# Influence of orientational relaxation on the electrostrictive coupling in $K_{1-x}Li_xTaO_3$

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## Abstract

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 $KTa_{1-x}Nb_xO_3$ (KTN). This coupling is shown to result in a resonance in the dielectric spectrum of the crystals. In KLT, polar nanoregions can reorient via 180° ($\pi$-relaxation) or 90° ($\pi/2$-relaxation) rotations. While the $\pi$-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 of the resonance, this relaxation alters its character from that of a resonance to that of a relaxation as the lithium reorientation frequency approaches and crosses the resonance. Experimental results from dielectric spectroscopy above and below this crossover are presented and discussed. Most significantly, the field strength needed to observe the polarization–strain coupling in KLT in the paraelectric phase is found to be 100 times smaller than it is needed for $SrTiO_3$ and $BaTiO_3$. This indicates that the electrostrictive coefficient is correspondingly 100 times larger in KLT and is due to the presence of polar nanoregions. © 1999 Elsevier Science Ltd. All rights reserved.

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## 1. 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. Höchli [1] and Vugmeister [2] 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 sites [3] 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. These regions, known as polar regions with a temperature dependent radius are responsible for modifying the 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 found [7] 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

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mechanical modes of vibration of the sample. Such a coupling in the paraelectric phase in a centro-symmetric system such as KTN and KLT is ruled out by symmetry arguments. However, the cubic symmetry is easily broken by application of a d.c. 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 reported [11] 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 reported [1] in KLT. The relaxation frequency or the relaxation time of both modes can be approximated by an Arrhenius law [1]

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

Here $\nu_0$ 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 about the lithium relaxation modes [12–15] in KLT, and the possibility, if any, of a coupling of these modes with electrostrictively induced stress.

On the basis of the ultrasonic measurements of KLT, Doussineau et al. [14,15] have established that one of the modes, known as $\pi$-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 $\pi$ reorientation is not accompanied by a change in the local strain field and therefore cannot couple to an external (normal) stress [16,17] 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 reorientation 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.

## 2. Case I: electrostrictive polarization–strain coupling

In the high temperature paraelectric phase KLT is macroscopically centro-symmetric. As is well known under such conditions, the crystal cannot possess any macroscopic polarization and hence exhibit a piezoelectric response. However, the center of symmetry can easily be broken by the application of a d.c. 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 d.c. 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 set-up. The electrostrictive coupling then manifests itself as a resonance in the dielectric response of the sample. In this section we briefly review the effect of electrostrictive polarization–strain coupling on the capacitance of the sample. A more detailed account of this discussion can be found in the monograph by Mason and coworkers [18,19]. Next we extend Mason's work [18] to include relaxation and damping.

## 3. 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 approximation [18] 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 linearized time-dependent strain can be written as

$$S_1(x,t) = s_{11}^E T_1(x,t) + 2M_{13}E_0 E_3(t) \qquad (2)$$

The first term on the right corresponds to Hooke's law and the second to the electrostrictive effect. Here $S_1$ is the strain, $T_1$ the stress, $s_{11}^E$ the elastic compliance at constant electric field, $M_{13}(= M_{1133})$ the relevant electrostrictive coefficient and $E_3$ the total electric field along the $z$-direction that consists of the d.c. bias field $E_0$, superposed onto a small signal a.c. field $E_3(t)$. Using expression (2) for the strain that is electrostrictively coupled to the external fields, Mason [18,19] has shown that the capacitance of the sample with boundaries that are free from mechanical stress is given by:

$$C(\omega, E_0) = \frac{wl}{d}\left[ \varepsilon_{33}^T - \frac{4M_{13}^2 E_0^2}{s_{11}^E} \right] + \frac{4M_{13}^2 E_0^2}{s_{11}^E} \frac{\tan\theta}{\theta};$$

$$\theta = \frac{\omega l}{2V} \qquad (3)$$

Here $\varepsilon_{33}^T$ 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. (3) above for the capacitance, we note that the condition for resonance is

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

where $\nu$ is the frequency and $\rho$ 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.

