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LETTER TO THE EDITOR

## Dielectric investigation of a solid solution of deuterated betaine phosphate<sub>0.95</sub>betaine phosphite<sub>0.05</sub>

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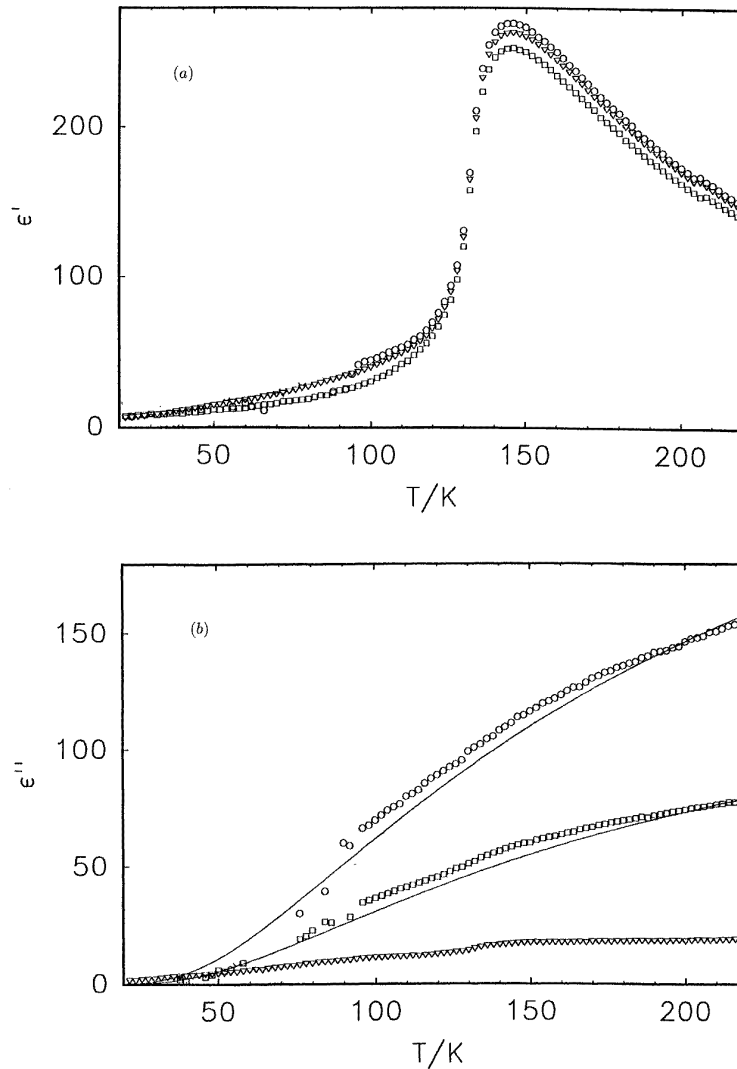
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**Abstract.** Measurements of the dielectric permittivity are reported for a solid solution of deuterated antiferroelectric betaine phosphate<sub>0.95</sub> and ferroelectric betaine phosphite<sub>0.05</sub> at frequencies in the range  $20 \text{ Hz} < \nu < 1 \text{ MHz}$ . This crystal orders antiferroelectrically at  $T_c = 140 \text{ K}$ . The dielectric response over the whole of the temperature region 50–300 K shows ac and dc conduction. The activation energy of the dc conduction was found to be  $E_b = 173 \text{ K}$  (0.015 eV).

The compounds 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. In both compounds the inorganic components ( $\text{PO}_4$  or  $\text{PO}_3$  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 K and 81 K [1]. Antiferroelectric order is established at  $T_c = 86 \text{ K}$  [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  $T_c = 216 \text{ K}$  [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 suppressed [4] and no spontaneous polarization occurs [5, 6]. The mixed crystal  $\text{BP}_{0.95}\text{BPI}_{0.05}$  exhibits dc and ac conductivity [7]. The activation energy of the thermally activated dc conductivity was found to be  $E_b = 464 \text{ K}$  (0.04 eV). The antiferroelectric phase transition was observed at  $T_c = 79 \text{ K}$ .

