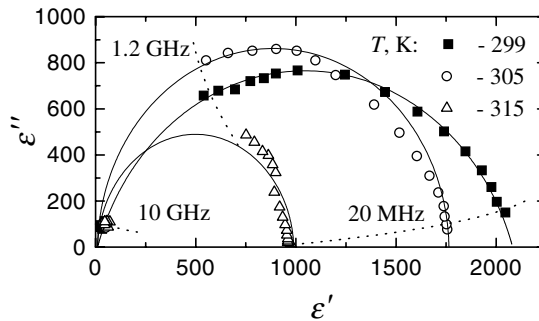
$$\epsilon(0) = \epsilon_{\infty} + \frac{C}{T_C - T} \quad (2)$$

with  $T_C = 299$  K and  $C = 3486$  K.

Temperature dependences of the complex dielectric permittivity  $\epsilon^* = \epsilon' - i\epsilon''$  at several frequencies in the dielectric dispersion region are shown in figure 2. The ferroelectric dispersion in the vicinity of  $T_C$  begins at about 20 MHz and ranges up to millimetre waves (figures 3 and 4). The characteristic minimum of  $\epsilon'$  appears at 1 GHz indicating a critical slowing down as in other H-bonded ferroelectrics [14, 21]. The ferroelectric dispersion nearly vanishes at 10 GHz near the phase transition temperature. Phenomenologically the ferroelectric



**Figure 3.** The frequency dependences of (a)  $\epsilon'$  and (b)  $\epsilon''$  of DBP<sub>0.01</sub>DBPI<sub>0.99</sub> at the different temperatures.



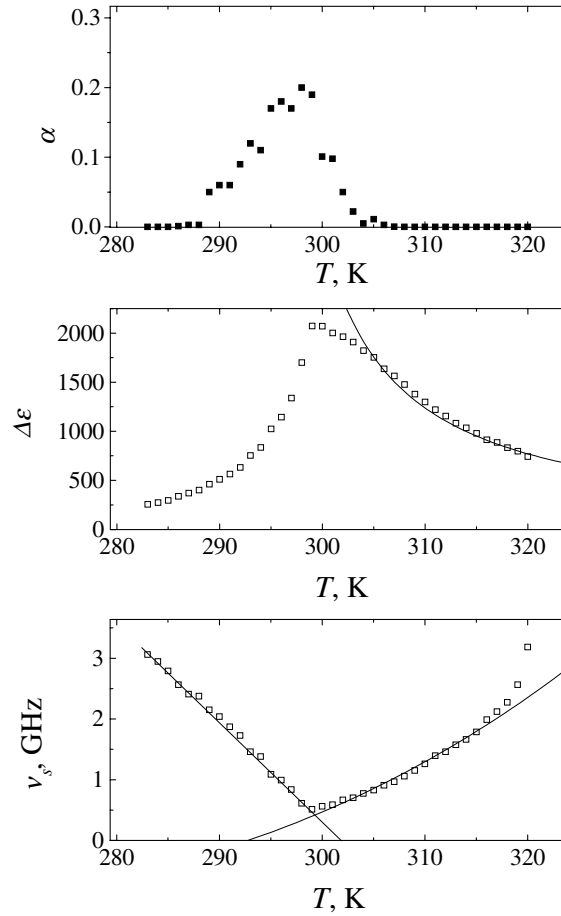
**Figure 4.** Cole–Cole diagrams of DBP<sub>0.01</sub>DBPI<sub>0.99</sub> at the different temperatures.

dispersion in the DBP<sub>0.01</sub>DBPI<sub>0.99</sub> crystal can be explained by the formula

$$\epsilon^* = \epsilon_\infty + \frac{\Delta\epsilon}{1 + (i\omega\tau)^{1-\alpha}} \quad (3)$$

which reduces to the Debye type formula when  $\alpha = 0$ . In this equation  $\Delta\epsilon$  is the strength of a relaxator,  $\tau$  is the relaxation time,  $\epsilon_\infty$  is the contribution of all higher-frequency modes and electronic polarization and  $\alpha$  is the relaxation time distribution parameter.

