Relaxation of Li-dipole pairs in the disordered perovskite $K_{1-x}Li_xTaO_3$ and the effect of external electric fields

R. K. Pattnaik and J. Toulouse
Physics Department, Lehigh University, Bethlehem, Pennsylvania 18015

Bolla George
Physics Department, Coe College, 1220 First Avenue NE, Cedar Rapids, Iowa 52402
(Received 10 November 1999; revised manuscript received 21 June 2000)

It has been well established by several studies that the relaxor perovskite $K_{1-x}Li_xTaO_3$ (KLT) exhibits two distinct relaxation modes in its dielectric spectrum, with respective barrier heights about 1200 and 2400 K. While the mode with the smaller barrier (known as $\pi/2$ relaxation) is responsible for the complex relaxor behavior of KLT, the relaxation connected with the larger barrier involves pairs of lithium dipoles reorienting as a single unit (known as π relaxation). A detailed study of this relaxation over a broad temperature range for nominal lithium concentrations 3.5% to 16% is presented here. The measured dielectric dispersion and absorption for all concentrations over this temperature range is shown to be in agreement with the Cole-Cole modification of the complex Debye dielectric response. Implicit in this modification is the recognition of a distribution of relaxation times in terms of two parameters α and τ_m. We find that the parameter α connected with the distribution function, increases with increasing concentration and decreasing temperature. Furthermore, α also decreases in presence of a dc bias field. In addition, the bias field reduces the dielectric loss and hardens the relaxation frequency. The distribution of relaxation times and its temperature evolution are explained in terms the random static electric fields due to frozen Li-dipole pairs.

I. 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 host crystal can be modified considerably by the collective effects induced by atomic substitution. 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) is such a system derived from the incipient ferroelectric $KTaO_3$ which is cubic at all temperatures. A large class of these mixed compounds and their properties has been reviewed by Höchli *et al.*[1] and Vugmeister and Glinchuk.[2] The origin of the anomalous behavior in this and similar systems lies in the fact that the substituted atoms (Li) occupy off-center sites[3] and exhibit relaxational motion between equivalent sites with a characteristic time that depends on temperature.[1,2] The Li^+ relaxation in KLT has been investigated by several groups using dielectric spectroscopy.[4–6] There is no dispute at present about the existence of two distinct relaxational modes in this system. The high frequency mode involves the reorientation of Li^+ between equivalent sites on orthogonal axes (barrier height $U_{\pi/2} \simeq 1200$ K), is termed a $\pi/2$ relaxation.[4] This relaxation, observed in KLT for all Li^+ concentrations, has been shown[4,6] to couple to external stress and is connected with the relaxor behavior of KLT.[7] By contrast the low frequency mode termed π relaxation is only present for higher concentrations. Its strength decreases as the concentration of Li^+ substitution decreases and on extrapolation, disappears below the critical Li^+ concentration ($x=2.2\%$). In fact, this relaxation was not observed at all in

a measurement of a 0.8% KLT sample. Also this relaxation does not couple to longitudinal sound waves in ultrasonic measurements. Based on these observations viz. concentration dependence and absence of coupling to longitudinal stress, Doussineau *et al.*[4] proposed that this relaxation most likely involves a pair of coupled dipoles (or a double dipole) reorienting along the same axis and have called it the π relaxation with a barrier height $U_\pi \simeq 2400$ K. If it were due to the π reorientation of single dipoles, one would expect a lower activation energy than for the $\pi/2$ relaxation since the π relaxation is not accompanied by the reorientation of the strain ellipsoid as we just mentioned and, in addition, this mode should be present at all Li^+ concentrations.

The purpose of the present study is to analyze the dielectric dispersion and absorption spectrum associated with the π relaxation for different Li^+ concentrations over a broad temperature range. In particular, we show that the Cole-Cole empirical form[8–10] of the dielectric response function satisfactorily fits the data. We then discuss the concentration and temperature dependence of the Cole-Cole parameter α, which accounts for a distribution of relaxation times.[8,9] The temperature dependence of this parameter is shown to arise from random static fields due to frozen or slowly relaxing dipolar units. Then, we discuss the results of measurements with a dc bias field and show that increased dipolar ordering leads to narrower distribution of relaxation times. We conclude that the distribution of relaxation times because of the asymmetry of the potential double well which is characteristic of disordered ferroelectrics.

