PHYSICAL REVIEW B VOLUME 46, NUMBER 9 1 SEPTEMBER 1992-I

Dipole-glass behavior of lightly doped $KTa_{1-x}Nb_xO_3$

P. M. Gehring, Henry Chou, S. M. Shapiro, J. A. Hriljac, and D. H. Chen
Department of Physics, Brookhaven National Laboratory, Upton, New York 11973

J. Toulouse
Department of Physics, Lehigh University, Bethlehem, Pennsylvania 18015

D. Rytz
Centre de Recherche en Optoélectronique, SANDOZ Huningue SA, F-68330 Huningue, France

L. A. Boatner
Solid State Division, Oak Ridge National Laboratory, Oak Ridge, Tennessee 37830

(Received 14 February 1992)

High-resolution x-ray diffraction measurements have been performed between 10 and 300 K on several single crystals of $KTa_{1-x}Nb_xO_3$ with $x \leq 0.157$. Contrary to the published phase diagram, no deviation from cubic symmetry is seen for $x \leq 0.060$. Instead, a low-temperature minimum in the cubic unit cell volume is observed at a temperature T_{min} which increases monotonically for $0.012 \leq x \leq 0.060$. Data for x=0.157, however, are consistent with the previously established sequence of structural transitions from cubic to tetragonal to orthorhombic to rhombohedral symmetries. We associate T_{min} with the onset of a dipolar glass transition. In addition, a radial broadening of the linewidths is observed at T_{min}, indicating the presence of strain in the lattice. Powdering small pieces from these single crystals suppresses the unit cell minimum and stabilizes the cubic phase down to 10 K, even for x=0.157.

I. INTRODUCTION

An enormous amount of scientific effort, both experimental and theoretical, has been devoted to the study of the behavior of isolated impurities in systems with soft phonon modes.[1-3] One of the most interesting and controversial questions concerns the nature of the low-temperature phase in such systems in the dilute limit. The mixed perovskite systems $KTa_{1-x}Nb_xO_3$ (KTN) (Refs. 4-6) and $K_{1-x}Li_xTaO_3$ (KTL) (Refs. 7-9) have played major experimental roles in this area of research. In the context of KTN the question is do low levels of the dipolar impurity Nb induce a true structural phase transition to a ferroelectric phase in $KTaO_3$, or does the addition of Nb produce instead a dipolar-glass phase with no change in structure?

Pure $KTaO_3$ is almost ferroelectric. Because the softening of the zone center transverse optic (TO) phonon mode is stabilized at low temperatures by quantum fluctuations, no change in symmetry occurs.[10] For this reason $KTaO_3$ is often called an "incipient" ferroelectric. By contrast, pure $KNbO_3$ transforms from a cubic paraelectric phase to a tetragonal ferroelectric phase at a transition temperature of 700 K, the change in symmetry being due to the displacement of the oxygen octahedra along the [001] direction.[11] At lower temperatures $KNbO_3$ undergoes two more structural transitions. A tetragonal to orthorhombic distortion is produced by the displacement of the O_6 octahedra along the [011] direction, followed by a transition to rhombohedral symmetry at even lower temperatures where the O_6 octahedra are displaced along the [111] direction.

It is widely accepted that concentrated KTN undergoes the same sequence of structural phase transitions as the pure niobate compound, but at progressively lower transition temperatures as the concentration of Nb is reduced. Measurements of the dielectric susceptibility as a function of temperature reveal these structural changes through the appearance of a peak at T_c, and form the basis for the current phase diagram.[12] There is, however, considerable debate about what happens at very low impurity levels. Measurements of the dielectric constant show only a single peak as a function of temperature for $x \leq 0.050$, implying a single transition.[13] Yet there is no consensus on whether this peak signals the appearance of a polar phase arising from a spontaneous displacement of the Nb ions below T_c and a corresponding change in symmetry, or the freezing of dipolar impurities in analogy to the appearance of a spin-glass phase and thus no change in symmetry.