## 4. Case II: in the presence of relaxation and damping

In the above calculation leading to Eq. (3) 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 $\tau$ 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 modifies the existing 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) leading to the following wave equation:

$$\rho\frac{\partial^2 u(x,t)}{\partial t^2} = \frac{1}{s_{11}^E}\frac{\partial^2 u(x,t)}{\partial x^2} + \eta(\omega,\tau)\frac{\partial}{\partial t}\frac{\partial^2 u(x,t)}{\partial x^2} \qquad (4)$$

The coefficient $\eta$ has dimension of viscosity. Such a viscous damping of acoustic waves has been discussed by several authors [20]. In the particular case of KLT the loss mechanism is the reorientation of the lithium impurities and the strength will depend on the relaxation time as well as the frequency of the applied field. For simplicity, we assume a Debye form for $\eta$:

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

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

$$T_1(x,t) = \left[\frac{g_{13}}{s_{11}^E}\frac{\cos k_c x}{\cos\dfrac{k_c l}{2}} - \frac{g_{13}}{s_{11}^T}\right]E(t) \qquad (5)$$

where $g_{13}$ and the complex wave vector $k_c$ are given by [20]

$$g_{13} = 2M_{13}E_0$$

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

Here $V$ is the sound velocity in the material whose density is $\rho$, and $\alpha$ is the acoustic attenuation coefficient.

Because of the polarization–strain coupling, we must also include the electrostrictive coupling into the equation relating the electric displacement $D$, and the applied electric field $E$:

$$\frac{\mathrm{d}D}{\mathrm{d}t} + \frac{1}{\tau}D = \frac{1}{\tau}[\varepsilon_s E(t) + g_{13}T_1(x,t)] \qquad (6)$$

where $\tau$ again is the mean residence time between reorientations of the lithium off-center ions. 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. (6) (earlier reports including Mason and others [18,19] assumed instantaneous relaxation $\tau = 0$). Hence $\varepsilon_s = \varepsilon(\omega = 0)$ is the static dielectric permittivity of the material.

Inserting Eq. (5) for the stress in Eq. (6), and following Daniel [21] and Mason [18], the real and imaginary permittivity are shown to be

$$\varepsilon'(\omega) = \frac{\varepsilon_s + \varepsilon_\infty\omega^2\tau^2}{\omega^2\tau^2 + 1} - \frac{1}{s_{11}^E}\frac{4E_0^2M_{13}^2}{\omega^2\tau^2 + 1}[1 - Y_r - \omega\tau Y_i] \quad (7)$$

$$\varepsilon''(\omega) = \frac{(\varepsilon_s - \varepsilon_\infty)\omega\tau}{\omega^2\tau^2 + 1} - \frac{1}{s_{11}^E}\frac{4E_0^2M_{13}^2}{\omega^2\tau^2 + 1}[\omega\tau - \omega\tau Y_r + Y_i]$$

$$(8)$$

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

$$Y_r = \frac{\theta\sin\theta\cos\theta + \beta\sinh\beta\cosh\beta}{(\theta^2 + \beta^2)(\cos^2\theta + \sinh^2\beta)} \qquad (9)$$

$$Y_i = \frac{\theta\sinh\beta\cosh\beta - \beta\sin\theta\cos\theta}{(\theta^2 + \beta^2)(\cos^2\theta + \sinh^2\beta)} \qquad (10)$$
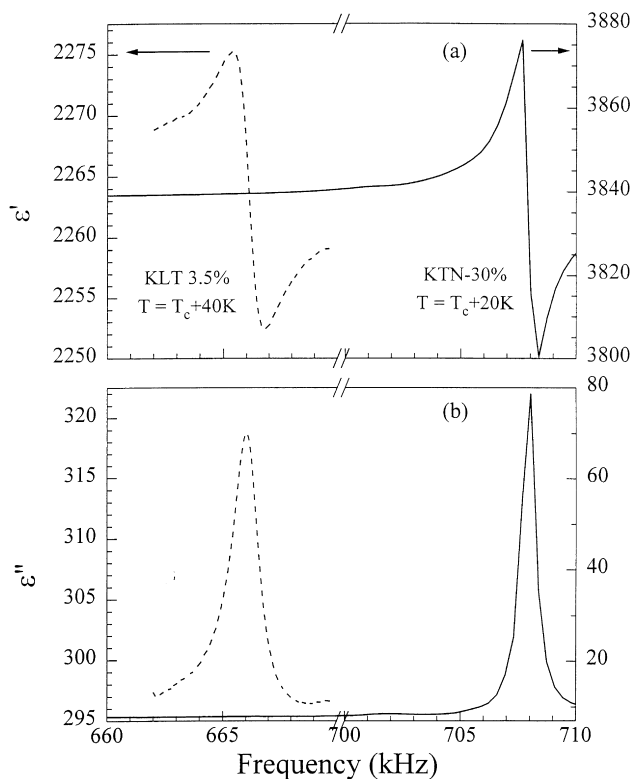
Fig. 1. Typical dielectric resonance data from KLT (3.5%) and KTN (30%) crystals. (a) Real part, and (b) imaginary part. Note the large absorption strength and broader linewidth of KLT even at 40 K above $T_c$.

