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Dielectric nonlinearity and spontaneous polarization of $KTa_{1-x}Nb_xO_3$ in the diffuse transition range

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$KTa_{1-x}Nb_xO_3$ (KTN) in an intermediate-concentration range ($x=15.7\%$) has been studied using dielectric-constant and spontaneous-polarization measurements. A large peak in the dielectric constant ($\epsilon_{max} \simeq 70\,000$) is observed at the temperature T_c^*. From room temperature down to T_c^*+20 K, ϵ obeys a Curie-Weiss law with $T_0 \sim 142.3$ K. Below, ϵ deviates from this law and *P-E* hysteresis loops are observed. These results indicate that the phase transition exhibits a diffuse character which is related to the appearance of microscopic polarized regions or cells. The ϵ peak at T_c^* exhibits a cusp shape and becomes flattened upon application of low dc-bias fields. A corresponding dielectric loss peak is also observed, the position of which reveals the relaxational character of the transition. Through measurements of $\epsilon(E,T)$ for different dc-bias fields, we have characterized the dielectric nonlinearities in the transition range; the first nonlinear coefficient, $\epsilon^{(2)}$, diverges in two distinct ranges, as $(T-T_c^*)^{-n}$, with $n \sim 9$ initially and with $n \simeq 2$ closer to T_c^*. These results suggest that diffuse phase transitions in mixed ferroelectrics are due to the ordering of polar cells modified by mutual strain interactions.

INTRODUCTION

Mixed ferroelectric systems can display properties that are very different from those of simple ferroelectrics. In particular, many of them are characterized by a diffuse phase transition, i.e., a phase transition taking place over a wide range of temperatures often called the Curie range.[1] $KTa_{1-x}Nb_xO_3$ (KTN) is of particular interest in trying to understand ferroelectric phase transitions in mixed systems; pure $KTaO_3$ remains cubic and paraelectric down to 0 K, while, at the other end of the phase diagram, $KNbO_3$ exhibits a ferroelectric transition from a cubic to a tetragonal structure at 701 K. In between, this system forms solid solutions with T_c varying continuously according to the formula $T_c=676x+32$ (Ref. 2) (for $x>4.7\%$). Below $x=4.7\%$, KTN may appear to offer an example of a dipolar glass,[3] while above $x \simeq 35\%$ it exhibits a first-order ferroelectric phase transition characteristic of $KNbO_3$.[4] In the intermediate range, we should expect that the Nb ions will interact cooperatively, giving rise to a transition, the nature of which is still not clear. Although it has often been thought that, above $x=4.7\%$, the transition is a "simple" ferroelectric one, earlier studies already showed that, in the intermediate-composition range, KTN behaves differently. Triebwasser's dielectric constant measurements[4] of an $x=20\%$ crystal revealed a second-order phase transition, while an $x=46\%$ crystal displayed a first-order transition as in $KNbO_3$. Courdille *et al.* showed similar results for $x=28\%$ and 40% crystals.[5] A recent ultrasonic study by the present authors also revealed an unexpected elastic behavior.[6,7]

In the present paper we report the results of dielectric constant and polarization measurements in the presence of a dc-bias electric field. The purpose of these measurements was to characterize the effect of substitutional disorder on the phase transition in mixed ferroelectrics and, in particular, the dielectric nonlinearities that are expected to be strong in the presence of such a disorder.

EXPERIMENT

Two crystals ($x=15.7\%$ and 14.4%) were used in this study, both grown from the melt by a slow-cooling method. The respective concentrations were estimated on the basis of the temperature, T_c^*, of the dielectric constant maximum. Upon inspection, the $x=15.7\%$ crystal was found to be homogeneous (no striations), whereas the $x=14.4\%$ crystal was not. The former was consequently more thoroughly studied. Thin plates ($\sim 1\times1\times0.1$ cm^3) were cut from these crystals for the measurements. Fresh aluminum electrodes were evaporated on both faces of the samples for each new run. Failure to do so leads to progressive detachment of the electrodes from the sample because of the strong electrostriction of the transition. This in turn results in the introduction of an extraneous series capacitance which can significantly depress the dielectric peak at T_c^*. For these reasons, the initial dielectric data published[8] should be ignored.