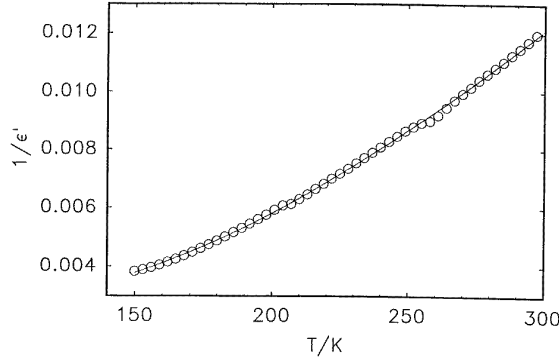
We now describe the experimental procedure. Deuterated  $\text{BP}_{0.95}\text{BPI}_{0.05}$  crystals ( $\text{DBP}_{0.95}\text{DBPI}_{0.05}$ ) were grown by controlled evaporation from  $\text{D}_2\text{O}$  solution. In such a way only the O–H $\cdots$ O connections were deuterated. The deuteration level was about 95% as follows from ENDOR measurements. 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 using a HP4284A capacitance bridge in the frequency range 20 Hz to 1 MHz. Measurements were made on three samples. They were thin plates of 0.8–0.2 mm thick and 12–17 mm<sup>2</sup> in area, coated with gold electrodes. The measurement voltage was 200 mV. For the temperature dependence measurements a Leybold VSK-4-320 cryostat was used. All of the measurements were performed during heating with a rate of about 0.1 K min<sup>-1</sup>.

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**Figure 1.** The temperature dependence of  $\epsilon'$  (a) at the frequencies (kHz):  $\circ$ , 0.1;  $\nabla$ , 1;  $\square$ , 1000, and of  $\epsilon''$  (b) at the frequencies (kHz):  $\circ$ , 0.1;  $\square$ , 0.2;  $\nabla$ , 1, for  $\text{DBP}_{0.95}\text{DBPI}_{0.05}$ . The line is the best fit according to the Arrhenius law (b).

We will now describe the results and discuss them. For  $\text{DBP}_{0.95}\text{DBPI}_{0.05}$  an anomaly in  $\epsilon'$  indicating the polar phase transition into the antiferroelectric state was observed at  $T_c = 140$  K (figure 1(a)). In the non-deuterated crystal the polar phase transition was observed at 79 K. The temperature shift of the phase transition due to the deuteration is 61 K. A Curie-Weiss law is not valid for  $\epsilon'$ . The temperature behaviour of the static dielectric constant can be explained by the modified one-dimensional Ising model [8, 9]. In this model the interaction between neighbouring dipoles in one-dimensional chains is treated exactly whereas all additional (weak) interactions are taken into account via the mean-field approximation. The treatment of this system yields for the static dielectric permittivity in



**Figure 2.** The temperature dependence of  $1/\varepsilon'$ . Points are experimental results, while the line shows the best fit. Please note that only each third point is plotted.

the high-temperature phase [9]:

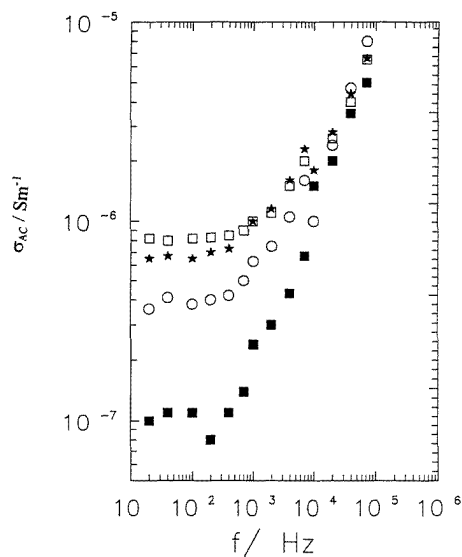
$$\varepsilon_s - \varepsilon_\infty = \frac{C}{T} \left[ \exp\left(\frac{2J_{\parallel}}{k_B T}\right) - \frac{J_{\perp}}{k_B T} \right]^{-1}$$

