New Dielectric Resonances in Mesoscopic Ferroelectrics

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A new type of dielectric resonance has been observed in several mixed ferroelectrics, $KTa_{1-x}Nb_xO_3$ (KTN), $K_{1-x}Li_xTaO_3$ (KLT), and $PbMg_{1/3}Nb_{2/3}O_3$ (PMN), also known as relaxor ferroelectrics. This resonance and its metastability (persistence over long periods of time) in KTN in the paraelectric phase provides clear evidence, in relaxors, for the presence of permanent polar nanoregions and strong polarization-strain coupling. The frequencies calculated from the elastic constant reveal the unexpected clamped nature of the resonance. These results point to the essential role of polar regions in the relaxor behavior. [S0031-9007(97)04675-9]

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It is well known, both experimentally and theoretically, that polarization can couple to elastic strains via the piezoelectric or the electrostrictive constants. However, piezoelectric effects can only be observed in noncentrosymmetric crystals (noncubic) and the electrostrictive effect is a second order and hence a weaker effect. In cubic systems, the application of an external dc bias field can always break the symmetry and induce a piezoelectric effect, but very large fields are required in order to induce any measurable macroscopic polarization. It was reported by Hubregtse *et al.* [1] that, in $BaTiO_3$, several kV/cm are necessary to induce such a polarization in the cubic phase and that this is only possible close to the transition. In the present Letter, we report a novel case in which the polarization-strain coupling can be "turned on" with much weaker fields (<50 V/cm) and as far as 20 K above the ferroelectric phase transition at T_c. We further show that, as far as 20 K above T_c, the field-induced macroscopic polarization is metastable and persists over long periods of time after removal of the field.

This novel case of polarization-strain coupling was observed recently in several mixed ferroelectrics that belong to the family of relaxor ferroelectrics, $KTa_{1-x}Nb_xO_3$ (KTN), $K_{1-x}Li_xTaO_3$ (KLT), and $PbMg_{1/3}Nb_{2/3}O_3$ (PMN), and may be a general feature of many others. The relaxor behavior is characterized by a frequency dependent position of the peak in the dielectric constant [2]. PMN has been long identified as a relaxor [3] but KLT [2] and KTN [4] were only recently shown to display this characteristic behavior as well. KTN, in particular, is a soft relaxor that has attracted considerable attention because of its large dielectric constant and tunable ferroelectric properties. Most of the present study is focused on this system.

In KTN, niobium is randomly substituted for tantalum and occupies an off-center position in the unit cell [5] which, as a result, acquires a permanent dipole moment. This moment can couple dynamically or statically to the surrounding host unit cells. As the temperature is decreased, this impurity-host coupling grows stronger and modifies the normal characteristics of the paraelectric phase of the system. Several anomalies have already been reported: The linear dielectric constant response departs from a Curie-Weiss law [6]; a finite remnant polarization [6], coercive fields, and polarization overtones [7] have also been shown to appear; and otherwise silent optic modes have been observed in Raman scattering [8], all approximately 20 K above T_c. These anomalies clearly indicate a lowering of the local symmetry on a nanometer scale [8,9] while x-ray diffraction [10] still gives the average symmetry as cubic. Because they have been reported either in polarization measurements, i.e., in the presence of a large electric field, or in Raman measurements, i.e., at high frequency, these anomalies could be due to a field-induced or dynamical symmetry lowering. In the present Letter, we show that these anomalies are the consequence of the condensation of polar regions, the permanence of which is stabilized by strain. We present evidence for such a condensation and, most surprisingly, show that this process occurs approximately 20 K above the phase transition for all concentrations studied between 1.2% and 30%.

Polar regions can form/condense when two or more Nb cells (along with their neighboring host cells), interacting in pairs or groups, begin to respond as a single polar unit. An essential feature of these regions is the local distortion that accompanies their local spontaneous polarization and leads to the modification of the normal characteristics of the paraelectric phase and to the polarization-strain coupling.

