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Ferroelectric-to-relaxor crossover and oxygen vacancy hopping in the compositionally disordered perovskites $KTa_{1-x}Nb_xO_3$:Ca

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It is shown that lattice disorder induced by Nb and Ca substitution has a strong influence on the dielectric and relaxational properties of $KTaO_3$. Both substituents are believed to occupy off-center positions at the Ta site, and the difference in valence between the Ca^{2+} and Ta^{5+} ions leads to the formation of oxygen vacancies (V_O). Specifically, for a $KTa_{1-x}Nb_xO_3$:Ca crystal with $x=0.023$ and with a 0.055 at. % Ca doping, we observe (i) a ferroelectric transition at atmospheric pressure (1 bar); (ii) a large enhancement of the transition temperature by Ca doping; (iii) a pressure-induced crossover from ferroelectric-to-relaxor behavior; (iv) the impending vanishing of the relaxor phase at high pressure; (v) the reorientation of the Ca-oxygen vacancy (Ca:V_O) pair defect; and (vi) the variation of the energetics and dynamics of this reorientation with pressure. Most of these effects are associated with Nb- and Ca-induced dipolar entities and appear to be general features of soft mode ferroelectrics with random-site polar nanodomains. The ferroelectric-to-relaxor crossover can be understood in terms of a large decrease with pressure in the correlation length among polar nanodomains—a unique property of soft ferroelectric mode systems.

I. INTRODUCTION

The static and dynamic properties of so-called relaxor ferroelectrics (or relaxors) have been of much recent interest.[1] On cooling, these materials exhibit slowing down of the relaxation of their orientational degrees of freedom, ultimately resulting in a frozen-in dipolar state which lacks long-range order. A universal signature of relaxors is a broad, frequency-dependent peak in the temperature-dependent susceptibility. The peak defines a dynamic freezing or ''glass'' transition temperature.

In ferroelectrics, relaxor behavior results from either frustration or compositionally induced disorder.[1–3] The latter type of disorder and related random fields are believed to be responsible for the relaxor properties of mixed ABO_3 perovskite oxides (Fig. 1) such as $Pb(Mg_{1/3}Nb_{2/3})O_3$ (or PMN), and La-modified $PbZr_{1-y}Ti_yO_3$ (or PLZT).[1–6] All of these materials involve structural and or chemical complexities which have made detailed understanding of the relaxor state difficult.

In the present work we have investigated a Ca-doped $KTa_{1-x}Nb_xO_3$ single crystal (henceforth designated KTN:Ca) and observed a number of properties which suggest that Ca-doped KTN may be a model system for studying the role of disorder in perovskites. Specifically, for our crystal with $x=0.023$ and 0.055 at. % Ca doping, we observe a ferroelectric (FE) transition at atmospheric pressure (1 bar); a large enhancement of the transition temperature with Ca doping; a pressure-induced crossover from FE-to-relaxor (R) behavior; the impending vanishing of the relaxor phase at high pressure; and the energetics and dynamics of the reorientation of the Ca-oxygen vacancy (Ca:V_O) pair defect. In this paper we first comment on the nature of Nb and Ca substitution in $KTaO_3$ and then describe briefly the experimental details followed by presentation of the results and their interpretation.

II. NATURE OF Nb AND Ca SUBSTITUTION IN $KTaO_3$

Pure $KTaO_3$ (KT) is the classic incipient perovskite ferroelectric. Its soft ferroelectric (FE) mode is stabilized at low temperatures by quantum fluctuations; consequently, the crystal does not undergo a FE transition and remains cubic down to the lowest temperatures.[7] However, the substitution of Nb for Ta at concentrations $x \geqslant 0.02$ yields mixed crystals which exhibit transitions to one or more FE phases depending on the composition.[8,9] At low Nb concentrations ($0.02 < x < 0.10$), the system exhibits a single cubic-rhombohedral transition.[9] Because the Nb^{5+} and Ta^{5+} ions have compa-

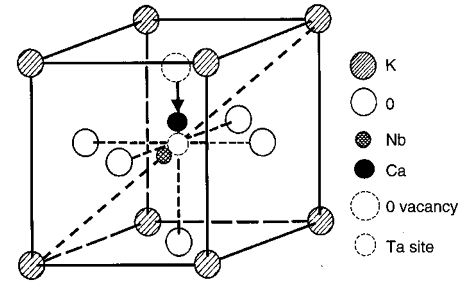

FIG. 1. The cubic perovskite structure of $KTaO_3$. On substituting for Ta^{5+} at the B site a Nb^{5+} ion occupies an off-center position along a ⟨111⟩ direction and a Ca^{2+} ion occupies an off-center position along a ⟨100⟩ direction. To preserve charge neutrality the substitution of Ca^{2+} for Ta^{5+} is accommodated by the formation of oxygen vacancies.

