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Nature of the phase transition in $K_{1-x}Na_xTaO_3$

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We present dielectric, elastic, and NMR measurements that point at the special character of the phase transition in $K_{1-x}Na_xTaO_3$ mixed crystals. At the onset of birefringence, a critical behavior is observed in the dielectric constant and in the elastic compliance, whereas the NMR measurements do not reflect any criticality. It is suggested that, related to the transition, an off-center displacement of the sodium ions of less than 0.1 Å occurs.

INTRODUCTION

Recently, mixed-crystal systems such as $K_{1-x}Li_xTaO_3$ and $KTa_{1-x}Nb_xO_3$ have attracted much attention.[1] The substitutional impurities Li (for K) and Nb (for Ta) considerably modify the properties of "pure" $KTaO_3$ which is known to remain in its cubic paraelectric state down to absolute zero. Addition of Li (with $0 \leq x \leq 0.04$) leads to a dipole-glass phase whereas addition of Nb (also with $0 \leq x \leq 0.04$) makes observation of a true ferroelectric state possible. In the present work, another mixed system, namely, $K_{1-x}Na_xTaO_3$, will be analyzed and discussed in the light of knowledge previously gained on the Li and Nb doped systems.

Mixed crystals of $K_{1-x}Na_xTaO_3$ were first investigated by Davis[2] and by Perry and Tornberg[3] in the concentration range $0.05 \leq x \leq 0.85$. Based on their study of dielectric properties and soft optical phonons, these authors indicate that the paraelectric-to-ferroelectric transition temperature T_c first increases with x to its maximum value $T_c = 65$ K for $x \approx 0.48$ and then starts to decrease in order to vanish for $x = 0.72$ where $T_c = 0$.

The range $0 \leq x \leq 0.28$ has been recently studied[4–6] and important deviations from classical ferroelectric behavior have been observed. They have been interpreted as a manifestation of quantum fluctuations[5] which are known to be important for $0 \leq T_c \leq 30$ K. In the quantum range, the most striking effect is the quadratic dependence of T_c as a function of the so-called "interaction parameter" s. Experimentally, s may be identified as the concentration x or as the hydrostatic pressure p. At ambient pressure, the law $T_c(\mathrm{K}) = 83\ (x - 0.12)^{1/2}$ has been obtained,[4] whereas $T_c(\mathrm{K}) = 16\ [6.6 - p\ (\mathrm{kbar})]^{1/2}$ at $x = 0.28$.[6] The exact nature of the "ferroelectric" phase is, however, still an open question and it should be emphasized that, to our knowledge, no ferroelectric hysteresis has been observed so far in $K_{1-x}Na_xTaO_3$.

The absence of a truly reversible polarization would imply an analogy between $K_{1-x}Na_xTaO_3$ and $K_{1-x}Li_xTaO_3$, where no spontaneous ferroelectric polarization is observed.[7] The properties of the latter system have been reviewed in detail in Ref. 8. Due to their off-center position, the Li^+ ions (substituting for K^+ in $KTaO_3$) create local dipoles. Collective effects between the dipoles occur below a concentration-dependent temperature T_g. The absence of criticality at the onset of these effects is reminiscent of the situation known in spin-glasses.

The question now arises of the nature of the low-temperature state in $K_{1-x}Na_xTaO_3$. In their pioneering work, Yacoby and Yust[9] deduced from their Raman-scattering experiments that both Li^+ in $K_{1-x}Li_xTaO_3$ and Na^+ in $K_{1-x}Na_xTaO_3$ occupy a site which is diplaced with respect to the very K^+ site in pure cubic $KTaO_3$. The off-center displacements indicated in the literature are given in Table I.

TABLE I. Off-center displacements of Li^+ and Na^+ ions in $KTaO_3$ according to several authors. The top row of the table indicates the references from which the data have been taken.

Ref.	9	8	10	11
	Raman	NMR	Dicke model	Point-charge model
Li^+	qualitative	0.9 Å	0.4 Å	~1.2 Å
Na^+	qualitative		0.08 Å	

In the present work, we will report on NMR, dielectric, elastic, and optic measurements in $K_{1-x}Na_xTaO_3$ with the purpose of gaining some insight into the transition mechanism.