where

$$\theta = \frac{\omega l}{2V} \qquad \text{and} \qquad \beta = \frac{\eta \omega^2 l}{4V^2 \rho}$$

Eqs. (7) and (8) are the desired expressions for the dielectric function in the presence of an electrostrictive polarization–strain coupling for a dipolar system undergoing a Debye-like relaxation. It can be verified that $\varepsilon'(-\omega) = \varepsilon'(\omega)$ and $\varepsilon''(-\omega) = -\varepsilon''(\omega)$, as required by the Kramers–Kronig relation.

The validity of the above model is limited to the range $\omega\tau \lesssim 1$ where the stress relaxes (the lithium can follow the stress wave). At low temperatures, when the relaxation time is long, i.e. $\omega\tau \gg 1$, the stress no longer relaxes and the model is no longer valid.

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 divided by its length. As can be seen from Eqs. (9) and (10) these two terms represent the strain contribution to the dielectric response near the mechanical resonance.

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 simple Debye. Nevertheless, the results of the model are useful for a qualitative comparison with the experimental results.

## 5. Experimental results

Several KTN and KLT crystals with different impurity concentrations were studied in the present work. However, most of the discussion presented here focuses 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 d.c. bias field was 300 V/cm or less and all measurements were made upon cooling the sample with the superposed a.c. excitation voltage no higher than 250 mV rms.

In Fig. 1 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 $T_c + 4$ and $T_c + 20$ K. It is interesting to note the contrast 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
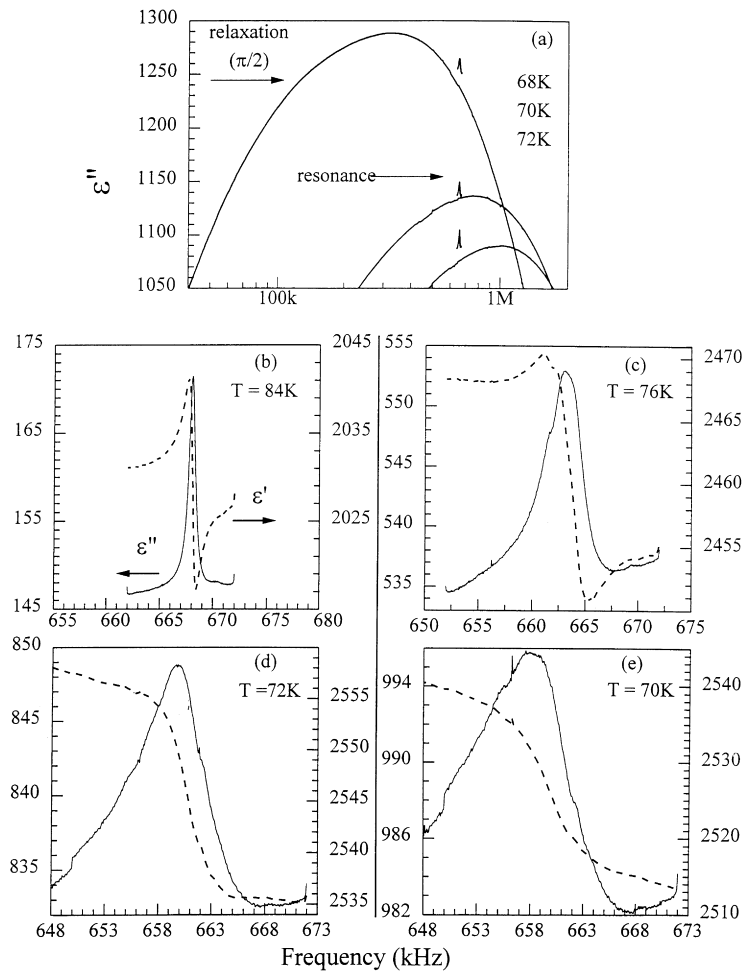
Fig. 2. (a) Crossing of the relaxation past the resonance. At 72 K the relaxation is at 1 MHz while the resonance is at 700 kHz. They cross each other near 70 K. Real (right axis) and imaginary (left axis) dielectric constant of KLT 3.5% crystal at different temperatures near the crossover. (b) At 84 and 78 K, the response is harmonic oscillator-like with a narrow linewidth. (c) As the relaxation approaches the resonance, the shape of the curve begins to change into the mixed responses of a resonance and a relaxation. (d) and (e) The resonant response completely changes into a relaxation as $\omega_{res}\tau \to 1$.

