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Ferroelectric/Antiferroelectric Phase Coexistence in the Intermediate Concentration Regions of the BA_xBP_{1-x} Phase Diagram

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Temperature and frequency dependent hysteresis loop measurements have been carried out along the phase diagram of ferroelectric (FE) betaine arsenate (BA) and antiferroelectric (AF) betaine phosphate (BP) mixed crystal system (BA_xBP_{1-x}). Coexistence regions characterized by competing ferro- and/or antiferroelectric interactions are detected by multiple hysteresis loops.

Keywords Ferroelectrics; antiferroelectrics; mixed phases; hysteresis loops

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Introduction

The temperature (T)-concentration (x)-pressure (p) phase diagram of BA_xBP_{1-x} is characterized by the appearance of a variety of coexistence regions in the intermediate concentration region [1–4]. The nature of the different mixed phases, transitions and relaxations of the phase diagram, that reveal themselves in the measurements of the dielectric function [1, 2] is still unclear and difficult to explain from structural [4] and spectroscopic data [3]. The typical features of the dipole glasses [5] do not exist in this system.

The nature of these coexistence regions will be discussed in terms of the different AF and FE contributions to the polarization, extracted from the measurements of the hysteresis loops.

Experimental

Mixed crystals were grown from aqueous solutions, and their concentrations analyzed by means of UV spectroscopy and density methods [1, 2]. Samples in the shape of thin

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slices (d < 0.5 mm) were oriented perpendicularly to the polar axis, and vacuum-deposited aluminium or gold films served as electrodes. The temperature (23–300 K) and hydrostatic pressure ($p < 500$ MPa) dependence of the dielectric hysteresis loops and the current curves were carried out at several frequencies with a home-built hysteresis bridge [1].

Results and Discussion

$BA_{0.62}BP_{0.38}$ is representative for the coexistence behavior [1–3]. This sample show, at low pressures, a single relatively broad anomaly in $\varepsilon'(T)$ at $T_{c2,a}$ (Fig. 1). A second peak at $T_{c2,b}$ is obtained by applying hydrostatic pressure. The appearance of this peak is correlated with the increase of the anomaly in tan $\delta(T)$ at T_d, indicative of the low temperature relaxation (Figs. 1 and 2).

Typical hysteresis and current curves are presented in Fig. 1. Figure 2 shows the temperature behavior of the corresponding critical fields. Coincident with $T_{c2,a}$ the system undergoes a transition into an AF phase: double hysteresis loops appear at T_{p1} (Fig. 2). A second AF component appears (P3 and P5) some degrees lower (T_{p2} in Fig. 2) with lower critical fields (internal loops). This indicates a transition at $T_{c2,b}$ into a pseudo AF phase in which two different AF orders coexist. This anomaly cannot be observed in the low pressure dielectric measurements due to the narrow temperature range between the two transitions. A FE component appears at lower temperatures due to the destabilization of the AF stability limit P3 (zero field crossing of the coercive field at T_{p3}, which coincides with T_d). A new component in the polarization tends to stabilize the AF structure (P2), and the result is a triple hysteresis loop at low temperatures. This process evidences the existence of interactions of different signs and it also shows a strong frequency dependence (Figs. 1 and 2). Increasing pressures changes the stability limits of the FE and AF components [7].

