Dipole ordering effects and reentrant dipolar glass state in $KTaO_3$:Li,Nb

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Dielectric permittivity and Raman-scattering studies reveal unconventional dipole ordering and structural effects that arise in the incipient ferroelectric $KTaO_3$ due to the simultaneous presence of off-center Li^+ and Nb^{5+} ions. A soft-mode-driven transition into a ferroelectric phase accompanied by the formation of a dipole glass in the Li^+ subsystem was identified at 39 K in a sample of composition $K_{0.9986}Li_{0.0014}Ta_{0.988}Nb_{0.012}O_3$. A second soft-mode transition was found at 30 K, whereas a transition into a phase identified as a ''reentrant dipolar glasslike state'' was observed at 15 K. Such a sequence of phases, diordered–long range ordered–reentrant glass, already known for disordered ferromagnets, is here reported for a highly polarizable matrix with soft modes.

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Ordering effects in systems of randomly distributed dipoles with orientational degrees of freedom in a polarizable matrix are an important topic in the physics of dielectric materials, the consideration of which goes back to Langevin's and Debye's works. In the past several years, new attention has been given to this subject due to the discovery that substitutional ions may induce ordering and even lead to ferroelectric instability in a highly polarizable matrix. A paradigmatic case is that of Li^+ or Nb^{5+} off-center ions substituting for K^+ or Ta^{5+} in the incipient ferroelectric $KTaO_3$ (KTO),[1–6] where the effective moment of the dipole centers is greatly increased with respect to other systems (e.g., alkali halides[7]), owing to the large value of the dielectric susceptibility at low temperature.

Actually the individual effects of the two impurities, Nb and Li, are relatively well established from the study of the compounds $K_{1-x}Li_xTaO_3$ (KLT) and $KTa_{1-y}Nb_yO_3$ (KTN). At concentrations of Li and Nb less than critical ones, $x_{c1} \approx 0.01$ for KTL (Ref. 8) and $y_{c1} \approx 0.008$ for KTN,[9,10] the system's behavior is close to that of $KTaO_3$, where ferroelectric ordering at low temperatures is prevented by quantum fluctuations. Above these thresholds, distinct manifestations take place in these two compounds. In KLT short-range ordering begins to develop with increasing Li concentration, giving rise to a dipole glass or mixed ferro-dipole glass state, with tetragonal microdomains.[4,5,9–14] At concentrations $x > 0.05$ long-range ferroelectric order develops.[15] These phenomena are specifically connected with the presence of slowly relaxing Li^+ off-center dipoles, which are characterized by large (~1.2 Å) ⟨100⟩ displacements and by indirect interaction via TO soft phonons in the highly polarizable perovskite-type matrix.

In KTN, there is evidence for a soft-mode-dominated transition to an ordered rhombohedral phase above a concentration of $y = 0.01$.[4,16] A sequence of three ferroelectric phase transitions (from tetragonal to orthorhombic to rhombohedral) is detected when $y > 0.03$.[4] These manifestations are ascribed to an instability of the Ta-O ferroelectric chain, which is usually attributed to the presence of fast-relaxing ⟨111⟩ displacements of substitutional Nb^{5+} ions. An understanding of the situation in which the two impurities are simultaneously present is not as well developed. This is the case for $K_{1-x}Li_xTa_{1-y}Nb_yTaO_3$ (KLTN) where there is the possibility of interplay between the Li^+ and Nb^{5+} dipolar subsystems. Prater, Chase, and Boatner[17] studied depolarization of light and Raman spectra in order to monitor the effects of Li additions with $x \geqslant 0.0025$ on the soft-mode phase transition (PT) of KTN, and they proposed a phase diagram for KLTN. At $x \leqslant 0.004$, all the essential features of the Nb-induced PT were evident, with the exception that the symmetry of the ferroelectric phase was found to be tetragonal rather than rhombohedral. Such a possibility was considered theoretically by Glinchuk.[18] With increasing Li content, the PT character turns to order-disorder, and its transition temperature is progressively raised.

