LETTER TO THE EDITOR

Betaine potassium iodide dihydrate: a new compound of betaine

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Abstract. Betaine potassium iodide dihydrate, $[(CH_3)_3N^+CH_2COO^-]_2.KI.2H_2O$, BKI for
short, is a new compound of the aminoacid betaine with a triclinic symmetry and the space group
$P\bar{1}$ at room temperature. The study of dielectric properties provided evidence for the existence
of a structural phase transition occurring around 100 K. The spontaneous electric polarization
is zero in both phases. A study of dielectric dispersion disclosed two relaxational modes with
different relevance in the high and in the low temperature phases. The main features observed in
BKI are consistently described by the Landau theory, by assuming a quadratic coupling between
the primary order parameter and the electric polarization.

Betaine compounds were extensively investigated in the last decade and some of them
present remarkable properties, like betaine calcium chloride dihydrate (BCCD) [1–3],
betaine arsenate (BA) [4, 5], the mixed compounds of betaine phosphate and phosphite
$(BP_{1-x}BPI_x)$ [6, 7] and betaine borate (BB) [8]. A new compound of the aminoacid betaine,
betaine potassium iodide dihydrate, $[(CH_3)_3N^+CH_2COO^-]_2.KI.2H_2O$, BKI for short, was
synthesized very recently and it presents unique features among the rich variety of properties
exhibited by the betaine family of compounds. In contrast to other well known betaine
compounds, that are orthorhombic (BCCD, BB) and monoclinic (BA, BP, BPI) at room
temperature, BKI is triclinic with space group $P\bar{1}$ [9].

    In the present work we report a detailed experimental study concerning dielectric and
pyroelectric properties of BKI. This study provided evidence for the existence of a structural
phase transition, very probably of first order, occurring very close to 100 K. The crystals
of BKI were grown from aqueous solution by the controlled solvent evaporation technique
and samples shaped as thin plates with dimensions $5 \times 4 \times 1.2$ mm^3 were cut perpendicular
to the c and $[\bar{1}10]$ directions and normal to the (110) plane, previously determined by x-ray
study. Gold foiled electrodes were used. The experimental details are reported elsewhere
[5, 10].

    The temperature dependence of real and imaginary parts of the complex dielectric
constant is depicted in figures 1(a) and (b) for the frequency of 100 kHz. For the three
directions referred to above, $\varepsilon'(T)$ exhibits always a step close to 100 K. These steps have
different sizes for the different directions. $\varepsilon''(T)$ shows, for the three mentioned directions,
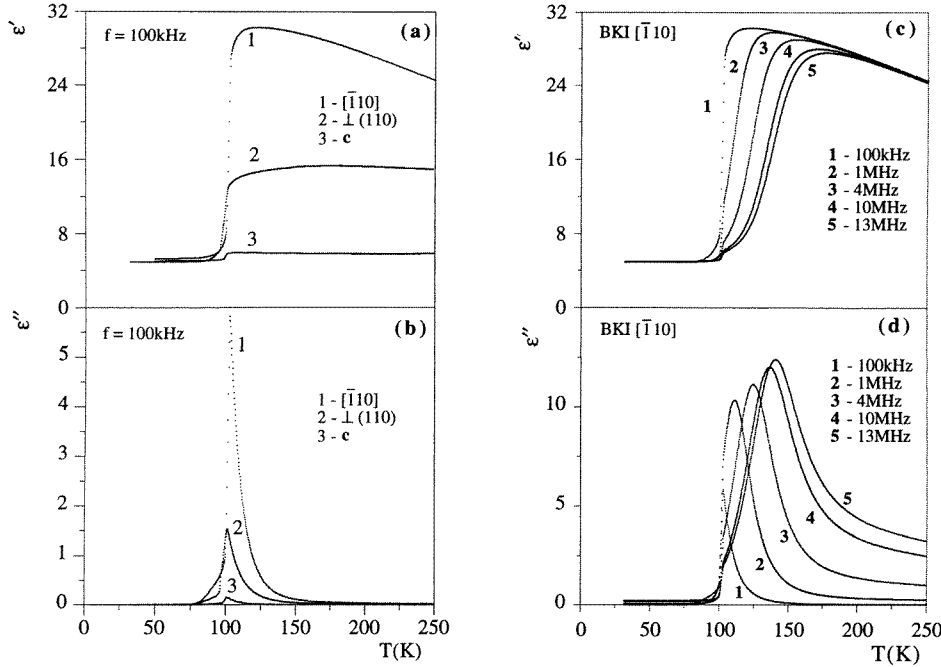broad peaks near T_c. We have studied the dielectric dispersion of BKI in the frequency

Figure 1. Temperature dependence of the complex dielectric constant in the c, $[\bar{1}10]$ and $\perp$ (110) directions for the frequency of 100 kHz: (a) $\varepsilon'(T)$ and (b) $\varepsilon''(T)$. Temperature dependence of the complex dielectric constant in the $[\bar{1}10]$ direction, in the frequency range 100 kHz–13 MHz: (c) $\varepsilon'(T)$ and (d) $\varepsilon''(T)$.

range 100 kHz–13 MHz along $[\bar{1}10]$ since it corresponds to the largest induced polarization by the a.c. electric field. The temperature dependence of ε' and of ε'' for some frequencies are depicted in figures 1(c) and (d).