The dielectric-constant measurements were performed with a general radio capacitance bridge (model 1615A) at 1 kHz with a 15 V/cm ac field. For the spontaneous-polarization measurements, we used a compensated Sawyer-Tower circuit. The temperature was controlled with a silicon diode sensor to better than 0.01 K.

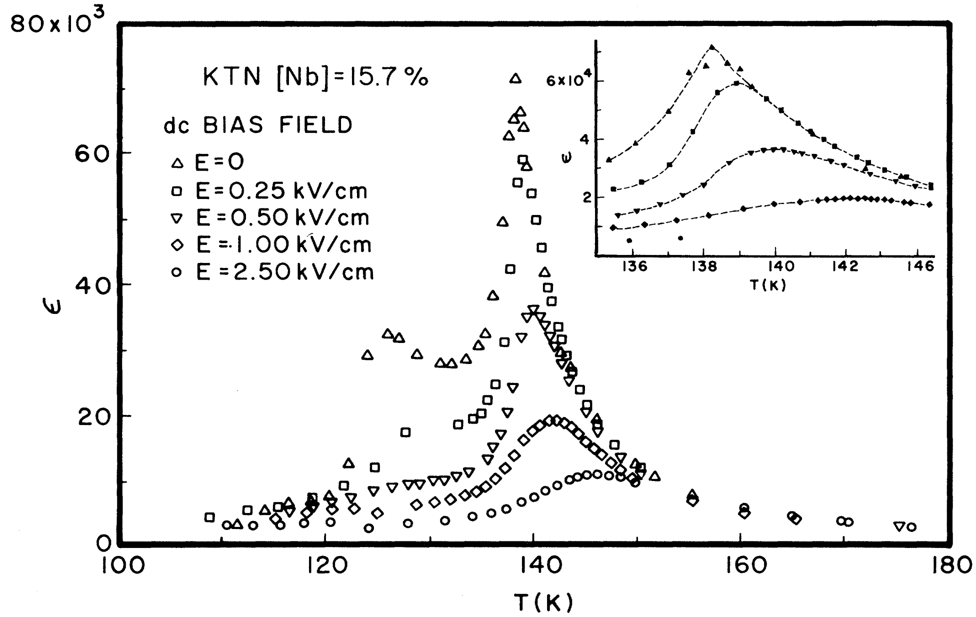

FIG. 1. Dielectric constant vs temperature for different dc-bias electric fields. Inset: expanded temperature scale.

RESULTS

Dielectric constant

The dielectric constant ϵ was measured for different applied dc-bias fields. The results are shown in Fig. 1. ϵ exhibits a very large peak at T_c^*, that shifts to higher temperatures with higher fields. On the low-temperature side of this peak, a discontinuity can be seen, that corresponds to the next lower transition. The respective characters of these two transitions can be inferred from Fig. 1. Both of them appear to be continuous and would normally be qualified as second order. Although one expects three successive transitions in simple perovskite ferroelectrics, the present results only clearly reveal two transitions. The nature of these remains an open question to which the rest of the paper attempts to find an answer. This explains why we have labeled the temperature of the main dielectric peak T_c^*, and why we do not refer to the corresponding transition as the cubic-tetragonal transition. The inset of Fig. 1 gives a magnified view of the dielectric-constant peak that reveals the cusp shape of the peak, and the flattening that results from the application of low dc-bias electric fields.

Upon cooling from room temperature, the approach to the ferroelectric transition is clearly seen in Fig. 2 to allow a Curie-Weiss law:

$$\epsilon^{-1} \simeq (\epsilon - 1)^{-1} = \frac{T - T_0}{C} \tag{1}$$

with $T_0 = 143.7$ K and $C = 101\,626$ K^{-1}. However, three features in Fig. 2 indicate that this transition is not of the usual second-order kind.[9] First, we note that, unexpectedly in this system, T_0 is higher than T_c^*. Second, a departure from a simple Curie-Weiss law becomes visible at ~ 160 K, i.e., approximately 20 K above T_c^*. Thirdly, unlike a second-order Landau transition, the slope on the low-temperature side is much less than twice that on the high-temperature side of the transition.