In this work we present results from a dielectric permittivity and Raman spectroscopy study for KLTN with $x \approx 0.0012$, i.e., with a smaller Li content than was used in Ref. 17. It appears that the phenomena induced in KLTN by a very small Li co-doping are quite complex, including a sequence of soft-mode driven transitions, the enhancement of dipolar relaxation, and the formation, at low temperature, of a phase that displays characteristic properties of a ''reentrant dipole glass'' phase. The behavior of the real ε' and imaginary ε'' parts of the permittivity is studied in the 100-

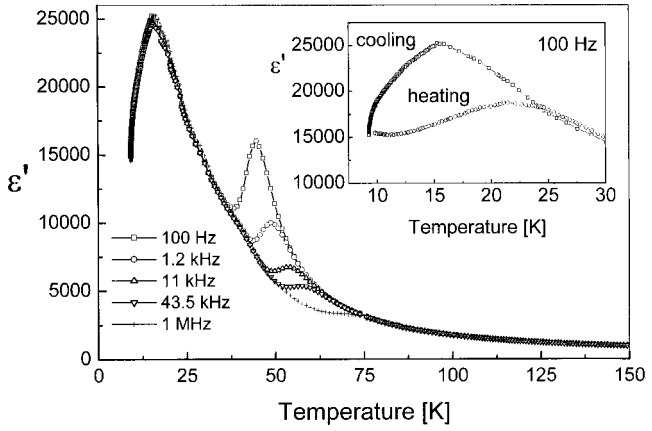

FIG. 1. Temperature dependence of the dielectric permittivity ε' in $K_{0.9986}Li_{0.0014}Ta_{0.988}Nb_{0.0012}O_3$ for several frequencies. The inset shows the behavior of ε' for successive cooling and heating in a 100-Hz reference ac electric field.

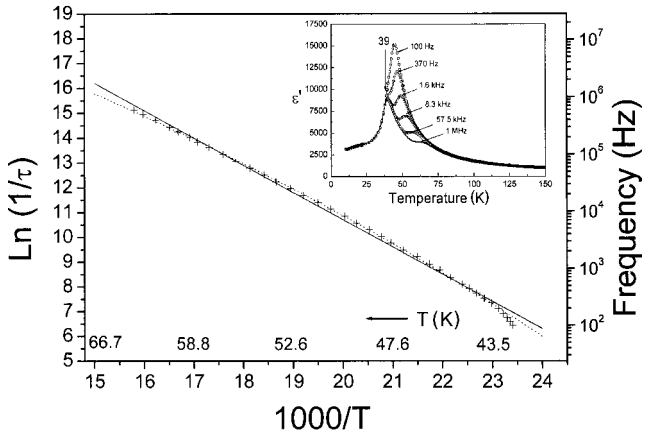

FIG. 2. Arrhenius plot for the temperature dependence of mean relaxation time in $K_{0.9986}Li_{0.0014}Ta_{0.988}Nb_{0.0012}O_3$. Experimental points (crosses) are determined from the position of the $\varepsilon''(T)$ maxima at different ac frequencies. The straight line presents an Arrhenius fit with $\tau_0 \approx 3\times10^{-14}$ s and $\Delta \approx 89.3$ meV. The dashed line is a Vogel-Fulcher fit with $\tau_0 \approx 1.3\times10^{-12}$ s, $\Delta \approx 55$ meV and $T_f = 11$ K. The inset shows the temperature dependence of the ε' heating run performed after specimen's cooldown to 10 K under 10 kV/cm of dc electric bias field.