These data were analysed by assuming that $\varepsilon^*(\omega)$, for different frequencies and at a fixed temperature, can be described by the Cole–Cole function [11]:

$$\varepsilon^*(\omega) = \varepsilon'(\omega) - i\varepsilon''(\omega) = \varepsilon(\infty) + \sum_{j=1}^{n} \frac{\Delta\varepsilon_j}{1 + (i\omega/\omega_{rj})^{\beta_j}} \qquad j = 1, 2, \ldots, n \qquad (1)$$

where $\varepsilon(\infty)$, $\Delta\varepsilon_j$, ω_{rj} and β_j are adjustable parameters: $\varepsilon(\infty)$ is the dielectric constant for high frequencies; $\Delta\varepsilon_j$ dielectric strength, ω_{rj} the relaxation frequency and β_j the dispersion coefficient for the jth relaxation mode. When the relaxation frequencies of the modes are very different they can be considered, usually, as independent ones.

The analysis of dynamical mechanisms of relaxation by fitting experimental data to expression (1) disclosed two relaxation modes being one more relevant in the range of temperatures above T_c (named the HT mode), while the other one (named the LT mode) is visible only below T_c. In the small interval 90–100 K they can be both detected. Figure 2(a) displays the dielectric strength of the HT mode ($\Delta\varepsilon_1$) and the dielectric strength of the LT mode ($\Delta\varepsilon_2$) as functions of temperature. Whereas the HT mode represents the main contribution to the real part of the dielectric constant, the LT mode contributes very weakly for ε', its contribution being $\sim$5 in the low temperature range. For the temperature intervals 150–300 and 20–100 K, the dispersive coefficients β_1 and β_2 are very close to unity (inset of figure 2(a)), showing the monodispersive character of BKI in these temperature ranges.
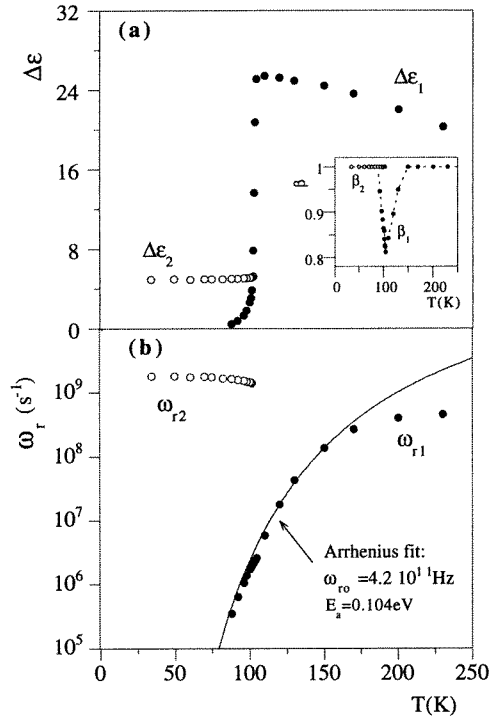
Figure 2. Temperature dependence of the Cole–Cole fitting parameters: (a) dielectric strengths of the HT ($\Delta\varepsilon_1$) and LT ($\Delta\varepsilon_2$) modes; inset of (a) dispersion coefficients of the HT (β_1) and LT (β_2) modes; (b) semilogarithmic plots of relaxation frequencies ω_{r1} (HT mode) and ω_{r2} (LT mode) and fit of $\omega_{r1}(T)$ to the Arrhenius law in the temperature range 96–150 K.

In the temperature interval 100–150 K the β_1 values decrease steeply down to 0.8 on approaching T_c from both sides of this temperature, indicating high critical fluctuations in the vicinity of the phase transition.

The logarithms of the relaxation frequencies of the HT ($\omega_{r1}(T)$) and of the LT ($\omega_{r2}(T)$) modes are depicted in figure 2(b). Whereas the frequency of the LT mode does not change significantly with the temperature there is a remarkable slowing down of the relaxation frequency of the HT mode on approaching the critical temperature. The fit of $\omega_{r1}(T)$ to the Arrhenius law ($\omega_{r1} = \omega_{r0}\,e^{(-E_a/k_B T)}$; k_B is Boltzmann's constant) in the temperature range 96–150 K determines the characteristic frequency $\omega_{r0} = 4.2 \times 10^{11}$ Hz and the activation energy $E_a = 0.10$ eV. The LT mode has a higher relaxation frequency than the HT mode and only the latter one seems related to the interactions that causes the phase transition.