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rable sizes and electronic polarizabilities, the Nb^{5+} ion would be expected to substitute for Ta^{5+} at the *B* site in the ABO_3 lattice (Fig. 1). However, there is strong evidence that the Nb^{5+} occupies an off-center position along the $\langle 111 \rangle$ direction both below and above the transition.[3,10] There are eight equivalent such positions in the perovskite lattice (Fig. 1), and the Nb^{5+} can hop among them. In the off-center position the Nb^{5+} is displaced[10] by ~0.14 Å and induces a relatively large dipole moment. The presence of strong, orientable dipolar entities in the highly polarizable KT host lattice provides just the ingredient that can trigger the onset of ferroelectricity.[3]

Very little is known about the details of Ca substitution in KT or KTN, and it is thus worthwhile to develop a hypothesis as to what can be expected. Intuitively, Ca^{2+} might be expected to substitute for K^+ at the *A* site (Fig. 1); however, size considerations (ionic radii, $r_i = 0.99$ A for Ca^{2+} vs 1.33 A for K^+) could make this substitution unfavorable. Alternatively, Ca^{2+} would substitute for Ta^{5+} ($r_i = 0.68$ A) at the *B* site. Electron spin resonance (ESR) studies of a number of divalent transition-metal ion (e.g., Mn^{2+}, Cu^{2+}, Co^{2+}) dopants in KT have shown that the substitution occurs at the *B* site.[11,12] These ions are intermediate in size between Ca^{2+} and Ta^{5+} suggesting that Ca^{2+} might also favor the *B* site. Indeed, the results to be discussed below support this assignment.

To preserve charge neutrality on substituting Ca^{2+} for Ta^{5+}, the Ca^{2+} ions would be accommodated by the formation of oxygen vacancies (V_O); 1.5 V_O's for each Ca^{2+}. Reference to Fig. 1 shows that this substitution leads to the formation of a $\langle 100 \rangle$ Ca:V_O pair defect on adjacent *B* and O sites. This pair is an electric dipole which in the ABO_3 lattice has six equivalent positions and may thus undergo reorientation among these positions. Such reorientation can take place simply by the hopping of the vacancy among the oxygen sites. As discussed later, we find evidence in the present work for this reorientation in applied ac fields, a conclusion that is supported by early ESR studies on divalent transition metal dopants[11,12] which revealed $\langle 100 \rangle$ axial spectra confirming the existence of such a pair defect and its reorientation.

An additional feature relevant to the present work is the fact that the Ca^{2+} and V_O have opposite effective charges and can thus be expected to be drawn together by Coulombic attraction. Indeed, the early ESR work on the transition-metal: V_O pairs in perovskites showed that the metal ion (e.g., Mn^{2+} in $SrTiO_3$) moves by a substantial distance (0.2 A) towards the oxygen vacancy.[13] We expect a comparable shift for Ca^{2+} in KT. The important point here is that the Ca^{2+} does not sit at a center of symmetry, but is off center. The presence of off-center Ca^{2+} and Ca^{2+}:V_O dipolar entities in the highly polarizable KT (or KTN) host lattice is another ingredient that can strengthen long-range correlations and the FE state.

III. EXPERIMENTAL DETAILS

The sample used in the present work was a light blue single-crystal plate ($0.2\text{-cm}^2 \times 0.1$-cm thick) cut from a Ca-doped KTN boule grown by solidification from a nonstoichiometric melt using a process similar to that originally described by Hannon.[14] The crystal was oriented using x-ray Laue back-reflection methods, sectioned along $\langle 100 \rangle$ directions, and the (100) faces were polished using colloidal silica. The Ca content was 0.055 at. % based on the amount of $CaCO_3$ added to the melt during growth. The Nb content was determined by inductively-coupled plasma (ICP) mass spectrometry and found to be 7900 ± 300 ppm by weight which translates to $x = 0.023$, or 2.3% of the Ta^{5+} ions replaced by Nb^{5+} ions. The sample was investigated by dielectric spectroscopy with measurements of the real (ε') and imaginary (ε'', or the dielectric loss, tan δ) parts of the dielectric constant performed as functions of frequency (10^2–10^6 Hz), temperature (4–300 K) and hydrostatic pressure (0–10 kbars). Helium was used as the pressure transmitting medium.

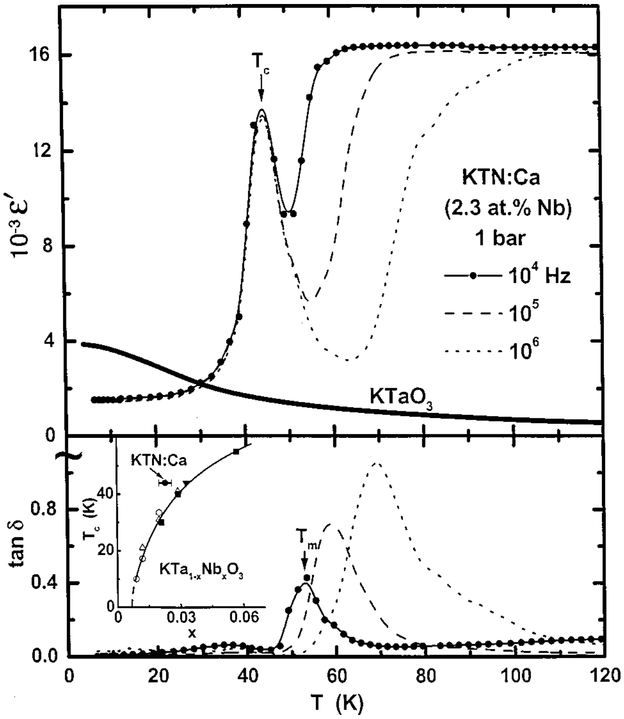

FIG. 2. Temperature dependences of the static dielectric constant (ε') and dielectric loss (tan δ) for a Ca-doped $KTa_{1-x}Nb_xO_3$ (or KTN) crystal with $x = 0.023$ measured at different frequencies. The inset shows the ferroelectric transition temperature (T_c) of this crystal relative to the T_c vs x phase diagram for KTN.