The outline of the paper is as follows. We present the experimental data for different KLT crystals studied with the fits of the Cole-Cole model and the results of measurements
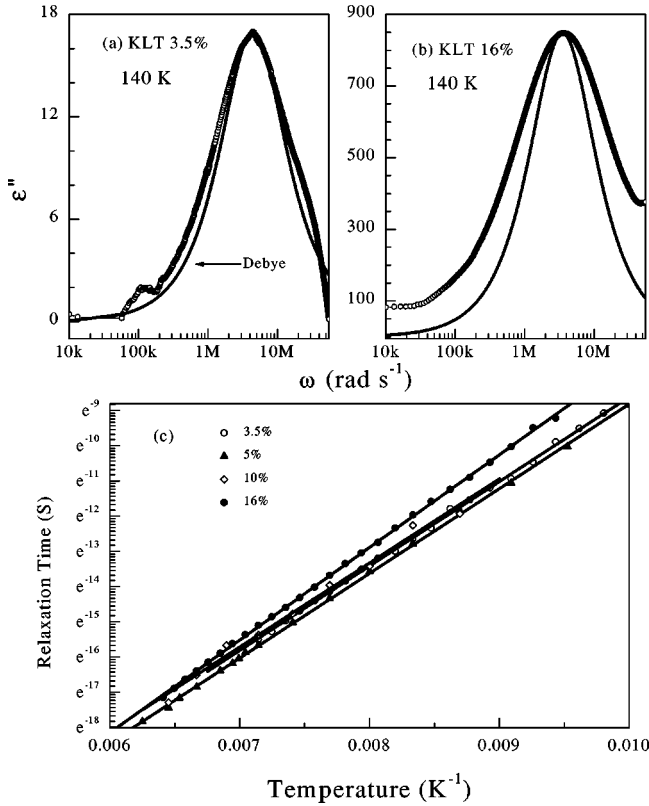
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TABLE I. Pre-exponential factor τ_0 and the activation energy U for different samples obtained from the fit of Arrhenius law to the temperature dependence of the dielectric absorption peak.

Conc.	τ_0 (S)	U(K)
3.5%	6.88×10^{-15}	2400
5%	5.32×10^{-15}	2405
10%	8.26×10^{-15}	2388
16%	1.81×10^{-15}	2633

cades for the 3.5% sample to 1.65 decades for the 16% sample, which may be contrasted with 1.14 decades in a Debye model.

The frequency ω_p at which the absorption reaches its peak value, provides an estimate of the average relaxation time $\tau = \omega_p^{-1}$, which is one of the most important parameters of any relaxation process. The temperature dependence of this relaxation time thus determined from the absorption peak is presented in Fig. 1(c) for all four different samples. Note that the y axis for all is in ln scale while the x axis is the inverse temperature. The data for all samples are seen to follow an Arrhenius law[1]

$$\ln \tau = \ln \tau_0 + \frac{U}{T}$$

FIG. 1. Dielectric absorption spectrum at 140 K (open circles) along with the Debye expression for absorption (solid line) for comparison. Note that as the concentration increases from (a) at 3.5% to (b) at 16% the width becomes larger. Also the maximum absorption increases. (c) Relaxation time (markers) in ln scale against inverse temperature for all the samples. The solid line is the Arrhenius fit to the data.

with a dc bias field. This is followed by a discussion of the results and, finally, the conclusion.

II. EXPERIMENTAL RESULTS

In the present work, we examined four different KLT samples with 3.5%, 5%, 10%, and 16% nominal concentrations, respectively. All crystals were in the (100) orientation and typically $(5 \times 5 \times 1)$ mm^3 except the 16% sample which was a cube 5 mm on the side. The measurements were carried out upon cooling the samples with the ac signal no more than 250 mV.