The unusual nature of the transition at T_c^* is further illustrated in Fig. 3 by the relative positions of the dielectric-constant and -loss peaks. In a normal transition, the two peaks would be found at the same temperature.[9] Here the two peaks are separated and the peak on one curve appears to coincide with the inflection point on the other curve. The inset corresponds to the curves expected from a Debye relaxation model for the real (constant) and imaginary (loss) parts of the complex dielectric constant and is discussed later in the paper.

The application of a dc-bias electric field has two effects. First, T_c^* is found to increase linearly with field, tending towards an upper limit at higher fields (>2.5

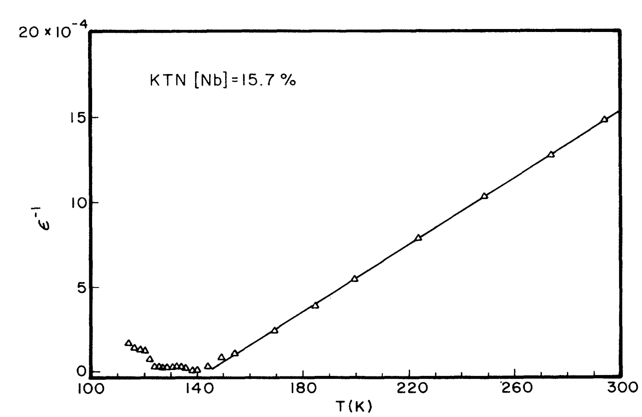

FIG. 2. Inverse dielectric constant vs temperature. The solid line is a Curie-Weiss fit to the data points above 170 K.

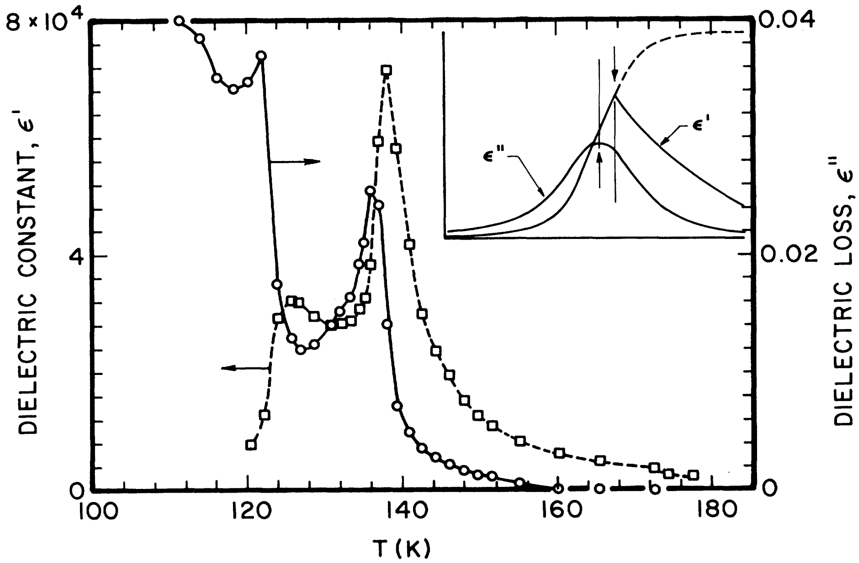

FIG. 3. Dielectric constant, ϵ', and dielectric loss, ϵ''/ϵ', for KTN (15.7%) measured at 1 kHz. Inset: Debye relaxation curves for ϵ'' and ϵ' modified as explained in the text.