Measurements of the inverse elastic compliance s_{11}^{-1} as a function of temperature on KTN samples with $x \leq 0.046$ by Höchli *et al.*[13] show a sharp jump in the same temperature range where the dielectric constant reaches a maximum. This has been interpreted as evidence of the symmetry breaking of the paraelectric (cubic) phase in KTN in the limit of small x. Prater *et al.*[4] also argue in favor of a low-temperature ferroelectric phase for $0.008 \leq x \leq 0.050$ on the basis of Raman scattering and optical-depolarization measurements. They claim the oxygen neighbors of the Nb impurity are more highly polarizable, producing long-range electric fields which stabilize the ferroelectric phase. In a recent Raman study on a KTN sample with x=0.012, the appearance of first-order scattering associated with the nonpolar TO_3 mode at 15.5 K clearly indicates the occurrence of a structural distortion.[14] The appearance of this Raman line coincides with the observation of a very sharp maximum in the dielectric constant, strongly suggesting that the transition is ferroelectric. By contrast, other recent Raman and inelastic neutron scattering measurements on the same KTN sample show that the energy of the zone center optic phonon only reaches a minimum of 0.9 meV at 20 K.[15,16] In addition, a strong pressure-induced low-frequency dispersion of $\epsilon(T, \omega)$ has been observed in KTN for x=0.020, suggesting instead that the low-temperature polar behavior of KTN in the dilute limit is glasslike.[5] As will be discussed below, x-ray diffraction experiments on this $x = 0.012$ KTN sample do not show any evidence of a structural phase transition down to 10 K.

A program of high-resolution x-ray diffraction experiments has been carried out to look for measurable changes in symmetry between 300 and 10 K in a series of single crystal specimens of KTN in the limit $x \leq 0.157$. Such a program is of obvious fundamental importance in view of the fact that no diffraction data, x-ray or neutron, has been used to corroborate the currently accepted phase diagram of KTN, particularly in the dilute limit.[17] From these measurements we observe no deviation from cubic symmetry at any temperature for $0.012 \leq x \leq 0.060$ within our experimental uncertainty. Instead, a striking minimum in the volume of the cubic unit cell is observed to occur at a characteristic temperature $T_{\rm min}$ which scales with the impurity concentration.

II. EXPERIMENTAL

The single crystal x-ray scattering measurements were performed on a four-circle Huber spectrometer using Ge(111) crystals as both monochromator and analyzer. A rotating Cu anode was used to produce the x rays. Typical operating conditions were 200 mA at a voltage of 40–50 kV. The wavelength used was 1.540 51 Å, corresponding to Cu $K\alpha_1$ radiation. At the (200) Bragg reflection, typical room-temperature in-plane longitudinal and transverse q widths (FWHM) were 0.0024 and 0.0030 Å^{-1}, respectively. All of the powder diffraction measurements were performed on beamline X7A at the National Synchrotron Light Source (NSLS). A Si(111) crystal was used to monochromate the incident x-ray beam and a Ge(220) crystal was used as analyzer.

Five samples were studied, having nominal Nb concentrations of x=0.012, 0.020, 0.030, 0.060, and 0.157. Typical sample dimensions were $9 \times 7 \times 0.7$ mm^3. Sample growth has been discussed elsewhere.[12] Each sample was mounted on a Cu holder such that its large surface (a polished [100] face) was accessible to the x-ray beam. The holder was capped with a Be top, filled with He exchange gas, then attached to the cold finger of a closed-cycle Displex refrigerator which varied the sample temperature between 10 and 300 K to within ±0.1 K. The refrigerator housing was fitted with a cylindrical Be window to allow passage of the incident and reflected x-ray beam.