(both real and imaginary parts) reveals little damping (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) $70 < T < 85$ 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 ceased 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 towards lower frequencies. This crossover is presented in Fig. 2(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 and at 68 K the relaxation is seen below the resonance. The evolution of the dielectric resonance in this temperature region is shown in Fig. 2(b)–(e) starting at 84 K. In this figure, the frequency range along the horizontal axis has been fixed at
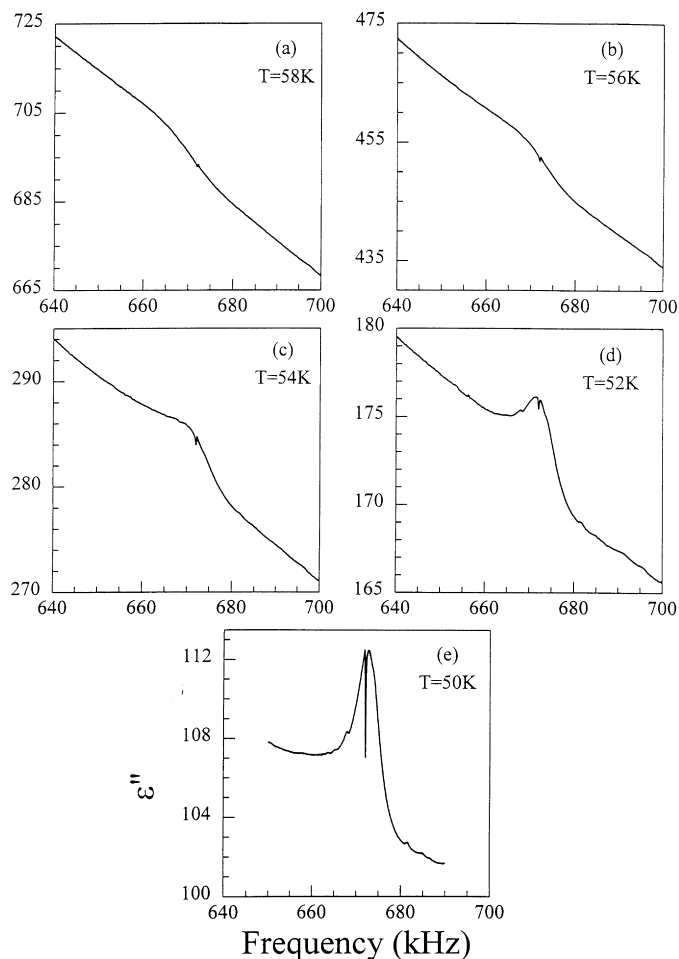
Fig. 3. Imaginary part of the dielectric constant after the crossover. (a) and (b) It is weaker in strength and almost unchanged between 58 and 56 K. (c) Below 56 K the strength is even weaker but the peak is more pronounced and has a narrower width. (d) and (e) At even lower temperatures the contrast of the peak increases with a split at the maximum that is reproducible.

