Field-Induced Sharp Ferroelectric Phase Transition in $K_{0.937}Li_{0.063}TaO_3$

H. Schremmer and W. Kleemann
Angewandte Physik, Universität Duisburg, D-4100 Duisburg, Federal Republic of Germany

D. Rytz
Hughes Research Laboratories, Malibu, California 90265
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Sharp first-order ferroelectric phase transitions as indicated by sharp peaks of the dielectric permittivity arise in $K_{0.937}Li_{0.063}TaO_3$ upon cooling or heating in electric fields $75 < E < 300$ kV/m. They cancel the random dipolar fields due to frozen-in off-center Li^+ ions, which destroy the phase transition and give rise to low-temperature domain states if $E = 0$. Sharp *zero-field* transitions with a dispersionless peak of ϵ' at $T_c^+ = 104.5$ K, which accurately follows the Landau-Devonshire theory at $T < T_c^+$, are observed after field cooling with $E > 75$ kV/m.

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The complex polar behavior of $K_{1-x}Li_xTaO_3$, $x \ll 1$, is known to be due to the interaction of the (nearly) softened host-lattice transverse-optic mode and the impurity dynamics.[1] The nature of its low-temperature phase is still controversial, since it reveals signatures of both glasslike[2] and long-range-ordered ferroelectric[3] behavior. Recently,[4] however, evidence of a well-defined phase boundary at $x_c \sim 0.022$ between both types of polar states was deduced from refractive index (n), linear birefringence (LB, Δn), and dielectric permittivity (ϵ') data. Whereas glassy disorder is frozen in below $T_g \lesssim 40$ K in samples with $x < x_c$, random-field- (RF-) induced domain states arise via first-order phase transitions (PT) below $T_c > 40$ K if $x > x_c$. The RF's are believed[4] to originate both from dipolar fields due to randomly frozen-in off-center[5] Li^+ ions and from their random strain fields.

The glasslike behavior of low-x samples has been convincingly evidenced, e.g., by the typical slow dynamics of the polarization P in external electric[2] and in strain fields,[6] respectively. On the other hand, the domain-state nature of high-x samples has only been indirectly demonstrated, e.g., by the absence of microwave-induced light scattering[7] or by the lack of secondary neutron Bragg-peak extinction in zero-field-cooled (ZFC) samples.[8] A smeared first-order PT into mesoscopic ferroelectric order was deduced from the thermal hysteresis of n, Δn, and ϵ' upon cycling through T_c.[4] However, the complete absence of any peaks of ϵ' at T_c^+ and T_c^- due to the claimed[4] condensation of the ferroelectric soft mode still raises doubts about the very existence of a well-defined, albeit smeared, PT.

In this Letter novel experimental data will be presented in order to remove this uncertainty. By applying moderate electric fields along [100] the random freezing of the Li^+ dipoles can effectively be suppressed so as to unsmear the PT and to create marked peaks in the ϵ' versus temperature T curves. For samples with $x = 0.063$, large enough field values may be chosen that are still smaller than the critical one, E_{cr}. At $E > E_{cr}$ the PT becomes smeared again, this time, however, by virtue of the *uniform* field. Only incomplete unsmearing of the PT was achieved on samples with smaller E_{cr} values, e.g., for $x = 0.026$. It should be noted that similar, albeit less spectacular, field-induced enhancements of ϵ' near the ordering temperatures of $K_{1-x}Li_xTaO_3$ with $x \sim 0.05$ were reported in previous papers.[9,10] They remained, however, either unexplained[9] or were interpreted in terms of the conventional Landau-Devonshire theory[11] without invoking the dominating RF effects for $E = 0$. Höchli *et al.*[12] subsequently argued against the idea of conventional ferroelectricity in $K_{1-x}Li_xTaO_3$[10] ($x = 0.026$) in view of the strongly dispersive nature of its dielectric function. We shall show that both properties are not at all contradictory.