We have registered at different fixed temperatures the values of the polarization P as a function of a.c. electric field along the direction [$\bar{1}$10] using electric fields up to 4 kV cm^{-1} near $T_c = 100$ K. BKI has no net spontaneous polarization in both temperature phases, and the slope of the lines $P(E)$ increases with the temperature, changing abruptly close to T_c. Pyroelectric current was measured along the sequence of thermal cycles: zero-field cooling (ZFC), field heating (FH), field cooling (FC) and zero-field heating (ZFH) along the direction [$\bar{1}$10], with a bias electric field of 1 kV cm^{-1}. Even for such a high field the polarization is smaller than 3 nC cm^{-2}. There is an excellent agreement for $P(T)$ obtained in cooling and heating runs at zero field. For the FH and FC runs the pyroelectric currents

are similar and only a negligible induced polarization of less than 0.1 nC cm^{-2} was detected in the ZFH run. Apparently there is no significative breaking of ergodicity in this betaine compound. A thermal hysteresis of about 2 K was found.

The experimental results here presented disallowed the identification of the primary order parameter related to the phase transition exhibited by the BKI at T_c, but even without this identification, we can describe its dielectric properties by using the Landau theory. The free energy density must verify the constraints imposed by the symmetry of the system. As BKI belongs to the space group $P\bar{1}$, the primary order parameter η has one component and the free energy density may be expanded in even powers of η and of the polarization P_k including coupling terms of the form $\eta^2 P_i P_j$. We shall limit ourselves to the case where only one component of the polarization is effective and so the free energy density has the form:

$$g = \frac{1}{2}a(T - T_0)\eta^2 + \frac{1}{4}b\eta^4 + \frac{1}{6}c\eta^6 + \frac{1}{2}\frac{P^2}{\varepsilon_{HT}} + \zeta\eta^2 P^2 - EP. \qquad (2)$$

a, b, c and ζ are independent temperature coefficients, all being positive except b, which is negative in a first order phase transition. ε_{HT} is the dielectric constant in the high temperature phase. As BKI does not exhibit any spontaneous polarization, we should take the term $\zeta\eta^2 P^2$ as positive. From the conditions of minimization of the free energy density and for $E = 0$ we obtain the solutions:

$$P_0 = \eta_0 = 0 \qquad\qquad \left(T > T_c = T_0 + \frac{3}{16}\frac{b^2}{ac}\right) \qquad (3)$$

$$P_0 = 0 \text{ and } \eta_0^2 = -\frac{b}{2c}\left[1 + \sqrt{1 - \frac{4ac}{b^2}(T - T_0)}\right] \qquad (T < T_c). \qquad (4)$$

The induced polarization (P) and the dielectric constant (ε) are given by the expressions:

$$P = \varepsilon_0\varepsilon_{HT}E \qquad \varepsilon = \varepsilon_{HT} \qquad T > T_c \qquad (\varepsilon_0 = \text{free space permittivity}) \qquad (5)$$

$$P = \frac{\varepsilon_0\varepsilon_{HT}}{1 + 2\varepsilon_{HT}\zeta\eta_0^2}E \qquad \varepsilon = \frac{\varepsilon_{HT}}{1 + 2\varepsilon_{HT}\zeta\eta_0^2} \qquad T < T_c. \qquad (6)$$
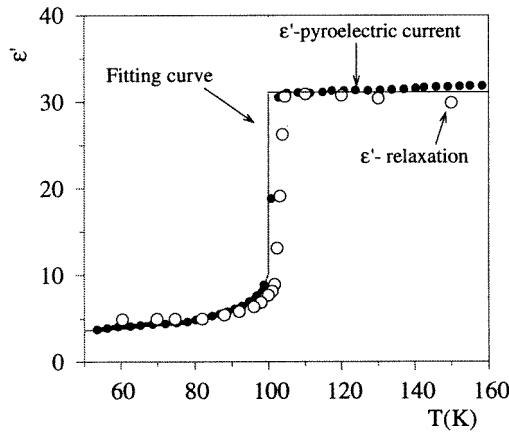

Figure 3. Temperature dependence of ε' obtained from pyroelectric current and dielectric relaxation and the fitting to expressions (5) and (6) (see text) obtained with a Landau model.

The polarization and the dielectric constant present a discontinuity at T_c, being:

$$\Delta\varepsilon_{T_c} = \Delta\varepsilon_{(T_c^+)} - \Delta\varepsilon_{(T_c^-)} = \frac{\varepsilon_{HT}}{1 - \frac{2}{3}c/(b\varepsilon_{HT}\zeta)}. \tag{7}$$

As can be seen in figure 3, there is an excellent agreement between ε' obtained from pyroelectric measurements and the static dielectric constant obtained from relaxation analysis. These data can be fitted to expressions (5) and (6) and the values of the adjustable parameters are $T_0 = 98.4$ K, $T_c = 100.1$ K and $\Delta\varepsilon_{(T_c)} = 20.4$.

From the study of dielectric, pyroelectric and polarization reversal here reported we can then conclude that BKI undergoes a phase transition at $T_c = 100$ K. Double hysteresis cycles for fields up to the electrical breaking down of the samples ($E = 10$ kV cm^{-1}) were not found, which very probably excludes the existence of an antiferroelectric phase in the low temperature range. As we have seen, a simple Landau model is able to describe qualitatively the main features of the dielectric constant behaviour. Work is in progress in order to identify the characteristics and symmetry of the order parameter and to determine the type of phase transition in BKI.

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