Strain-induced quadrupolar ordering of dipole-glass-like $K_{1-x}Li_xTaO_3$

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Linear birefringence measurements on dipole-glass-like $K_{1-x}Li_xTaO_3$ with $x=0.011$, 0.016, and 0.022 reveal logarithmic time dependences of long-range dipolar ($\langle P_z^2\rangle$) ordering due to natural built-in strains at low temperatures. This explains recent observations of time-dependent elastic-neutron-scattering intensities of an $x=0.017$ sample, rapidly cooled below its glass temperature. For $x=0.022$ both dipole-glass and ferroelectric-domain state properties are found as predicted previously.

In the past decade the formation of defect-induced polar states in the "incipient" ferroelectrics $KTaO_3$ and $SrTiO_3$ has attracted considerable interest.[1] However, the experimental situation is not simple and far from being completely understood. On doping with different cations, many dipole glasses and ferroelectrics with quite different individual properties became apparent. Evidently the concentration of impurities plays a crucial role, since it determines the interaction between the polarization clouds surrounding the impurity dipoles at low temperatures.[2]

Recently,[3] in one particular case, $K_{1-x}Li_xTaO_3$ ("KTLi"), it proved possible for the first time to determine a phase boundary between low-x glasslike and high-x ferroelectric compositions at $x=x_c\simeq 0.022$. Most of the previous experiences[4,5] fit well with this picture. In particular, it allows for a simple interpretation of recent elastic neutron scattering data.[6] Large Bragg peak intensities were observed on an $x=0.04$ sample below $T_c\sim 50$ K. These are compatible with a spatially incoherent ferroelectric domain state,[7] which is due to quenched random fields (RF) as discussed previously.[3,8] On the other hand, upon cooling in an electric field the Bragg peaks are as small as in the paraelectric phase. Evidently long-range dipolar order, $\langle P_z\rangle\neq 0$, is created with a high degree of spatial coherence, which favors the tendency of secondary neutron extinction.[6]

The opposite situation is found with $x=0.017$, where secondary extinction suppresses the (004) Bragg reflex nearly completely in an as-quenched sample.[6] However, over several hours the intensity gradually increases under isothermal conditions, $T<T_g\simeq 40$ K, where T_g is the freezing temperature of the dipole glass.[3] As remarked previously,[3] we believe that this behavior is crucially determined by built-in strains. Being due to crystal growth and sample preparation, they may produce quadrupolar ordering on their inherent macroscopic length scale ("domains"). Similarly, as under the action of an external electric field,[4] a typical time dependence may be expected. The sample approaches its equilibrium state in a field which is inhomogeneous by nature. Spatial inhomogeneity, determined by more or less random distributions of $\langle P_x^2\rangle$, $\langle P_y^2\rangle$, and $\langle P_z^2\rangle$ domains, eventually allows for large Bragg peak intensities.[6]

In this Brief Report the existence of natural built-in strains and their influence on the quadrupolar ordering of glassy samples of KTLi will be shown. We shall report on linear birefringence (LB) data of samples with $x=0.011$, 0.016, and 0.022, which prove to depend on both the cooling rate and the time under isothermal conditions. Logarithmic time dependences, similar to those found in spin glasses,[9] are detected *without* applying any *external* field. Whereas well-defined freezing temperatures T_g emerge for $x=0.011$ and 0.016, the sample with near-critical concentration, $x=0.022$, rather exhibits an extremely smeared first-order phase transition.

The samples used in this investigation were (001) plates with typical size $2\times 1\times 0.2$ mm^3, cut from crystals with nominal concentrations $x=0.011$, 0.016, and 0.022. LB data were taken on microscopically selected sample sections (typically 20×20 μm^2 wide), appearing homogeneous between crossed polarizers under both conditions, asquenched or slowly cooled down to $T\sim 10$ K. As described previously,[3] large homogeneous sections on a millimeter scale are found in nominally strain-free glasslike samples ($x<x_c$). Figures 1(a) and 1(b) show micropolarigrams of a sample with $x=0.016$, rapidly ($\Delta t\sim 500$ s) and slowly ($\Delta t\sim 2$ h) cooled down from about 60 to 10 K, respectively. Visibly, strain-induced inhomogeneity arises upon slow cooling, whereas the rapidly cooled sample appears homogeneously dark except in the vicinity of heavily strained regions (i.e., sample edges and growth imperfections).