The concentration dependence of the cubic lattice parameter a was measured at room temperature for three of the powdered KTN single crystal samples spanning the concentration range $0.012 \leq x \leq 0.157$. The lattice parameter a varied linearly as a function of the Nb concentration x, consistent with Vegard's law.

III. RESULTS

A. Single crystal data

At sufficiently high concentrations of the dipolar impurity Nb, KTN undergoes a sequence of three structural phase transitions.[12,11] In order to verify this behavior, the cubic (420) Bragg reflection of a single-crystal specimen of KTN with x=0.157 was monitored as a function of temperature. The (420) reflection was chosen because it was the highest order reflection attainable using the four-circle spectrometer, and thus gave the largest available peak splitting in the tetragonal, orthorhombic, and rhombohedral phases. An alignment of the crystal was performed after equilibrating at each temperature.

Data for the (420) reflection are shown in Fig. 1 for x=0.157 at five different temperatures which span the range over which these transitions occur. The data were taken cooling from room temperature. In each case the spectrometer was set to scan the momentum transfer along the radial direction. Thus the reciprocal lattice units (rlu) in this figure correspond to $4a^*/\sqrt{4^2+2^2} = 2a^*/\sqrt{5}$, where $a^* = 2\pi/a = 1.5745$ Å^{-1}. The spec-

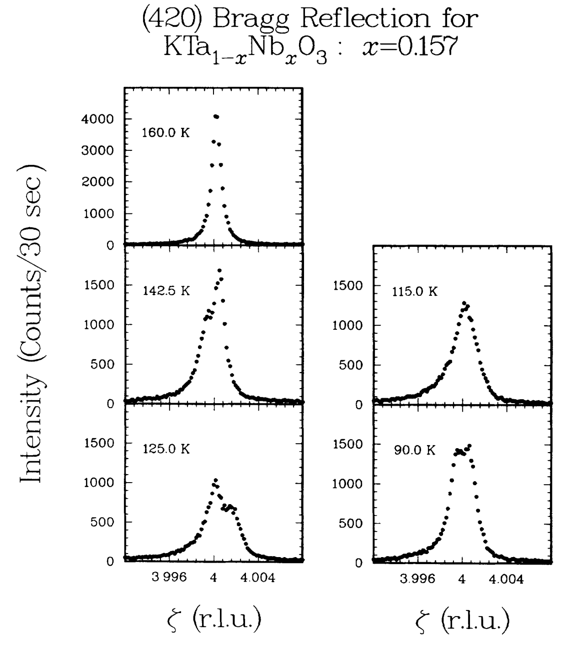

FIG. 1. Radial scans through the (420) Bragg reflection as a function of temperature taken on a rotating anode four-circle diffractometer. The sequence of splittings is consistent with three structural phase transitions starting from a high-temperature cubic phase and ending with a low-temperature rhombohedral phase.

trometer resolution was improved by using the (333) reflection of the Ge analyzer instead of the (111) reflection since then the sample scattering angle $2\theta_S$ (119.52°) more closely matched that of the analyzer $2\theta_A$ (90.14°). In this configuration, room-temperature in-plane longitudinal and transverse q widths (FWHM) at (420) are 0.0028 and 0.0058 Å^{-1}, respectively.

A single, sharp peak is observed from room temperature down to 160 K, which is consistent with a cubic structure. Upon further cooling to 142.5 K the peak splits into two peaks having unequal intensities, due to unequal domain populations. Although not well resolved, this splitting signals a clear change in structural symmetry. At 125 K the splitting increases significantly and the relative peak intensities change, indicating a change in the relative domain populations and yet another change in symmetry. Below 115 K the line shape becomes symmetric, indicating that the domain populations are balanced, but the peak remains split down to 10 K. Although these measurements cannot uniquely specify the crystal symmetry at each temperature, they do indicate the presence of three structural phase transitions and are thus consistent with the published phase diagram.[12]