kV/cm). Secondly, in Fig. 4, we show the effect of the dc-bias field on the shape of the ϵ peak measured upon cooling with or without the field on. The higher peak, obtained with field cooling is the dielectric analog of a similar effect observed in spin glasses with a dc magnetic field applied. Finally, the electric-field dependence of the dielectric constant is shown in Fig. 5, in which ϵ is seen to decrease with increasing bias field. The solid lines are the results of a fitting of the experimental points to an expansion of the form

$$\epsilon=\epsilon_L+\epsilon^{(2)}E^2+\epsilon^{(4)}E^4 , \quad (2)$$

where ϵ_L represents the normal linear part of the dielectric constant. The temperature dependence of the first two nonlinear coefficients, $\epsilon^{(2)}$ and $\epsilon^{(4)}$, is presented on a log-log scale plot in Fig. 6; both are seen to diverge in two distinct stages as $(T-T_c^*)^{-n}$. In the first stage the divergence is very strong with $n\sim 9$ for $\epsilon^{(2)}$ and appears to be even stronger for $\epsilon^{(4)}$. Closer to T_c^*, the divergence is weaker with $n\simeq 2$ for both coefficients. We note that the higher exponent is subject to the choice of T_c which may not be equal to T_c^*. However, plots obtained with different choices of T_c still show a two-step divergence with a high exponent in the higher-temperature range. For the lower range, T_c^* is the temperature at which $\epsilon^{(2)}$ and $\epsilon^{(4)}$ reach their maximum and the exponent of 2 is therefore considered to have a clear physical significance.

Polarization

The total polarization was measured using a compensated Sawyer-Tower circuit, i.e., in the presence of a large

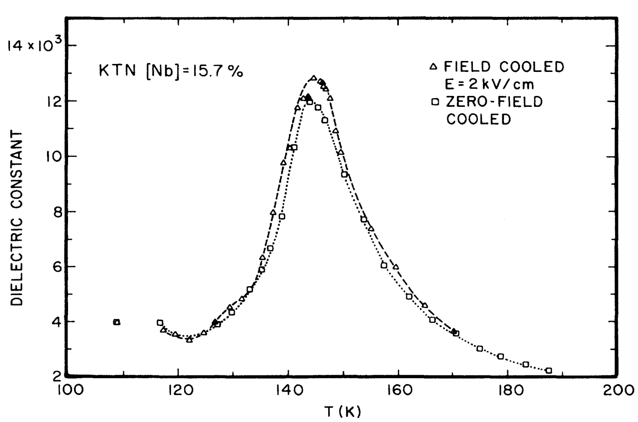

FIG. 4. Dielectric constant of KTN (15.7%) cooled with a 2 kV/cm dc-bias field on and with zero-bias field, respectively.

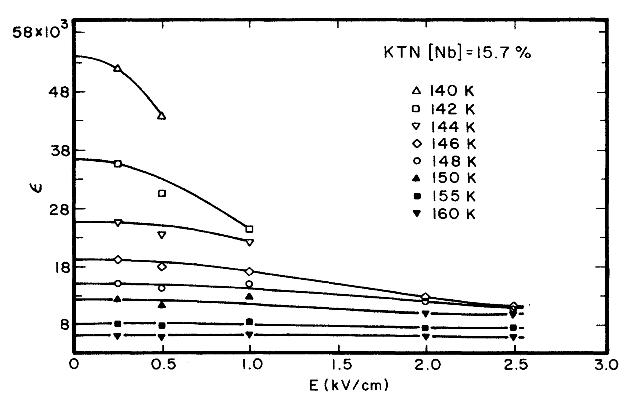

FIG. 5. Dielectric constant vs dc-bias electric field at different temperatures. The solid lines represent fits of the $\epsilon(E)$ expansion as given by Eq. (2) to the data points. The 0.5-kV data point at 140 K has been corrected, based on the departure of the 0.5-kV points at the higher temperatures.

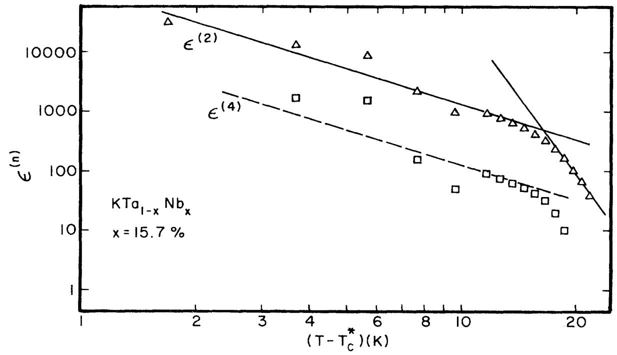

FIG. 6. Log-log plot of $\epsilon^{(2)}$ and $\epsilon^{(4)}$, coefficients of the first and second nonlinear terms of the $\epsilon(E)$ expansion, vs $(T-T_c)$ with $T_c = T_c^*$ (138.3 K). The solid lines have slopes of -9 and -2, respectively.

