

Dielectric relaxation and resonance in relaxor ferroelectric $K_{1-x}Li_xTaO_3$

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Polar regions are shown to mediate a strong coupling between polarization and strain in the paraelectric phase of the mixed ferroelectric $K_{1-x}Li_xTaO_3$ (KLT) and $KTa_{1-x}Nb_xO_3$ resulting in a field-induced piezoelectric response. The coupling is shown to result in a resonance in the dielectric spectrum of the crystals. In KLT, polar nanoregions can reorient via 180° (π relaxation) or 90° ($\pi/2$ relaxation) rotations. While the π relaxation is of no consequence, the $\pi/2$ relaxation has a strong influence on the overall character of the resonance. In addition to providing a mechanism for loss and degradation of the quality factor, this relaxation alters the character of the resonance as the two cross. Experimental results from dielectric spectroscopy above and below this crossover are presented and discussed. A simple theoretical Debye model involving the electrostrictive polarization-strain coupling is presented and the calculated spectrum is shown to reproduce the experimental spectrum. The parameters derived from the model are discussed. Most significantly, the electrostrictive coefficient of KLT is found to be 100 times larger than that of $BaTiO_3$, and is due to the presence of polar nanoregions. [S0163-1829(99)13833-5]

INTRODUCTION

Mixed ferroelectrics have been the focus of much fundamental and applied research for several years. Interest in the study of these materials arises from the fact that the physical properties of the crystal can be modified considerably by the collective effects induced by the impurity. These modifications include impurity-induced fluctuations, metastable polarization, phase transition leading to an ordered or dipolar glassy state, etc. $K_{1-x}Li_xTaO_3$ (KLT) and $KTa_{1-x}Nb_xO_3$ (KTN) are two such systems, both derived from the same incipient ferroelectric $KTaO_3$ which is cubic at all temperatures. Höchli¹ and Vugmeister² have reviewed the development of research in these materials up to the early nineties. The origin of the anomalous behavior in these two systems lies in the fact that the impurities (Nb or Li) occupy off-center sites³ and exhibit relaxational motion between equivalent sites with a characteristic time that is temperature dependent.^{1,2} In addition, this off-center occupancy of the impurity has the consequence of polarizing an extended region of host cells surrounding it. From Raman measurements^{4,5} on KLT it has been shown that even 100 K above T_c interacting (isolated) lithium impurity centers (or clusters) form regions known as polar regions. These reorienting polar regions are responsible for modifying the static and dynamic properties of the undoped host crystal. For instance, first order Raman coupling, which is forbidden in the paraelectric phase by symmetry arguments, becomes active both in KTN and KLT, clearly revealing a lowering of the local symmetry.⁴⁻⁶ Anomalous ferroelectric behavior has also been reported: the dielectric response has been found⁷ to exhibit relaxor behavior and to depart from the Curie-Weiss law. In the polarization hysteresis measurements,⁸ a frequency-dependent remnant polarization has been observed at temperatures well above the actual ferroelectric transition.

An essential characteristic (of great interest for applications) common to all ferroelectrics is the polarization-strain coupling^{9,10} which results in a strain that is linearly dependent

on polarization through the piezoelectric effect. The work we present in this paper concerns this polarization-strain coupling in KLT. This coupling, as is well known,^{9,10} manifests itself as a resonance in the dielectric spectrum at a frequency which is determined by the mechanical modes of vibration of the sample. Such a coupling in the paraelectric phase of a centro-symmetric KTN and KLT is ruled out by symmetry arguments. However, the cubic symmetry is easily broken by application of a dc electric field leading to a polarization-strain coupling through a second order piezoelectric or electrostrictive interaction. A study of this coupling in KTN has been reported¹¹ and this report also provides important evidence for the existence of the polar regions in KTN. In KLT, this electrostrictive effect is of even greater interest for the following reasons. First, KLT is a relaxor exhibiting strong dielectric dispersion (unlike KTN) over a broad frequency range. More importantly, and unlike KTN in which no dielectric relaxation is observed in the MHz range, two relaxational modes have been reported¹ in KLT. The relaxation frequency or the relaxation time of both modes can be approximated by an Arrhenius law¹

$$\nu = \nu_0 e^{-U/T} \quad \text{or} \quad \tau = \tau_0 e^{U/T}. \quad (1)$$

Here ν_0 is the attempt frequency, U the (temperature independent) energy barrier (separating the equivalent sites) in units of the Boltzmann constant, and T the temperature. The purpose of this work is to study the effects of the lithium relaxation on the polarization-strain coupling. However, before we proceed further, it is important to know the lithium relaxation modes¹²⁻¹⁵ in KLT, and the possibility, if any, of a coupling of these modes with an electrostrictively-induced stress.

On the basis of ultrasonic measurements of KLT, Doussineau *et al.*^{14,15} established that one of the modes, known as π relaxation, involves a reorientation of lithium ions between sites situated along the same axis. The other mode, identified by the same group as a $\pi/2$ relaxation, involves reorientation

of lithium ions between sites situated on orthogonal axes. The π reorientation is not accompanied by a change in the local strain field and therefore can not couple to an external (normal) stress¹⁶ while the $\pi/2$ mode, which changes the symmetry of the strain upon reorientation, can respond. Because the relaxation frequency is strongly temperature-dependent [see Eq. (1)] the lithium relaxation frequency and the resonant frequency of the fundamental mechanical mode of vibration can become equal to each other. Thus, KLT provides a unique opportunity to study the interaction between a relaxation and a resonance, or between local atomic reorientations and acoustic modes.

The paper is organized as follows. We first present a model (for a Debye system) in which we calculate the complex dielectric constant, including an electrostrictive polarization-strain coupling, in centrosymmetric crystals. This is followed by a report on the experimental dielectric resonance measurements in KLT and a discussion of the results.