Longitudinal scans through the (200) Bragg peak were measured as a function of temperature for the lower concentrations, $x \leq 0.030$. Such scans are sensitive only to tetragonal and orthorhombic distortions in the presence of different domains. After a tetragonal distortion, for example, residual strains in the lattice cause the crystal to break up into domains in which the unique tetragonal c axis can point along any one of the three pseudocubic crystallographic axes. A longitudinal scan through (200) will then see both the a- and c-axis lattice spacings and two peaks will appear. In the case of a single domain, only one peak would be present. In general, the relative intensities of each peak will likely differ because the relative populations for each domain will differ. Such is the case for the presumed cubic-tetragonal transition for the x=0.157 sample, where the splitting at 142.5 K produces two peaks with different intensities (see Fig. 1).

The temperature dependence of the cubic lattice spacing a, determined from the position of the (200) reflection, is shown in Fig. 2. The most striking feature of these data, aside from the absence of any detectable change in symmetry down to 10 K, is the minimum in a that appears in each of these dilute single crystal samples. Equally striking is the fact that the minimum value of a occurs at a temperature $T_{\min}$ which scales with concentration, as is shown in Fig. 3.

In order to check for other possible changes in symmetry, the (420) Bragg peak was also monitored as a function of temperature between 300 and 10 K for x=0.030 and 0.060 as had been done for the x=0.157 sample. This reflection has the advantage over Bragg peaks of the form (h00) of being sensitive to rhombohedral distortions. These should manifest themselves as a splitting of the (420) peak along both the longitudinal or radial direction as well as along the transverse direction. Nevertheless, no splitting of the (420) Bragg peak was seen at any temperature for either concentration. The minimum in the cubic lattice spacing, however, remains. In addition, a significant homogeneous broadening of the Bragg peak occurs at a temperature which corresponds well to $T_{\min}$. This is shown in Fig. 4. The small anomaly at 100 K is not understood, but unlike the broadening at $T_{\min}$, it is not a reproducible feature of the data.

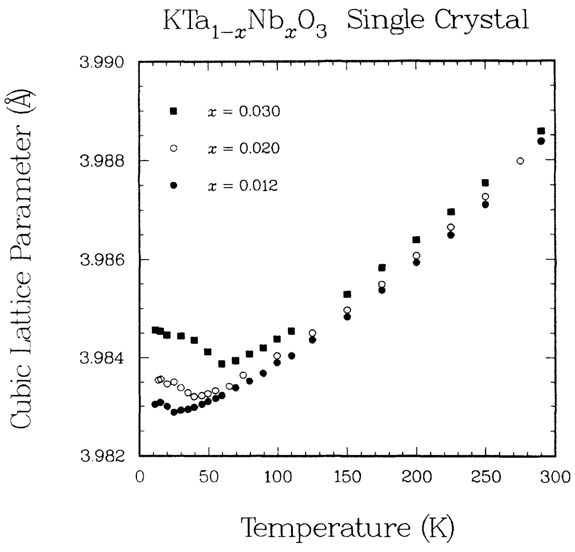

FIG. 2. Temperature dependence of the cubic lattice parameter for $x \leq 0.03$. Data were taken while cooling from room temperature.

The spectrometer q resolution at (420) using the Ge(333) reflection for the analyzer was not measured directly, but from the longitudinal q width of the (420) Bragg peak (taken at high temperature) we can state that it is no worse than 0.0018 Å^{-1}. From this a limit of $1 \pm (5 \times 10^{-4})$ can be put on the ratio c/a. In addition, an upper bound of 0.017° can be placed on any rhombohedral distortion. By comparison, the rhombohedral distortion observed for pure KNbO$_3$ at 230 K (33 K below the transition temperature) is 0.182° ± 0.008°.[11]