The frequency dependence of the real and imaginary parts of dielectric permittivity (figure 3) as well as Cole–Cole diagrams (figure 4) confirms the Debye-type nature of the dielectric dispersion. However, on approaching the phase transition temperature the parameter



**Figure 5.** The temperature dependences of the fit parameters  $\alpha$ ,  $\Delta\epsilon$  and  $\nu_r = 1/2\pi\tau$ .

$\alpha$  deviates from its zero value and reaches a maximum of 0.2 at 298 K. This variation is more clearly developed than in pure BPI [14] ( $\alpha = 0.04$  at  $T_C$ ) or DBPI [15] ( $\alpha = 0.12$  at  $T_C$ ). It means that an admixture of only 1% betaine phosphate into the betaine phosphite crystal leads to a remarkable deviation from a pure monodispersive behaviour of the dielectric dispersion expected for a relaxational mode type of phase transition. The relaxation time,  $\tau$ , the strength of the relaxator,  $\Delta\epsilon$ , the distribution parameter,  $\alpha$ , and  $\epsilon_\infty$  were obtained according to the Cole–Cole formula by the best fit. The obtained parameters are presented in figure 5. The temperature dependence of the relaxation frequency  $\nu_r = 1/(2\pi\tau)$  shows a curvature in the high-temperature phase. The temperature dependence of the relaxation frequency according to the quasi-one-dimensional Ising model [13] is given by

$$\nu_r = \nu_\infty \exp\left(-\frac{\Delta U}{kT}\right) \left[ \cosh\left(\frac{2J_{\parallel}}{kT}\right) \right]^{-1} \left[ \exp\left(-\frac{2J_{\parallel}}{kT}\right) - \frac{J_{\perp}}{kT} \right] \quad (4)$$

where  $\Delta U$  is the activation energy for the reorientation of the dipole, and  $\nu_\infty$  is the attempt frequency. Using the parameters  $J_{\parallel}$  and  $J_{\perp}$  obtained by means of equation (1), the best fit according to equation (4) results in the following values:  $\Delta U = 1093$  K (0.095 eV) and  $\nu_\infty = 3.89$  THz.

Within the frame of the model the transition temperature  $T_C$  is determined by the condition

$$kT_C \exp\left(-\frac{2J_{\parallel}}{kT_C}\right) = J_{\perp} \quad (5)$$

which results to  $T_{C \text{ Ising}} = 290.95$  K. The mismatch with the real phase transition temperature  $T_C = 299$  K shows also that the phase transition under investigation is not purely of the quasi-one-dimensional Ising type or it can be also slightly of first order or diffused. In the ferroelectric phase the relaxation frequency follows the classical law  $\nu_r = A(T_C - T)$  with  $A = 0.162$  GHz K<sup>-1</sup>.

#### 4. Conclusions

A small admixture such as 1% BP is already able to change noticeably the character of the phase transition as well as the quasi-one-dimensional feature of deuterated betaine phosphite. The temperature behaviour of the static dielectric permittivity of DBP<sub>0.01</sub>DBPI<sub>0.99</sub> can be rather well explained with the quasi-one-dimensional Ising model. In agreement with that model, the behaviour of the dielectric dispersion indicates the ferroelectric phase transition at  $T_C = 299$  K to be of relaxational mode type. The ferroelectric dynamics is described in terms of the soft relaxational mode associated with the deuteron flipping motion in a double-well potential with an activation energy  $\Delta U = 0.095$  eV and attempt frequency  $\nu_{\infty} = 3.9 \times 10^{12}$  Hz. However, the phase transition temperature calculated from the fit parameters of the quasi-one-dimensional Ising model differs slightly from the experimental one, and, also, the dielectric dispersion behaves close to the transition temperature as not strictly monodispersive as expected for a relaxational mode.

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