ELECTROSTRICTIVE POLARIZATION-STRAIN COUPLING

In the high temperature paraelectric phase KLT is macroscopically centrosymmetric. As is well known, under such conditions the crystal cannot possess any macroscopic polarization and hence cannot exhibit a piezoelectric response. However, the center of symmetry can easily be broken by the application of a dc bias field. Because of the preferential alignment of the ions, a macroscopic polarization P_0 is then induced which can electrostrictively couple to the mechanical strain. If a small alternating electric field is superposed onto the dc bias field, the induced macroscopic polarization will oscillate about P_0 with a frequency equal to the frequency of the small ac field. Such an experimental arrangement is easily realized in our dielectric measurement setup. The electrostrictive coupling then manifests itself as a resonance in the dielectric response of the sample. In this section we review the effect of electrostrictive polarization-strain coupling on the capacitance of the sample. First, we consider the ideal case where the effects of relaxation and damping are ignored. A more detailed account of this discussion can be found in the monograph by Mason¹⁷ and others.¹⁸ Next, we extend Mason's work¹⁷ to include relaxation and damping.

Case I: In the absence of relaxation and damping

Let us consider a sample of length l , width w , and thickness d such that the length is much greater than the other two dimensions. Let the length be along the x axis, and the thickness along the z axis. The long surfaces ($l \times w$) are fully electroded and all the fields are applied across the thickness d . Since the width and thickness are much smaller than the length, it is a good approximation¹⁷ to set the stress along these directions equal to zero throughout the crystal. With these assumptions, a time- and space-dependent stress and strain will exist only along the length. The strain can be written as

$$S_1(x,t) = s_{11}^E T_1(x,t) + M_{13} E_3^2. \quad (2)$$

The first term on the right corresponds to Hooke's law and the second to the electrostrictive effect. Here S_1 is the strain, T_1 is the stress, s_{11}^E the elastic compliance at constant electric field, $M_{13} (= M_{1133})$ is the relevant electrostrictive coefficient, and E_3 is the total electric field along the z direction that consists of the dc bias field E_0 , superposed onto a small signal ac field $E_3(t)$. This quadratic term can be linearized¹⁷ to

$$E_3^2 = (E_0 + E_3(t))^2 \approx E_0^2 + 2E_0 E_3(t)$$

and the variable strain then becomes

$$S_1(x,t) = s_{11}^E T_1(x,t) + g_{13} E_3(t), \quad (3)$$

where $g_{13} = 2M_{13}E_0$. Using the above expression for the strain that is electrostrictively coupled to the external fields, Mason^{17,18} has shown that the capacitance of the sample with boundaries that are free from mechanical stress is given by

$$C(\omega, E_0) = \frac{wl}{d} \left[\epsilon_{33}^T - \frac{g_{13}^2}{s_{11}^E} \right] + \frac{g_{13}^2 \tan \theta}{s_{11}^E \theta}, \quad \theta = \frac{\omega l}{2V}. \quad (4)$$

Here ϵ_{33}^T is the constant stress dielectric permeability in the absence of any polarization-strain coupling and the sound speed V is defined as

$$V^2 = \frac{1}{\rho s_{11}^E}.$$

From Eq. (4) above for the capacitance, we note that the condition for resonance is

$$\theta = \frac{\omega l}{2\nu} \quad \text{or} \quad \nu = \frac{1}{2l} \sqrt{\frac{1}{\rho s_{11}^E}},$$

where ν is the frequency and ρ the density. In a thin bar sample, the mode whose wavelength is twice the length of the specimen is the fundamental mode of vibration. Thus, a resonance occurs when the dielectric measurement frequency equals the frequency of the resonant standing wave in the sample. From the first two terms in the above expression, we also note that the electrostrictive coupling has the added effect of suppressing the free dielectric constant far away from the resonance.

Case II: In the presence of relaxation and damping

In the above calculation leading to Eq. (4) for the capacitance, the effects of relaxation and damping were ignored. However from our measurements, we find that the relaxation has a strong influence on the resonant response and is in fact the focus of this paper. We therefore extended the calculations of the preceding section to include damping and relaxation. To the best of our knowledge such a calculation has not been reported elsewhere. Therefore, we present the calculation in some detail.

As discussed earlier [Eq. (1)], the lithium ion undergoes thermally-activated motion between equivalent sites with a relaxation time τ that depends on temperature. Following this reorientation the displaced host ions that surround the impurity will also relax to new equilibrium positions. Thus, the lithium reorientation generates a stress that modifies the ex-

isting stress distribution around the impurity sites and provides an anelastic mechanism for damping. To incorporate the loss, a strain rate-dependent stress is now introduced into Eq. (2)

$$\frac{1}{s_{11}^E} S_1(x, t) + \eta(\omega, \tau) \frac{\partial S_1(x, t)}{\partial t} = T_1(x, t) + \frac{g_{13}}{s_{11}^E} E_3(t)$$

leading to the following wave equation:

$$\rho \frac{\partial^2 u(x, t)}{\partial t^2} = \frac{1}{s_{11}^E} \frac{\partial^2 u(x, t)}{\partial x^2} + \eta(\omega, \tau) \frac{\partial}{\partial t} \frac{\partial^2 u(x, t)}{\partial x^2}. \quad (5)$$

The coefficient η has dimensions of viscosity. Such a viscous damping of acoustic waves has been discussed by several authors.¹⁹ In the particular case of KLT, the loss mechanism is the reorientation of the lithium impurities and its strength will depend on the relaxation time as well as on the frequency of the applied field. For simplicity, we assume a Debye form for η :

$$\eta(\omega, \tau) = \eta_0(T) \frac{\omega \tau}{1 + \omega^2 \tau^2}, \quad (6)$$

where $\eta_0(T)$ is a temperature dependent viscosity.