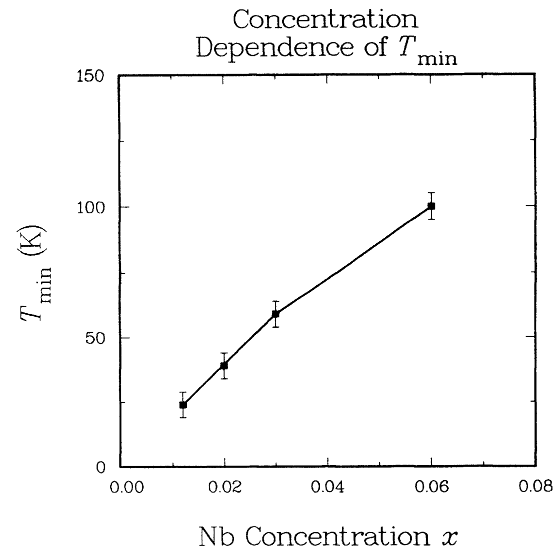

FIG. 3. Dependence of $T_{\min}$ on the Nb concentration, x.

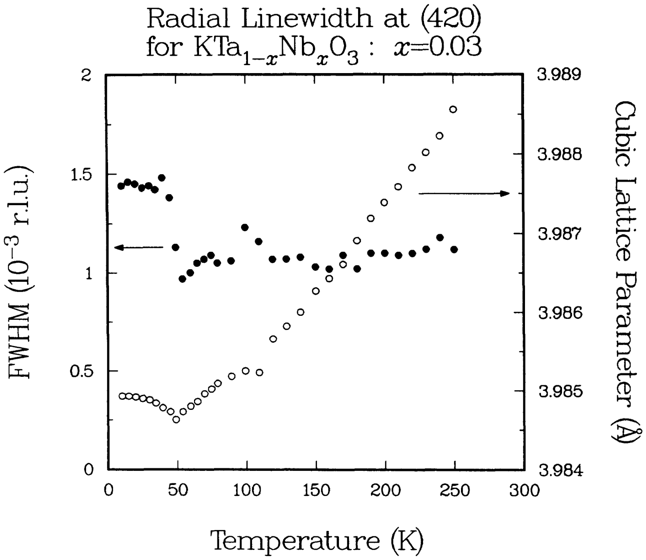

FIG. 4. Full width at half maximum (FWHM) in rlu (reciprocal lattice units) for the (420) Bragg reflection for x=0.030 as a function of temperature. The onset of broadening coincides with the minimum in the lattice parameter at T_{min}.

B. Powder diffraction data

X-ray diffraction measurements were carried out at beamline X7A at the NSLS on polycrystalline samples of KTN, with x=0.02, 0.03, 0.06, and 0.16. The use of powders permitted the study of more Bragg peaks than were accessible in the single crystal experiments. Moreover, with powder samples, the question of domains is no longer a concern since all domains are seen with equal probability. These samples were prepared from appropriate mixtures of K_2CO_3, Nb_2O_5, and Ta_2O_5. The mixtures were thoroughly mixed and ground, fired to 850 C, reground, and then fired at 1100 C. The samples appeared pure based on x-ray diffraction measurements, but small amounts of $K_2(Nb,Ta)_4O_{11}$ impurities were discernible in the synchrotron x-ray data.

The (200), (220), and (222) Bragg peaks were measured as a function of temperature for these powder samples between 300 and 10 K. The wavelengths used varied from 0.70 to 1.20 Å. The corresponding q widths and q resolution at (222) ranged between 0.008–0.007 $Å^{-1}$ and 0.0019–0.0012 $Å^{-1}$, respectively.[19]

Surprisingly, the dilute powder samples did not exhibit the minimum in the cubic lattice parameter that had been seen in the single crystal samples. Therefore, as a check, small pieces were broken off from the single crystal samples, powdered by grinding in an agate mortar, and then measured in exactly the same way. Again no minimum was found. The cubic lattice spacing a increased monotonically with increasing temperature. Moreover, the peak widths remained constant in both cases over the entire temperature range. Typical data are shown at the (222) Bragg peak for two concentrations, x=0.020 (powdered single crystal) and 0.030 (polycrystalline) in Fig. 5.