In Figs. 1(a) and 1(b) we show the imaginary part of the dielectric constant ϵ'' (open circles) at 140 K for the 3.5% and 16% KLT. The frequency axis has been kept the same for better comparison. We have also plotted a Debye absorption spectrum (continuous curves) to compare and contrast with the experimental data. The first point to note is that the absorption profile for both concentrations depart from the Debye form and more so for higher concentrations. Conversely, this suggests that the relaxation may approach the Debye limit at very low concentrations. Second, the absorption strength $\epsilon''_{\max}$, increases from approximately 17 for the 3.5% sample to about 850 for the 16% sample. In contrast, the full width at half maximum does not show as significant a trend with concentration, only increasing from 1.38 de-

and a fit of the above form yields a straight line, which is also shown in Fig. 1(c) as a solid line along with the data. The fitting parameters obtained τ_0 and U are presented in Table I. We notice that the attempt time τ_0 and the activation energy U are almost the same for the three lower concentrations and are consistent with values reported in the literature.[1,4–6] A deviation of about 10%, observed in the 16% sample may be due to a temperature gradient that may have existed across the sample because of its large size.

We note from Figs. 1(a) and 1(b) that, although the absorption profile for both these samples (and also for the other two) deviates from a Debye response, it nevertheless is largely symmetric. In view of this, the Cole-Cole modified dielectric dispersion[8,9]

$$\epsilon^* = \epsilon_\infty + \frac{\epsilon_0 - \epsilon_\infty}{1 + (i \omega \tau)^{1-\alpha}} \qquad 0 < \alpha \leq 1 \qquad (1)$$

was chosen to fit the data. Here ϵ_0 is the static permittivity, ϵ_∞ is the optical permittivity, τ the relaxation time, and ω the frequency of measurement. Implicit in the above modifications is the idea of a distribution of relaxation times[8–10]—controlled by the parameter α—in contrast to the single relaxation time ($\alpha = 0$) assumed in a pure Debye model. The best fits (solid lines) along with the data (open circles) at 140 K are shown in Fig. 2(a) for the 3.5% and in Fig. 2(b) for the 16% sample. We notice that, except at the low and high frequency ends of the spectrum, the Cole-Cole form fits the data reasonably well. The associated fitting parameters α and the mean relaxation time τ_m for each sample are also provided in the plots. Similar fits were made at all lower temperatures, and the one at 110 K for the 3.5% sample is shown in Fig. 2(c) along with the data. The Cole-Cole parameter α obtained from the fits is presented in Fig.
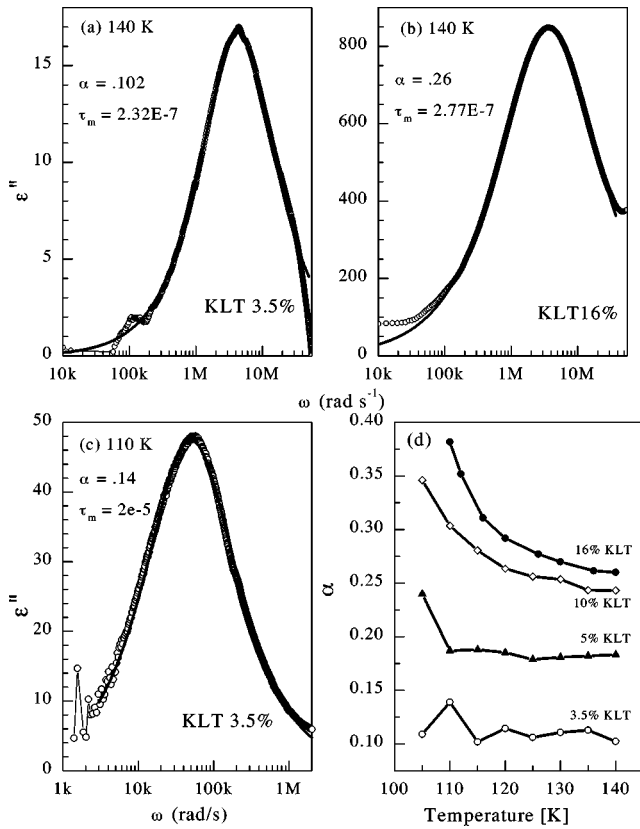
FIG. 2. Fit of Cole-Cole modified dielectric absorption (solid line) to the data (open circles) at 140 K for (a) KLT 3.5% and (b) KLT 16%. (c) Fit at a lower temperature of 110 K for the KLT 3.5%. (d) The temperature evolution of the Cole-Cole empirical parameter α for all the concentrations. For the 3.5% and 5% samples it stays nearly independent of temperature but for the higher concentration samples it increases.