Choosing the origin at the center of the bar sample, the wave Eq. (5) can be solved with stress-free boundary conditions $T(\pm l/2) = 0$, leading to the following expression for the stress:

$$T_1(x, t) = \left[\frac{g_{13}}{s_{11}^E} \frac{\cos k_c x}{\cos \frac{k_c l}{2}} - \frac{g_{13}}{s_{11}^T} \right] E(t), \quad (7)$$

where the complex wave vector k_c is given by¹⁹

$$k_c = k - i\alpha = \frac{\omega}{V} - i \frac{\eta \omega^2}{2V^3 \rho}.$$

Here V is the sound velocity in the material whose density is ρ , and α is the acoustic attenuation coefficient.

Before we couple the above stress to the electric displacement vector, let us recall that, in the presence of a relaxation, the equation relating the electric displacement and the applied electric field is written as²⁰

$$\frac{dD}{dt} + \frac{1}{\tau} D = \frac{\epsilon_s}{\tau} E(t),$$

where τ again is the mean residence time between reorientations of the lithium off-center ions. Because of the polarization-strain coupling, we must also include the electrostrictive coupling into the above equation:

$$\frac{dD}{dt} + \frac{1}{\tau} D = \frac{1}{\tau} [\epsilon_s E(t) + g_{13} T_1(x, t)]. \quad (8)$$

As mentioned in the beginning of this section to the best of our knowledge we do not know of any previous investigation of dielectric relaxation including a coupling term as given in Eq. (8), (earlier reports including Mason¹⁷ and others¹⁸ assume $\tau=0$). Here $\epsilon_s = \epsilon(\omega=0)$ is the static dielectric permittivity of the material.

Inserting Eq. (7) for the stress in Eq. (8), and following Daniel²⁰ and Mason,¹⁷ the real and imaginary permittivity can be obtained:

$$\epsilon'(\omega) = \frac{\epsilon_s + \epsilon_\infty \omega^2 \tau^2}{\omega^2 \tau^2 + 1} - \frac{1}{s_{11}^E} \frac{4E_0^2 M_{13}^2}{\omega^2 \tau^2 + 1} [1 - Y_r - \omega \tau Y_i], \quad (9)$$

$$\epsilon''(\omega) = \frac{(\epsilon_s - \epsilon_\infty) \omega \tau}{\omega^2 \tau^2 + 1} - \frac{1}{s_{11}^E} \frac{4E_0^2 M_{13}^2}{\omega^2 \tau^2 + 1} [\omega \tau - \omega \tau Y_r + Y_i]. \quad (10)$$

Here the functions Y_r and Y_i are proportional to the mechanical strain, and are given by

$$Y_r = \frac{\theta \sin \theta \cos \theta + \beta \sinh \beta \cosh \beta}{(\theta^2 + \beta^2)(\cos^2 \theta + \sinh^2 \beta)}, \quad (11)$$

$$Y_i = \frac{\theta \sinh \beta \cosh \beta - \beta \sin \theta \cos \theta}{(\theta^2 + \beta^2)(\cos^2 \theta + \sinh^2 \beta)}, \quad (12)$$

where

$$\theta = \frac{\omega l}{2V}, \quad \beta = \frac{\eta \omega^2 l}{4V^2 \rho}.$$

Equations (9) and (10) are the desired expressions for the dielectric function in the presence of the polarization-strain coupling for a dipolar system undergoing a Debye-like relaxation. It can be verified that $\epsilon'(-\omega) = \epsilon'(\omega)$ and $\epsilon''(-\omega) = -\epsilon''(\omega)$, as required by Kramers-Kronig relation.

The validity of the above model is limited to the range $\omega \tau \leq 1$ in which the reorientation-induced stress relaxes fully (the lithium can follow the stress wave). At low temperatures, when the relaxation time is long, i.e., $\omega \tau \gg 1$, the reorientation-induced stress no longer relaxes. This invalidates the applicability of Eq. (8) and thus the model breaks down below the crossover temperature where $\omega \tau \gg 1$.

In physical terms, $g_{13} Y_r$ and $g_{13} Y_i$ are the real and imaginary amplitude of the average strain, i.e., the strain integrated over the length of the bar and then divided by the length. As can be seen from Eqs. (11) and (12) these two terms represent the strain contribution near the mechanical resonance to the dielectric response. The overall shape of these two calculated curves depend on the product $\omega_{\text{res}} \tau$. We plot them in Figs. 1(a) and 1(b) for different relaxation times. The parameters used are given in Table I. We notice in particular that, when $\omega_{\text{res}} \tau \ll 1$, the real part resembles the response of a harmonic oscillator and has a narrow full width at half maximum (FWHM). But as $\omega_{\text{res}} \rightarrow \tau^{-1}$, the shape evolves into that of a relaxation and the imaginary part Y_i becomes significantly broader suggesting that the strain does not get enough time to relax to its normal value.

Before we conclude this section we remark that the model discussed here has been developed for the case of a Debye relaxation. However in most systems, including the disordered ferroelectrics studied in the present work the relaxation is more complex than a simple Debye. Nevertheless, the results of the model are useful for a qualitative comparison with the experimental results as we now show.

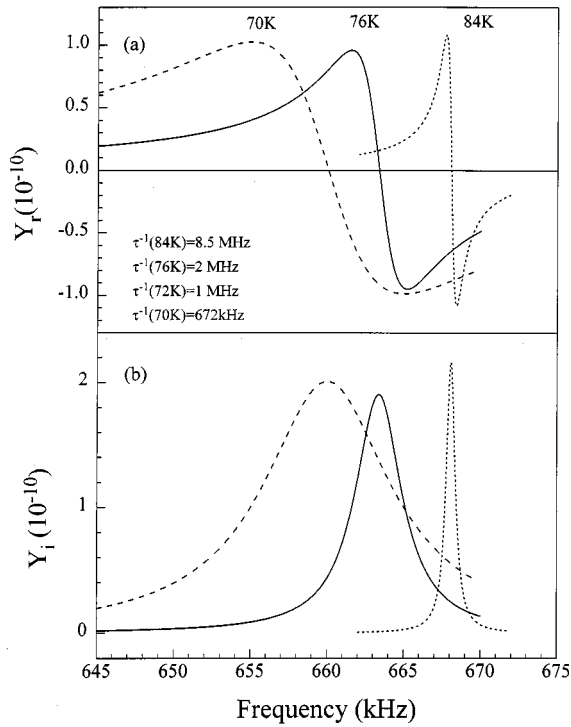


FIG. 1. Calculated strain [using Eqs. (11) and (12)] involving the polarization-strain coupling. The various parameters used are given in Table I and the associated lithium ion relaxation times in the plot. (a) Real part. (b) Imaginary part. Note that in the limit $\omega_{\text{res}}\tau \ll 1$ the anelastic strain relaxes producing a resonant response (84 K). But as $\omega_{\text{res}}\tau \rightarrow 1$ the resonant response changes into a relaxation (70 K).

