Diffuse Ferroelectric Phase Transition and Long-Range Order of Dilute $KTa_{1-x}Nb_xO_3$

W. Kleemann and F. J. Schäfer
Angewandte Physik, Universität Duisburg, D-4100 Duisburg 1, Federal Republic of Germany

and

D. Rytz
Hughes Research Laboratories, Malibu, California 90265

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Refractive-index and linear-birefringence measurements on $KTa_{1-x}Nb_xO_3$, with $x=0.008$, 0.012, and 0.02, reveal smeared phase transitions into long-range order. In accordance with previous caloric, second-harmonic–generation, dielectric, and x-ray results, the crystal optical data can be explained on the basis of a "cooperative dipole glass" model. This involves local ordering within the finite Curie region of a diffuse phase transition followed by a strain-induced collective reorientation of frozen-in microdomains.

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The influence exerted by impurities on systems undergoing structural phase transitions (PT) has been discussed very thoroughly in the last few years.[1] Particular interest has been focused on soft defects, which do not *a priori* break the symmetry seen by the local ordering coordinate, but which nevertheless enhance the actual PT temperature of the system. The way in which soft defects really initiate the PT by coupling of the local and the bulk soft modes has been the subject of quite a number of investigations.[2–4] Fundamental differences are expected if the critical region is attained such that the defects are already frozen-in or such that they are still mobile between their off-center potential wells. In the latter case, true long-range order (LRO) with somewhat modified critical behavior is likely to occur rather generally.[5] For the frozen-in–type defects the very existence of a unique transition temperature T_0 and of a low-temperature phase with true LRO is still a matter of controversy. There is much evidence that LRO is suppressed by random symmetry-breaking defects in systems, where the order parameter has either only one (Ising-type symmetry[4]) or an infinite number of components (continuous symmetry[6]). The influence of random fields exerted by the defects in the case $1 < n < \infty$ still lacks theoretical studies.[1]

One of the most extensively investigated doped systems, suitable for studies of soft defects, is $KTaO_3$ containing small amounts of Nb^{5+} (KTN). Whereas $KTaO_3$ is an incipient ferroelectric, which does not undergo any PT, $KTa_{1-x}Nb_xO_3$ ($x > 0.008$) seems to exhibit a cubic-to-rhombohedral PT at finite temperature.[7,8] It has been argued[9] that as a result of the short hopping time of the Nb^{5+} ions the defect-centered clusters may reorient themselves near T_0 to give a phase with true LRO. This seems to be proven by measurements of the spontaneous polarization P_s.[10,11] Moreover, electric-field–induced Raman scattering of the soft mode in KTN with $x \leq 0.05$ did not reveal any evidence for Nb^{5+} being a symmetry-breaking defect.[12] Additional experimental results, which are compatible with LRO, are available from investigations of second-harmonic generation,[13] of ^{35}K NMR,[14] and of first-order Raman spectra.[12,15]

Very recently, however, the occurrence of LRO in ferroelectric KTN has been questioned[16] on the basis of dielectric-relaxation measurements as a function of temperature and hydrostatic pressure. The observed dispersion in the range 10^2–10^6 Hz was analyzed in terms of a simple Debye model for relaxing Nb^{5+} dipoles. At atmospheric pressure, the Nb^{5+} occupies an off-center position, thus creating a dipole, which at high temperatures may reorient itself, while the Nb^{5+} is hopping among equivalent positions. At low temperatures, the Nb^{5+} is frozen in one of the potential minima. Within this interpretation, KTN is expected to exhibit no LRO, but only frozen-in short-range order (SRO), which resembles spin-glass order in some respect. Hence, contrary to the mobile–soft-defect model,[9] dilute KTN seems to be a system with a four-component order parameter containing random symmetry-breaking defects which suppress LRO. This picture provides a possible explanation for the absence of anomalies in the specific heat of KTN at the apparent transition temperatures.[17]

