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LOW TEMPERATURE DIELECTRIC RELAXATION IN MIXED CRYSTALS OF BETAINE PHOSPHATE AND BETAINE PHOSPHITE

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ABSTRACT:We compare dielectric relaxation in the mixed Betaine Phosphate Phosphite system BP_xBPI_{1-x} for x=.40, .70 and .85 at low temperatures. In all cases, broad relaxation peaks were detected below 20K. We present a frequency dependent parameterization based upon the Kohlrausch-Williams-Watts formalism. It is found that the KWW relaxation time is Arrhenius and that β_{kww} is strongly temperature dependent. For the case of x=.85, β_{kww} increases with decreasing temperature.

INTRODUCTION

Antiferroelectric Betaine Phosphate[1] (BP:$(CH_3)_3NCH_2COO{\cdot}H_3PO_4$) and ferroelectric Betaine Phosphite[2] (BPI:$(CH_3)_3NCH_2COO{\cdot}H_3PO_3$) are molecular crystals of the amino acid betaine and the phosphoric or phosphorus acids, respectively. Both of these compounds have been shown to undergo high temperature structural phase transitions at 365K [BP][1] and 355K [BPI][3]. BP exhibits two additional phase transitions at 86K and 81K. Antiferroelectric order is established in BP at T_c=86K. At T_c, the O-H $\cdots$ O bonds order along one-dimensional chains and the chains are linked antiferroelectrically. By contrast, BPI shows ferroelectric order below T_c=216K. Because these compounds are almost isostructural, it is possible to form solid solutions of $(BP)_x(BPI)_{1-x}$ [BP100·x] at any concentration. Crystals with low-x tend to be more difficult to grow[4]. One is thus able to study as a function of concentration the change from a system with antiferroelectric order to one with ferroelectric order. At intermediate concentrations the long range electric order is suppressed[5]. Recently, we have reported dielectric measurements[6] showing that while a proton glass state exists in BP40, dc and ac conductivity is observed in BP95. The mixed system BP:BPI is thus the most recent addition to the ever-growing family of those systems which show a proton glass state. Proton glass behavior has been detected in the phosphate systems $Rb_{1-x}(NH_4)_xH_2PO_4$[7,8] [RADP] and $Rb_{1-x}(ND_4)_xD_2PO_4$[9,10] [D-RADP]. A few studies have been reported in the arsenate systems $Rb_{1-x}(NH_4)_xH_2AsO_4$[11,12] [RADA] and $Rb_{1-x}(ND_4)_xD_2AsO_4$[13] [D-RADA] which confirm proton glass behavior. The phosphate system $K_{1-x}(NH_4)_xH_2PO_4$[14,15] [KADP] and its aresnate variant, $K_{1-x}(NH_4)_xH_2AsO_4$[16] [KADA] have also been shown to exhibit proton glass behavior. The Betaine-phosphite -phosphate mixed crystals mark a significant departure from these above mentioned systems in that it is presently the single example of a proton glass state occurring in a system which does not strictly possess a PO_4 or an AsO_4 group. Instead, we see that proton glass behavior occurs due to a mixing of the PO_3 and PO_4 groups in this system.

EXPERIMENTAL

In order to obtain frequencies from 10^{-2}Hz to 10^6Hz over a temperature range of 5K to 300K, several different experimental setups were used. Coverage of the frequency range from 10^{-2} to 10^5 Hz [LF] was obtained by using a Solatron/Schlumberger 1260 Impedance/Gain-Phase Analyzer supplemented by the high-impedance Chelsea Dielectric Interface. The Hewlett-Packard 4274A Multi-Frequency LCR meter was used to measure frequencies from 10^1 Hz to 10^7Hz [AF]. A home-built continuous-flow cryostat capable of providing temperatures down to 2K was used with both the LF and AF bridges in order to make measurements below 20K. A cryogenic refrigeration system was also used in conjunction with the LF and AF bridges in order to provide temperatures between room temperature and approximately 20K. In all cases, the temperature controller was the Lake Shore DRC-91C temperature controller.