EXPERIMENTAL RESULTS

KTN and KLT crystals with different impurity concentrations were studied in the present work. However, most of the discussion presented here will focus on KLT 3.5% ($T_c = 46$ K) since this sample was studied in somewhat more detail. The samples were typically 1 mm thick, 2 mm wide, and 5 mm long, all single crystals with [100] orientation. The main surfaces were fully aluminum coated. The dc bias field was 300 V/cm or less and all measurements were done upon cooling the sample with the superposed ac excitation voltage no higher than 250 mV rms.

In Fig. 2 we present the real and imaginary parts of the dielectric spectrum showing the resonance in two different crystals, KLT-3.5% and KTN-30%, measured respectively at $T_c + 40$ K and $T_c + 20$ K. It is interesting to note the contrast

TABLE I. Calculated parameters [Eqs. (9) and (10)] at different temperatures for the electrostrictive coefficient, static and high frequency dielectric constants, the viscosity, and the acoustic attenuation coefficient.

Temp. (K)	M_{13} (m^2/V^2)	ϵ_∞	ϵ_s	η_0 (Poise)	α (m^{-1})
84	1.4×10^{-17}	150	2070	1.2×10^3	0.3
76	3.2×10^{-17}	850	2640	1.75×10^3	1.65
72	4×10^{-17}	1290	3100	1.8×10^3	2.65
70	5×10^{-17}	1535	3500	2.5×10^3	4

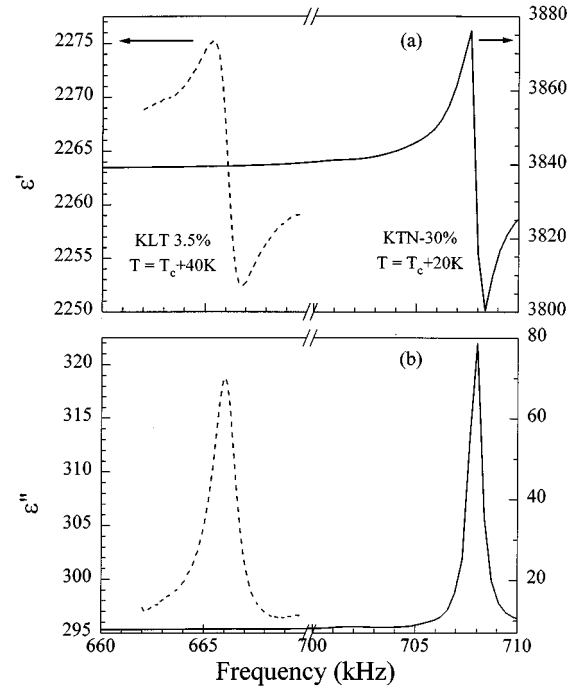


FIG. 2. Typical dielectric resonance data from KLT (3.5%) and KTN (30%) crystals. (a) Real part. (b) Imaginary part. Note the large absorption strength and broader linewidth of KLT even at 40 K above T_c .

between them. Even though the KTN crystal was doped about 10 times more and the temperature was two times closer to T_c , the overall shape of the resonance (both real and imaginary parts) reveals little damping (the absorption FWHM < 1 kHz). By contrast, the shape of the resonance for the more dilute KLT, even twice as far from T_c , already reveals a large damping or internal friction with the absorption peak about four times as great and a FWHM ~ 2 kHz. This shows that the lithium relaxation, because of its slow dynamics, has a much stronger influence on the mechanical resonance of KLT. In KTN, the Nb dynamics is much faster than the time period of the strain response, so as to have little or no influence at all.

The experimental results can be broadly divided into three temperature ranges: (1) $T > 85$ K; (2) $70 \text{ K} < T < 85$ K; and (3) $T < 70$ K. We present the results successively in the three regions.

(1) Although all measurements were started from 160 K, no significant changes are noticed in the shape of the resonance until about 85 K. The resonance is seen to occur at a frequency $\nu = V/2l$, and also to shift to higher frequencies as the temperature is decreased. This trend ceases near 100 K where the resonance begins to shift to lower frequencies.

(2) In this intermediate temperature region, the relaxation, initially at a higher frequency, crosses the resonance to end at lower frequencies. This crossover is presented in Fig. 3(a). We see that, at 72 K, the relaxation peak is near 1 MHz while the resonance is near 700 kHz. This crossover occurs around 70 K and, at 68 K, the relaxation is seen below the resonance. The evolution of the dielectric resonance in this temperature region is shown in Figs. 3(b)–3(e) starting at 84 K. In this figure, the frequency range along the horizontal