In order to help clarify this controversial situation we have undertaken linear-birefringence (LB) measurements on KTN with $x=0.008$, 0.012, and 0.02. In the case of frozen-in SRO with $\langle P_z \rangle = 0$, but $\langle P^2 \rangle \neq 0$, no LB is expected below the freezing temperature. The crystal remains optically isotropic because of the absence of uniformly distorted regions. Similar arguments recently helped to shed light on the true nature of a related system, $KTaO_3$:Li, which seemed to be a "polar glass." The detection of spontaneous LB,[18] however, gave strong evidence for a transition into a state with $\langle P_z \rangle \neq 0$. Anticipating the main result of our present study, the same inference

applies to KTN at low temperatures. However, in order to understand simultaneously the relaxational behavior[16] and the absence of c_p anomalies,[17] the aim of this Letter cannot simply be a rejection of the glassy-state idea[16] in favor of a LRO model implying normal ferroelectricity. We rather believe that the onset of SRO due to softening of local modes is the primary process in dilute KTN. The appearance of LRO, on the other hand, is interpreted as a secondary effect due to cluster interaction. In order to confirm this novel idea, we have additionally measured the temperature dependence of the refractive index (RI), which is sensitive to both SRO and LRO.[19] If we compare the RI anomaly with the LB it can be shown that SRO only partially transforms into LRO at low temperatures. Hence, unlike a conventional ferroelectric, KTN rather behaves like a "cooperative dipole glass."

The experiments were carried out on single-crystal (001) platelets[20] with typical size $1\times2\times0.2$ mm^3. With use of a computer-controlled and microscopically monitored interferometric device[19] the temperature dependences of the RI and of the LB could be measured with accuracies of $\delta n\sim10^{-5}$ and $\delta(\Delta n)\sim10^{-7}$, respectively. We report here on investigations between 4.5 and 100 K measured at 589.3-nm light wavelength over sample areas of 5×5 to 50×50 μm^2. All results were reproducible on cycling of the temperature.

Figure 1 shows the temperature dependence of the RI of KTN with $x=0.008$, 0.012, and 0.02. If we start at 100 K, all of the $n(T)$ curves coincide and exhibit a nearly linear T variation. This can be attributed to the host crystal, $KTaO_3$. However, before reaching a convex maximum for $T\rightarrow0$ all of the curves bend down and exhibit concave anomalies. After passing inflection points (Fig. 1, arrows) at $T_c=10$ K ($x=0.008$), 17 K ($x=0.012$), and 31.5 K ($x=0.02$), respectively, they saturate at concave relative minima below 5 K. Clearly, the anomalies are due to ferroelectric ordering. Within the indicatrix perturbation approach[19,21] one readily obtains the contribution to the RI,

$$\delta n=-(n_0^3/6)(g_{11}+2g_{12})\langle P^2\rangle, \quad (1)$$

due to the time- and space-averaged square of the polarization, $\langle P^2\rangle$, measured within a cubic (001) plane. The direction of **P** is assumed to be along $\langle111\rangle$[7,8] and the electro-optical coupling constants g_{ij} refer to the cubic phase of KTN.

The δn anomalies are not at all in conflict with the dipole glass model[16] exhibiting merely SRO. They measure the autocorrelation function $\langle P^2\rangle$,[19] which is expected to saturate at $T\rightarrow0$. On the other hand, Eq. (1) may also describe a normal ferroelectric. In that case SRO occurs above T_c in the precursor region[19,22] and switches into LRO below T_c. Consequently, in Eq. (1) $\langle P^2\rangle$ must be read as $\langle P\rangle^2+\langle\delta P^2\rangle$ below T_c. The onset of spontaneous polarization $P_s=\langle P\rangle$ at a well-defined PT temperature normally[19] gives rise to a distinct change of the slope of δn at T_c. This is not observed for KTN. Hence, either LRO is absent, as proposed,[16] or the PT are smeared, where the degree of smearing obviously increases with decreasing x.

From Eq. (1) with $\delta n(5\text{ K})=-0.0003$, -0.0008, and -0.0026, respectively, $n_0=2.26$,[23] and g_{11}, g_{12}, and g_{44} equal to 0.13, -0.03, and 0.12 m^4 C^{-2}, respectively,[24] one obtains $\langle P^2\rangle^{1/2}=47$, 77, and 140 mC/m^2 for $x=0.008$, 0.012, and 0.02, respectively. As discussed above, these values may be taken either as a