2(d) for all concentrations as a function of temperature. The two main observations concerning α are (i) that it increases with concentration and (ii) that it is more flat at higher temperature but curves upward with decreasing temperature, and the more so at higher concentrations.

In an effort to examine the effects of a dc bias field on the relaxation, measurements were conducted with different bias voltages on the KLT 10% sample upon cooling. The 10% sample was specifically chosen with the thought that, at an intermediate concentration, the effects of the external field would be more perceptible than at a lower concentration while still remaining simple. In Figs. 3(a) and 3(b) we present the absorption spectrum ϵ'' at 120 and 105 K, respectively, for different bias field strengths. We notice that, at temperatures above 120 K, a field of 2000 V/cm (the largest the impedance analyzer could tolerate) has minimal effect both on the shape and strength of the absorption. The spikes in Fig. 3(a) are presumably due to polarization-strain coupling[11,12] (a resonant response in the dielectric spectrum is noticed when one of the mechanical modes of vibration of the specimen matches the excitation frequency). It is clear that, as the temperature is decreased, the absorption becomes progressively more sensitive to the field [open circles in Fig. 3(b)]. In addition to an overall reduction, the absorption peak shifts to higher frequency with increasing field strength [see Fig. 3(b)]. In Fig. 3(b) at 105 K we also present the Cole-
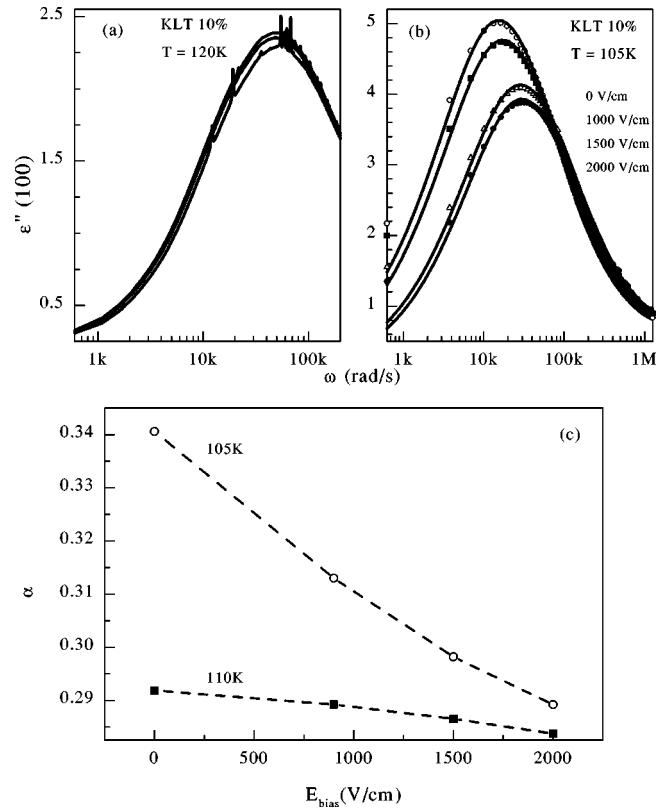

FIG. 3. (a) Dielectric absorption for the KLT 10% samples with different bias fields at 120 K. The spikes noticed are resonances due to polarization-strain coupling. (b) Note that the effect of the field becomes progressively stronger at lower temperature (105 K) with a suppression of the low frequency end followed by a shift of the peak to higher frequency. The solid line is the Cole-Cole fit to the data. (c) The field strength dependence of the Cole-Cole parameter α at 110 and 105 K. Notice the decrease of α with field strength.