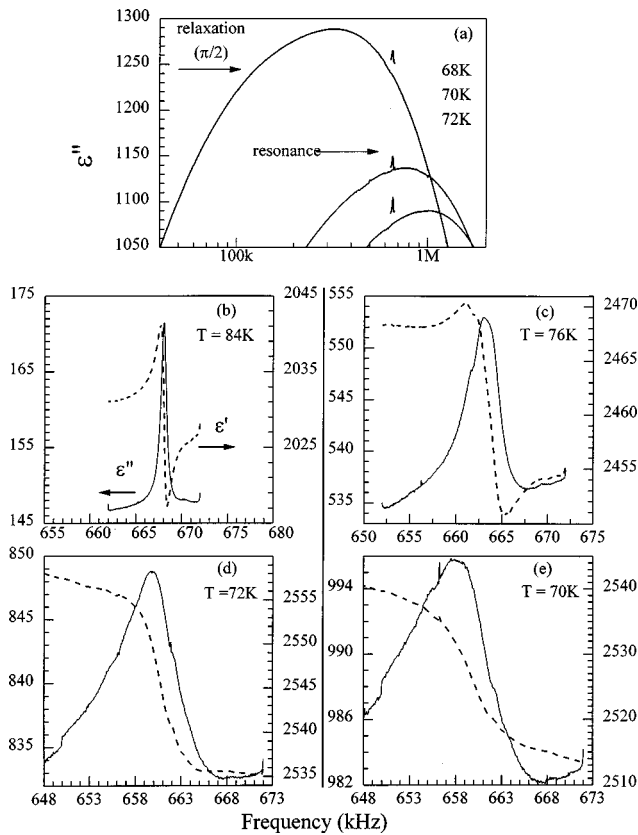


FIG. 3. (a) The crossing of the relaxation past the resonance. At 72 K the relaxation is at 1 MHz while the resonance is at 700 kHz. They cross each other near 70 K. Real (right axis) and imaginary (left axis) dielectric constant of KLT 3.5% crystal at different temperatures near the crossover. (b) At 84 and 78 K it has a harmonic oscillatorlike response with a narrow linewidth. (c) As the relaxation approaches the resonance the shape of the curve begins to change into a mixed response of a resonance and a relaxation. (d), (e) The resonant response completely changes into a relaxation one as $\omega_{\text{res}}\tau \rightarrow 1$.

axis has been fixed at 25 kHz for all plots to better show the evolution of the shape of the resonance line with temperature. At 84 K (about 40 K above T_c), the dielectric absorption peak [Fig. 3(b) solid curve] is quite narrow (~ 1 kHz) and small. The shape of the real (dashed curve) and imaginary (solid curve) parts resemble the response of an underdamped harmonic oscillator driven at resonance. It is also evident, from the baseline slope of the resonant absorption peak, that the dielectric relaxation peak is approaching the resonance from the high frequency side. We further notice that they both coincide near 70 K. This progression of the lithium relaxation crossing the resonance towards lower frequencies has two most noticeable effects: (i) an increase in the linewidth of the absorption; starting from about 1 kHz at 84 K, the half width increases to approximately 20 kHz at 70 K; and more importantly (ii) a change in the character of the resonance. These changes are more visible in the real part of the dielectric constant than in the absorption part. Starting from a harmonic oscillatorlike response at 84 K [Fig. 3(b)], the shape of the resonance gradually transforms into the relaxationlike response [Figs. 3(c) and 3(d)] of an order-disorder system. Also to be noted in Figs. 3(b)–3(e) is that the line shape is asymmetric even starting from high tem-

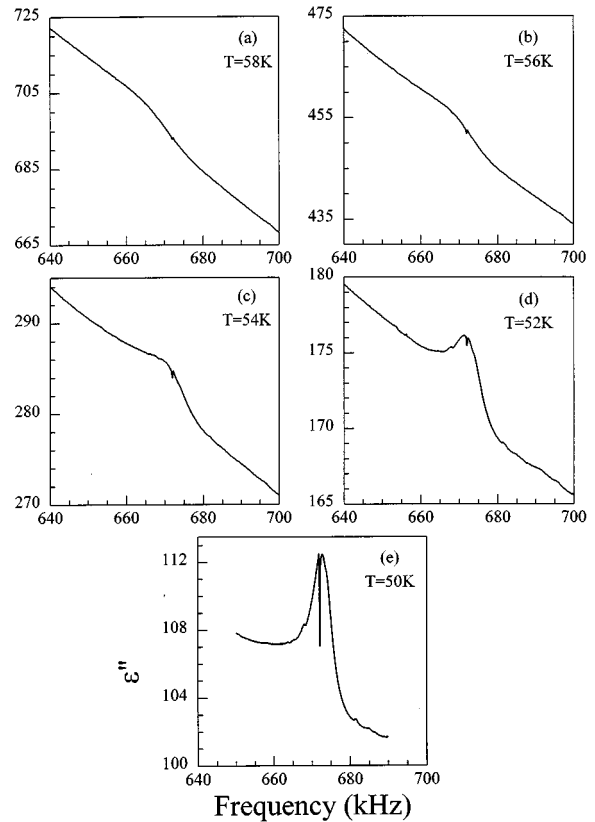


FIG. 4. Imaginary part of the dielectric constant after the crossover. (a),(b) It is weaker in strength and almost intractable between 58 and 56 K. (c) Below 56 K the strength is even weaker but the peak is better pronounced with a narrower width. (d),(e) At even lower temperatures the peak increases and a reproducible split appears at the maximum.

peratures. Finally, the absorption peak can be seen to shift from 665 kHz at 84 K to 657 kHz at 70 K.

(3) Once the relaxation peak has fallen below the resonance frequency, a new dynamic range begins in which the relaxation time is longer than the resonance time period. The most important effects noticed are (i) the resonance frequency that was earlier shifting to lower frequencies increases again below the crossover, i.e., the acoustic modes participating in the resonance hardens, and (ii) the resonance becomes broader, loses strength, and is almost unobservable near 60 K. However, at still lower temperatures, when the relaxation peak is well below the resonance frequency, the resonance reappears with growing strength. In Fig. 4, a sequence of resonance lines in the 50 K range is presented. The fact that the relaxation peak lies well below the resonance frequency is also seen in the flatness of the “background” of the resonance peak.

It is also interesting to note a sharp split between 662 kHz and 665 kHz that grows stronger as the temperature is decreased. This feature is reproducible and is therefore not an experimental artifact, but it is beyond the scope of the present paper.

