Existence of a ferroelectric phase in the $KTaO_3$:Li crystal

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(Submitted 10 November 1982)
Pis'ma Zh. Eksp. Teor. Fiz. **37**, No. 1, 30–33 (5 January 1983)

It has been established on the basis of acoustic, dielectric, pyroelectric, and optical experiments that in potassium tantalate crystals with noncentral lithium impurity a phase transition to the ferroelectric phase, rather than to the "polar glass" phase, occurs.

PACS numbers: 77.80.Bh

The introduction of noncentral impurities into a strongly polarized paraelectric lattice, as shown theoretically in Refs. 1 and 2, can lead to the appearance of a ferroelectric state. The most appropriate object for checking the theory is potassium tantalate with a lithium impurity. Indeed, $KTaO_3$ is distinguished by high dielectric constant ($\epsilon \sim 4 \times 10^3$ at $T \lesssim 40$ K) and remains a paraelectric (point group O_h) down to 0 K, while the lithium impurity, due to the small ionic radius, occupies, as follows from differential *KP* spectra,[3] a noncentral position in the $KTaO_3$ lattice with a displacement ~0.5 Å and has a dipole moment. However, there is now no unique point of

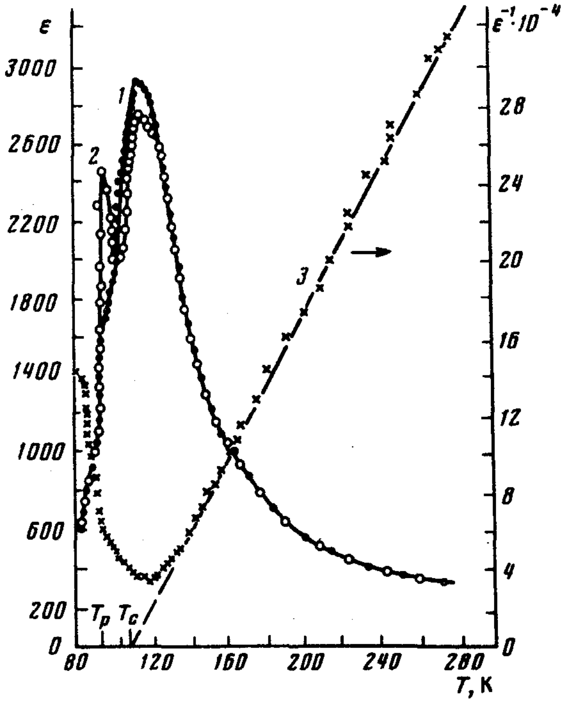

FIG. 1. Temperature dependences of the dielectric constant ϵ for multidomain (curve 1) and single-domain specimens in a field $E_0 = 3$ kV/cm (2) ϵ^{-1} (3). The frequency is 1 kHz.

view on the nature of the phase transition in the system $K_{1-x}Li_xTaO_3$. Thus, although in a number of works on optical scattering[4,5] and birefringence[6] indications of a ferroelectric state are mentioned, it is asserted in Refs. 7–12 that in this system (for $x \leqslant 0.24$) a "polar glass" state, in which there is no macroscopic spontaneous polarization and no exactly fixed transition point, is formed. There is only an extended region of "vitrification" and the observed critical anomalies of the dielectric constant and its dispersion are attributed to the presence of slowly relaxing clusters.[10] The presence of "polar glass" phases was deduced, in particular, from the absence of any anomalies in the elastic compliance S_{11}, measured by the resonance method.[7,8]

The purpose of the present work is to study the phase transition and the low-temperature phase in the crystal $K_{1-x}Li_xTaO_3$. Crystals were grown from a solution in the melt Ta_2O_5,$K_2CO_3 + Li_2CO_3$ and the content of the lithium impurity was determined from the charge. Dielectric and optical measurements were performed on specimens with average sizes $5 \times 5 \times 1$ mm; silver electrodes were deposited on the large faces perpendicular to [100]. The results of the measurements of the temperature dependence of ϵ are presented in Fig. 1. We see in Fig. 1 that the dependence $\epsilon(T)$ follows the Curie–Weiss law with $C = 5.3 \times 10^4$ K^{-1} and $T_c = 103$ K. By creating a single-domain specimen by cooling it to temperature $T \simeq 78$ K in a constant electric field E_0 applied along [100], an additional sharp peak appears in $\epsilon(T)$ at T_p whose position does not depend on the frequency of the measuring field and the magnitude of