IV. RESULTS AND DISCUSSION

Experimentally, Nb and Ca substitution produces remarkable changes in the dielectric properties of KT. Figure 2 contrasts the temperature dependence of ε' of our KTN:Ca sample with that of KT. Above 50 K, $\varepsilon'(T)$ of KT obeys a Curie-Weiss law, and below this temperature ε' increases less rapidly with decreasing temperature than is predicted by this law due to quantum fluctuations.[7] Ultimately, $\varepsilon'(T)$ reaches a plateau as $T \rightarrow 0$ K as required by the third law of thermodynamics, and ε' is very large (~4000). This $\varepsilon'(T)$ response, which is frequency independent in the audio frequency range, is well understood in terms of soft-mode theory.[7] Specifically, the frequency ω_s of the soft FE mode (a $q = 0$ TO phonon) of KT in the cubic paraelectric phase decreases with decreasing T accounting for the Curie-Weiss $\varepsilon'(T)$ response and deviations thereof, since ω_s and ε' are related by a Lyddane-Sachs-Teller relationship such that $\omega_s^2\varepsilon'=\text{const.}$ ω_s becomes sufficiently small at low temperatures, but is prevented by quantum fluctuations from vanishing and precipitating a FE transition. Consequently, KT does not undergo a FE transition down to the lowest temperatures.[7]

The dielectric spectrum of KTN:Ca is remarkably different as shown in Fig. 2. First ε' increases with increasing T, rises to a sharp, frequency-independent peak at 44 K and then decreases in a Curie-Weiss-like fashion on further heating. These are the characteristics of a FE transition with $T_c=44\,\text{K}$, and the results to follow support this contention. The second main feature in the $\varepsilon'(T)$ response is the turnaround in ε' with increasing T above T_c. This turnaround is strongly frequency dependent and is also marked by a large relaxational peak in tan $\delta(T)$ as shown in the lower portion of Fig. 2. Above this feature ε' reaches a very large and nearly temperature- and frequency-independent value. We believe that this feature in the dielectric response, which is absent in KTN samples of the same composition but without Ca doping, is associated with the hopping motion of the Ca:V_{O} pair defect as we shall shortly justify.

It should be noted in passing here that a weak relaxational peak in tan $\delta(T)$ is known to occur in both ''pure'' and intentionally doped KTaO$_3$.[15] The peak is observed at ~40 K (at 1 kHz), has a characteristic activation energy of $E=440\,\text{K}$, and an intensity that is sample dependent. It has been attributed to the presence of extended defects located around rhombic Fe^{3+} ions associated with oxygen vacancies,[15] but this assertion has not been definitely confirmed. In the present work, this relaxation peak is swamped by the much larger dielectric losses associated with the phase transition at 44 K and with the hopping of the Ca:V_{O} pair defect which occurs at higher temperatures. Thus we shall not deal with the 40 K relaxational peak in the present paper.

The two main features in the dielectric response of our KTN:Ca crystal at 1 bar are thus the FE phase transition and the hopping motion of the Ca:V_{O}. Fortunately, these two phenomena are sufficiently separated in temperature to allow us to study them and the effects of pressure on them separately. We begin with the ferroelectric transition.

A. Ferroelectric transition and ferroelectric-to-relaxor crossover

Figure 3 shows the dielectric response associated with this FE transition as well as the influence of pressure on this response. (In this figure we have subtracted the part of the total response well above T_c due to the hopping motion of V_{O} and associated Ca:V_{O} dipolar pair.) At 1 bar the response is the classic ferroelectric signature: it is essentially frequency independent, the weak frequency dispersion at the peak and above T_c being a vestige of the large ε' and tan δ associated with the Ca:V_{O} reorientation (see Fig. 2). The inset in Fig. 2 shows the transition temperature $T_c=44\,\text{K}$ for our sample relative to the T_c vs x phase diagram[9] for KTN. It is seen that the relatively small amount of Ca in the $x=0.023$ KTN sample has a remarkably strong influence on T_c, raising it from ~32 to 44 K. Evidently the presence of even a few Ca:V_{O} dipoles in the highly polarizable KTN host strongly enhances the long-range correlations among dipolar entities, thereby raising T_c.

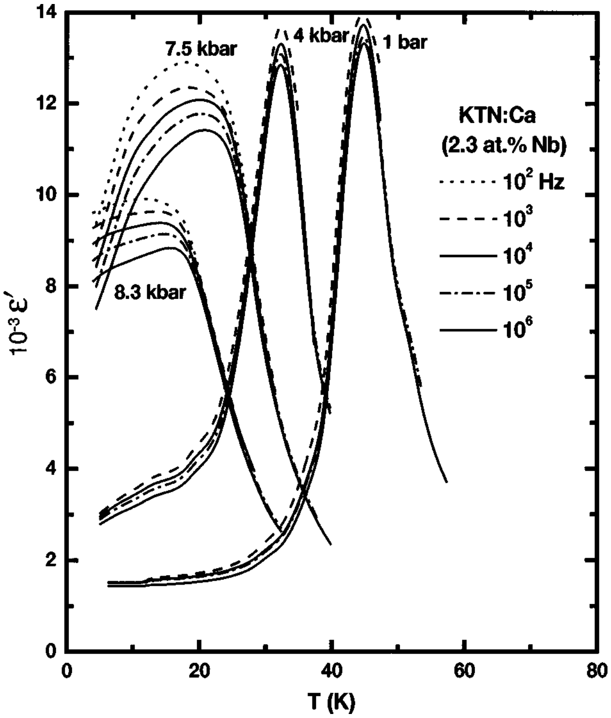

FIG. 3. Temperature dependence of the static dielectric constant of KTN:Ca measured at different frequencies and hydrostatic pressure. The crystal exhibits a pressure-induced normal ferroelectric-to-relaxor crossover as can be seen by comparing the 4- and 7.7-kbar isobars.