In order to compare the temperature evolution of the two processes (relaxation and resonance), we plot in Fig. 5 the temperature dependence of the respective peak frequencies. The relaxation frequency was determined from an earlier

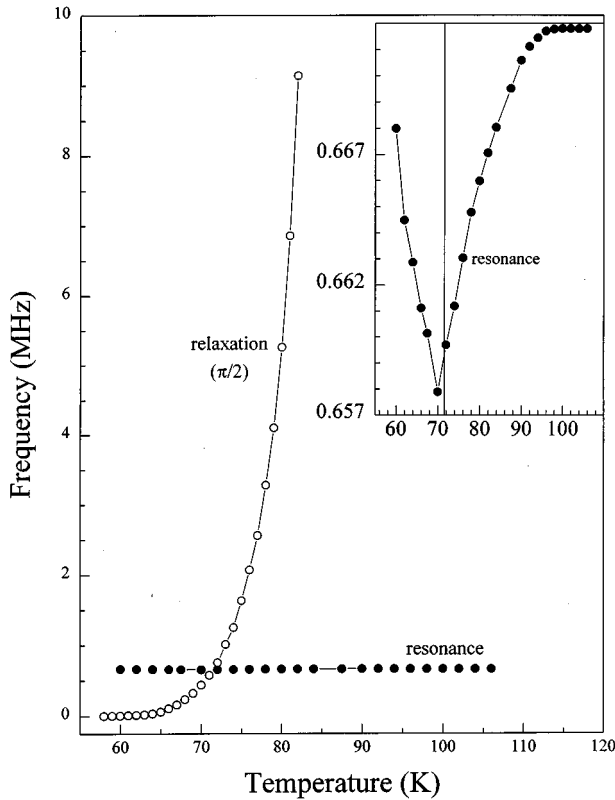


FIG. 5. The $\pi/2$ lithium relaxation crosses over the resonance near 70 K. Inset: Enlarged view. After the crossover, the resonance hardens, i.e., it shifts to higher frequencies with decreasing temperature.

measurement without any dc bias field. The two curves intersect each other near 70 K, which is the crossover temperature. An expanded view of this intersection is provided in the inset. This shows that the resonance shifts to lower frequency as the temperature is decreased towards the crossover near 70 K whereupon it begins to increase again, thus indicating hardening.

DISCUSSION

It is worth emphasizing that two dynamic processes are monitored here. The first one is the dielectric resonance, driven by the polarization-strain coupling, and the other is the lithium $\pi/2$ relaxation which is a thermally activated process. The two processes are shown in Fig. 3(a) to cross each other near 70 K. Accordingly, three different dynamic regimes can be identified. (i) At high temperatures ($T > 85$ K), the lithium relaxation peak is at much higher frequency than the resonance ($\omega_{\text{res}}\tau \ll 1$). (ii) In the crossover region between 85 and 70 K ($\omega_{\text{res}}\tau \approx 1$), the lithium relaxation peak, approaching from the high frequency side, crosses the resonance near 70 K. (iii) In the low temperature region (below 70 K), the relaxation peak is below the resonance ($\omega_{\text{res}}\tau \gg 1$).

As shown earlier in the present experimental configuration, the polarization along the z direction of the crystal produces an electrostrictive (normal) stress and strain along the length (x axis) of the specimen. In addition, the reorientation of the lithium impurity contributes an anelastic component to

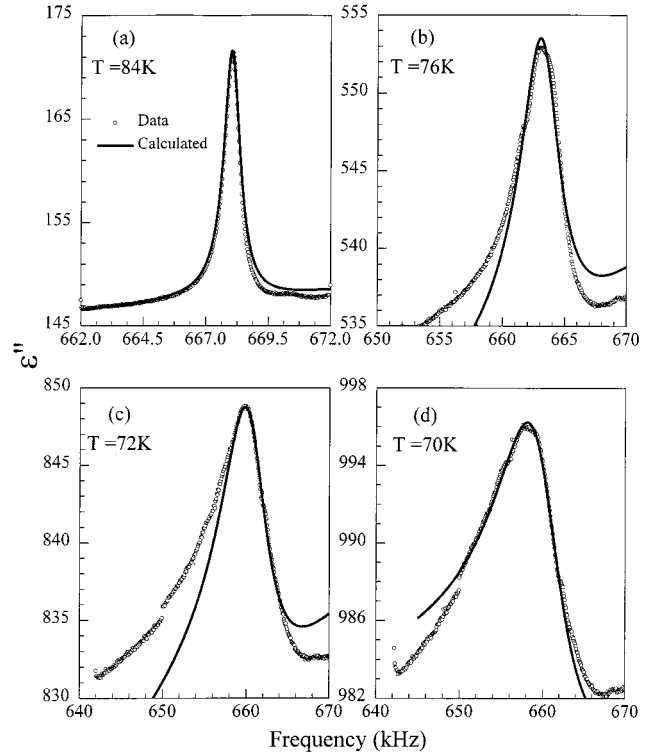


FIG. 6. Calculated [Eqs. (9) and (10)] real and imaginary dielectric constant at different temperatures compared with experimental result. The parameters are given in Table I. Note that the asymmetry and linewidth predicted by the model is in good agreement with the data.

the electrostrictive stress. In a small frequency range around the resonance frequency the stress becomes large and can lead to a stress-induced reorientation of the lithium impurities. At high temperature, because the relaxation frequency is much higher than the resonance frequency, lithium can reorient almost instantly in the presence of the resonance stress. Consequently the viscosity parameter η , which was assumed of the Debye form, has only a small frequency dispersion resulting in a sharp dielectric resonance, as observed at high temperatures.

From Eqs. (9) and (10) we note that the contribution of the strain to the dielectric response is contained in the terms Y_r and Y_i . In the small $\omega\tau$ limit these functions resemble the real and imaginary components of the resonant response of a harmonic oscillator. The dielectric spectrum at 84 K, shown in Fig. 3(b), indeed illustrates such a response. The calculated imaginary dielectric constant at 84 K is shown in Fig. 6(a) along with the experimental data. The parameters are provided in Table I and they are analyzed at the end of this section.