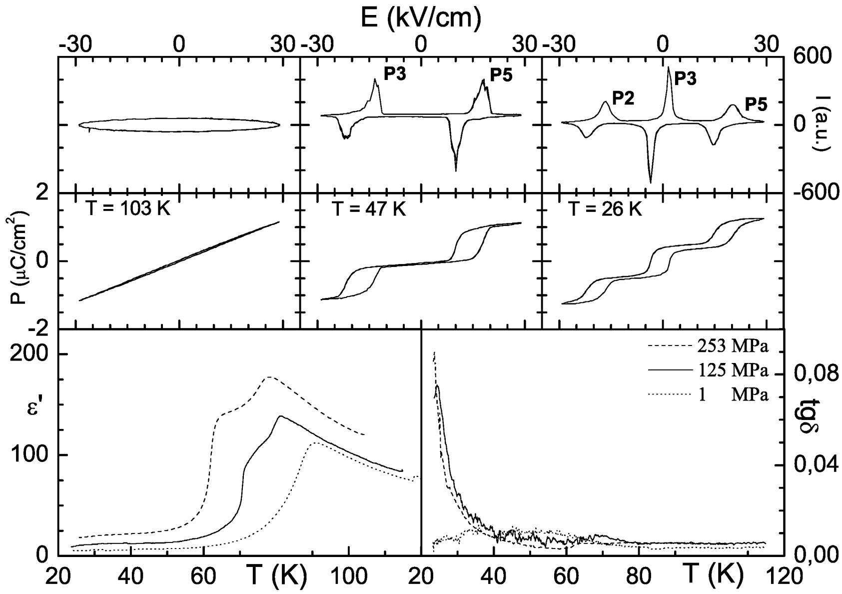

FIGURE 1 Typical hysteresis loops (above) and current curves (below) for $BA_{0.62}BP_{0.38}$ at $p = 10$ MPa in the different regions of the anomaly diagram. $\nu = 10$ Hz, sinus. Below: $\varepsilon'(T)$ (left) and tan $\delta(T)$ (right) by cooling at different pressures and $\nu = 1$ kHz

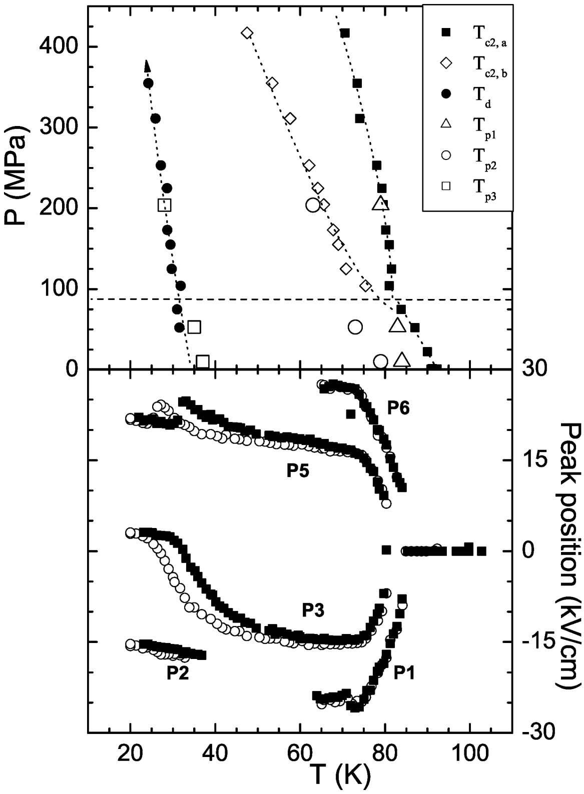

FIGURE 2 Above: (T, p) phase diagram for the $BA_{0.62}BP_{0.38}$ sample from the peaks detected in the dielectric measurements (cooling; $\nu = 1$ kHz) and the critical fields from the current curves (cooling; $\nu = 1$ Hz). Below: Behavior of the critical fields taken from the peaks in the current curves for $BA_{0.62}BP_{0.38}$ at 10 MPa. The numbers correspond to the peaks in Fig. 1. $\nu = 1$ and 10 Hz, sinus.

A phenomenological model can reproduce the main features of the system [6, 7]. The only condition for the appearance of phase separation is that the competing FE and AF states have to present a small energy difference that the disorder can counteract.

Conclusion

Competing ferro- and/or antiferroelectric contributions to the polarization are responsible for the different mixed regions observed in the phase diagram of BA_xBP_{1-x}. This suggests two systems of ordered units and it is tempting to assume the AsO_4- and PO_4-tetrahedra as these independent units [3]. The existence of disorder, which compensates the small energy difference between the competing states, is responsible for the main features of the phase diagram [6, 7].

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