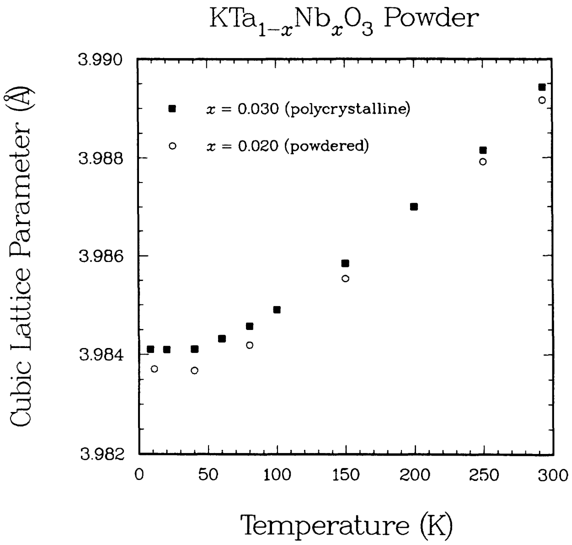

FIG. 5. Line shape as a function of scattering angle 2θ for a powdered sample taken from the x=0.157 single crystal. No evidence of any structural transition is seen down to 10 K.

As a final test, a small piece was broken off from the x=0.157 crystal and powdered. Whereas the single crystal sample exhibits the three structural transitions shown in Fig. 1, the powdered sample remained cubic down to the lowest temperature. This is seen in Fig. 6(a) where the (222) Bragg peak profile is shown at 300, 150, 125,

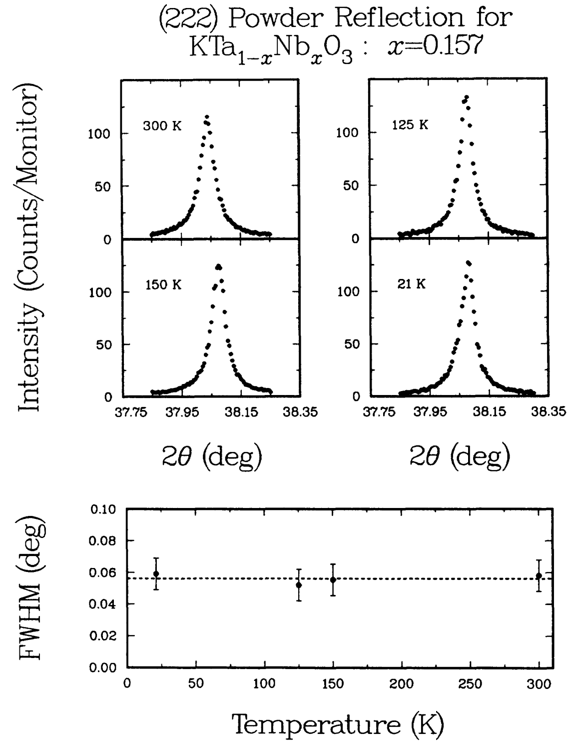

FIG. 6. Temperature dependence of the cubic lattice parameter for a polycrystalline sample with x=0.030, and a powdered sample taken from the x=0.020 single crystal. Data were taken on cooling from room temperature. No minimum is observed in the lattice parameter above T=10 K.

and 21 K as a function of 2θ. No splitting of the peak is seen at any temperature. Moreover, the 2θ linewidth, plotted in Fig. 6(b) as a function of temperature, remains constant at 0.056°, which corresponds to a q of 0.0077 Å^{-1}. (The data for this sample do not cover a sufficiently wide range in 2θ to determine whether particle size or strain were primary factors in the excess broadening of the peak width.) Thus the process of powdering KTN samples appears to stabilize the cubic phase in all samples studied down to 10 K. It should be emphasized, however, that the gross temperature dependence of the cubic lattice parameter is not affected by the powdering. This can be seen by comparing Fig. 2 with Fig. 5. Aside from a very small difference in the absolute lattice spacing of order 0.0002 Å (probably due to a minute zero offset between the X7A diffractometer and the rotating anode three-circle diffractometer), the overall temperature dependence for the x=0.020 sample is the same before and after powdering. Only the low-temperature minimum is absent.