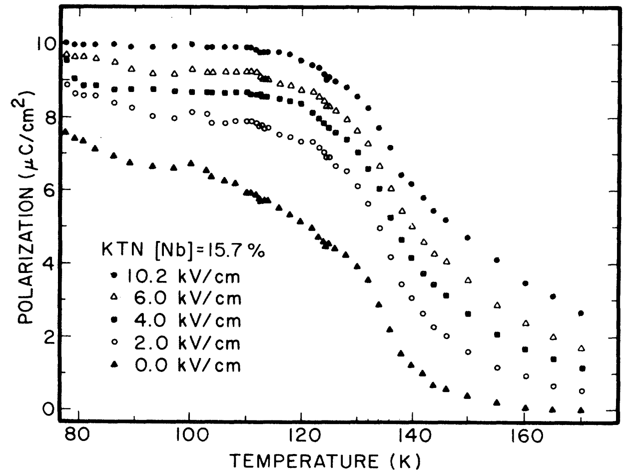

FIG. 8. Total polarization vs temperature. The different curves were obtained from the upper branch of the hysteresis loops observed with a maximum applied field of 10.2 kV/cm and at a frequency of 40 Hz. The 0.0-kV/cm curve corresponds to the remnant polarization.

applied electric field; hysteresis loops were observed over a wide range of temperatures, as far up as $T_c^* + 20$ K, which is also where we report a deviation from a Curie-Weiss law.

Examples of the observed hysteresis loops are given in Fig. 7. Pictures 7(a) and 7(b) were taken at 135 K, i.e., below T_c^*, with an applied field frequency of 40 and 5 Hz, respectively. Pictures 7(c) and 7(d) were taken at 160 K, i.e., well above T_c^* at the same two frequencies. The area inside the loop clearly increases with decreasing frequency, indicating that the existence of a loop is due to a stable polarization and not just to slow kinetics relative to the field frequency. Further measurements taken at 0.1 Hz (not shown) were similar to the 5-Hz measurements. Spontaneous polarization does therefore appear to exist above T_c^*, an observation suggesting the existence of polar cells that will be the main focus of our discussion below. As measured from the hysteresis loops observed with a 10.2 kV maximum field, the total polarization and the remnant polarizations are plotted in Fig. 8 as a function of temperature and for different fields along the upper branch of the loops. The remnant polarization is seen to increase smoothly from about 165 K downwards. The inflection points for all fields occur at approximately 136.5 K, i.e., below T_c^*, where the dielectric-constant peaks.

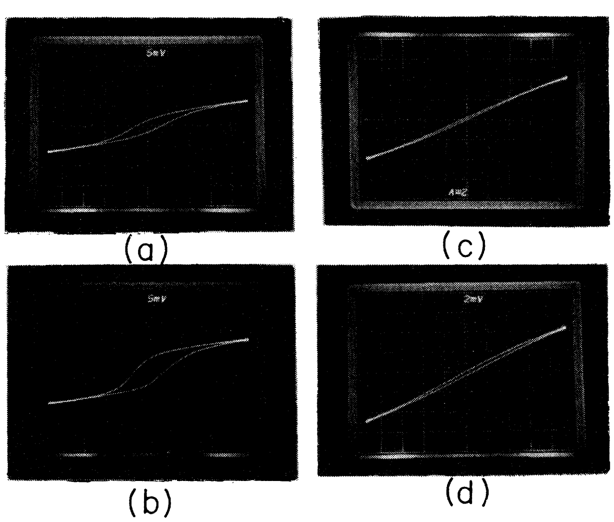

FIG. 7. P-E hysteresis loops taken at 135 K and (a) 40 Hz, (b) 5 Hz, and at 160 K and (c) 40 Hz, (d) 5 Hz.