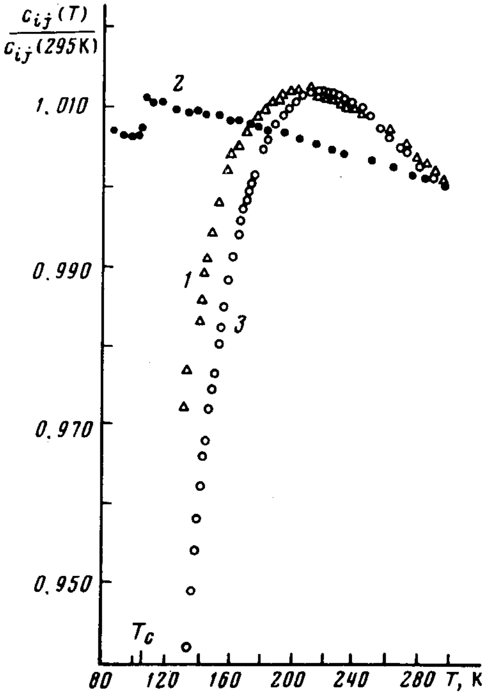

FIG. 2. Temperature dependences of relative changes in the elastic moduli: c_{11} (curve 1), c_{44} (2), and $\frac{1}{2}(c_{11} - c_{12})$ (3) for a multidomain specimen.

E_0 (Fig. 1, curve 2). The peak in ϵ at T_p was observed both with heating of the specimen to some temperature T_{meas} and with the subsequent cooling, but only if T_{meas} does not exceed T_c; in the opposite case, the dependence $\epsilon(T)$ becomes the same as in the starting state of the specimen (i.e., curve 1 in Fig. 1). In a single-domain specimen, a peak was also observed at T_c in the pyroelectric response measured by the dynamic method,[13] as well as birefringence and dielectric hysteresis loops for $T < T_c$.

Acoustic measurements were performed on a specimen with $x = 0.1$ and dimensions ~ 1 cm^3, whose faces were oriented along [100] and [110]. The velocity of elastic waves was measured by the method used in Ref. 14 at a frequency of 30 MHz with relative accuracy 10^{-4}. The temperature dependence of the relative changes in the elastic moduli c_{11}, c_{44}, and $\frac{1}{2}(c_{11} - c_{12})$ are shown in Fig. 2. The characteristic (for a phase transition[15]) jump in the modulus c_{44} at $T_c = 103$ K is interesting. As T_c is approached from the direction of the paraelectric phase, damping of all types of elastic waves increased (see Fig. 3) and, in addition, for waves determined by the moduli c_{44} and $\frac{1}{2}(c_{11} - c_{12})$ the damping is so high that in a multidomain specimen these moduli could be measured only in the high-temperature phase. It should be noted that an anisotropy is observed in the temperature dependences of the elastic constants (Fig. 2), while for a transition to the glass state it is expected that the anomalies in the elastic constants, corresponding to shear deformations (i.e, c_{44} and $\frac{1}{2}(c_{11} - c_{12})$) are identical.

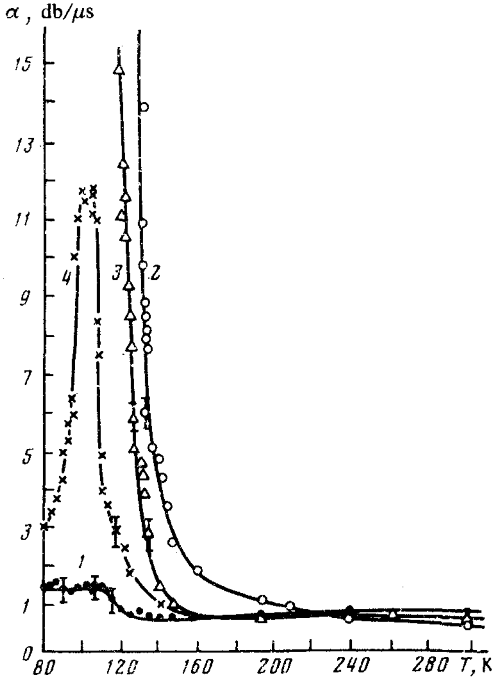

FIG. 3. Temperature dependences of damping of elastic waves with frequency 30 MHz propagating along [110]. Curve 1 shows the slow transverse wave (with velocity determined by c_{44}; curve 2 shows the fast transverse wave ($\frac{1}{2}(c_{11} - c_{12})$) and longitudinal wave in a multidomain (3) and single-domain specimen in a field $E_0 = 3$ kV/cm (4).

Damping of elastic waves in a single-domain (using the same method as in measuring ϵ) specimen is less than in a multidomain specimen (Fig. 3, curves 3 and 4), as is usually observed in ferroelectrics.[15]

Thus, based on the available experimental data we can conclude the following about the nature of the phase transition: First, there exists a phase-transition point T_c, fixed by the jump in the elastic modulus c_{44}; second the pyroelectric effects observed for $T < T_c$ and the decrease in damping in the single-domain specimen, together with the appearance of birefringence and dielectric hysteresis loops, indicate the ferroelectric nature of the low-temperature phase. The reason for anomalies at T_p remains unclear and requires further study.

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Translated by M. E. Alferieff
Edited by S. J. Amoretty