EXPERIMENTAL

$K_{1-x}Na_xTaO_3$ crystals were grown using a slow-cooling method already described for other $KTaO_3$-derived mixed systems.[12] The concentration x was deduced from the T_c measurements (see below) using the T_c vs x law. A set of five crystals was employed having $x = 0$, 0.05, 0.17, 0.19, and 0.21.

The effect of the transition on the dielectric constant ϵ (measured at 1 kHz) and on the inverse elastic compliance s_{11}^{-1} (deduced from electromechanical resonance frequencies in the 300–500-kHz range) is shown in Figs. 1 and 2, respectively. No transition occurs if $x < 0.12$. If $x > 0.12$, ϵ reaches its maximum value at T_c. The dielectric peak is associated with an elastic step. No effort was made to check the frequency dependence of both features. It should, however, be pointed out that the T_c's gained from the dielectric and acoustic measurements correspond to the onset of birefringence when viewing the samples with $x > 0.12$ between crossed polarizers.

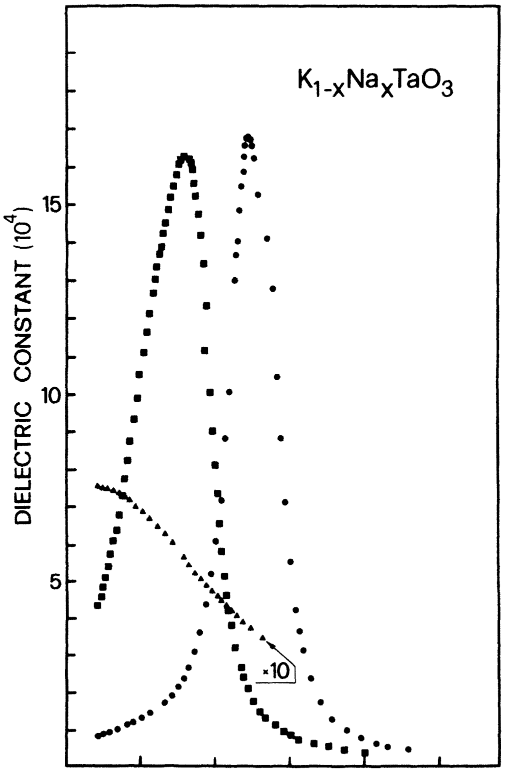

FIG. 1. Temperature dependence of the dielectric constant in $K_{1-x}Na_xTaO_3$ crystals with $x = 0.05$ (▲), 0.17 (■), and 0.21 (●).

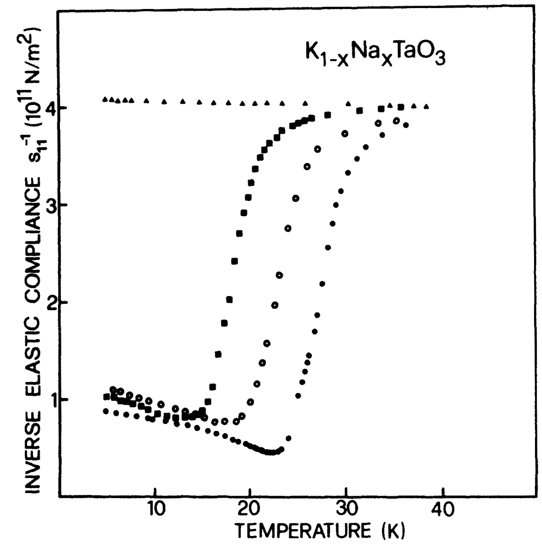

FIG. 2. Temperature dependence of the inverse elastic compliance s_{11}^{-1} in $K_{1-x}Na_xTaO_3$ crystals with $x = 0.05$ (▲), 0.17 (■), 0.19 (○), and 0.21 (●).

