

Dipolar Centers in Quantum Paraelectrics: Mn and Fe in KTaO_3

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Motivation—Random lattice disorder produced by chemical substitution in ABO_3 perovskites can lead to the formation of dipolar impurities and defects that influence the static and dynamic properties of these materials. Because of the high polarizability of the ABO_3 host lattice, associated with its soft ferroelectric mode, dipolar entities polarize regions around them forming polar nano-/microdomains whose size is determined by the temperature-dependent correlation length, r_c , in the host. When these dipolar entities possess more than one equivalent orientation, they may undergo dielectric relaxation in an applied *ac* field. At sufficiently low concentration, each polar domain behaves as a non-interacting dipolar entity with a single relaxation time, but at higher concentrations of disorder, the polar domains can interact, leading to the formation of a glass-like relaxor state, or even an ordered ferroelectric state.

Accomplishment—We have investigated the dipolar relaxational properties of the disordered quantum paraelectric KTaO_3 , where the disorder is produced by dilute Mn and Fe impurities. A significant aspect of this work is the influence of hydrostatic pressure on these properties. KTaO_3 is a model soft ferroelectric (FE) mode system whose long wavelength TO phonon frequency softens with decreasing temperature (T), but never quite vanishes because of quantum fluctuations at sufficiently low temperatures. The soft mode imparts unto KTaO_3 a strongly T-dependent r_c , making the behavior of dipolar centers in this crystal quite interesting. We have determined the temperature and pressure dependencies of r_c as shown in Fig. 1. The Mn^{2+} center results from the off-center displacement ($\approx 0.9 \text{ \AA}$) from the K^+ site along one of six equivalent [001] directions. At a concentration of 0.01 at.%, the Mn^{2+} centers are, on the average, farther apart than r_c and there is no measurable anomaly in

the real part of the dielectric susceptibility, but there is a loss ($\tan \delta$) peak at $\sim 50\text{K}$. r_c at this temperature is two unit cells long ($2a_o$ in Fig. 1), and thus there is no overlap or correlations among the polar nanodomains. At a concentration of 0.3 at.% Mn, however, one in every ~ 300 unit cells has a Mn^{2+} ion, and in this case, for $r_c = 2a_o$ there is some overlap and correlations among the nanodomains. The result is weak relaxor behavior that is reflected in both the dielectric susceptibility (or ϵ') and $\tan \delta$ as shown in Fig. 2. Pressure reduces r_c (Fig. 1) resulting in weaker correlations and smaller ϵ' and $\tan \delta$ anomalies.

Iron produces two dipolar centers in KTaO_3 , an Fe^{3+} -oxygen interstitial complex and an Fe^{2+} center most likely produced by an off-center position of Fe^{2+} . Unlike Mn doping, Fe doping at the 0.3 at.% level does not lead to any measurable anomalies in $\epsilon'(T)$, the Fe centers behaving as non-interacting nanodomains with $\tan \delta$ peaks at $\sim 150\text{K}$ and $\sim 185\text{K}$ (Fig. 3). The absence of $\epsilon'(T)$ anomalies is easily understood from the results in Fig. 1. In the 150-200K range, r_c is only $\approx 1a_o$ so that the nanodomains are much smaller than in the case of Mn (where $r_c \approx 2a_o$) at its $\tan \delta$ peak and, thus, there is essentially no overlap or correlation among the Fe center.

Significance—Soft mode systems such as KTaO_3 are ideal hosts for studying the onset and evolution of correlations among dipolar centers because the correlation length for dipolar interactions in these hosts can be delicately tuned by either temperature or pressure, as shown in Fig. 1. This property is unique to soft mode systems where the soft mode frequency is determined by a delicate balance between short-range and coulombic forces. In turn, the dielectric signature of dipolar centers provide an indirect probe of soft mode behavior.