When a coupling between polarization and strain is present, various mechanical modes of vibrations can be excited electrically, by modulating the macroscopic polarization. This can easily be done experimentally by superposing on the dc bias field a small ac field. The dc field serves to induce a macroscopic polarization and the small ac field to excite vibrations which become significant in amplitude when the ac frequency of the small field matches a resonant frequency of the bar or plate sample. In Fig. 1, we display the frequency spectrum of the dielectric constant ε' and loss $D = \varepsilon''/\varepsilon'$, (a) for a KTN crystal measured at $T_c + 15$ K under several dc bias fields, (b) for the
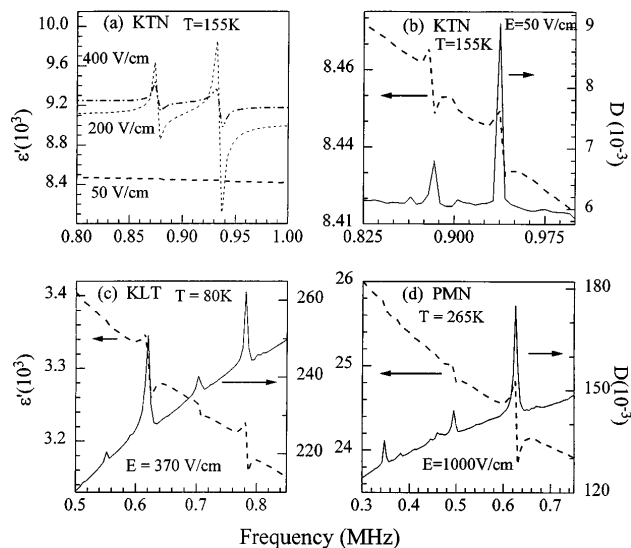
FIG. 1. (a) Dielectric resonances in KTN crystal for different dc bias fields. (b) Details of the 50 V/cm data from (a) along with loss tangent D. (c) ε' and D of KLT at 80 K ($T_c + 35$ K), and (d) of PMN (triangle-shaped sample). Left axis in all four figures corresponds to ε', while right axis corresponds to the loss tangent D.

same KTN crystal at the lower field on an expanded scale, (c) for a crystal of KLT, and (d) for a crystal of PMN. In all cases, the dc bias field was applied perpendicular to the major faces of the plate sample. The KTN spectrum clearly reveals two large resonances near 1 MHz. In Fig. 1(b), even for the very low field, the resonance is extremely strong. Moreover, as the ferroelectric transition is approached, even smaller dc bias fields can trigger these resonances. These results clearly confirm the presence, in KTN above the transition, of permanent polar regions that possess a local spontaneous polarization and the local distortion associated with it. If it were not for the presence of polar regions, KTN would require several kV/cm to overcome internal fields and induce a macroscopic polarization, as is the case in $BaTiO_3$ [1]. In this novel case, the effect of the dc bias field is simply to align these polar regions and, thus, induce a macroscopic polarization. Because the local spontaneous polarization of each polar region is necessarily accompanied by a local distortion, the alignment of the regions also results in a macroscopic strain that can be modulated by modulating the macroscopic polarization, hence the field-induced polarization-strain coupling which here corresponds to a field-induced d_{31} piezoelectric coefficient. It is important to note that no resonance is observed in the absence of a small dc bias field. The same explanation holds true for KLT and PMN, although there,

because the local distortions are increasingly more important (harder relaxors), higher fields are necessary.