Modest pressure has a strong influence on the dielectric response as shown in Fig. 3. Initially and up to 6 kbars, the main influence of pressure is a shift of T_c to lower temperatures with $dT_c/dP=-3.0\,\text{K/kbars}$. This slope is comparable to those of many other soft mode ferroelectrics.[7] The influence of pressure on T_c is readily understood in terms of soft mode theory.[7] Specifically and simply, pressure increases ω_s making it necessary to go to lower temperatures (hence a lower T_c) to destabilize the mode and precipitate the transition.

Above 6.5–7.0 kbars, the dielectric response changes qualitatively as shown for the 7.5- and 8.3-kbar isobars in Fig. 3. The broad $\varepsilon'(T)$ peaks and the strong frequency dispersion on the low-temperature side at these pressures are the hallmarks of a relaxor phase. Thus our KTN:Ca sample exhibits a pressure-induced crossover from normal ferroelectric to relaxor behavior. Evidence for this crossover is also seen in the dielectric loss, tan δ, which becomes both larger and frequency dependent in the relaxor phase.

In the relaxor phase, the $\varepsilon'(T)$ peak defines a dynamic glasslike transition temperature which is designated by T_m. Pressure suppresses T_m at about the same rate as T_c. Although T_m is dependent on frequency, its pressure derivative is weakly frequency dependent.

There has been considerable recent interest in the properties of relaxors and the normal ferroelectric (FE)-to-relaxor (R) crossover; however, the physics of relaxors and the mechanism for this crossover phenomenon are still not settled.[1] As already noted, relaxor behavior is very prevalent in composionally disordered perovskites. The early conventional wisdom (the Smolenskii model) has been that relaxor behavior and the associated diffuse phase transitions in mixed perovskite ferroelectrics at 1 bar are induced by compositional fluctuations leading to large fluctuations in transition temperatures.[2,16] Thus a common approach of studying these properties has been to vary the composition, and thereby the degree of disorder, in order to induce relaxor behavior.[1,4] However, this approach introduces complications such as added randomness, lattice defects, lattice strains, and altered interatomic forces. Consequently, there is considerable vagueness in the interpretation and understanding of the experimental results.

Illuminating new insight into the physics of systems of this type has recently come from high pressure experiments on La-modified $PbZr_{1-x}Ti_xO_3$ (or PLZT) samples.[6] Starting with compositions that exhibit normal FE behavior at 1 bar, it was demonstrated that pressure induces a crossover to a relaxor phase. Since pressure clearly does not induce increased compositional fluctuations and disorder in samples of fixed compositions, the pressure results brought into question the early mechanisms proposed to account for relaxor behavior in perovskites. In contrast to changing the composition at 1 bar, the application of pressure changes only the interatomic interactions and the balance between long- and short-range forces making it easier to get to the essential physics.

The present results on KTN:Ca, earlier work[3] on a KTN sample with $x=0.02$ and the PLZT results[6] suggest that the pressure-induced FE-*R* crossover is a general feature of soft-mode ferroelectrics with dipolar impurities or polar nanodomains. We attribute this crossover to the unique pressure dependence of the soft-mode frequency ω_s, which controls the polarizability of the lattice as we now demonstrate.

The decrease of ω_s with decreasing T in the PE phase causes the polarizability of the lattice and thereby the correlation length (r_c) for polar fluctuations (which is inversely related to ω_s) to increase rapidly as $T \rightarrow T_c$. Because ω_s is determined by a delicate balance between long-range and short-range interactions, it is very strongly pressure (or volume V) dependent.[7] A measure of this dependence is the soft mode Grüneisen parameter, $\gamma \equiv -(\partial \ln \omega_s / \partial \ln V)_T$. For ordinary dielectrics γ for transverse optic (TO) phonons is on the order of 1–2 and is very weakly temperature dependent. However, for soft ferroelectric (TO) mode systems, like KT, PZT's, and other perovskites, γ is very large and strongly temperature dependent—approaching values of several hundred near T_c.[7]

The large value of γ translates to a large increase (decrease) in ω_s (r_c) with pressure. Figure 4 shows the variation of r_c with temperature at 1 bar and at elevated pressures for our KTN:Ca specimen. These results are deduced from the pressure and temperature dependences of ε'.[3,17] We cannot determine the absolute value of r_c in this way, but we can evaluate the relative change in this quantity. Hence in Fig. 4, r_c is given in arbitrary units. The 1-bar results show the large increase in r_c with decreasing temperature, a remarkable feature of the large, temperature dependent polarizability of the lattice. The decrease of r_c with pressure is nonlinear and is largest near T_c where it is estimated to be about 10^3 larger than the decrease in the lattice constant of the host.[3] For example, at 44 K in Fig. 4 r_c decreases by about a factor of 8 between 0 and 8.5 kbars, and the corresponding decrease in correlation volume is very large.