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. 2(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 under-damped harmonic oscillator driven at resonance. It is also evident, from the baseline slope of the resonance peak, that the dielectric relaxation peak is approaching from the high frequency side. We further notice that both the resonance and the relaxation coincide near 70 K. This progression of the lithium relaxation crossing the reso-nance and then shifting to lower frequencies below has two most noticeable effects: (i) an increase in the line-width 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 char-acter of the resonance. These changes are more visible in

the real part of the dielectric constant than in the absorp-tion part. Starting from a harmonic oscillator-like response at 84 K (Fig. 2(b)), the shape of the resonance gradually turns into a relaxation-like response of an order–disorder system (Fig. 2(c) and (d)). Also to be noted in Fig. 2(b)–(e) is that the line shape is asymmetric even starting from high temperatures. Finally, the absorp-tion peak can be seen to shift from 665 kHz at 84 K to 657 kHz at 70 K.

3. Once the relaxation 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 that was earlier shifting to lower frequencies moves towards higher frequencies below the crossover, i.e. the acoustic modes participating in the resonance harden; and (ii) the resonance becomes broader and loses its strength and is almost unobservable near 60 K. However,
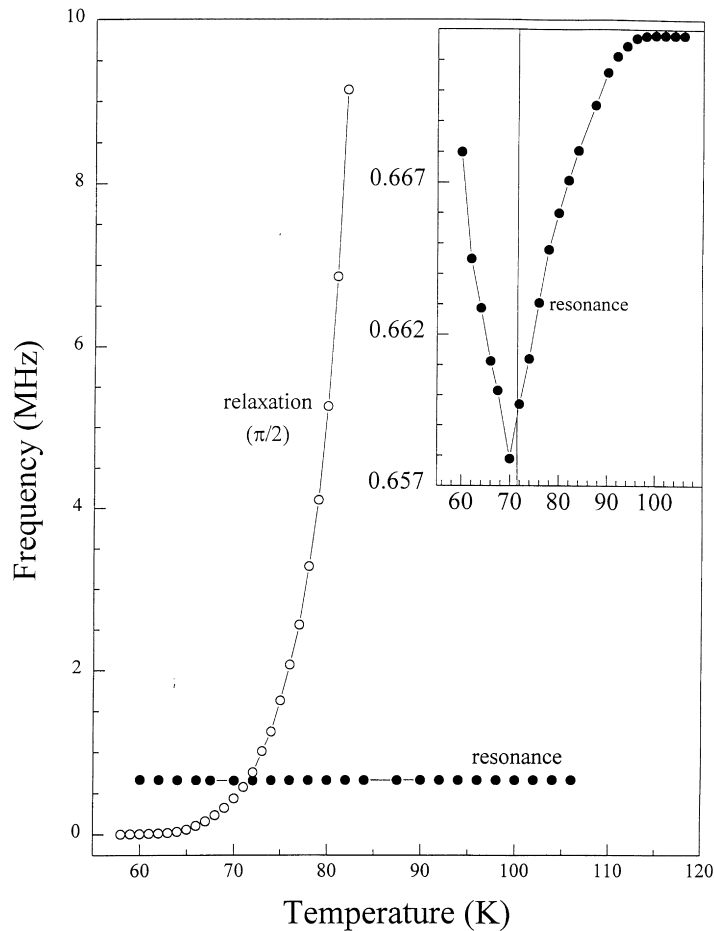
Fig. 4. The π/2 lithium relaxation crosses over the resonance near 70 K. Inset: enlarged view. After the crossover, the resonance hardens i.e. it shifts to higher frequencies with decreasing temperature.

at still lower temperatures, when the relaxation peak is well below the resonance frequency, the resonance reappears with growing strength. In Fig. 3, 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 the sharp split between 662 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. 4 the temperature dependence of the respective peak frequencies. The relaxation frequency was determined from an earlier measurement without any d.c. bias field. The two curves intersect near 70 K, which corresponds to 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 down to the crossover near 70 K whereupon it begins to increase again thus indicating hardening.

## 6. 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 π/2 relaxation which is a thermally activated process. The two processes are shown in Fig. 3(a) crossing over near 70 K. Accordingly, three different dynamic regimes depending on the temperature can be identified. (i) At high temperatures ($T > 85$ K), the lithium relaxation peak is at much higher frequency than the resonance ($\omega_{res}\tau \ll 1$). (ii) In the crossover region between 85 and 70 K ($\omega_{res}\tau \lesssim 1$), 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 ($\omega_{res}\tau \gg 1$).