At concentrations $x>x_c$, ferroelectric 90° domains frequently appear on a μm scale[3] (see, e.g., Fig. 4 of Ref. 10). Similar, albeit fuzzier structures are also observed on a sample referring to the phase boundary $x=0.022\sim x_c$, as shown in Fig. 1(c) (bottom). Simultaneously, however, also large-scale LB patterns similar to those observed on glassy samples [Fig. 1(b)] are recognized [Fig. 1(c), upper two-thirds]. Contrasting with $x<x_c$ samples, however, the LB distribution as a whole does not vary visibly on changing the cooling rate. Small, but finite effects are only perceivable, on *measuring* the LB. This is shown in Fig. 2, where the LB vs T of rapidly

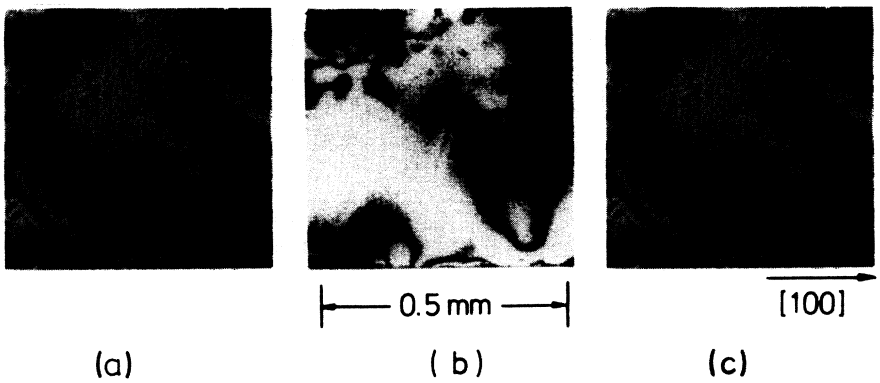

FIG. 1. Typical sample sections of KTLi with thickness $d \sim 0.2$ mm and $x = 0.016$ [(a) and (b)] and 0.022 [(c)], rapidly [(a)] and slowly [(b) and (c)], respectively, cooled to $T = 10$ K and viewed between crossed polarizers, which were oriented under $\pm 45°$ with respect to [100].

cooled samples with $x = 0.011$, 0.016, and 0.022 is compared for slow-heating ($\Delta t \sim 2$ h; curves 1, 3, and 5, respectively) and subsequent slow-cooling runs ($\Delta t \sim 2$ h; curves 2, 4, and 6, respectively). It is seen that slow-cooling enhances the low-T LB by about 100% for $x < x_c$ (curves 1–4), whereas an enhancement of less than 10% is characteristic for $x \sim x_c$ (curves 5 and 6). Nevertheless, in all cases the absolute differences $\delta\Delta n \sim (0.5\text{–}2.5) \times 10^{-4}$ are of the same order of magnitude. Moreover, as will be discussed below, slow relaxation towards the slow-cooling LB is observed for all concentrations, $0.011 \leq x \leq 0.022$. This shows in particular that some glasslike nature is also inherent in samples with $x \sim x_c$.

On the other hand, there is also strong evidence for RF ferroelectric behavior characterizing the $x = x_c$ sample. Apart from the above-mentioned typical 90° domains, it is observed that its low-T LB is more than one order of magnitude larger than that of $x < x_c$ samples, and a hysteresis loop appears around $T \sim 45$ K. This, however, is very narrow ($\Delta T \sim 1$ K) and nearly completely rounded.