Single crystals of BP:BPI used in this investigation were procured from J. Albers (Fachbereich Physik, Universität des Saarlandes, Federal Republic of Germany). These high quality crystals were grown by controlled evaporation from aqueous solutions. For the dielectric spectroscopy, samples in the shape of thin slices oriented along the monoclinic b-axis[2] were gold-plated in a sandwich configuration so that the crystal was between gold plates. Copper leads were attached to the gold plates with silver paint. In order to circumvent possible problems resulting from any hydroscopic nature associated with these crystals, exposure to the ambient atmosphere was limited after gold plating.

RESULTS and DISCUSSION

In Figure 1, we show temperature dependent data for ϵ'' in the melt concentrations of 40%, 70% and 85% for frequencies between 1Hz and 10^6Hz. Each of the intermediate concentrations we have investigated show some sort of low-temperature relaxation. Starting with BP85, we see that ϵ'' increases in magnitude with decreasing concentration and then assumes the appearance one expects from a true glass-like relaxation with the 40% concentration. The solid lines shown here are fits to a phenomenalogical parameterization involving powers of a Bessel function of fractional exponent together with a Lorentzian which is able to rather completely describe our low temperature data in all concentrations. For some of the data below 10K only the parameterization is show in order to clarify the figure.

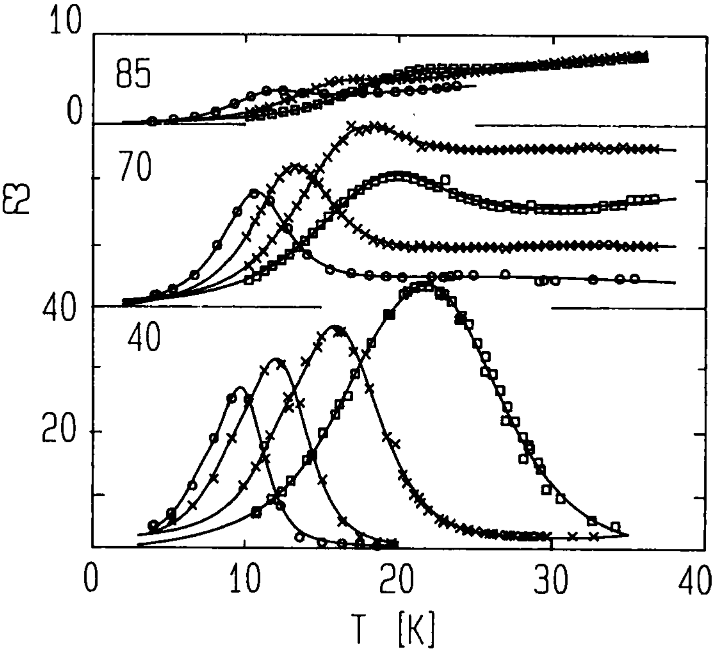

FIGURE 1. ϵ'' vs. temperature for BP85, BP70, and BP40. The lowest frequency (1Hz) is indicated by circles while the highest frequencies (10^4Hz, 10^5Hz, and 10^6Hz respectively) are indicated by open squares. Intermediate frequencies are denoted by crosses.

The fact that high temperature data in BP85 and BP70 show some ac conductivity may explain the unusual behavior seen above roughly 25K in these two systems. By contrast, we see almost no high-temperature ac conduction in BP40 and correspondingly, the relaxation curve for this compound exhibits no unusual increase with temperature.