where  $\varepsilon_s$  is the static dielectric constant for the soft mode,  $\varepsilon_\infty$  is the dielectric permittivity due to all higher-frequency modes, and  $J_{\parallel}$  and  $J_{\perp}$  are the nearest-neighbour intrachain and the effective mean-field interchain coupling constants, respectively. From the best fit (figure 2) we got the parameters  $C = 7602$ ,  $\varepsilon_\infty = 3$ ,  $J_{\parallel} = 205.4$  K (0.018 eV),  $J_{\perp} = -19.4$  K (0.0017 eV). In the antiferroelectric system, the effective mean-field coupling constant  $J_{\perp}$  can be regarded as a sum of two contributions [8]:  $J_{\perp} = J_{\perp}^{(1)} + J_{\perp}^{(2)}$ , where  $J_{\perp}^{(1)}$  denotes the mean-field coupling between dipoles within the same subsystem. All of the dipoles within each subsystem are parallel which means that  $J_{\perp}^{(1)} > 0$  is always valid.  $J_{\perp}^{(2)}$  characterizes the mean-field coupling between dipoles of different subsystems. In an antiferroelectric system, where the two subsystems order antiparallel to each other,  $J_{\perp}^{(2)} < 0$  is valid. The transition temperature  $T_c$  is determined by the condition [10]

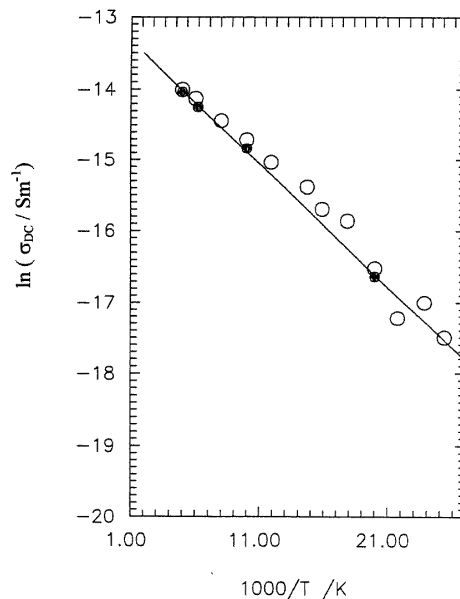
$$k_B T_c \exp\left(-\frac{2J_{\parallel}}{k_B T}\right) = J_{\perp}^{(1)} - J_{\perp}^{(2)}.$$

From this equation we get  $J_{\perp}^{(1)}$  and  $J_{\perp}^{(2)}$ :  $J_{\perp}^{(1)} = 0$  K (0 eV) and  $J_{\perp}^{(2)} = -19.4$  K (0.0017 eV). Our results are quite close to the ones obtained for the BP and DBP [8].

Starting from high frequencies the loss increases smoothly with decreasing frequency, clearly indicating the presence of electric conductivity. But the increase in the deuterated sample is slower than that in the non-deuterated [7] one (figure 1(b)) and the dielectric loss at the same temperature and frequency is lower in DBP<sub>0.95</sub>DBPI<sub>0.05</sub> than in the non-deuterated sample. We do not observe any increase of losses due to the dielectric dispersion related to the soft mode because the soft-mode frequency lies at much higher frequencies ( $\nu_s > 100$  GHz) [8]. Figure 3 shows the frequency dependence of the conductivity  $\sigma = \varepsilon_0 \omega \varepsilon''$  above and below the antiferroelectric phase transition temperature. These results clearly show the limiting dc conductivity at low frequencies. Unfortunately our frequency range was not wide enough to make a fit as in reference [7] for the ac conductivity  $\sigma_{ac}$ . At 50 Hz  $\sigma_{dc}$  is already the main component of  $\sigma$ . We used an Arrhenius law to fit the temperature dependence of  $\sigma_{dc}$ :  $\sigma_{dc} = \sigma_0 \exp(E_b/kT)$ , as indicated in figure 4 by the solid



**Figure 3.** The frequency dependence of the conductivity of  $\text{DBP}_{0.95}\text{BPI}_{0.05}$  at the temperatures (K):  $\square$ , 200;  $\star$ , 161;  $\circ$ , 100;  $\blacksquare$ , 50.



**Figure 4.** The temperature dependence of the dc conductivity  $\sigma_{dc}$  ( $\bullet$ , the fit from figure 2;  $\circ$ , at 50 Hz).

line with  $\sigma_0 = 1.93 \times 10^{-6} \Omega \text{ m}^{-1}$  and  $E_b = 173 \text{ K}$  (0.015 eV). The activation energy  $E_b$  is significantly lower than in  $\text{BP}_{0.95}\text{BPI}_{0.05}$  [7], but the critical relaxation rate observed in the non-deuterated sample [7] was 200 K, which is approximately the same as we observe.

Also as in the non-deuterated sample the antiferroelectric phase transition does not influence the conductivity, and most probably the limiting barriers for  $\sigma_{dc}$  are not influenced by the phase transition.

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