We now show that the resonances displayed in Fig. 1 are associated, albeit in a peculiar way, with longitudinal mechanical vibrations of the plate sample. The fundamental resonant frequency of a plate or bar sample can be obtained from the simple condition $2L = \lambda$, in which L is the length of the sample and λ is the wavelength of the acoustic wave. This condition leads to the following expression for the resonant frequency [11]:

$$\nu = \frac{1}{2L}\sqrt{\frac{1}{\rho S_{11}}},$$

in which ρ is the density and S_{11} is the elastic compliance measured at constant stress. It is important to note that the resonance of a plate or bar sample leads to free vibrations, which, therefore, take place at constant stress while the propagation of sound waves in a solid takes place at constant strain [12]. For a plate sample, one expects two longitudinal resonances, corresponding to the two major dimensions of the sample, as we indeed observe in Fig. 1. Using the above relation, the frequencies of the resonances can be calculated from a knowledge of the elastic compliance. By means of ultrasonics, we have also independently measured the elastic constants [13] C_{11} and C_{12} from which S_{11} can be estimated. For the 1.2% sample when calculating the resonance frequency from the measured elastic compliance [14], we find a 50% discrepancy with the observed resonance frequency. However, the agreement is quite good with the frequency calculated from the elastic stiffness constant C_{11} (within 7%). The agreement is even better for the 15.7% KTN. (See Table I. The percentages represent the deviation between measured and calculated values.)

The overall very good agreement between the resonant frequencies calculated from C_{11} and those measured is a surprising one which suggests that the resonances are not excited at constant stress but, effectively, at constant strain and correspond to the internal generation of sound waves propagating in the plane of the sample, i.e., perpendicular to the applied field. This point is further discussed at the end of the paper.

Another argument in support of the above analysis is provided by the temperature dependence of the elastic constants, determined independently from ultrasonic measurements. These measurements reveal a significant softening of C_{11} from which one would predict a decrease in the frequency of the dielectric resonances as temperature is decreased towards the transition. This is indeed what is

TABLE I. Comparison of measured and calculated resonant frequencies at $T = T_c + 20$ K for different KTN crystals.

Concentration	Dimension (mm²)	ν_1(calc) (kHz)	ν_1(meas) (kHz)	ν_2(calc) (kHz)	ν_2(meas) (kHz)
1.2% ($T_c = 12$ K)	8.2 × 5.3	486	451 (7.2%)	767	727 (5.2%)
15.7% ($T_c = 139$ K)	3.8 × 4	902	908	949	952
26% ($T_c = 225$ K)	3.5 × 4.4	748	770 (3%)	948	960 (1.2%)

observed and displayed in Fig. 2 for two concentrations. The agreement is again remarkable and further supports our explanation for the observed resonances and the fact that it is C_{11} and not $1/S_{11}$ that must be used in calculating the resonant frequencies.

As indicated earlier, the observation of these resonances in KTN was not limited to one sample or concentration, but was, in fact, made for all Nb samples studied, with concentration ranging from 1.2% to 30%. This is illustrated in Fig. 3 for three concentrations. The resonant frequencies are the ones appearing in Table I. This figure, however, also reveals another remarkable fact that is particular to KTN: For all three concentrations, the resonances appear approximately 20 K above the ferroelectric transition, i.e., at $T^* \cong T_c + 20$ K, even though T_c itself depends on concentration [6] (see Table I). Because of this universal character of T^* in KTN, it is believed that the polar regions form as a result of a condensation process, similar to the condensation of water droplets in a supersaturated vapor. The suggestion of a possible condensation was recently made in another publication [6] but could not be confirmed until the presence of permanent polar regions was clearly established, which is one of the purposes of the present Letter. Although the resonances reported here reveal the presence of polar regions in relaxors, the formation process of these regions is not the same in all of them. While, in KTN, it appears to take place as a condensation process at $T^* \cong T_c + 20$ K, in KLT, these regions form at approximately 200 K for all Li concentrations. This difference between the two systems has been attributed to the magnitude of the local distortion energy of the Li or Nb centers relative to the interaction energy between centers [15].