Cole fit (solid line) along with the data (open circles) for different field strengths and note that the parameter α decreases with increasing field strength. The overall dependence of α on the field strength at 110 and 105 K is plotted in Fig. 3(c).

III. DISCUSSION

The essential features of the results presented in the last section are that (i) the dielectric dispersion and absorption are largely symmetric about $\omega\tau = 1$ but deviate increasingly from a Debye form with increasing concentration; (ii) τ follows an Arrhenius law and the macroscopic or average activation energy U for relaxation and the associated attempt time τ_0 obtained from it are almost concentration independent; (iii) the Cole-Cole modification of the Debye dielectric response function describes the absorption spectrum reasonably well over a broad temperature range; (iv) the parameter α increases with concentration, and also with decreasing temperatures; and, finally, (v) a dc bias field has the effect of hardening the relaxation frequency while suppressing the absorption.

A spectral width broader than the Debye value of 1.14 decade as noticed in Fig. 1 is often attributed[9] to a distribution of relaxation times around a mean or most probable

value. Such an attempt to fit the dielectric absorption data of KLT with a Gaussian distribution of relaxation times has been made by Christen *et al.*[5] However their report does not contain any temperature evolution of the distribution function and any possible explanation of its origin. The main cause of this distribution that would be specific of disordered ferroelectrics[13] is the local fields which should be concentration and temperature dependent. Each impurity dipole cluster experiences a slightly different local field and relaxes with its own intrinsic time. In this respect a distribution of relaxation times is a manifestation of the distribution of local fields or dipole-dipole interaction strengths. Another point to note is that each coupled dipole pair can experience a field due to other coupled pairs and also due to unpaired or individual dipoles. But since the relaxation frequency of unpaired dipoles is much higher ($U_{\pi/2} = 1200$), their contribution will, on the average, be negligibly small. Thus the local fields at Li^+ sites will largely come from dipole-pair clusters that are quasistatic or slowly reorienting. Evidently this contribution will increase with concentration (because of a smaller mean separation between Li^+ centers) and also with decreasing temperature as more and more pairs become frozen. As we discuss below, the larger absorption width in Fig. 1(b) for the higher concentration samples originates from these random local fields.

In order to obtain further details of this distribution function, we turn to the Cole-Cole fit of the data presented in Figs. 2(a)–2(c). The most important features in this figure [Fig. 2(d)] are that α increases with concentration n and also with decreasing temperature and more so for higher concentrations. The increase of α with concentration implies that the distribution of relaxation times progressively broadens as the concentration increases. This is expected since, at higher concentrations, there will be a higher density of dipole clusters. The other feature to note in Fig. 2(d) is the near independence of α on temperature for lower concentration samples. This is an indication that, above 100 K, the distribution of local fields in these samples is nearly independent of temperature. It is likely that the coupled pairs of dipoles are sufficiently far apart at low concentrations not to influence each other. The remaining temperature-dependent α is most likely due to some larger more complex dipole clusters, presumably consisting of more than two dipoles, that are already frozen. These frozen clusters with a larger dipole moment provide a background of stationary random local fields. That the population of such large frozen moments is small follows from the narrow width of the distribution function. In contrast, for the higher concentration samples, α is first of all larger implying a broader distribution function as already mentioned and second, α increases with decreasing temperature. Such an increase of α with decreasing temperature must be due to the changing dynamics of dipole clusters (slowing down with decreasing temperature). At higher concentrations, a slowing down of the dynamics is more likely since the dipoles will, on the average, be more closely spaced. As the temperature is decreased, the fraction of dipole pairs that are freezing will increase leading to a temperature-dependent local field distribution.