The experiments were carried out with samples and techniques described previously.[4] The dielectric permittivity was measured with a Hewlett-Packard 4192A impedance bridge, which allows for biasing voltages up to 200 V at frequencies between 5 Hz and 13 MHz. We shall report here only on the most clear-cut data obtained on $x = 0.063$ samples. Figure 1 shows LB vs T cycles at $E = 0$, 210, and 360 kV/m, respectively. The particularly large low-T LB for $E = 0$ proves more complete absence of 90° domains than reported previously (Ref. 4, Fig. 1, curve 4). The field reduces both the width and the height of the thermal hysteresis loop. It shifts the PT towards higher temperatures, and induces high-T LB tails. All of these features map well onto the Landau-Devonshire theory of the ferroelectric polarization at a first-order PT.[11] In particular, vanishing hysteresis and smearing of the originally sharp jumps of Δn indicate the destruction of the PT at large enough fields, $E > E_{cr}$ (curve 3). It should be noted, however, that $\Delta n \propto P^2$ does not distinguish between single and multiple 180°-domain states. A clear hint of the claimed[4] zero-field

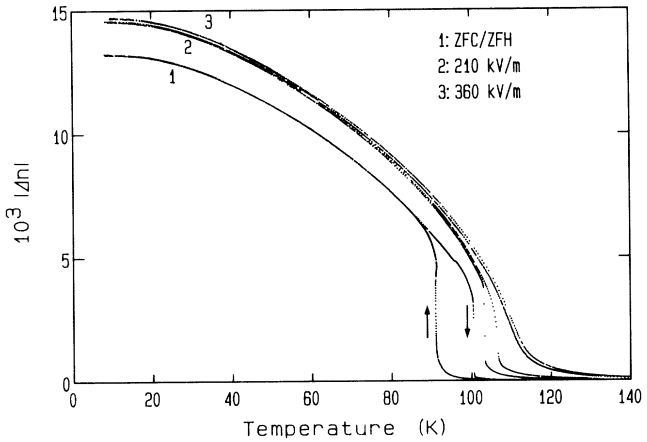

FIG. 1. Temperature cycles of the linear birefringence in quadrupolar-ordered $K_{0.937}Li_{0.063}TaO_3$ at various external fields.

domain state is, however, given by the low saturation LB, which is about 10% smaller than that of the poled sample. Very probably,[4] this difference is due to the disorder inherent in the domain walls.

Figure 2 shows ϵ' vs T, measured at $f=1$ kHz in the vicinity of $T_c\sim 100$ K (Fig. 1) on cooling [2(a)] and heating [2(b)] in various external fields. The predominating feature of the ZFC curve [Fig. 2(a), curve 1] is the broad Li^+ dipole-pair relaxation peak[13] at $T\sim 125$ K. The suspected ferroelectric PT is merely indicated by a gentle drop of ϵ' vs T below $T_c^-\sim 90$ K. It is interesting to note that the drop becomes sharper on reducing the cooling rate. This hints at domain growth while slowly passing the "critical" regime, an effect well-known from magnetic RF systems.[14]

Field cooling (FC) with increasing fields first sharpens the drop [Fig. 2(a), curve 2, $E=32$ kV/m] and then produces a sharp spike at $T_c^-=98.4$ K [Fig. 2(a), curve 3, $E_0=75$ kV/m]. At larger fields a peak evolves, which, however, gradually broadens until eventually merging with the dipolar relaxation peak at 113.2 K [Fig. 2(a), curve 7, $E=360$ kV/m]. ϵ'' vs T data (not shown) obtained under the same conditions confirm the creation and subsequent rounding of a peak at $E_0=75$ kV/m and $E\gtrsim 200$ kV/m, respectively. On the other hand, on field heating (FH) after ZFC somewhat larger threshold fields, $E_0\sim 100$ kV/m, are needed in order to reveal sharp peaks of ϵ' and ϵ'' at T_c^+.

Obviously, during both FC and FH the dipolar RF are more or less canceled by the external field. On FC the Li^+ dipoles become aligned from the beginning and dipolar RF are quite naturally avoided. Upon FH after ZFC, on the other hand, the frozen-in microdomains have to be aligned before reaching T_c^+ from below. Owing to the electret properties of $K_{1-x}Li_xTaO_3$,[2] this requires larger fields than the single-dipole alignment upon FC.