Although the results reported so far provide a strong indication of the existence of polar regions in relaxor ferroelectrics, the strongest piece of evidence yet is the metastability of these resonances and, therefore, the metastability of the induced macroscopic polarization above the transition. As an example, we show in Fig. 4 the result of a cycle in which a KTN crystal was measured at different temperatures upon cooling, with a 650 V/cm dc bias field on and then measured at the same temperatures upon warming without the field. Upon cooling, the resonances are observed starting at about 180 K, but rapidly increase
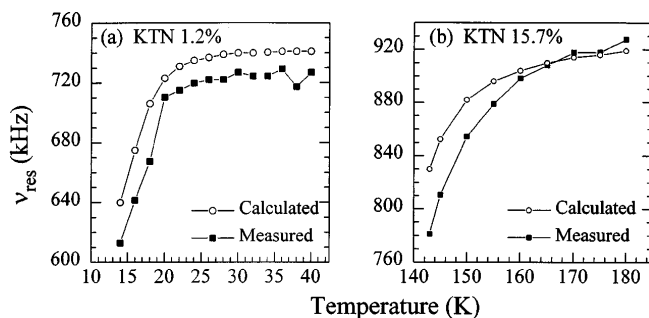
in amplitude around 160 K ($\cong T_c + 20$ K), as shown by the changing vertical scale. At 150 K ($= T_c + 11$ K), the dc field was turned off and, upon warming, the resonances were measured at the same temperatures. Although smaller in amplitude, the resonances clearly persist and again decrease rapidly around 160 K. It is also interesting to note that, in the second part of the experiment (warming with the bias field off), the KTN spectrum displays all of the same details that are visible upon cooling, e.g., double peaks, shoulders, etc.

The metastability of the resonances indicates that the origin of the macroscopic polarization is different above and
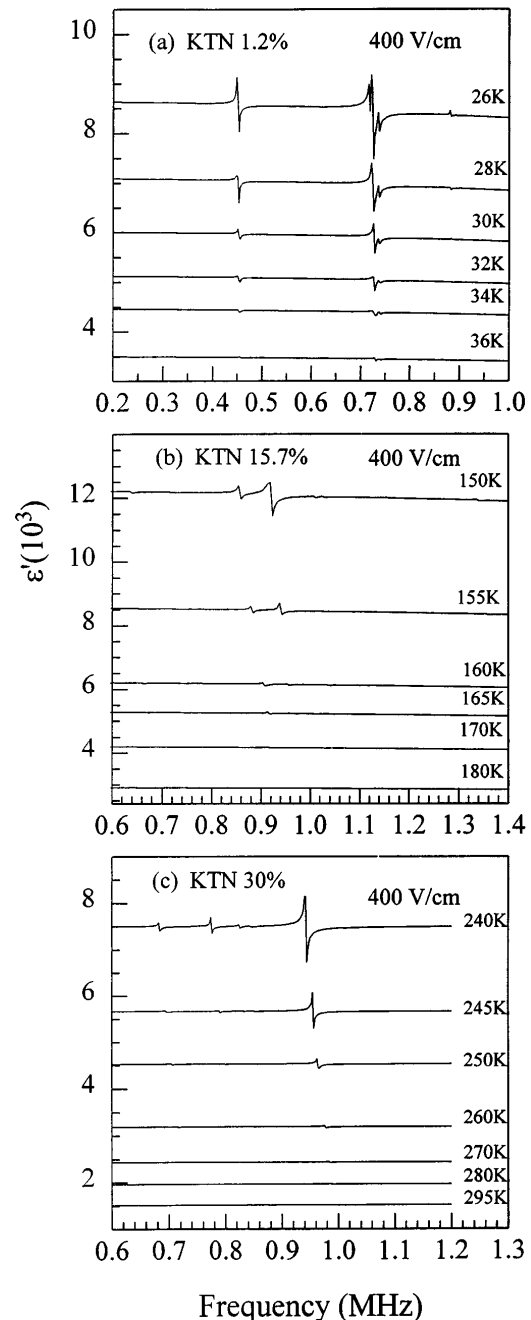
FIG. 3. ε' of KTN at different temperatures in the presence of a dc bias field. (a) 1.2%, (b) 15.7%, and (c) 30%.