Hz–1-MHz frequency range and in the 9–300-K temperature range with approach described in Ref. 19. Low-energy Raman spectra, taken in a 90° geometry were used to study the TO_1 soft-phonon mode in the range of 15–100 K, using the methods described in Ref. 20. Observations were performed at different temperatures, after cooling the sample to about 15 K, at a rate of 1 K/min and then heating to the successive points of measurement. KLTN single crystals were provided by Oak Ridge National Laboratory. About 0.012 wt % of Cu was added to facilitate the crystal growth. From the concentration in the melt, and using empirical rules,[21] the estimated Li concentration in the samples was $x = 0.0014$. The estimated concentration of Nb, according to the phase diagram of KTN,[22] was $y = 2.4\%$. A direct determination performed by electron microprobe analysis, supported by the comparison to reference KLTN specimens in which the Nb concentration was accurately determined using microprobe and photometry methods, gave a value of $y = 1.2 \pm 0.6\%$. Specimens, in the form of thin, polished, and electroded slabs were prepared for dielectric measurements, and a rectangular parallelepiped was used for Raman experiments. The samples were oriented along ⟨100⟩ cubic axes.

Figure 1 shows the temperature dependence of ε' at different frequencies, as recorded in cooling runs. Two prominent features are apparent: (i) a pronounced dielectric relaxation developing in the 40–90-K region; and (ii) an intense cusp-shaped $\varepsilon'(T)$ maximum at 15.3 K, with a small dispersion and strong temperature hysteresis (inset of Fig. 1). At $T > 50$ K relaxation indicates characteristics of a Debye type. The magnitudes of $\varepsilon'(T)$ and respective $\varepsilon''(T)$ maxima decrease, and their position shifts to higher temperatures with ac frequency. At a given temperature, the positions of $\varepsilon''(f)$ maxima and the ε' inflection point coincide. The dielectric relaxation is usually analyzed by the relation between the monitoring frequency ω and the temperature T_m at which $\varepsilon''(T)$ is at its maximum. Assuming that at T_m the characteristic macroscopic mean relaxation time is $\tau_m = 1/\omega$, an ''Arrhenius plot'' (ln τ versus $1/T$) is then employed. Figure 2 gives the respective Arrhenius plot, which shows that, at least down to 45 K, the temperature dependence of the relaxation time determined from the positions of the $\varepsilon''(T)$ maxima at different frequencies, was satisfactorily described by an Arrhenius law $\tau = \tau_0 \exp(\Delta/k_B T)$, with $\tau_0 \approx 3 \times 10^{-14}$ s and an activation energy $\Delta \approx 89.3$ meV, that are well-known relaxation parameters for 90°-orientation ''hops'' of Li^+ centers.[3] However, a Vogel-Fulcher (VF) law $\tau = \tau_0 \exp[\Delta/k_B(T - T_f)]$, with $\tau_0 \approx 1.3\times10^{-12}$ s, $\Delta \approx 55$ meV and a freezing temperature $T_f = 11$ K, provided a better fit consistent with the deviation from behavior typical of noninteracting relaxators. Below 45 K, the relaxation time $\tau(T)$ is slowing down abruptly and ceases to fit the VF law.

Coincidently, it is remarkable that for $T > 50$ K, the total permittivity, defined as ε' (100 Hz) obeys a Curie-Weiss law with $T_C = 39-40$ K and $C = 1.25\times10^5$ K, suggesting a ferroelectric PT in the same temperature region where the dielectric relaxation freezes. The inset of Fig. 2 presents the $\varepsilon'(T)$ behavior for a heating run performed after a successive specimen cooldown to 10 K in a dc field of 10 kV/cm, removing the dc field, and then shorting and opening the electrodes. The dc field depresses the low-temperature cusp entirely. The nonrelaxing part of the permittivity ε'_{nr} has a maximum, and the Li^+ off-center related relaxation decreases at the same temperature 39 K. Therefore the experiments suggest that 39 K is both the critical temperature of a ferroelectric PT mainly of the second order (no hysteresis) and the point of condensation of a dipole glass state. Such a coincidence implies a coupling of the soft lattice and the Li related relaxation modes. The dynamics of such a PT can be of a central-peak type, as was considered in Ref. 23 for a system of relaxators in small concentration, coupled with the TO soft mode. At the same time, in a plot of $1/\varepsilon'$ (1 MHz) vs T, $\varepsilon'_{nr}(T)$ is easily identified as a baseline that can be fit by a Curie-Weiss law with $T_C \sim 30-31$ K, which suggests the possible presence of another soft-mode driven PT.