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. Moreover, the reorientation of the lithium impurity contributes an additional anelastic component to the existing electrostrictive stress. The stress becomes significantly large in a small frequency range around the resonance frequency and can lead to 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, leading to a sharp dielectric resonance as observed.

In the crossover temperature range, with the relaxation time becoming longer, the anelastic component of the stress that is proportional to the strain rate (d$S$/d$t$) takes a progressively longer time to fully relax leading to damping over a broader frequency range. The relaxational character grows stronger as $\tau$ becomes even longer and overdamping is evident from (the real part of) the data (dashed lines) in Fig. 2(d) and (e). It is interesting to note in Fig. 2(b)–(d) that the height of the peak stays almost the same from 84 to 70 K in contrast to about a 10-fold 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 Fig. 2(d) and (e) is also consistent with the large attenuation observed near and below the crossover temperature in the ultrasonic measurements [13,14].

Another point to note in Fig. 2 is that the line shape is asymmetric, and that this asymmetry is more pronounced in the imaginary part $\varepsilon''(\omega)$ than in the real part $\varepsilon'(\omega)$. At excitation frequencies above the resonance frequency, the crystal is clamped i.e. the stress and strain are out of phase by 180°. Consequently, for $\omega > \omega_{res}$, the lithium reorientation is prevented, leading to a rapid decrease of the resonant 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. 4 at 54 K the relaxation frequency is less than 3 kHz while the resonance is at about 670 kHz. As a result of this large difference relative to the strain wave period, 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.

As shown in the inset of Fig. 4, the resonant frequency (or the speed of sound wave propagation) undergoes a 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 lithium relaxation is accompanied by reorientation of the polar regions that increase in size as the transition temperature is approached. As estimated from Raman scattering [4] and diffuse neutron scattering [22] measurements, these polar regions are approximately 35 Å (8 unit cells) in size close to $T_c$. The reorientation-induced stress and the accompanying strain has the effect of increasing the compressibility of the crystal (see Refs. [16,17]) hence decreasing the bulk modulus (which is inversely proportional to the compressibility). Thus, in this temperature range, the sound speed, being inversely proportional to the square root of the bulk modulus, decreases. By contrast, below the crossover, the reorientation becomes progressively more difficult with decreasing temperature, which has the effect of decreasing the compressibility of the crystal. The observation of an increase in the resonant frequency below the crossover is consistent with this explanation. The modification of compressibility by reorienting impurities in metals has been discussed in detail by Robrock [16,17]. In the temperature region above 100 K, the compressibility is essentially unaffected by the relaxation. Consequently as temperature is decreased, the ionic crystal exhibits the normal behavior of increasing stiffness due to anharmonic effects.

The electrostrictive coefficient in KLT can be qualitatively compared with those of SrTiO$_3$ and BaTiO$_3$. As reported by Rupprecht and Winter [10] for SrTiO$_3$, at 243.3 K this parameter is $1.723 \pm 0.002 \times 10^{-19}$ m$^2$/V$^2$. For BaTiO$_3$ according to Caspari and Merz [9] it is $-3.333 \times 10^{-19}$ m$^2$/V$^2$ at room temperature. In the work for BaTiO$_3$ the later group 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 BaTiO$_3$ or SrTiO$_3$. Fitting of the results and precise estimate of the electrostrictive coefficient for KLT is in progress and will be published elsewhere.

## 7. 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 d.c. bias field) provides sufficient macroscopic polarization for the piezoelectric response to become effective. As compared to conventional ferroelectrics such as SrTiO$_3$ and BaTiO$_3$ the coupling in KLT requires field strengths that are two orders of magnitude smaller. This we believe is due to the enhancement of

the coupling by the presence of the off-center lithium in polar regions. The anelastic strain caused by the lithium reorientation has a reduced 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 each other. The most important modifications are observed near the crossover region namely: transformation of mechanical resonance and dielectric resonance to a relaxation and increase of bulk compressibility. The fact that the $\pi/2$ relaxation is low enough in KLT to interact with the mechanical strain may be the reason for the classification of KLT as a hard relaxor.

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