The Relaxational Properties and Phase Behavior of $Pb(Sc_{0.5}Ta_{0.5})O_3$

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Motivation—Many oxides with the ABO_3 perovskite structure exhibit large dielectric constants and strong electromechanical coupling. These properties arise from an easily polarized (soft) crystal lattice due to a low-frequency transverse optic phonon. Of particular interest are perovskites with chemical disorder due to mixed cations on the A sites (corners of a simple cube) or the B sites (center of the cube). One example is $Pb(Sc_{0.5}Ta_{0.5})O_3$ or PST with disordered Sc and Ta on the B site and two distinct phases, a high-temperature cubic phase with local non-cubic distortions (polar nanoregions) and a low-temperature polar or ferroelectric phase. We have employed hydrostatic pressure to better understand the dielectric response and phase behavior of PST.

Accomplishment—The size of the polar nanoregions (PNRs) and correlations between them are determined by the polarizability of the host lattice. In particular, the polarizability can increase with decreasing temperature (T), leading to larger polar regions and stronger correlations. In PST these regions reach macroscopic size at low temperature, and a spontaneous transformation to a ferroelectric (FE) state occurs. This phase transition is reflected in the dielectric constant ε′ for a PST ceramic sample versus increasing T at ambient pressure (P) shown in Fig. 1. As T increases, there is a rapid rise in ε′ near 250 K with little frequency dependence. This rise marks a transition from a FE state with macroscopic polar domains to a relaxor (R) state with dynamic PNR's and a strong frequency dependence in the dielectric constant. At higher temperatures, the thermal fluctuations in these PNRs increase, resulting in a dispersive peak (T_{max}) in ε′. The inset in Fig. 1 shows the thermal hysteresis expected in the first-order FE transition but not in the R state.

Hydrostatic P decreases the polarizability of the lattice, thus decreasing both the size of the PNR's and correlations between them and suppressing the FE transition. This suppression is shown in Fig. 2 where we compare ε′ versus increasing T at 1 bar, 4 kbar and 9 kbar. There is no evidence for a FE state at the two elevated pressures. Data at 2 kbar (not shown) show a small anomaly in ε′ (T) near 235 K, indicating that the FE transition is still present.

The phase behavior of PST is summarized on the Temperature-Pressure phase diagram in the inset of Fig. 2. Both the temperature of the ε' peak, T_{max}, in the R state (shown at 10^4 Hz) and the FE transition temperature, T_c, decrease with increasing P. The FE transition decreases at a faster rate, extending the R state over a wider T range, and completely vanishes between 2 and 4 kbar (shown as a star), allowing a continuous FE-to-R crossover (from point A to point B) without crossing a phase boundary.

Significance—The results show that the R state is the ground state of disordered PST at high P (reduced volume). The termination of a phase line at a point (the star in the inset of Fig. 2) is a very unusual feature in the phase diagram of a solid. From a thermodynamic point of view it is akin to the gas-liquid critical point for a fluid; however, in the present case it is associated with a pressure-induced FE-to-R crossover. Its existence allows one to define a path such as A-B that allows PST to undergo the crossover without crossing a phase boundary.

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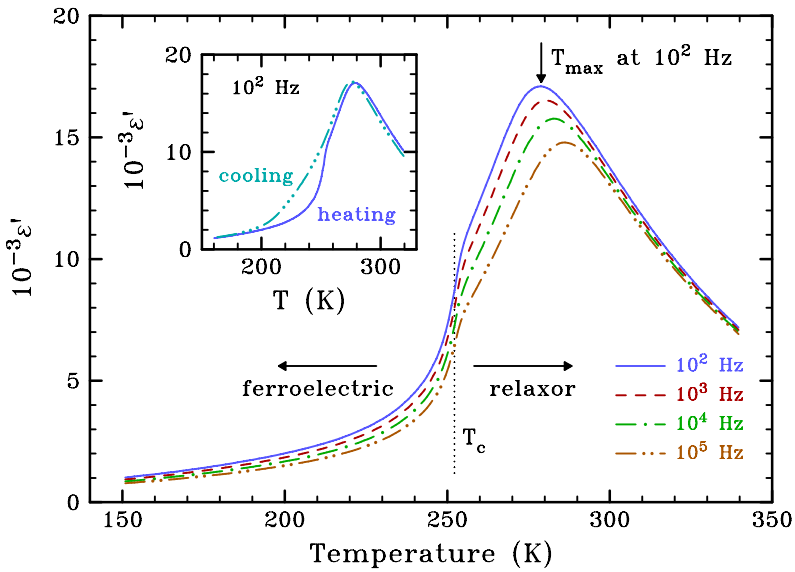

Figure 1. Dielectric data ε′ (T) measured during heating reveal a transition from a ferroelectric (FE) state below T_c (near 250 K) to a relaxor (R) state above T_c. The inset shows the thermal hysteresis expected in the first-order FE transition but not in the R state.

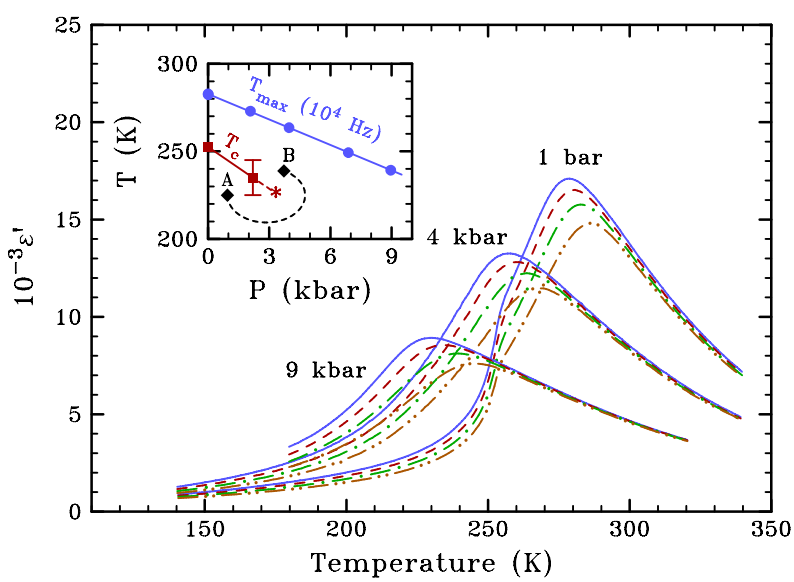

Figure 2. Hydrostatic pressure decreases ε′ (T) and suppresses the FE state. Isobaric heating data at 4 and 9 kbar show only the R state at all temperatures, in contrast to the data at 1 bar. Inset: The temperature of the ε′ peak, T_{max}, in the R state and the FE transition, T_c, during heating decrease with pressure. The FE transition vanishes between 2 and 4 kbar (indicated by a star), allowing a continuous path from point A to point B without crossing a phase boundary.