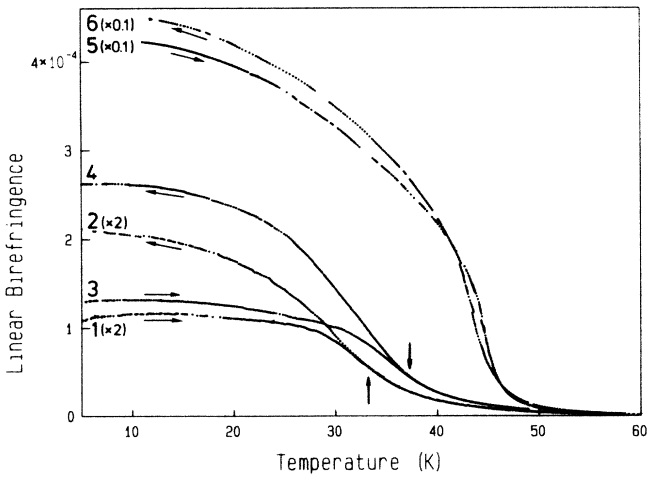

FIG. 2. LB vs T of rapidly quenched KTLi with $x = 0.011$, 0.016, and 0.022 on slow heating (1, 3, and 5, respectively) and subsequent slow cooling (2, 4, and 6, respectively). The glass temperatures for $x = 0.011$ and 0.016 are indicated by arrows.

According to ideas of Imry and Wortis[11] this is expected[3] for $x = x_c$, where glasslike cluster freezing ($x < x_c$) and RF ferroelectric ordering ($x > x_c$) become undistinguishable, or, in other words, the RF microdomains (not resolved by LB contrast) are degenerating into frustrated dipolar clusters. A peculiarity due to the borderline character of the $x = x_c$ sample is the crossing of the LB vs T curves 5 and 6 observed at 42 K (Fig. 2), where the sample's nature changes from quenched-glass-like to overheated-domain-like, both states being thermodynamically metastable in a different sense.

The purely glasslike samples, $x = 0.11$ and 0.16 are characterized by well-defined limits of metastability. At the glass temperatures, $T_g = 33.5$ and 37.5 K, respectively (arrows in Fig. 2), slow- and rapid-cooling LB curves merge into one another. These temperatures agree perfectly with those obtained from dielectric permittivity[3] and piezoelectric data ($x = 0.016$).[4] Below T_g, the LB is very clearly time dependent. This is shown for $x = 0.016$ in Fig. 3 at six different constant temperatures, $T_0 = 4.7$, 10.0, 14.4, 19.3, 23.3, and 28.3 K. It is seen that $\Delta n(t)$ gradually approaches the asymptotic value $\Delta n(\infty)$ tentatively taken from the slow-cooling data of Fig. 2 (curve 4). Note that the initial values $\Delta n(0)$ were obtained after quenching the sample from $T = 50$ K to T_0 within about 500 s. They do not agree, hence, with $\Delta n(T_0)$ as given by the slow-heating curve 3 in Fig. 3, since this involves partial annealing before reaching T_0 from below. For the highest temperature, $T_0 = 28.3$ K, $\Delta n(6000\text{ s})$ seems to approach $\Delta n(\infty)$ without indicating saturation. In that case, we believe that the inserted value, $\Delta n(28.3\text{ K})$, referring to curve 4 of Fig. 2, is substantially smaller than expected for $t \to \infty$ because of the finite cooling rate involved. Furthermore, we remark that similar Δn vs t curves emerge for $x = 0.011$ and 0.022, both exhibiting similar growth rates of the LB, e.g., $d(\Delta n)/dT \sim 10^{-18}\,\mathrm{s}^{-1}$ for $T = 20$ K and $t \to 0$.