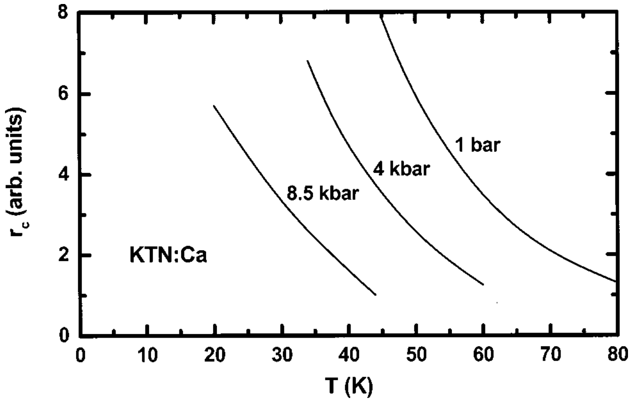

FIG. 4. Variation of the correlation length for dipolar interactions with temperature at different pressures for KTN:Ca.

On the basis of the above results and discussion, the dielectric response of KTN:Ca can be understood as follows. It is clear from the data in Figs. 2 and 3 that the presence of localized, oscillating Nb-induced and $Ca^{2+}:V_O$ dipoles in the highly polarizable KT host lattice greatly increases the polarizability of the crystal in the high-temperature PE phase. We envision each dipole inducing polarization (or dipoles) in adjoining unit cells and forming a dynamic polarization "cloud" whose extent is determined by the correlation length for dipolar fluctuations, r_c. At high temperatures r_c is small and the polarization clouds are effectively polar (FE) nanodomains. With decreasing T at low pressures ($\leqslant$6–7 kbars), the rapidly increasing r_c couples these nanodomains into rapidly growing polar clusters and increases their Coulombic interactions. Ultimately, these clusters percolate (or permeate) the whole sample and precipitate a static, cooperative long-range ordered FE state at $T \leqslant T_c$. At sufficiently high pressure (7.7 kbars in Fig. 3) on the other hand, the clusters increase in size on decreasing T in the PE phase, but do not become large enough to permeate the whole sample (or grains) and precipitate a FE transition. Rather, the clusters exhibit a dynamic "slowing down" of their fluctuations at $T \leqslant T_m$ leading to the observed relaxor behavior. Because r_c decreases continuously with increasing pressure, the polar clusters become smaller with increasing pressure—a fact that accounts for the observed increase in the frequency dispersion and suppression of the dielectric anomaly (e.g., compare the 7.5- and 8.3-kbar response in Fig. 3). It is thus seen that the FE-to-*R* crossover results simply from the large decrease in r_c with pressure—a unique property of soft FE mode materials.

B. Random fields and domain state

The dipolar entities formed by the substitution of Nb^{5+} and Ca^{2+}, of course, create random electric fields in the host $KTaO_3$ lattice. The lattice strains x_{ij} associated with these substituents also couple to the polarization via terms of the form $x_{ij}P_kP_1$ setting up additional random fields or enhancing their presence. There has been much interest in the influence of random fields on long-range order. Quite sometime ago it was shown theoretically[18,19] that when the order parameter has continuous symmetry, the ordered state of a large system of less than $d=4$ dimensions is unstable against an arbitrarily weak random field, i.e., a field much weaker than the interactions which favor the ordered state. Instead of a long-range ordered state, it becomes energetically favorable for such a system to break up on cooling into sufficiently large domains to form a so-called low-temperature domain state. The size of the domains is determined by a balance between the domain-wall energy and the statistics of the random field.[18]

For systems with uniaxial or cubic anisotropy, long-range order for $d=3$ can exist in equilibrium, if the width of the random-field distribution δ does not exceed a critical value δ_c. A quantitative estimate of δ_c was obtained by Schneider and Pytte[20] for an Ising spin model with infinite-ranged interaction with statistically independent site fields with a Gaussian distribution. More recently, Vugmeister[21] examined the existence of long-range (or ferroelectric) order in random-site dipole systems with electric dipole moments possessing cubic anisotropy. He showed that in disordered random-site systems, the critical concentration for the appearance of long-range order is determined by a balance between two competing effects: (i) the interaction energy of the dipolar entities separated by a mean distance r and (ii) the width of the static random-field distribution. Using an Ising model Hamiltonian with random fields h_i of the form

$$H=-J\sum_{i\neq j} S_iS_j-\sum_i h_iS_i, \tag{1}$$

where the ''spins'' $S_{i,j}$ located on sites i and j are electric dipoles with $(+/-)$ orientations that have an interaction potential of the form

$$J(r)=J_0\exp(-r/r_c^*) \tag{2}$$

and with a Lorentz form of the static field distribution. Vugmeister calculated the phase diagram for the system in terms of the quantity nr_c^{*3}, where n is the density of dipoles and r_c^* is the critical separation needed for the onset of long-range order.

In the dilute limit, the system considered by Vugmeister[21] produces a dipolar glasslike phase, and the long-range-ordered state appears only after exceeding a certain critical concentration of dipoles which determines the critical separation r_c^*. Interpreted in terms of this model, the concentration of dipoles n for our KTN:Ca crystal exceeds the critical concentration below ~6 kbars, and the crystals exhibit a long-range-ordered FE state at low temperatures. With increasing pressure, n scales with the density—a very small effect, i.e., n is essentially constant, but r_c^* decreases rapidly, ultimately falling below the critical value for $p>\sim 7$ kbars. Consequently, the dipolar system can no longer achieve long-range order and thus forms a relaxor phase at low temperatures. This is effectively the argument we advanced in Sec. IV A above and in an earlier study[3] on KTN. Here we take r_c^* to be essentially equivalent to the correlation length r_c.