The foregoing analysis establishes the existence of a distribution of relaxation times that depends on temperature particularly strongly at higher concentrations. However as we recall from Arrhenius law, the relaxation time depends on the intrinsic parameters U and τ_0. This should entail a distribution of U or τ_0 or both and hence, a temperature dependent U and/or τ_0. Yet we note from Fig. 1(c) that the relaxation time obeys an Arrhenius law and yields temperature-independent U and τ_0 that are also nearly concentration independent (see Table I). The temperature independence of U and τ_0 follows from the absence of any noticeable curvature in the Arrhenius plot.[14] Thus, there seems to be a conflict between the implications of the Cole-Cole modification of the Debye dielectric response and the Arrhenius dependence of the relaxation time. In order to resolve the conflict we propose the following model. In the presence of local fields, it is more appropriate to replace the symmetric double well potential by an asymmetric double well potential. The equilibrium positions are no longer degenerate; one site becoming more stable than the other. Since there is no specific preference as to which well becomes deeper or which one becomes shallower, the structure of a symmetric double well on the average is preserved with an activation energy that is independent of temperature. Thus the average activation energy and attempt time, as obtained from the Arrhenius fit, should not reveal any temperature dependence while the shape of the relaxation peak would.

In view of the assertion made earlier that the random local fields are an essential source for a distribution of relaxation times, it may then be argued that ordered—in contrast to random—local fields can produce a discernible change in the distribution of relaxation times. In an attempt to verify this prediction, measurements with a dc bias field were conducted on the KLT 10% sample and the results are shown in Figs. 3(a) and 3(b). We note from Fig. 3(b) that, with a field strength of 2 kV/cm, the relaxation time is approximately 0.33×10^{-4} s while the same without any field is approximately 0.63×10^{-4} s. This shows that, as the degree of ordering increases, the relaxation time becomes shorter. In order to determine whether or not the field has any influence on the parameter α, the Cole-Cole expression for absorption was used to fit the data at 110 and 105 K. From Fig. 3(b) we note that the fit (solid line) is reasonably good and that, as shown in Fig. 3(c), α decreases with increasing field strength. Since the limit $\alpha \to 0$ corresponds to the Debye model, it would mean that the external field has the effect of narrowing the distribution of relaxation times. The external field aligns an increasing fraction of the dipoles with decreasing temperature which results in a smaller variance of the local fields. This confirms the assertion made earlier that the random local fields play an essential role in causing the distribution of relaxation times.

We may remark here about the possible influence that these coupled dipole pairs may have on the phase transition characteristics of KLT. It was pointed out by Vugmeister and Glinchuk[2] that the static random fields due to individual Li^+ dipolar units are not sufficient to explain a critical concentration of 2.2% and that additional random fields must therefore be present. Doussineau *et al.*[4] and Wickenhöfer *et al.*[15] proposed, and our present results suggest, the same explanation, namely that that additional static random fields arise from coupled Li^+-dipole pairs that begin freezing well above the phase transition.

We point out here that the various modifications to the

single relaxation time Debye dielectric response are based on the analysis of a large volume of data rather than on any fundamental scientific reasoning. In this respect, there is no justification, *a priori*, to recognize a Cole-Cole distribution of relaxation times in KLT for the analysis of the data. Any other symmetric distribution, such as Fuoss-Kirkwood or Gaussian form could well have been chosen with the same success. However, independent of the specific choice of the distribution, the conclusions—distribution of relaxation times, concentration-independent mean values, temperature-dependent local random fields, etc.—will nonetheless be the same.

In summary we have shown that the π relaxation in KLT, for nominal Li^+ concentrations from 3.5% to 16%, is well described by a Cole-Cole modification of the Debye relaxation function over a broad temperature range. Based on the temperature dependence of the Cole-Cole parameter α, we conclude that, the distribution of τ is due to a corresponding distribution of fields from frozen dipole pairs or larger clus-ters. The presence of frozen random field implies that the double potentials, within which dipole pairs reorient, are asymmetric. It is then also possible to resolve the apparent contradiction between temperature-independent average activation energy and attempt time. This is done by noting that in a random distribution, there will be an equal number of positive and negative asymmetry. Finally we have shown that, as expected from our model, a dc bias field reduces the degree of randomness and consequently also reduces the width of the distribution. Such a distribution of asymmetric double well potential may be a general characteristic of polar compounds with off-center ions.

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