IV. DISCUSSION

Because the dilute KTN samples remain cubic down to 10 K, the low-temperature minimum in the lattice spacing a implies a corresponding minimum in the volume of the KTN cubic unit cell. This is a phenomenon that has been observed in mixed single crystals of ferroelectric RbH_2PO_4 and antiferroelectric $NH_4H_2PO_4$, a dipolar glass known more commonly as $(RDP)_{1-x}(ADP)_x$.[18] Thus the x-ray diffraction data would seem to support the presence of a low-temperature dipolar-glass phase for dilute KTN in which a transition from frozen impurity behavior to relaxing impurity behavior takes place. It can of course be argued that the experimentally observed broadening of the Bragg peaks at $T_{\min}$ results from a structural distortion of the lattice into various domains and that the subsequent peak splitting is not resolved because of inadequate q resolution. This cannot, however, account for the minimum in the unit cell volume except in the extremely unlikely case where the crystal volume probed by the x-ray beam is composed of a single domain. Indeed, this would have to be the case for each of the four dilute KTN single crystals studied. The data in Fig. 1 clearly show the x=0.157 crystal is not composed of a single domain.

Instead, it is likely that small, ordered clusters of dipoles form below the freezing temperature ($T_{\min}$) in dilute KTN, thereby inducing a strain in the crystal, as this would be a plausible explanation for the broadening of the radial linewidths of the (420) Bragg reflection seen in Fig. 4. But, because no change in symmetry was detected, these clusters must be randomly oriented so that the average symmetry of the KTN system as seen with x rays remains cubic. The existence of such clusters is consistent with the pressure-dependent data of Samara, who reported clear evidence for a distribution of relaxation times in a single crystal of KTN with x=0.020.[5] This conclusion differs from that based on Raman studies in which new peaks are observed to develop with decreasing temperature, indicative of a breaking of symmetry.[14]

As for the suppression of the sequence of structural transitions in the x=0.157 sample, and the low-temperature minimum in the unit cell volume of dilute KTN samples, there are at least two possible explanations: (1) a random-strain-field effect is produced upon grinding the samples into powders and (2) a strong finite particle-size effect is present. KCN is an example of the first possibility. In pure KCN, different sample treatments were used to introduce random-strain fields into the lattice.[20] In some cases the low-temperature noncubic phases were supressed and a quadrupolar-glass state was formed instead, analogous to that induced by introducing Br ions in $(KBr)_{1-x}(KCN)_x$.[21] The second explanation finds precedence in ferroelectric $BaTiO_3$, which exhibits a cubic to tetragonal phase transition temperature in bulk material at 401 K. Below a critical particle size of 0.12 μm T_c is found to drop below room temperature (see Ref. 23). This phenomenon has been explained in the context of an induced internal pressure $P = 2\gamma/R$, where γ is the surface tension and R the particle radius.[22,23] Since an increase in P reduces T_c,[24] an increase in γ or a decrease in R will have the same effect. This simplistic description does not, however, take into account the particle-size effect on the softening of the phonon mode which contributes to the spontaneous polarization of the material.

V. SUMMARY

High resolution x-ray diffraction measurements taken on a series of KTN samples with $x \leq 0.060$ show no detectable change in symmetry between 300 K and 10 K. Instead, a low-temperature minimum in the cubic unit cell volume, a feature seen in other dipolar glasses, is observed at a temperature $T_{\min}$ which increases with increasing impurity concentration. The lack of evidence of any structural phase transition seen by the x-ray diffraction experiments along with the systematic dependence of $T_{\min}$ on x argue in favor of a dipolar-glass description for the low-temperature polar phase in dilute KTN.