There has been considerable effort aimed at seeking evidence for the existence of a domain state in mixed perovskites. For example, Bednorz and Müller[22] investigated the system $\mathrm{Sr}_{1-x}\mathrm{Ca}_x\mathrm{TiO}_8$ and observed relatively sharp $\varepsilon'(T)$ peaks for $0.0018<x<0.016$ which were attributed to a transition to a low-temperature quantum FE state. For $x>0.016$ these peaks give way to much broader rounded peaks whose intensities decrease and breadths increase with increasing x. These rounded peaks, whose peak temperature is frequency independent, were attributed to the formation of a random-field-induced low-temperature domain state. A puzzling aspect of this work, however, is why the domain state is not obtained for $x<0.016$ given that Ca-substitution-induced random fields exist below this composition. The authors[22] and others[23] noted this concern and offered possible explanations, but the issue is not yet resolved. In another example, Schremmer, Kleemann, and Rytz[24] noted that a domain state exists in $\mathrm{K}_{0.937}\mathrm{Li}_{0.063}\mathrm{TaO}_3$ below ~90 K. This state is attributed to the random dipolar fields associated with frozen-in off-center Li^+ ions, and its signature is a ''gentle drop'' (a change in slope) in $\varepsilon'(T)$ below 90 K. These random fields are cancelled by applied electric fields which induce a sharp FE transition. In a third example, Westphal, Kleemann, and Glinchuk[25] have argued that random fields are responsible for the observed strong slowing down of the dynamics of the best-known and most-studied relaxor PMN and for its eventual freezing into a domain state.

It is clear from the above three examples that there appears to be no common, or unique, dielectric signature for the transition to a ''domain state,'' and that the presence of weak random fields does not seem to suppress the FE transition in dilute $\mathrm{Sr}_{1-x}\mathrm{Ca}_x\mathrm{TiO}_3$. More generally, the existence of a domain state in the perovskites remains an unsettled issue as does the distinction between such a state and a relaxor state that consists of critically slowed down, randomly oriented nanodomains which ultimately freeze in a dipolar glasslike fashion at sufficiently low temperature. For our KTN:Ca sample, the sharp $\varepsilon'(T)$ peaks we observe for $p\leqslant 6$ kbars are signatures of FE transitions, and the broad peaks and strong low-temperature frequency dispersion that set in for $p>7.5$ kbars are the universal signatures of the relaxor state.

The existence of Nb^{5+}- and Ca^{2+}-induced polar nanodomains in KTN:Ca should be manifested at temperatures considerably higher than T_c or T_m. These domains will be randomly oriented so that the net polarization of the sample ΣP should be zero. However, ΣP^2 will not be zero, and the existence of the polarization will be reflected in properties that depend on P^2. Two such properties are electrostriction as evidenced in the linear thermal expansion,[2] $(\Delta l/l)$, and the quadratic electrooptic effect evidenced in the temperature dependence of the index of refraction n.[26] Measurements of $(\Delta l/l)$ and n vs T on KTN:Ca should be quite revealing in this regard. In our picture, the nanodomains grow with decreasing T as a result of the increase in correlation length and lead to the formation of a FE state at T_c if they become sufficiently large to permeate the whole sample or grains thereof; otherwise, they exhibit a critical slowing down and form a relaxor state below T_m.

C. Oxygen vacancy hopping

We now turn our attention to the second main feature in the dielectric response of KTN:Ca in Fig. 2 which we attribute to the hopping motion of the oxygen vacancy. An earlier ESR study[11] investigated the reorientation of the Mn^{2+}-V_O dipole in KT:Mn which involves hopping of the V_O within the next-nearest shell of the paramagnetic Mn^{2+} ion. The Arrhenius temperature dependence of the width of the Mn^{2+} ESR line yielded $E=0.115\,\mathrm{eV}$ for the barrier height between equivalent orientations and $\omega_0=4.4\times10^{13}\,\mathrm{s}^{-1}$ for the jump frequency. A later study revealed relaxation in the dielectric response of KT doped with a number of transition-metal ions.[27] The signature of this relaxation is a Debye-type loss peak of the form

$$\tan\delta=\frac{\delta\varepsilon'}{\varepsilon'}\cdot\frac{\omega\tau}{1+\omega^2\tau^2}, \tag{3}$$

where $\delta\varepsilon'$ is the difference between the relaxed (low frequency) and unrelaxed (high frequency) dielectric constant, ω is the angular frequency and τ is the relaxation time. The relaxation time exhibited Arrhenius temperature dependence of the form

$$\tau^{-1}=\omega_0\exp(-E/kT) \tag{4}$$

from which the activation energy E and pre-exponential factor, or jump frequency, ω_0, were obtained. For the particular case KT:Mn^{2+} the results were $E=0.11\,\mathrm{eV}$ and $\omega_0=5\times10^{13}\,\mathrm{s}^{-1}$ in excellent agreement with the ESR results. This agreement clearly establishes that the relaxational $\tan\delta(T)$ peak in KT:Mn^{2+} is associated with the reorientation of the Mn^{2+}-V_O pair defect.