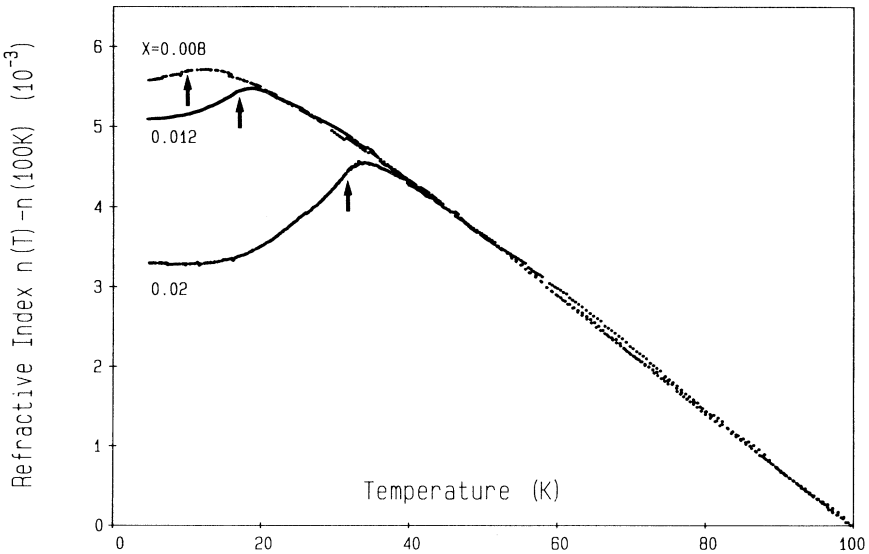

FIG. 1. Temperature dependence of the refractive index of KTN with $x=0.008$, 0.012, and 0.02 measured with $\lambda=589.3$ nm between 4.5 and 100 K and plotted relative to $n(100\text{ K})=2.25$. Inflection points are marked by arrows.

measure of local SRO, or in the case of true LRO, as a measure of $P_s \sim \langle P^2 \rangle^{1/2}$. The decision on this question is brought about by the LB experiment. As shown in Fig. 2, spontaneous LB does arise in the vicinity of T_c. This is only compatible with symmetry breaking on a scale given by the sample volume tested (about $50 \times 50 \times 200$ μm^3) and, hence, proves LRO.[18] The LB measures P_s via the relation[21]

$$|\Delta n| = (n_0^3/3) g_{44} P_s^2, \quad (2)$$

which is valid for rhombohedral LB measured in the (001) plane. From the low-temperature Δn data (Fig. 2) one obtains $P_s = 13$, 39, and 62 mC/m^2 for $x = 0.008$, 0.012, and 0.02, respectively. These data are significantly smaller than those obtained from the RI anomaly (see above). Evidently δn contains appreciable contributions ($\sim 90\%$ for $x = 0.008$!) due to order-parameter fluctuations, $\langle \delta P^2 \rangle$, which are undetected by LB for symmetry reasons. These may be dynamic (quantum fluctuations?) or static (remnant of the initial glassy state; see discussion below). Note that care was taken to obtain maximum, quasi-single-domain LB on homogeneously distorted sample areas, which have generally linear dimensions of the order 0.1 mm with irregular shapes. It is noteworthy to remark that our optical P_s values are significantly larger than those obtained by integration of the pyroelectric current.[10,11] As stated previously[22] the LB measurement seems to yield more reliable results than the conventional method.

The LB results seem to disprove Samara's glassy-state model of KTN.[16] As for conventional ferroelectrics it is possible to fit Δn vs $t = 1 - T/T_0$ by power laws with critical exponents $2\beta \sim 1$ and $T_0 \sim T_c$, if data points from the convex parts of the LB curves within a limited interval ($\Delta t \sim 0.1$) are chosen (Fig. 2). This procedure, however, is not unambiguous and may be seriously cast in doubt in the low-x limit, where the LB curves become appreciably smeared. Evidently the initial assumption of well-defined PT into conventional LRO cannot be maintained. At first sight one might consider macroscopic concentration gradients to be responsible for a respective T_0 distribution and, hence, LB smearing. However, no reduction of the LB tail widths is found on reduction of the probed sample area by a factor of 100. Hence, the shapes of the LB curves seem to be intrinsic and due to homogeneous x on a macroscopic scale (≥ 5 μm). Only the absolute value and the sign of Δn may change on scanning of the entire sample area as a consequence of domain competition.

With regard to the intrinsic nature of the smeared LB curves it is plausible to assume that the PT of KTN is "diffuse" in the sense reviewed by Lines and Glass.[25] As a result of structural disorder and compositional fluctuations on a microscopic scale, presumably far below the micron limit, the PT starts on cooling by freezing of the local soft mode of comparatively large Nb^{5+} clusters. The subsequent freezing of less-concentrated clusters and, finally, isolated Nb^{5+} ions defines what is frequently called the "Curie region." It is well known[25] that P_s, the c_p anomaly, and the RI vary slowly throughout the Curie range rather than exhibit abrupt changes at T_0. Moreover,[25] temperature-