In addition, the process of powdering KTN samples is seen to suppress the low-temperature minimum in the unit cell volume, and even the structural transitions observed in the more concentrated KTN sample with x=0.157. However the gross temperature dependence of the lattice constant is left unaffected. This observation places previous experimental work on KTN powders under some degree of suspicion. It is hoped therefore that these results will stimulate a check of previous powder data taken on KTN samples and serve as a motivation for further experimental work.

ACKNOWLEDGMENT

Work at Brookhaven National Laboratory was carried out under Contract No. DE-AC02-76CH00016, Division of Materials Sciences, U.S. Department of Energy.

[1] See, for example, the review of orientational glasses by U. T. Hóchli, K. Knorr, and A. Loidl, Adv. Phys. **39**, 405 (1991), and references therein.

[2] B. I. Halperin and C. M. Varma, Phys. Rev. B **14**, 4030 (1976).

[3] K. H. Höck and H. Thomas, Z. Phys. B **27**, 267 (1977).

[4] R. L. Prater, L. L. Chase, and L. A. Boatner, Phys. Rev. B. **23**, 221 (1981).

[5] G. A. Samara, Phys. Rev. Lett. **53**, 298 (1984).

[6] U. T. Höchli, K. Knorr, and A. Loidl, Adv. Phys. **39**, 405 (1990).

[7] U. T. Höchli, Phys. Rev. Lett. **48**, 1494 (1982).

[8] L. L. Chase, E. Lee, R. L. Pratner, and L. A. Boatner, Phys. Rev. B **26**, 2759 (1982).

[9] J. J. van der Klink and F. Borsa, Phys Rev **3**, 52 (1984).

[10] J. D. Axe, J. Harada, and G. Shirane, Phys. Rev. B **1**, 1227 (1970).

[11] A. W. Hewat, J. Phys. C **6**, 2559 (1973).

[12] D. Rytz and H. J. Scheel, J. Cryst. Growth **59**, 468 (1982).

[13] U. T. Höchli, H. E. Weibel, and L. A. Boatner, Phys. Rev. Lett. **39**, 1158 (1977).

[14] J. Toulouse, P. DiAntonio, B. E. Vugmeister, X. M. Wang, and L. A. Knauss, Phys. Rev. Lett. **68**, 232 (1992).

[15] K. B. Lyons, P. A. Fleury, H. Chou, J. Kjems, S. M. Shapiro, and D. Rytz (unpublished).

[16] H. Chou, S. M. Shapiro, K. B. Lyons, J. Kjems, and D. Rytz, Phys. Rev. B **41**, 7231 (1990).

[17] A diffuse peak was seen for x=0.017 in an x-ray scattering study by Andrews at 30 K, S. R. Andrews, J. Phys. C **18**, 1357 (1985), but no evidence of long-range structural order.

[18] H. Terauchi, Jpn. J. Appl. Phys. **24**, 75

[19] D. E. Cox, B. H. Toby, and M. M. Eddy, Aust. J. Phys. **41**, 117 (1988).

[20] K. Knorr, Phys. Rev. Lett. **66**, 3016 (1991).

[21] J. M. Rowe, J. J. Rush, D. J. Hinks, and S. Sussman, Phys. Rev. Lett. **43**, 1158 (1979).

[22] T. Kanata, T. Yoshikawa, and K. Kubota, Solid State Commun. **62**, 765 (1987).

[23] K. Uchino, E. Sadanaga, and T. Hirose, J. Am. Ceram. Soc. **72**, 1555 (1989).

[24] G. A. Samara, Phys. Rev. **151**, 378 (1966); Ferroelectrics **2**, 277 (1971).