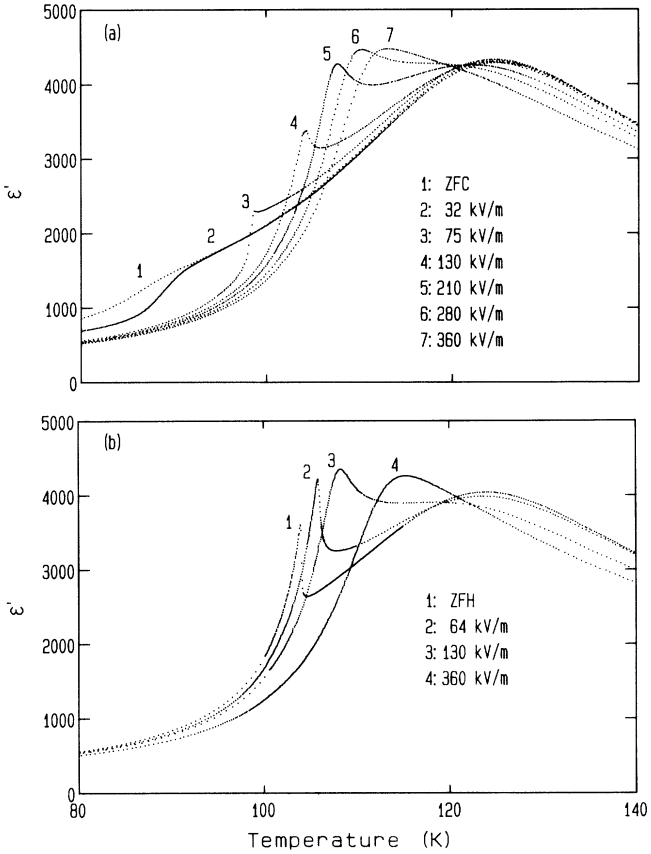

FIG. 2. Temperature dependence of the real part of the dielectric permittivity measured at $f=1$ kHz and various external fields (a) on cooling, and (b) on heating after cooling in $E=360$ kV/m.

Clearly, both T_c^- [Fig. 2(a)] and T_c^+ as indicated by the new anomalies of ϵ' and ϵ'' shift towards higher temperatures with increasing fields. The clearest data are revealed by ϵ' data obtained on a FC sample on heating as shown in Fig. 2(b) (cooling field $E_c=360$ kV/m, heating fields $0\le E_h\le 360$ kV/m). A particularly sharp spike arises under zero-field-heating (ZFH) conditions at $T_c^+(0)=104.5$ K. Rounding occurs at $E_h\gtrsim 130$ kV/m, although sharp discontinuities are still seen in the LB up to $E\sim 300$ kV/m (Fig. 1). Possible reasons for the strong rounding tendency of ϵ' vs T will be discussed below. Here we use the criterion of vanishing hysteresis in order to determine the critical field. This results in $E_{cr}\sim 300$ kV/m from both Δn *and* ϵ',ϵ'' vs T data. Remnant small hysteresis ($\Delta T\sim 2$ K) of *both* quantities (Fig. 1) at $E>E_{cr}$ is probably due to asymmetric freezing and unfreezing behavior of the Li^+ dipoles as discussed above.

It should be stressed that E_{cr} is independent of the cooling field. Essentially the same curves ϵ' vs T as in Fig. 2(b) are observed for *all* fields, $0\le E_c\le 300$ kV/m, provided that E_h exceeds some threshold value, E_h^{min}.

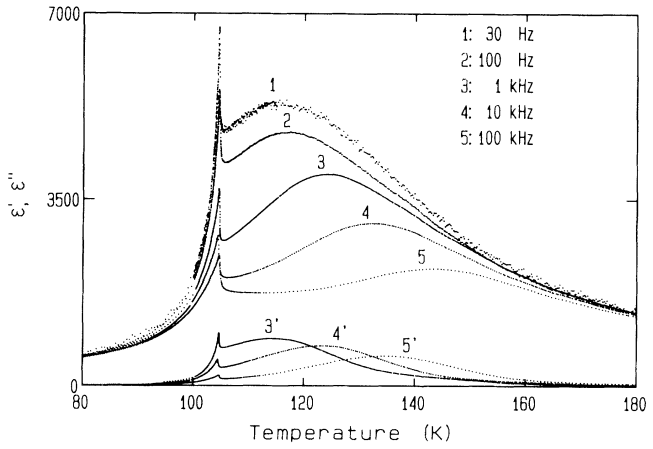

FIG. 3. Temperature dependence of the real (curves 1–5) and of the imaginary parts (curves 3′–5′) of the dielectric permittivity measured on zero-field heating at various frequencies after field cooling under $E=360$ kV/m.