It is remarkable that in past work on KLTN of similar compositions[17] only a ferroelectric PT, at about the same temperature, was reported. Ordering in the Li^+ subsystem, at such a small concentration of Li as observed here can be explained by considering that the presence of Nb enhances the permittivity ε' and the corresponding correlation radius $r_c \sim \varepsilon'^{1/2}$ of indirect dipole-dipole interaction.[1,2] Moreover, our dielectric experiments indicate that a second ferroelectric PT takes place at ~30 K and a further transformation occurs, accompanied by a permittivity maximum around 15 K.

The outstanding feature of this peak is its cusplike shape. In heating runs, it was shifted to about 22 K, evidencing a marked temperature hysteresis (see the inset of Fig. 1). Dispersion in this region was negligible, but relaxation occurred on very long time scales. A stretched exponential (Kohlrausch) law $\varepsilon' \sim \varepsilon'_0 \cdot \exp[-C \cdot t^{1-n}/(1-n)]$ satisfactorily describes the relaxation process in this region. This behavior is typical for glasses[24] evidencing the presence of a hierarchy of states and that the relaxing system goes through a set of the intermediate potential barriers. Furthermore, the magnitude and the relaxation rate appeared to be sensitive to the specimen history. After cooling from 36 to 15 K, the parameter n in the Kohlraush law at 15 K appeared to be 0.64 and 0.82 for cooling rates of 0.4 K/min and 4 K/min, respectively. These facts clearly evidence the system's nonergodicity in the cusp temperature region. At $T \geqslant 25$ K the long-time dielectric relaxation vanishes.

The presence of the cusp-shaped peak sheds new light on the structural processes in KLTN at low temperature. Its peculiar shape,[8] together with the characteristics of temperature hysteresis, long-time relaxation, and suppression by a dc field, indicate a transformation to another glasslike ordering at ~15 K. A similar sequence with a ''reentrant'' glass state succeeding to higher temperature PT's with long-range ordering is known for disordered ferromagnets with competing interactions (see, e.g., Refs. 24 and 25). However, in order to confirm this unexpected observation of a transition into a reentrant glass state for a dipole system with soft modes, additional evidence in favor of the presence of a long-range order PT (at least at $T \sim 39$ K) should be found.

Figure 3 shows the Raman spectra in the low-frequency region, that is of concern for the TO_1 soft mode. The weak structureless spectrum, observed above 40 K, is identified with soft-mode scattering, activated by polar disorder in the paraelectric phase. This is usual for $KTaO_3$ containing low Li concentrations.[12] Below that point, a well-identified TO_1 spectrum emerges rather quickly from the background, showing a clear separation in two components. These appear to arise in succession below 40 K, growing rapidly as temperature decreases. In analogy with past indications, we identify them as the A and E species of the TO_1 mode, although a direct determination of their symmetry was not carried out. For $T < 35$ K, this spectrum was successfully analyzed as a sum of two damped oscillators, and the best-fit values of oscillator frequencies are plotted in Fig. 4. The two components are clearly split below 35 K, indicating that the system is in a long-range-ordered, ferroelectric phase. From these facts it follows that the phase-transition point locates a few degrees higher, in agreement with the indication of 39–40 K from the dielectric results. Additionally, the two frequencies follow a different evolution. As temperature decreases, the A component hardens continuously, stabilizing somewhere between 27 and 30 K. In the same range, the E component undergoes a marked variation, inverting its trend from softening to hardening. This is consistent with the dielectric results and clearly indicates that at ~30 K a second stage of the structural transformation takes place, following that occurring at higher temperature. On further cooling, both frequencies become nearly constant, with a final splitting of about 12 cm^{-1}. Notice, however, that a kink is present