FIG. 2. Elastic constant of KTN crystals determined from the dielectric resonances (open circles) and measured using ultrasonics (solid squares).
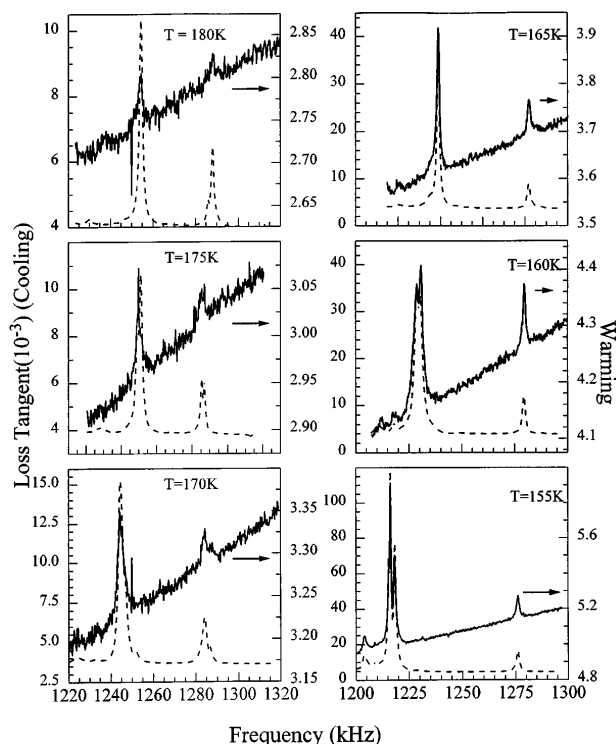
FIG. 4. Polarization metastability of KTN at different temperatures upon cooling to 150 K with bias field (left axis and dotted lines) and heating up to 180 K without bias field (right axis and solid lines).

below the condensation temperature T^*. In the high temperature range, the local polarization is primarily induced by the application of the dc bias field; although the external field aligns the Nb-centered dipoles giving rise to a small macroscopic polarization, these dipoles are only weakly correlated in the sense that their dynamics is dominated by thermal effects and, consequently, the macroscopic polarization disappears instantly upon removal of the field. By contrast, below T^*, neighboring Nb-centered dipoles become strongly correlated, forming permanent polar regions characterized by a local spontaneous polarization; the macroscopic polarization is then essentially due to the alignment of the polar regions and it is stabilized by the polarization-strain coupling. For low niobium concentrations, the polar regions are more remotely spaced and, hence, not as strongly correlated as they are for higher concentrations. As a result, upon removal of the bias field, the induced alignment persists, but over a shorter time for lower concentrations.

The present results indicate that, given an ensemble of randomly distributed dipoles in a highly polarizable solid, nanoscopic regions with a local spontaneous polarization can develop that are stabilized by the local strain. These, then, can be regarded as giant electric dipoles giving rise to superparaelectric behavior and field-induced piezoelectricity. It is important to note, however, that the latter piezoelectricity is not induced in the conventional manner in which the field induces a uniform polarization in the solid. Here, the field merely aligns the giant dipoles

or local polarization moments and, consequently, a much weaker field is required. The corresponding alignment of the local distortion fields gives rise to a macroscopic strain. Modulating the macroscopic polarization with a small ac field amounts to coherently modulating the orientational order of the giant dipoles and, thus, internally generating sound waves in the sample. This explains why the resonant frequency is determined by the elastic constant C_{11}, rather than by the elastic compliance S_{11}. Finally, the present results confirm the explanation proposed for the unusual dielectric and polarization behavior of relaxor ferroelectrics. The relaxor behavior is due to the presence of very small (nano/meso) polar regions which would suggest that relaxors be identified as *mesoscopic ferroelectrics* or even *mesoelectrics* for short. In KTN, these regions can be very easily reoriented and KTN can be qualified as a soft relaxor. By contrast, in KLT, and even more so in PMN, the distortions are greater and the polar regions, to be reoriented, require higher bias fields; KLT is thus a harder relaxor than KTN and PMN is a harder relaxor still. This classification is supported by the fact that the ferroelectric transition is continuous (second order) in KTN, it is first order in KLT, and it is absent in PMN.

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