In the crossover temperature range, with the relaxation time becoming longer, the anelastic component of the stress that is proportional to dS/dt takes a progressively longer time to fully relax, leading to damping over a broader frequency range. Because of this, the functions Y_r and Y_i begin to display a relaxational character. The data at 76 K in Fig. 3(c) is evidence of this mixed response. The relaxational character grows stronger as τ becomes even longer and overdamping is evident from (the real part of) the data (dashed

lines) in Figs. 3(d) and 3(e). The calculation shows that, as τ increases, the spectral width of the resonant strain undergoes noticeable broadening and not so significant an increase in amplitude. It is interesting to note in Figs. 3(b)–3(e) that the height of the peak stays almost the same from 84 to 70 K, in contrast to about a tenfold increase in the linewidth. Thus, it may be said that it is not the magnitude of the anelastic stress but rather the associated relaxation time that plays the most important role.

The overdamping observed in Figs. 3(d) and 3(e) is also consistent with the large attenuation observed near and below the crossover temperature in the ultrasonic measurements.^{13,14} The calculated and measured imaginary parts at different temperatures are shown in Figs. 6(a)–6(d) and the parameters are given in Table I. At high temperatures, the model agrees with the measurements but begins to depart as the temperature is decreased. This is due to the fact that the model was developed assuming a Debye-type relaxation, i.e., uncorrelated or isolated dipoles. In the case of KLT, which displays the relaxor behavior, this assumption becomes increasingly invalid when approaching the transition.

Another point to note in Figs. 3(b)–3(e) is that the line shape is asymmetric, and that this asymmetry is more pronounced in the imaginary part $\epsilon''(\omega)$ than in the real part $\epsilon'(\omega)$. At excitation frequencies above the resonance frequency, the crystal is clamped, i.e., the stress and strain are out of phase by 180° (Y_r undergoes a change of sign). Consequently, for $\omega > \omega_{\text{res}}$, the lithium reorientation is prevented leading to a rapid decrease in absorption.

The reappearance of the resonance (with narrowing width) at lower temperatures is most likely due to the fact that the relaxation frequency is then far below the resonance. As shown in Fig. 5 at 54 K, the relaxation frequency is less than 3 kHz while the resonance frequency is at about 670 kHz. As a result of this large difference, the lithium and the accompanying distortion appear frozen and the anelastic strain does not come into play. This in turn leads to reduced attenuation and a reappearance of the resonance.

In the model used, we note that the resonance frequency is unaffected by the lithium relaxation. But as shown in the inset of Fig. 5, the resonant frequency (or the speed of sound wave propagation) undergoes softening, goes through a minimum and then increases again below the crossover. A qualitative explanation of this behavior can be provided as follows.

The lithium reorientation-mediated stress and strain contribute to the compressibility of the crystal over and above the elastic stress and strain. In the temperature range between 100 and 70 K, as the relaxation time nears the period of vibration of the resonance, the anelastic stress has ample time to fully relax. Thus the reorientation of the polar regions is accompanied by a local mechanical distortion. The size of these polar regions estimated from Raman scattering⁴ and diffuse neutron scattering²¹ measurements, is approximately 35 Å (eight unit cells) close to T_c . The reorientation-induced stress and the accompanying strain in this temperature range has the effect of increasing the compressibility of the crystal (see Robrock¹⁶), hence decreasing the bulk modulus (which is inversely proportional to the compressibility). Thus, in this temperature range, the sound speed, which is inversely pro-

portional to the square root of the bulk modulus, exhibits a reduction. By contrast, below the crossover, the reorientation becomes progressively more difficult with decreasing temperature, which has the effect of increasing the stiffness of the crystal or decreasing its compressibility. The observation of an increase in the resonant frequency below the crossover is consistent with this explanation. Such modification of the compressibility by reorienting impurities in metals has been discussed by Robrock.⁶ In the temperature region above 100 K, the compressibility is essentially unaffected by the relaxation. Consequently as the temperature is decreased the crystal, being ionic, exhibits the normal behavior of increasing stiffness due to anharmonic effects.

DISCUSSION OF THE PARAMETERS OBTAINED FROM THE FIT

In Table I the electrostrictive coefficient M_{13} of KLT is seen to increase with decreasing of temperature. At 70 K it is about four times as large as it is at 84 K. This parameter can be compared with those of SrTiO₃ and BaTiO₃. As reported by Rupprecht and Winter, at 243.3 K this parameter for SrTiO₃ is $(1.723 \pm 0.002) \times 10^{-19} \text{ m}^2/\text{V}^2$. According to Caspari and Merz it is $-3.33 \times 10^{-19} \text{ m}^2/\text{V}^2$ for BaTiO₃ at room temperature. Our values in the temperature range 85 to 70 K is seen to be about 100 times greater. This much larger value of the electrostrictive coefficient in KLT is supported by the simple experimental fact that Caspari and Mertz in their work for BaTiO₃ had to apply an electric field of 30 000 V/cm while a similar effect in KLT can be observed with a field of only 300 V/cm. This clearly proves that the polarization-strain coupling is much stronger in KLT than it is in either BaTiO₃ or SrTiO₃.

The high frequency dielectric constant ϵ_∞ is observed to increase at lower temperatures. This is an anomalous behavior since ϵ_∞ is normally independent of temperature. While this temperature independence may be true in the optical frequency ($\sim 10^{14}$ Hz) range where the electrons only contribute with the ions providing a stationary background, it may not be true when the measurement frequency is far below the phonon band. Our best explanation is that this is due to an increase in the local fields created by the defect-induced distortions which grow in size as the temperature is decreased. These local fields can enhance the high frequency ionic polarizability and lead to a large temperature dependent ϵ_∞ . Recently Vugmeister²² has proposed that ϵ_∞ in relaxor ferroelectrics can be as high as 1000.

The static dielectric constant ϵ_s is also seen to increase with decreasing temperature which indeed is expected from a Curie-Weiss law.