Nuclear magnetic resonance and relaxation experiments have been performed on ^{23}Na and ^{39}K in one of the crystals ($x = 0.21$, $T_c = 24.2$ K). We have also unsuccessfully searched for the ^{181}Ta resonance, which is easily detected in pure $KTaO_3$.[13] All experiments were performed in an 8-T external field, observing the absorption spectra after quadrature Fourier transformation of the free-induction decay. The rotating rf field H_1 was always larger than 50 G. Both on the ^{23}Na and ^{39}K resonances, quadrupolar echoes[14] were observed at all temperatures and all data reported refer to the central $+\frac{1}{2} \leftrightarrow -\frac{1}{2}$ transition only, unless otherwise stated. Amplitude and position of the ^{23}Na resonance are shown in Fig. 3 as a function of inverse temperature. The straight line in the top part of the figure reflects Boltzmann's law, and implies that no second-order broadening of the line occurs at T_c. The lower part shows that the second-order frequency shift, if present, is less than half a linewidth, so that we can estimate that ν_Q (^{23}Na) < 150 kHz. The distribution of satellite frequencies, as derived from the quadrupolar echo, is ~ 25 kHz full width at half maximum.

The ^{23}Na spin-lattice relaxation time T_1 is shown as a function of temperature T in Fig. 4. The straight line corresponds to $T_1^{-1} \propto T^{\alpha}$ with $\alpha = 1.8$. For quadrupolar Raman relaxation and a simple Debye spectrum for the phonons, one expects $\alpha = 2$,[15] but values around 1.8 have been found also in, e.g., NaI.[16] These deviations probably reflect the inadequacy of a Debye spectrum in solids with widely varying ionic masses. The experimental curve goes

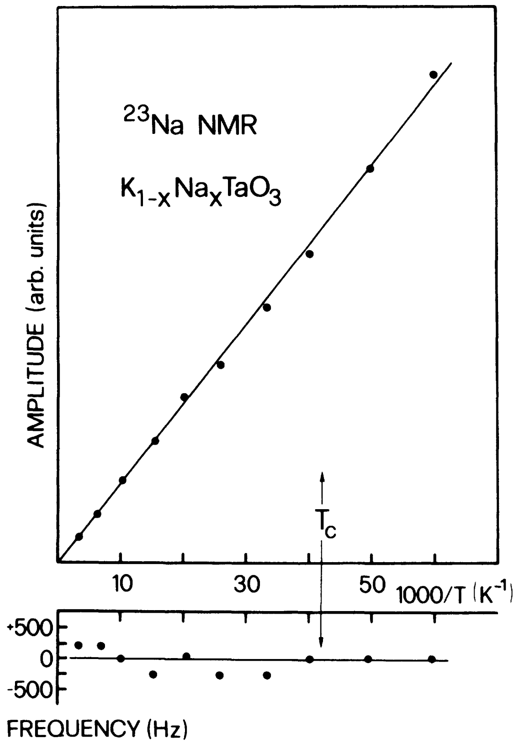

FIG. 3. Amplitude and position of the ^{23}Na resonance as a function of inverse temperature in a $K_{1-x}Na_xTaO_3$ crystal with $x = 0.21$ and $T_c = 24.2$ K (see text).

smoothly through T_c, without showing critical effects. The deviations of the lowest-temperature point from the line, if significant at all, might be due to mode softening, similar to what is observed on ^{35,37}Cl relaxation in the antifluorite K_2PtCl_6,[17] but at these values of T_1^{-1} paramagnetic impurities may become important.

The NMR data for ^{39}K are somewhat scantier and less accurate than those on ^{23}Na, due to poor sensitivity and longer relaxation times. In the temperature region studied (see Fig. 4) the behavior is similar to that of ^{23}Na and the width of the quadrupolar echo indicates a similar static distribution of field gradients. Also in Fig. 4 are a few points taken on a pure sample of $KTaO_3$. It is seen that the Na doping has no substantial effect on the ^{39}K relaxation. Note, however, that, if the ^{23}Na and ^{39}K relaxations were different only through Sternheimer factors and quadrupole moments, we would expect the ^{23}Na relaxation to be slower than that for ^{39}K by a factor 1.7 instead of faster by about a factor of 4, as observed. This enhancement of the relaxation rate might be due to the greater anharmonicity of the local potential around Na^+, as compared to that around K^+, so that the "local field" effective in causing spin-lattice relaxation through the anharmonic Raman process is bigger on ^{23}Na then on ^{39}K. If the distribution of field gradients on the ^{181}Ta nucleus is similar to that on ^{23}Na and ^{39}K, one expects the central transition to be so severely broadened by second-order quadrupole effects that in fact it might become unobservable.