Following recent ideas[9] to describe the time dependence of the magnetization in spin glasses in an external magnetic field, we have plotted the normalized quadrupolar order parameter,

$$[\Delta n(t)/\Delta n(\infty)]^{0.5} \propto [\langle P_z^2(t)\rangle/\langle P_z^2(\infty)\rangle]^{0.5} ,$$

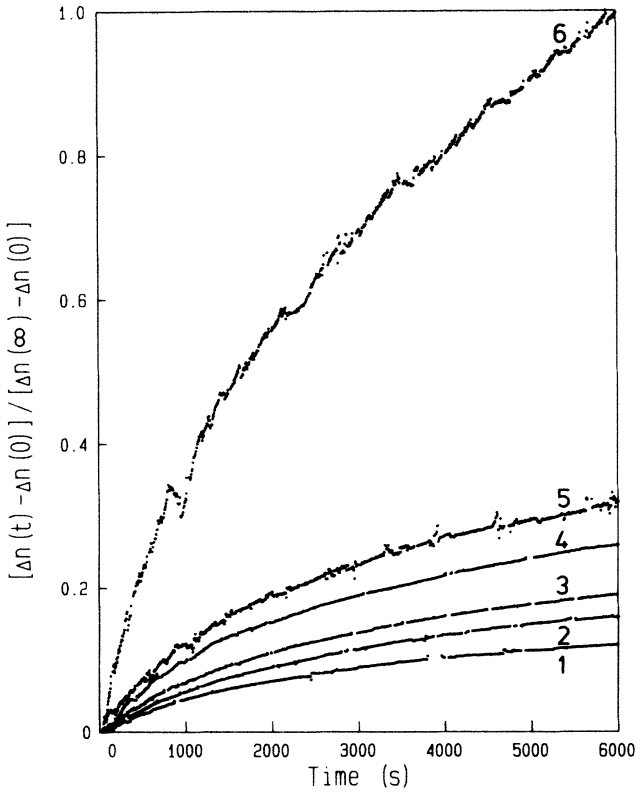

FIG. 3. Normalized strain-induced LB variation, $[\Delta n(t) - \Delta n(0)]/[\Delta n(\infty) - \Delta n(0)]$ vs time for $x = 0.016$, and $T_0 = 4.7$, (1), 10.0 (2), 14.4 (3), 19.3 (4), 23.3 (5), and 28.3 K (6), respectively.

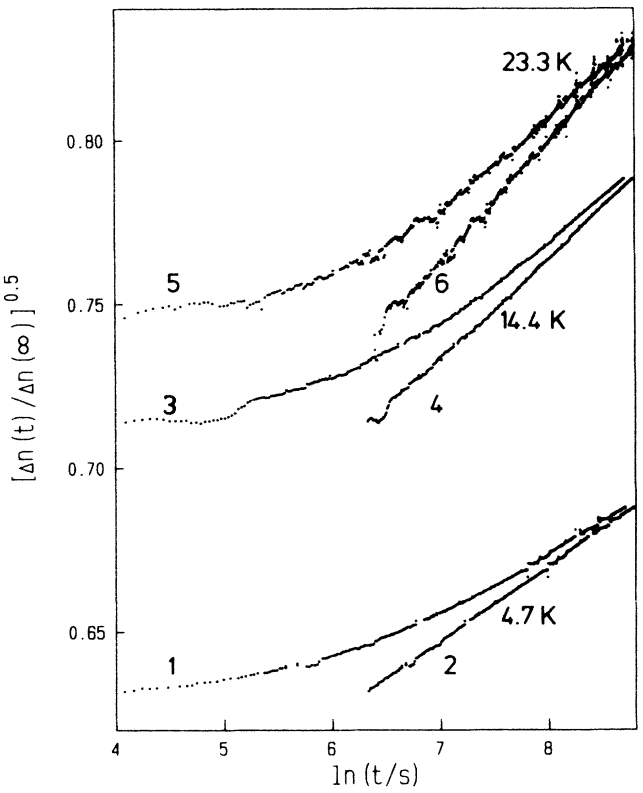

FIG. 4. $[\Delta n(t)/\Delta n(\infty)]^{0.5}$ vs $\ln(t/s)$ for $x = 0.016$ and $T_0 = 4.7$, 14.4, and 23.3 K, where the time $t > 0$ is counted immediately *after* (1, 3, 5) and 550 s *before* reaching T_0 by rapid quench (2, 4, 6, respectively).