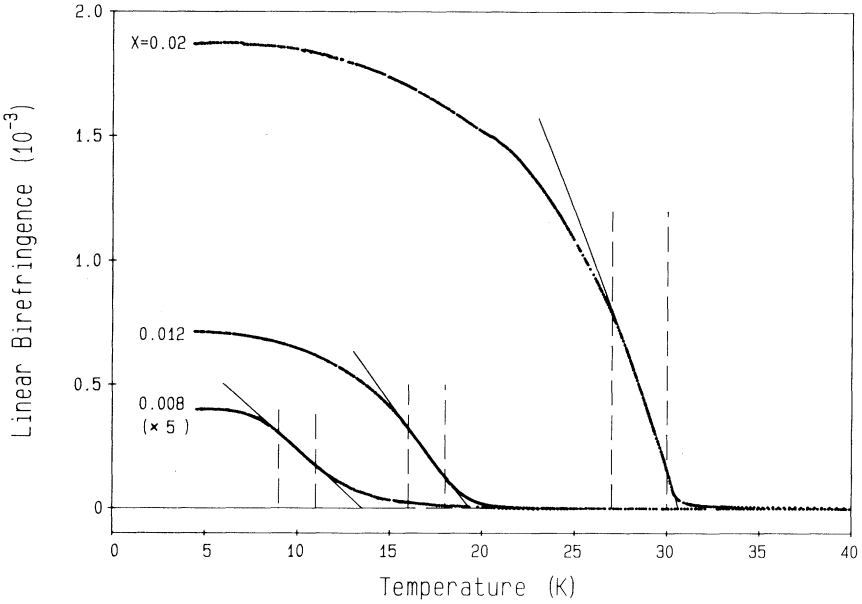

FIG. 2. Temperature dependence of the linear birefringence of KTN (same as in Fig. 1) between 4.5 and 40 K. Solid lines denote power-law best fits of the data between the dashed and vertical bars. Note the change of scale ($\times 5$) for the $x = 0.008$ curve.

dependent dielectric relaxation with pronounced dispersion and strong sensitivity to external fields (E or p) is expected within a model of individually ordering microregions. All of these predicted properties compare well with the experimental data collected for KTN.

Nevertheless, the still relatively sharp onset of Δn and the large saturation values of P_s require an additional coupling mechanism between the ordered microregions. With regard to the large tails observed in the RI or in the second-harmonic–generation experiments,[13] which significantly exceed those of the LB, it is clear that local symmetry breaking by static or dynamic clusters starts far above the onset of LRO. Obviously a collective ordering process of individual distorted microregions starts to work after reaching a critical concentration and establishes static LRO. This process, however, remains smeared and, hence, does not involve diverging correlation lengths. It is highly probable that the ordering mechanism is due to long-range strain fields, which accompany the locally ordered clusters. The relatively high mobility of the Nb^{5+} ions near their freezing temperature[9] allows the initial multimicrodomain structure to be transformed—at least partially (see discussion above)—into macroscopic quasi single domains. The above-pictured ordering process defines what might be called a "cooperative dipolar glass." It excludes a c_p singularity[17] as a result of the absence of criticality.

The true nature of ferroelectric LRO in dilute KTN is still unknown. There is some evidence for inhomogeneity of the distortion (viz., P_s) on a microscopic scale. Recent high-precision x-ray studies[26] seem to hint at virtually vanishing bulk distortion of dilute KTN ($c/a = 1.0 \pm 2\times10^{-4}$ for $x = 0.017$ at 10 K). On the other hand, by use of empirical relationships[27] between the atomic displacement and T_c or P_s, respectively, much larger values are calculated ($c/a \sim 1.0014$ for $x = 0.012$ at 5 K). This apparent contradiction can be resolved by the assumption of large local distortions within microdomains, which are polarized by virtue of initial random Nb^{5+} clusters and single impurities, whereas the host lattice in between merely carries a very small bias distortion. It should be possible to check this conjecture by small-angle x-ray scattering. The average microdomain size should also be available from Raman linewidth[12,15] analysis.

In conclusion, our present crystal optical data and previous caloric,[17] second-harmonic–generation,[13] dielectric,[16] and x-ray[26] results on dilute KTN can be explained within the model of a "cooperative dipole glass." Presumably the same model applies to $KTaO_3$:Li too.[18] Quantitative aspects of the ordering processes involved will be discussed in a forthcoming paper on the basis of LB, RI, and novel Raman-scattering data. Consequences of our new model for the concept of quantum ferroelectricity[8] will need further consideration.

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