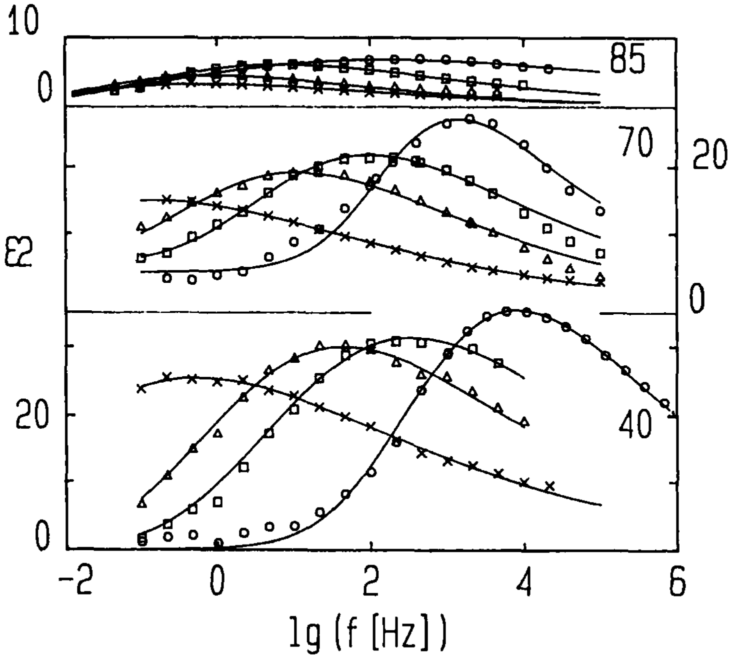

FIGURE 2. ε" as a function of frequency for the three concentrations. The temperatures are roughly 15K(circles), 13K(squares), 11K(triangles) and 9K(crosses).

In Figure 2, we show a diagram of ε" as a function of frequency for several temperatures. The lines shown are fits to the (semi-infinite) Fourier transform of the KWW[17] stretched exponential including an offset for the case of BP70. We find that for BP40, the KWW parameterization provides an excellent description with only slight departures at lower frequencies. For BP70 and BP85, this parameterization misses slightly at low and high frequencies, respectively. Never-the-less, this parameterization is rather successful in describing such broad relaxation peaks as observed in these systems. For BP40, the relaxation curves show a continuous broadening as temperature is decreased. The relaxation data on BP70 shows a narrowed temperature independent relaxation for temperatures above 30K. Below 30K, one observes a general broadening and corresponding increase in relaxation times with decreasing temperatures. By contrast, the relaxation in BP85 shows the unusual property of being rather broad at higher temperatures and then narrowing at lower temperatures. This type of behavior has been reported in $K_{0.989}Li_{0.011}TaO_3$ by Kleemann et. al.[18] and it has also been observed to occur in 40%$Ca(NO_3)_2$+60%$K(NO_3)$[19]. According to Ngai[20] such an unusual shift in the distribution of relaxation times can be explained by the second universality relation.

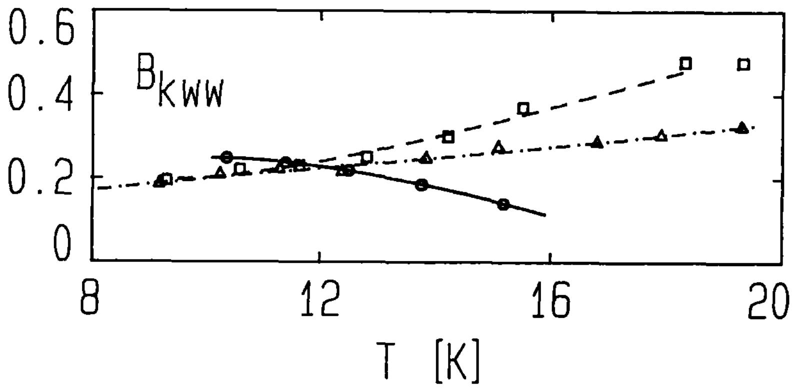

FIGURE 3. β_{kww} as a function of temperature for the three concentrations: 85%(circles), 70%(squares) and 40%(triangles). Lines are to guide the eye.

In Figure 3, we show the temperature dependence of the β_{kww} parameter. In BP70, β_{kww} approaches unity at higher temperatures and is fairly insensitive to temperature. At temperatures below 20K, β_{kww} shows a dramatic decrease and at the lowest temperatures, it is in agreement with the value obtained in BP40. The β_{kww} measured in BP85, however, shows an increase with decreasing temperature. At the lowest temperatures, β_{kww} for BP85 is slightly in excess of that seen in BP70 and BP40. The KWW relaxation times obtained for each of the three concentrations show a purely Arrhenius behavior as a function of temperature with energy barriers of 174K(BP85), 206K(BP70), and 235K(BP40) which is in good agreement with the energy barrier obtained for BP40 over a larger temperature range[6].

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