DISCUSSION

The three surprising results of the present study are the appearance of a nonzero polarization, approximately 20 K above T_c^*, the strong and peculiar nonlinearity exhibited by the dielectric constant also from $T_c^* + 20$ K downwards, and the shape and position of the dielectric-constant and loss peaks at and near T_c^*.

The first result provides definite evidence for the appearance of stable polarized microregions or cells, which can be aligned in an external electric field. Once aligned in the electric field, these cells can no longer contribute to the large susceptibility or dielectric constant, hence the explanation for the departure from a normal Curie-Weiss law. As is apparent from the reported results, this departure coincides with and is therefore probably due to the onset of a negative nonlinearity in the dielectric constant ($\epsilon^{(2)} < 0$). The peculiarity of this nonlinearity resides in the fact that none of the exponents measured have the value that is expected from a mean-field theory. In a mean-field Landau theory, usually applicable to simple ferroelectrics, it can easily be shown that the nonlinear coefficient $\epsilon^{(2)}$ is related to the linear ϵ_L as $\epsilon^{(2)} \sim \epsilon_L^{(4)}$. Assuming a Curie-Weiss temperature dependence for ϵ_L, the temperature dependence of $\epsilon^{(2)}$ is predicted to be $(T-T_c^*)^{-4}$. Instead, our present results for $\epsilon^{(2)}$ reveal two regions with respective exponents ~ -9 and ~ -2, indicating a deviation from the mean-field behavior normally associated with very long-range interactions.

A possible interpretation of these results can be obtained from an analysis of the shape and position of the dielectric-constant and loss peaks at and near T_c^*. We shall therefore summarize the three major experimental observations on this subject. (1) The dielectric-constant peak at T_c^* exhibits a cusp shape (rounding off is restricted to less than 1 K) which is significantly flattened by even moderate dc-bias fields; (2) below T_c^*+20 K, the dielectric constant measured in a field-cooled sample is higher than when cooled in zero field; (3) a dielectric-loss peak is observed with its maximum located on the low-temperature side of the dielectric-constant peak at T_c^*. Observations (1) and (2), together with the observation of a hysteresis loop and a deviation of the susceptibility from a Curie-Weiss law for above T_c^*, are typical of spin glasses[10] with the dielectric constant replaced by magnetic susceptibility. Also characteristic of spin glasses is the strong divergence of the nonlinear coefficients of the susceptibility. This is most certainly true of our dielectric constant in the first part of the transitional region $[\epsilon^{(2)} \sim (T-T_c^*)^{-9}]$. The change over to a weaker divergence ($n \sim -2$) can be logically interpreted as a departure from a pure spin (or dipolar) glass behavior due to the strain interactions between polar cells. This interpretation is supported by a recent ultrasonic study of the same crystal.[7] In this study, we have observed, at approximately the same temperature, a strong softening of the C_{44} elastic constant, a departure of the C_{11} constant to a weaker divergence, and a sharp rise in the ultrasonic attenuation.