versus $\ln(t/s)$ in Fig. 4 for $T = 4.7$, 14.4, and 23.3 K, respectively. We thus assume linear coupling between the inherent local strain field with $\langle P_z^2 \rangle^{0.5}$ in analogy with the well-known coupling between an electric field E_z, and the polarization $\langle P_z \rangle$.[3-5] It is seen that proportionality is achieved only after large times, if $t = 0$ is counted from the start of the experiment *after* reaching T_0 (curves 1, 3, and 5). However, in reality the quadrupolar ordering starts already *during* the cooling process, since we are not able to remove the built-in strain before reaching T_0 within a finite time. It is, hence, reasonable to shift the origin of the time scale by some value t_0, being close to the real cooling times from 60 K to T_0 (~ 500 s in all cases). This is accomplished in Fig. 4 for the curves 2, 4, and 6 by choosing $t_0 = -550$ s, which yields nearly perfect linearization of all curves within 550 s $< t <$ 6550 s. Empirical laws of the form

$$[\Delta n(t)/\Delta n(\infty)]^{0.5} = a + b \ln(t/s) , \quad (1)$$

are obtained with $a = 0.488$, 0.520, and 0.504, and $b = 0.022$, 0.030, and 0.037, for $T = 4.7$, 14.4, and 23.3 K, respectively. Note that our data clearly indicate but *one* characteristic relaxation time. The short-lived component reported previously[6] presumably was due to sluggish thermal equilibration of the cryostat involved.

Clearly, the monotonic increase of the slope parameter b with increasing temperature, reflects the thermal activation involved in the microscopic reorientation processes governing the quadrupolar ordering. As proposed for relaxing spin glasses[9] one might introduce a virtual barrier height $W_c = k_B T \ln(t/\tau_0)$, which allows the rescaling of all data onto a single master curve. Indeed, a preliminary plot of $\Delta n(t)^{0.5}$ vs $T \ln(t/\tau_0)$ for all data of Fig. 4 with an attempt time $\tau_0 \sim 10^{-8}$ s appears quite reasonable, although more data would be required for a thorough check. At the present stage, however, other descriptions like algebraic or stretched-exponential time dependences[12] may not be excluded to appropriately describe the relaxation of KTLi towards its equilibrium state $\langle P_z^2(\infty) \rangle$. We did not attempt to test all of these possibilities owing to the present experimental uncertainties, i.e., uncontrollable intrinsic strain fields and ill-defined zeros of the time scale. These are hoped to be overcome in future experiments, which are planned to be done under well-defined external stress.

In conclusion, by using time-resolved and spatially resolved LB measurements the crucial role of internal strains, determining quadrupolar order and "domain" distributions of glassy KTLi at low temperatures, could be evidenced. It will be interesting to compare the time dependences of both the quadrupolar and the dipolar ordering processes under constant stress and electric field,[4] respectively. Although $\langle P_z^2 \rangle$ and $\langle P_z \rangle$ are closely linked to one another, different dynamics may be encountered as was recently demonstrated on $KBr_{1-x}(CN)_x$.[13]

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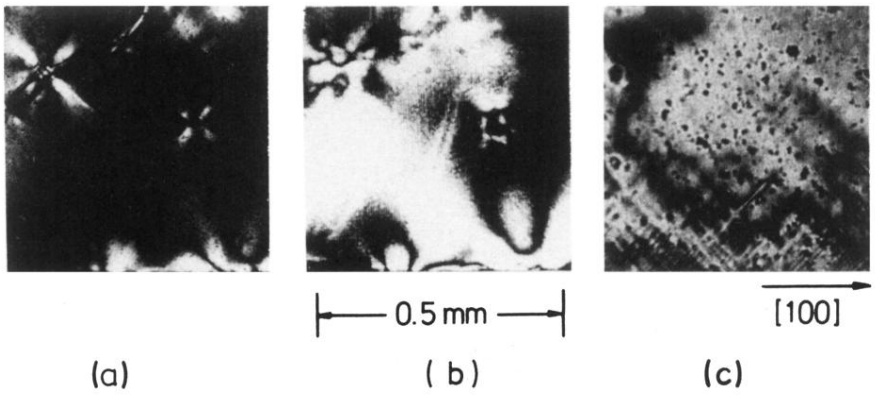

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