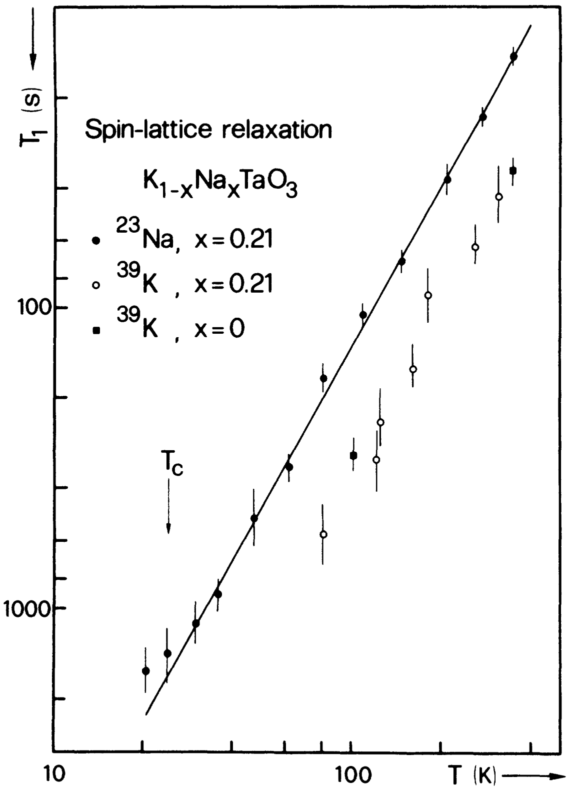

FIG. 4. Spin-lattice relaxation times T_1 of ^{23}Na and ^{39}K as a function of temperature in a $K_{1-x}Na_xTaO_3$ crystal with $x = 0.21$ and $T_c = 24.2$ K and of ^{39}K in a $KTaO_3$ crystal.

DISCUSSION

The observed behavior of the dielectric constant and the inverse elastic compliance is, of course, compatible with the old picture of a ferroelectric transition occuring in $K_{1-x}Na_xTaO_3$. This system cannot, however, be treated as a standard ferroelectric when considering the local properties investigated by NMR. The most puzzling feature of the experimental data is the clear absence of critical effects on the ^{23}Na spin-lattice relaxation rate T_1^{-1} in Fig. 4, as found in normal ferroelectric perovskites such as $NaNbO_3$ and $NaTaO_3$.[18] In fact, *all* nuclear relaxation rates (for nuclei with a suitable quadrupole moment) in *all* ferroelectric systems studied so far, be they of order-disorder or of displacive character, show such effects (for a review see, e.g., Ref. 19), with the single exception of ^{7}Li in $K_{1-x}Li_xTaO_3$.[8] In that case, a slowing-down of thermally activated hopping of Li ions through 90° between equivalent sites displaced from the cubic position along the [100] axes creates a nonzero time-averaged local polarization on longer and longer times scales, and a structure analogous to a spin-glass is thought to occur. The hopping shows up in the T_1^{-1} vs T plot as a distinct Arrhenius behavior, with a barrier height of about 1000 K.

The present data on ^{23}Na show no such behavior, but rather the T^2 dependence characteristic of a Raman-type process. For this to dominate a maximum in the relaxation rate due to thermal hopping supposedly present somewhere in the temperature range studied, the displacement of the Na ion has to be less than ~0.1 Å, comparable to the calculated displacement in Ref. 10 (see Table I). The data in Fig. 3 lend support to the idea of a displacement of the Na ions, rather than of a deformation of the oxygen octahedra, as in $NaNbO_3$ and $NaTaO_3$, where important static quadrupole effects on the Na site are observed in the low-temperature phases. The calculated value of the quadrupolar frequency ν_Q for a displacement of 0.08 Å is ~7 kHz, so the satellite structure would be contained in the distribution of field gradients, and no second-order effects would be observed.

In summary our data indicate that, in $K_{1-x}Na_xTaO_3$, a small displacement ($\leq$0.1 Å) of the sodium ion is the main source of polar behavior, and that a dipole-glass type of transition, characterized by gradual slowing down, is more likely than a ferroelectric transition, where one expects critical slowing down. Whether the Na motion is thermally activated or rather oscillatory cannot be decided from the present experiments.

ACKNOWLEDGMENT

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