Sponsors for various phases of this work include: DOE Office of Basic Energy Sciences

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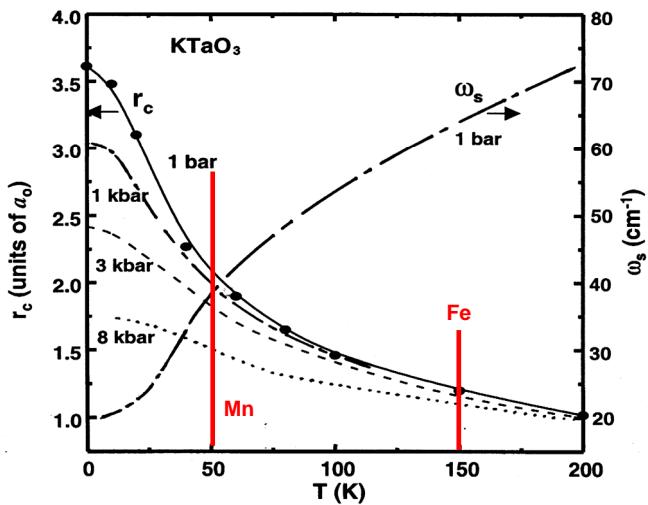


Figure 1. Temperature dependence of the ferroelectric soft mode frequency (ω_s) and of the correlation length (r_c) for dipolar correlations of KTaO_3 . The influence of pressure on $r_c(T)$ is also shown.

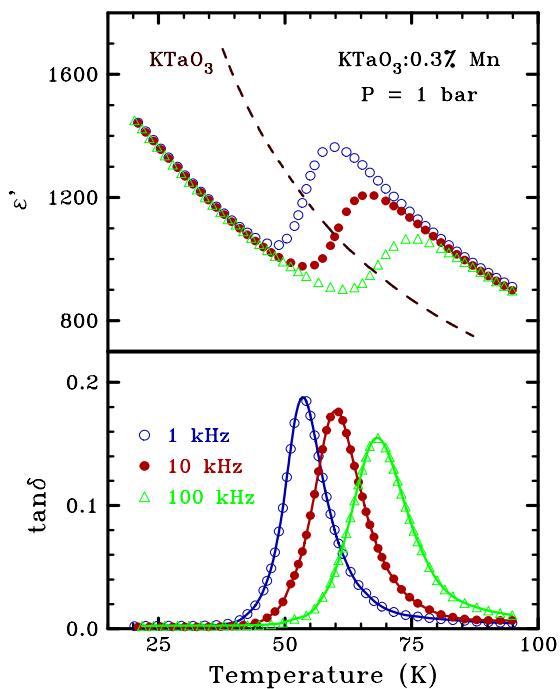


Figure 2. Temperature dependence of ϵ' and $\tan \delta$ at 1 bar of a KTaO_3 crystal with 0.3 at % Mn showing the relaxational character of the response. The non-relaxational $\epsilon'(T)$ response of undoped KTaO_3 is shown (dashed line) for comparison.

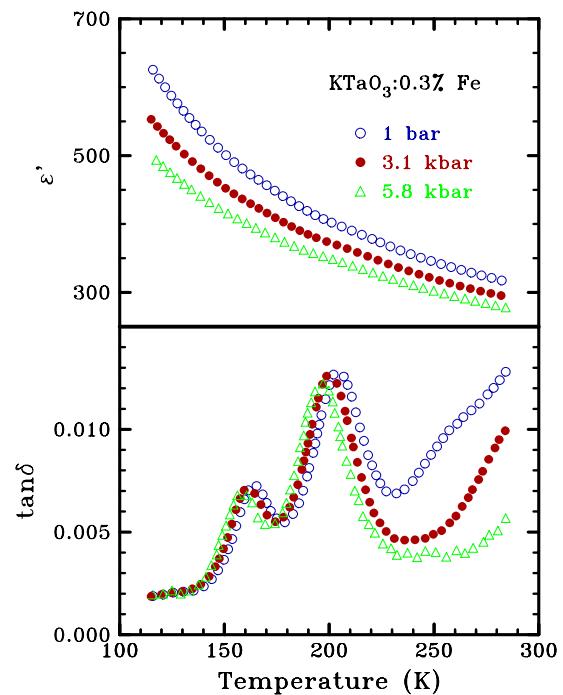


Figure 3. Temperature dependences of ϵ' and $\tan \delta$ at different pressures of a KTaO_3 crystal doped with 0.3 at % Fe.