For the present KTN:Ca^{2+} case, $\tan\delta(T)$ peaks such as those in Fig. 2 measured at different frequencies show that $\tau^{-1}(T)$ obeys Eq. (4) as shown in Fig. 5. At 1 bar $E=0.081\,\mathrm{eV}$ and $\omega_0=3.6\times10^{12}\,\mathrm{s}^{-1}$. Comparison of these parameters with the earlier results on KT:Mn^{2+} and KT:Co^{2+} reveal trends which strongly indicate that this dielectric relaxation in KTN:Ca^{2+} is indeed associated with the hopping motion of V_O of the Ca^{2+}-V_O pair defect. These trends are summarized in Table I. It is seen that E for the KTN:Ca^{2+} defect is somewhat smaller than that for KT:Mn^{2+} consistent with its loss peaks occurring at lower temperatures (only the values of $T_{\max}$ at 10^3 Hz are shown in the table). For KT:Co^{2+}, E is much larger also consistent with its much higher $T_{\max}$. We have also listed in Table I the ionic radii of the dopant ions in comparison with that of Ta^{5+} (0.68 A). Viewed against these radii, the E's in the table reveal a distinct trend, namely an inverse relationship between E and r_i. The Co^{2+} ion is nearly the same size as Ta^{5+} and causes little local distortion or relaxation of the oxygen octahedron around it (Fig. 1). Hopping of V_O is relatively difficult in this case. The Mn^{2+} ion, which is significantly larger than Ta^{5+}, causes more local relaxation and a lower E. Ca^{2+} causes the largest relaxation and leads to the lowest E. Evidently, the larger the relaxation, the easier the hopping of the M^{2+}-V_O pair (where M^{2+} is a divalent metal ion). Undoubtedly in KTN:Ca the presence of off-center Nb would have some influence on V_O hopping, but the results suggest that this influence is not major at the Nb concentrations involved.

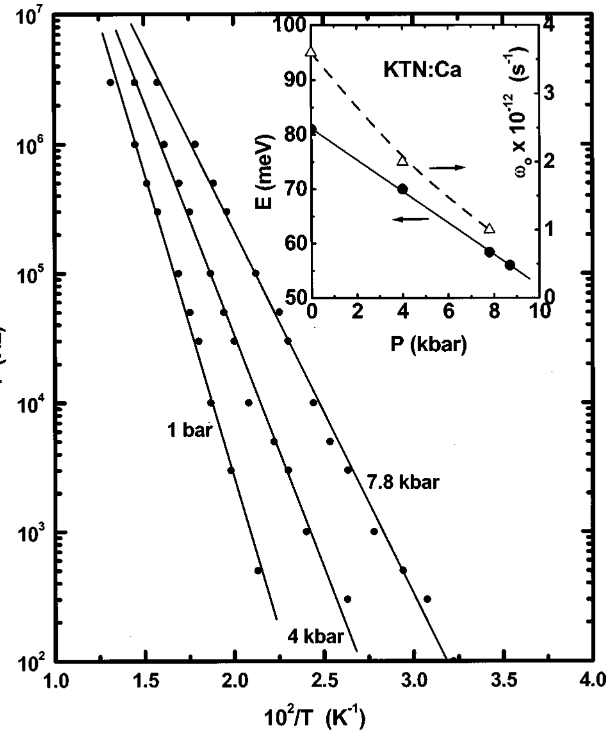

FIG. 5. Arrhenius plot of the reciprocal of the relaxation time of the hopping motion of the oxygen vacancy of the Ca^{2+}-V_O pair defect in KTN:Ca measured at different pressures. The inset shows the pressure dependence of the activation energy and the jump frequency for the process.

Our observation that the larger the local relaxation, the lower is the activation energy for the hopping of the M^{2+}-V_O pair begs the question, why? We believe that the issues here are essentially the same as those recently raised by Nowick, *et al.*[27] concerning the two observations that these activation energies in perovskites, which fall in the range 0.1–0.4 eV, are: (i) much smaller than the activation energy for dc ionic conductivity (~1.0 eV for KT), and (ii) also much smaller than the migration energy for the oxygen vacancy (>1.0 eV) obtained from computer simulations. As for these latter two observations, Nowick *et al.* suggest that the answer lies in the off-symmetry (or off-center) configuration of the M^{2+}-V_O defect. In this configuration the ions surrounding the defect undergo sufficient relaxation to create a lower symmetry configuration than would be the case if the defect pair occupied normal lattice sites. In an applied ac field the defect can then flip among equivalent low-symmetry configurations, a process that should involve

TABLE I. Values of the $\tan\delta$ peak temperature ($T_{\max}$), activation energy (E) and attempt frequency (ω_0) associated with the hopping motion of the oxygen vacancy in KT:Ca. Values of the ionic radii (r_i) of the Ca^{2+}, Mn^{2+}, and Co^{2+} ions are also listed.

	$T_{\max}$@10^3 Hz (K)	E (eV)	ω_0 (s^{-1})	r_i (Å)
KT:Ca^{2+}	44	0.08	4×10^{12}	0.99
KT:Mn^{2+}	56	0.11	5×10^{13}	0.80
KT:Co^{2+}	186	0.36	4×10^{13}	0.73

smaller motions and, consequently, lower E than for the flipping of the unrelaxed configuration with the defect occupying normal sites.[27] The essential feature of the explanation is that sufficiently large ionic displacements occur around the M^{2+} dopant so as to greatly facilitate the hopping of the pair. As noted in Sec. II, the ESR data provide strong evidence for large off-center displacements for this defect in perovskites.