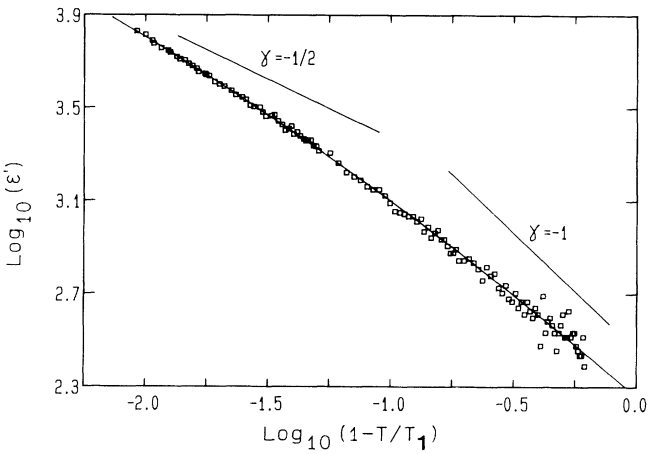

FIG. 4. Double-logarithmic plot of ϵ' vs $1-T/T_1$ for $T<T_1=105.5$ K, measured with $f=30$ Hz on ZFH after FC (Fig. 3, curve 1) and best fitted by Eq. (3) (solid line). Straight lines, denoted as $\gamma=-\frac{1}{2}$ and -1, respectively, indicate the expected asymptotic slopes, Eq. (3).

For ZFC samples, $E_c=0$, we find $E_h^{\min}\sim 100$ kV/m, which is sufficient to cancel the RF by taking advantage of the finite domain mobility just below $T_c^+(E_h)$. Hence, the role of E_c is *not* just to align certain regions of the sample, which then respond as a ferroelectric up to $E_{cr}\sim E_c$.

Obviously, a classic first-order PT characterizes the FC sample measured on ZFH [Fig. 2(b), curve 1]. Indeed, at frequencies 30 Hz $\leq f\leq$ 100 kHz both ϵ' and ϵ'' are sharply peaked at an invariable temperature, $T_c^+(0)=104.5\pm 0.1$ K (Fig. 3). This behavior fundamentally contrasts with that of the broad dipolar relaxation peaks, which emerge at $T>T_c^+(0)$ and exhibit Debye-type dispersion with Arrhenius-type relaxation times.[13] Evidently collective behavior of the order parameter, P, in the sense of a PT from long-range order into the paraelectric state is probed *below* T_c^+. Coupling between the collective and the impurity modes is merely reflected by a gradual decrease of the ϵ spikes, roughly in proportion to that of the relaxational peaks (Fig. 3) with increasing frequency.

A Landau-Devonshire analysis[11] of the free energy

$$G=G_0+(b/2)(T-T_0)P^2-(c/4)P^4+(d/6)P^6 \quad (1)$$

yields the familiar T dependence of P undergoing a first-order PT at $T_c=T_0+3c^2/16bd$, and the static dielectric permittivities

$$\epsilon_-^{-1}=b(T-T_0)\,,\quad T>T_0\,, \quad (2)$$

and

$$\epsilon_+^{-1}=4b(T_1-T)+2c(b/d)^{1/2}(T_1-T)^{1/2}\,,\quad T<T_1\,. \quad (3)$$

T_0 and T_1 are the thermodynamic limits of metastability upon cooling and heating, respectively. Whereas $\epsilon_-=4\epsilon_+$ at T_c, ϵ_+ exceeds ϵ_- at higher T until diverging as $T\rightarrow T_1$.