The viscosity parameter, η_0 is seen not to increase so significantly between 84 to 70 K. At 70 K it is about twice as large as at 84 K. This would suggest that the reorientation-induced stress does not increase as significantly as the crossover is approached, consistent with the fact that the absorption peak does not increase as much as its width [Figs. 3(b)–3(e)]. In this relaxor it is the reorientation time or the relaxation time that plays the most significant role in modifying the properties of the host. The mean viscosity parameter $\bar{\eta}$ [Eq. (6) averaged over the frequency range of calculation] can be compared with quartz. As discussed by Ballato

(see Ref. 18), for quartz, η/C is about 10^{-14} sec, where C is the elastic constant. In the present case, with our own ultrasonic measurement of C_{11} of KLT, $\bar{\eta}/C_{11}$ is of the order of 10^{-10} sec at 85 K. This may be consistent with the fact that the quality factor of the KLT crystal is more than four orders of magnitude smaller than the quality factor of quartz (which is in the range of several million²³).

Finally, the attenuation coefficient α is seen to increase significantly over the same temperature range. This follows from the fact that α depends on the inverse cube of the speed of sound ($\alpha \sim V^{-3}$). The largest decrease of sound speed is observed between 84 and 70 K explaining such a large temperature variation. We could not make a meaningful comparison of this coefficient with the available ones as they all have been measured at much higher ultrasonic frequencies.

CONCLUSIONS

In the present paper we have shown that, in mixed ferroelectrics, precursor polar regions significantly enhance the piezoelectric properties by allowing a strong electrostrictive coupling between polarization and strain. The alignment of the polar regions (by a small dc bias field) provides sufficient macroscopic polarization for the piezoelectric response to become effective. As compared to pure ferroelectric such as BaTiO₃ and (incipient) SrTiO₃ the coupling in KLT requires field strengths that are two orders smaller. This we believe is

due to the enhancement of the coupling due to the presence of the off-center lithium in polar regions. The anelastic strain caused by the lithium reorientation has a limited effect at temperatures above and below a crossover region where the relaxation time and the period of the mechanical strain waves are far away from to each other. By contrast, in the crossover region, the interaction between the two dynamic processes results in a variety of anomalous behaviors namely: transformation of mechanical resonance and dielectric resonance into a relaxation, increase of the bulk compressibility. A simple Debye model taking the electrostrictive coupling into account has been presented and the results of the calculations match the trends observed in the experiments. The fact that the lithium $\pi/2$ reorientation in KLT can couple to the mechanical strain and, moreover, that the associated relaxation frequency can cross the acoustic resonance frequency (before the phase transition) may be the reason for relaxor behavior in KLT. By contrast, in KTN the fact that Nb relaxation always stays well above the resonance (in fact, it is not observable at all in the low frequency range) may be the reason for it not to display any pronounced relaxor behavior.

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- ¹U. T. Höchli, K. Knorr, and A. Loidl, *Adv. Phys.* **39**, 405 (1990).
²B. E. Vugmeister and M. D. Glinchuk, *Rev. Mod. Phys.* **62**, 993 (1990).
³O. Hanske-Petipierre and Y. Yacoby, *Phys. Rev. B* **44**, 6700 (1991).
⁴B. E. Vugmeister, P. DiAntonio, and J. Toulouse, *Phys. Rev. Lett.* **75**, 1646 (1995).
⁵P. DiAntonio, B. E. Vugmeister, J. Toulouse, and L. A. Boatner, *Phys. Rev. B* **47**, 5629 (1993).
⁶K. B. Lyons, P. A. Fleury, and D. Rytz, *Phys. Rev. Lett.* **57**, 2207 (1986).
⁷J. Toulouse and R. Pattnaik, *J. Phys. Chem. Solids* **57**, 1473 (1996).
⁸L. A. Knauss, R. Pattnaik, and J. Toulouse, *Phys. Rev. B* **55**, 3472 (1997).
⁹M. E. Caspari and W. J. Merz, *Phys. Rev.* **80**, 1082 (1950).
¹⁰G. Rupprecht and W. H. Winter, *Phys. Rev.* **155**, 1019 (1967).
¹¹R. Pattnaik and J. Toulouse, *Phys. Rev. Lett.* **79**, 4677 (1997).
¹²J. Toulouse, B. E. Vugmeister, and R. Pattnaik, *Phys. Rev. Lett.* **73**, 3467 (1994).
¹³P. Doussineau, C. Frnois, A. Levelut, J. Toulouse, and S. Ziolkiewicz, *Ferroelectrics* **150**, 59 (1993).
¹⁴P. Doussineau, Y. Farssi, C. Frènois, A. Levelut, K. McEnaney, J. Toulouse, and S. Ziolkiewicz, *Europhys. Lett.* **24**, 415 (1993).
¹⁵Hans-Martin Christen, U. T. Höchli, André Châtelain, and Saul Ziolkiewicz, *J. Phys.: Condens. Matter* **3**, 8387 (1991).
¹⁶A. S. Nowick and B. S. Berry, *Anelastic Relaxation in Crystalline Solids* (Academic, New York, London, 1972); Karl-Heinz Robrock, *Mechanical Relaxation of Interstitials in Irradiated Metals* (Springer-Verlag, Berlin, 1990).
¹⁷Warren P. Mason, *Crystal Physics of Interaction Processes* (Academic, New York and London, 1966).
¹⁸Thyrgve Meeker, in *Precision Frequency Control*, edited by Edward A. Gerber and Arthur Ballato (Academic, New York and London, 1985), Vol. 1.
¹⁹H. F. Pollard, *Sound Waves in Solids* (Pion limited, London, 1977).
²⁰Vera V. Daniel, *Dielectric Relaxation* (Academic, New York and London, 1967).
²¹G. Yong and J. Toulouse (private communication).
²²B. E. Vugmeister and H. Rabitz, *Phys. Rev. B* **57**, 7581 (1998).
²³Takuro Ikeda, *Fundamentals of Piezoelectricity* (Oxford University Press, London, 1990).