The explanation for our observation that the larger the ionic dopant (which results in larger off-center displacements and larger local relaxations), the easier the hopping motion of the M^{2+}-V_{O} pair then simply follows from the above considerations. Also related to this is the strength of the M^{2+}-V_{O} dipole. As we noted earlier, the M^{2+} ion and V_{O} attract each other. Large off-center ionic displacements bring the pair closer together reducing its dipole moment. A smaller dipole moment should make it easier to flip the orientation among equivalent configurations, i.e., a lower E.

With increasing pressure the tan δ peaks shift to lower temperatures reflecting the influence of pressure on the kinetics and energetics of the relaxation process. Some of the results are shown in Fig. 5. We find that E decreases linearly with pressure at a rate of 2.8 meV/kbar over the range of the measurements, and ω_0 decreases by $\sim$ a factor of 4 between 0 and 8 kbars.

Analysis of our data indicates that essentially a single relaxation time defines the V_{O} hopping process, i.e., the process is a Debye relaxation. This can be seen in the following way. From Eqs. (3) and (4) we note that a plot of tan δ vs $1/T$ gives a symmetric peak for a Debye process. It can be shown[27] that the width $\Delta(1/T)$ at half maximum of this peak is given by $\Delta(1/T) = 2.635\,\mathrm{k/E}$. A distribution of relaxation times would lead to a wider peak. Some of our results are shown in Fig. 6 for one frequency. The Δ's obtained from such plots yielded E's that are only $\sim$15% smaller than those determined from the Arrhenius plots as in Fig. 5, indicating that essentially a single relaxation time is involved. This finding is in accord with the light Ca doping of our sample which implies a weak interaction among Ca^{2+}-V_{O} pairs and between these pair defects and the off-center Nb ions.

Going back to Fig. 1 we note that it is the reorientation of the Ca^{2+}-V_{O} dipoles that enhances the polarizability of the lattice and causes the upturn in $\varepsilon'(T)$ near and above the tan $\delta(T)$ peaks. At temperatures significantly above the peaks, these dipoles are freely reorienting leading to the observed saturation in $\varepsilon'(T)$. Here it is worth emphasizing again that the Ca^{2+}-V_{O} dipoles reside in a highly polarizable (or soft FE mode) KTN lattice so that their polarizing influence extends over many interatomic spacings. This feature appears to be largely responsible for the very large values of ε' at high temperatures despite the low Ca^{2+} concentration in the sample. Another contributing factor may be the possibility of having some Ca^{2+} on the K^{1+} site resulting in free-carrier absorption and high conductivity.

V. CONCLUDING REMARKS

The mixed KTN:Ca crystal investigated here exhibits a richness of properties and effects related to the presence of disorder in perovskite oxides. The present results, along with our earlier findings on KTN (Ref. 3) and PLZT's,[6] strengthen the conclusion that the pressure-induced FE-R crossover is a general phenomenon in soft-mode ferroelectrics with random site disorder. It is a manifestation of the large decrease with pressure in the correlation length for the interaction among polar domains. The apparent large enhancement of the FE transition temperature of our KTN crystal due to the small amount (0.055 at. %) of Ca^{2+} doping is an important finding that deserves further study in KTN and other perovskites. It relates to the issue of how random dipolar entities can strengthen long-range correlations in these materials, an issue that runs counter to conventional wisdom based on random-field considerations as discussed in Sec. IV B.

Finally, more detailed studies of the influence of pressure on the energetics and dynamics of the hopping motion of metal ion/oxygen vacancy pair defects in KTN and related perovskites should improve our understanding of these defects and their interactions with other dipolar entities in these materials.

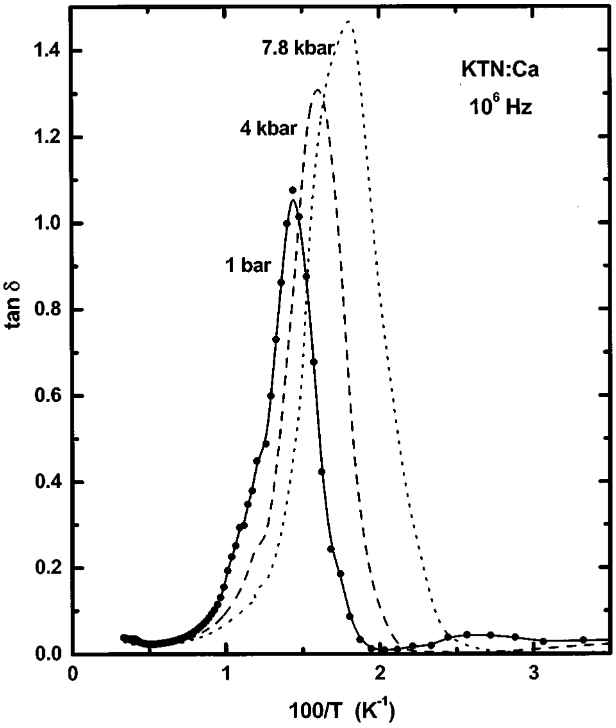

FIG. 6. Plot of tan δ vs $1/T$ for KTN:Ca at one frequency and different pressures. The width at half maximum of each peak is inversely proportional to the activation energy of the relaxation process of the hopping of the oxygen vacancy.

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