Obviously our FC-ZFH experiments [Figs. 2(b) and 3] correspond to the situation $T_c<T_c^j\lesssim T_1$ with nearly diverging ϵ'. Indeed, from a best fit of the ϵ' data by Eq. (3) we find $T_1=105.5$ K, whereas $T_c=T_1-c^2/16bd=103.7$ K is obtained by using the best-fit parameters $b=1.03\times 10^{-5}$ and $c^2/d=2.99\times 10^{-4}$. A log-log plot of ϵ' vs $t=1-T/T_1$ (Fig. 4) reveals the high quality of the fit with its marked "crossover" from t^{-1} to $t^{-1/2}$ behavior as $t\rightarrow 0$. This analysis suggests that contributions of individual and aggregated Li^+ dipoles to the permittivity may be neglected *below* T_c^+. Only *above* T_c^+, in the absence of long-range order, does dipolar permittivity dominate and give rise to large shoulders. We did not attempt to separate dipolar and collective contributions to ϵ' and ϵ'' at $T>T_c^+$ [Figs. 2(b) and 3].

It is interesting to note that the computed value $T_0=T_1-c^2/4bd=98.2$ K nearly coincides with the T_c^- value as obtained with $E_0=75$ kV/m [Fig. 2(a), curve 3], but by far exceeds the ZFC value, $T_c^-\sim 90$ K, as obtained form both LB (Fig. 1) and the ϵ' step [Fig. 2(a), curve 1]. We believe this extra lowering of T_c^- by about 8 K to be due to the nonordering RF, as similarly predicted for magnetic RF systems.[15] Indeed, within $0\leq E\lesssim E_0$, T_c varies much more strongly than in the subsequent range, $E_0\lesssim E<E_{cr}$, where $dT_c/dE\sim$const, as predicted for small enough fields.[11] It is the low-field regime where the minimal domain size should gradually increase until reaching infinity at the threshold, $E\sim E_0$, in the sense discussed by Andelman and Joanny.[16] Their arguments are expected to hold for both unstrained or accidentally strained $K_{1-x}Li_xTaO_3$, i.e., for an RF system with cubic[17] or Ising anisotropy.

The extrapolated critical temperature, $T_{cr}=T_1+c^2/5bd=111.3$ K, is compatible with the LB data (Fig. 1). They suggest the critical curve with vertical tangent and vanishing discontinuity to occur at $107<T_{cr}<112$ K, where $210<E_{cr}<360$ kV/m. From Fig. 2(a) one finds, more precisely, $280<E_{cr}<360$ kV/m in agreement with the above estimated value, $E_{cr}\sim 300$ kV/m.

Finally the severe rounding of the ϵ' (and ϵ'') vs T curves in fields as low as $E\gtrsim E_{cr}/2$ (Fig. 2) has to be considered. Firstly, a larger sensitivity to rounding is expected for the derivative function, $\epsilon\propto dP/dE$, than for the order parameter, P, itself. Hence, if P undergoes some RF-induced precursor rounding as discussed by Imry and Wortis[18] for a first-order PT, the ϵ vs T curve will be affected by a much greater extent. In addition, rounding will become more important at reduced discontinuities of P, i.e., in large fields, in agreement with our observations. Secondly, we believe the random strain mechanism to be responsible for the still appreciable rounding. Owing to the statistical distribution of Li^+, it will survive in any large electric field. Hence, complete sharpness of the PT is never achieved. Fortunately, however, rounding is nearly negligible in the limit $E=0$ (FC-ZFH sample, Fig. 3). Obviously, "wrong" phase droplets[18] evolve merely on the scale of the coherence length ξ on approaching T_c^+ from below. At $E\neq 0$, presumably, the interface energy between polarized and unpolarized material is lowered. Hence, droplets of size $l>\xi$ are eventually stabilized near T_c^+, thus initiating rounding[18] as observed.

It will be interesting to investigate electric field effects on $K_{1-x}Li_xTaO_3$ with different impurity concentrations. Presently, it is not yet very clear why unsmearing of the first-order PT is much harder to achieve in low-x samples (e.g., $x=0.026$). Presumably this is connected with a crucial increase of $|d\ln T_c(x)/dx|$ with decreasing x, which favors the condition $l>\xi$ and, hence, rounding.[18]

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