The dynamics of the interacting polar cells can be understood on the basis of observation (3) above, namely, the relative positions of the dielectric-constant and loss peaks. The shift between the two peaks suggests a relaxation mechanism which is illustrated in the inset of Fig. 3. In the inset, we show the normal behavior of the real and imaginary (or loss) parts of the dielectric constant, ϵ' and ϵ'', for a Debye-type relaxation process. In particular, ϵ' exhibits a step while ϵ'' peaks at a temperature corresponding to the midpoint of this step $[\omega\tau(T)=1]$. This behavior is typical of an ensemble of permanent dipoles, the motion of which is impeded by external interactions. In the present case, the dipoles are not permanent but only appear at a temperature $T_d \simeq T_c^*+20$ K, hence the unusual rise in ϵ' instead of the flat high-temperature region normally observed. The low-temperature side of the ϵ' peak, however, corresponds to the normal step in ϵ'; thus ϵ'' peaks at a temperature which is shifted down from the peak in the dielectric constant. As expected for a relaxation, the low-temperature side of the ϵ' peak also shifts to higher temperatures when measured at higher frequencies (not shown), while the high-temperature side remains unchanged, being simply due to the formation of the dipoles. The frequency dependence is also observed to become smaller as the niobium concentration is increased. This model thus provides a qualitative description of the dynamics of the polar cells near T_c^*. The relaxation cannot, however, be simply of a Debye form, the latter being strictly applicable only to isolated dipoles, with no mutual interactions. This is obviously not the case here since we have shown that the polar cells do interact via their mutual strain fields as well as, necessarily, in dipole-dipole interactions. In the case of spin glasses, a similar relaxational behavior is observed and the peak of the real susceptibility is found to coincide with the inflection point of the imaginary part, as can also be seen here in Fig. 3.[11,12] The similarity between the present results and those obtained on spin glasses indeed suggest the existence of a frozen-in disorder. A possible model for the transition can then be suggested, in which unit cells containing niobium distort rhombohedrally at a temperature T_d, i.e., Nb becomes frozen in a particular [111] direction, contributing to the [100] component of the polarization. Yet, four equivalent [111] rhombohedral orientations can still give rise to the same [100] polarization. Hence the transition at T_c^* would indeed be ferroelectric but it would also coincide with the freezing-in of elastic quadrupoles resulting in an orientational glass. Such a model is presently under investigation. It would be consistent with a recent neutron-scattering study which has revealed a strong increase in the intensity of the Bragg peak near T_c^*, presumably due to the relief of extinction.[13] Such a model also shows similarities with the model proposed for KBr-KCN.[14]

CONCLUSION

The present dielectric and polarization results clearly reveal the diffuse character of the ferroelectric transition in the mixed KTN system at intermediate concentrations. The departure of $\epsilon(T)$ from a Curie-Weiss law and the concurrent observation of hysteresis loops starting at T_c^*+20 K signal the appearance of microscopic polarized regions or cells. It is these cells that contribute to the spontaneous polarization above T_c^* and are responsible for the nonlinearities in the dielectric constant. Furthermore, the cusp shape of the zero-field dielectric-constant peak and the divergence of the first nonlinear coefficient $\epsilon^{(2)}$ suggest the dielectric equivalent of a spin-glass behavior of the system. The existence of polar cells has already been demonstrated experimentally at lower concentrations[15] (dipolar glass range). At intermediate concentrations, the present results indicate that the ferroelectric transition in KTN is not a classical second-order Landau transition but that it takes place in two steps: (i) the progressive appearance of polar cells around single or groups of a few niobium ions; (ii) the collective ordering of the individual electric dipoles modified by mutual strain interactions between the cells. Near and below T_c^*, the transition exhibits a relaxational character which is also typical of spin glasses. Only for niobium concentrations above $x = \sim 40\%$ does the transition in KTN become a classical ferroelectric transition of the first order.[4]

ACKNOWLEDGMENTS

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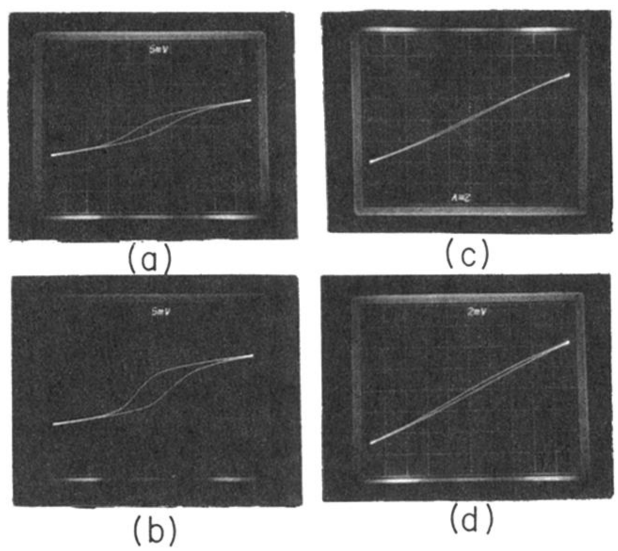

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