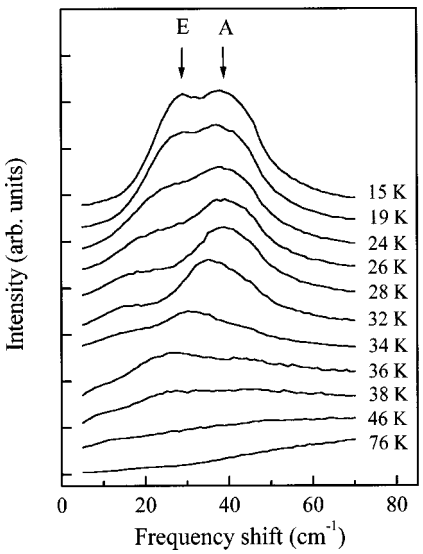

FIG. 3. Low-frequency Raman spectra in $K_{0.9986}Li_{0.0014}Ta_{0.988}Nb_{0.012}O_3$ at different temperatures. The arrows identify the positions of the soft-mode components.

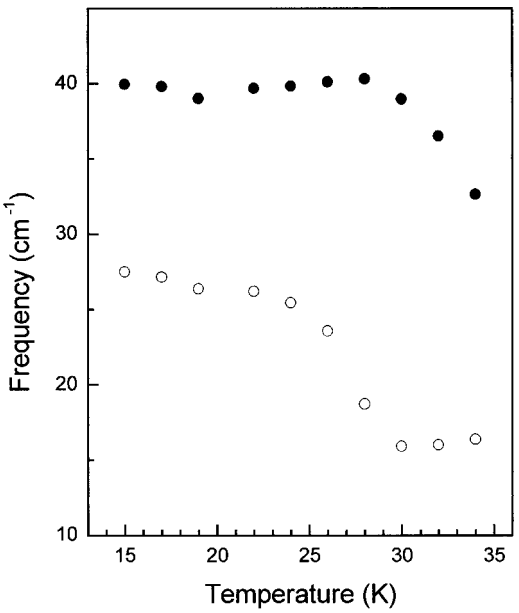

FIG. 4. Temperature dependence of the oscillator frequencies for the soft-mode components: E (open symbols) and A (full symbols). The data have been obtained by fitting the spectra to a sum of damped oscillators.

around 20 K, i.e., in the same region where the low temperature ε' maximum is observed in heating runs.

The Raman-scattering results prove the soft-mode character for the PT at 39 K, and give additional evidence for the observation of a PT into a reentrant glass state in dipolar systems with soft modes, i.e., into a collective dipole glass state occurring, on cooldown, not from the paraelectric phase, but from a ferroelectric one. A complex sequence of PT's has also been observed in $(Pb_{1-x}La_x)(Zr_yTi_{1-y})O_3$ (PLZT) ceramics,[26] but the presence of a long-range-ordered state in ceramics cannot be proven. The transitions observed in order-disorder-type ferroelectrics like $Rb_{1-x}(NH_4)_xH_2AsO_4$ (RADA) (Ref. 27) also have very little in common with the present case.

In conclusion, it is shown that in KLTN, on approaching the Nb-induced ferroelectric PT with a correspondingly high magnitude of ε', the Li-related dipolar ordering is strongly enhanced with respect to the case of KLT having a similar Li content. Eventually, the coupling between the soft TO lattice mode and the relaxation mode of Li dipoles leads to the simultaneous appearance of ferroelectric order and of a dipole-glass phase. The instability with respect to long-range ordering of different symmetries, which is typical for KTN, plus frustration and competition with the coexisting Li^+-center-related dipole glass subsystem lead, on further cooldown, to another PT transition into a phase with characteristic properties of a glasslike state, i.e., into a reentrant dipole glass state. The experimental results presented here clearly manifest the formation of several phases on cooldown of the present KLTN composition. In fact, we observed a soft-mode-driven PT from the paraelectric phase to a long-range ferroelectric one and then to a dipolar nonergodic glasslike phase at lower temperatures, which can be interpreted as a reentrant dipole glass state.

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