Contribution from Structural Jahn–Teller Ions to the Elastic and Ferroelectric Properties of Lithium Niobate and Lithium Tantalate

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Abstract—Elastic and ferroelectric characteristics of single crystals of lithium niobate and tantalate are investigated in a wide range of temperatures by complex acoustooptic means. The contribution from Jahn–Teller NbO_6 and TaO_6 systems to the characteristics of elastic moduli, ultrasonic attenuation, and nonlinear optical coefficients is analyzed using a new phenomenological model. It is hypothesized that the displacement of Nb^{5+} and Ta^{5+} ions, which exhibit the second-order Jahn–Teller effect along trigonal axis $\overline{C}$, and the subsequent ordering of octahedral, result in unusual elastic and ferroelectric properties.

INTRODUCTION

Lithium niobate and tantalate ($LiNbO_3$ and $LiTaO_3$) are known to have exceptional ferroelectric, pyroelectric, piezoelectric, elastic, and nonlinear optical properties. They are naturally used widely in opto- and acoustoelectronics [1−3]. While the primary focus was initially on crystals doped with iron-group and rare-earth ions, it has shifted over the past two decades to pure crystals used as bases for periodic domain structures. The mechanisms behind the abovementioned unusual physical properties and the potential to adjust them in the temperature interval of 77−500 K (the one most important for applications) became major subjects to be explored. Both materials have one high-temperature structural phase transition (T_C) from the centrosymmetric paraelectric structure ($R\overline{3}C$) to the noncentrosymmetric ferroelectric one ($R3C$) with Li, Nb, and Ta cations arranged along trigonal axis $\overline{C}$ ($T_C = 1480$ and 938 K, respectively). In both materials, niobium and tantalum ions are in a hexagonal close arrangement and occupy the central positions in octahedra formed by O ions in the $R\overline{3}C$ phase. At room temperature (i.e., below T_C), they are displaced along axis $\overline{C}$ by 0.25 (Nb) and 0.20 Å (Ta). Although the values of T_C are high, their basic physical properties are shaped below T_C.

Several theoretical and experimental studies [4−9] into the nature and the type of phase transitions, and thus the unusual physical properties of $LiNbO_3$ and $LiTaO_3$, have been performed over the last few decades. It was assumed earlier that the phase transitions were of the order−disorder type for Li ions and the displacement type for Nb and Ta ions. However, the analysis of phonon spectra and molecular dynamics in [10] led to the development of a new model based on Nb^{5+} and Ta^{5+} ions being second-order Jahn−Teller (JT) ions. It was assumed that the phase transition is not of the displacement type, but of the order−disorder type with a strong correlation between displaced Nb or Ta ions; and that the potential (elastic) energy decreases as the centrosymmetric structure is disrupted and the volume of a unit cell, which contains ten atoms, changes. Another feature of this model is the crucial role of interaction between JT Nb and Ta ions and their immediate environment, which is reflected in the Nb−O or Ta−O distance in much the same way as was proposed earlier for JT ions with triple orbital degeneracy in manganites [11, 12]. In both cases, the degeneracy of the initial symmetric electron configuration is lifted at $T < T_C$, and the direction of symmetry axes of the low-temperature phase is definitely related to the ordered displacement of JT ions. Cooperative ordering of distorted NbO_6 or TaO_6 octahedra along axis $\overline{C}$ then occurs with a reduction in temperature at $T < T_C$. The results from analyzing the density of electronic states in [10] revealed that valence bands are formed primarily by O $2p$ orbitals hybridized with Nb $4d$ or Ta $5d$ orbitals of NbO_6 or TaO_6 complexes, respectively, while conduction bands are formed by Nb $4d$ or Ta $5d$ t_{2g} orbitals hybridized with O $2p$ bands. The degrees of covalency of Nb−O
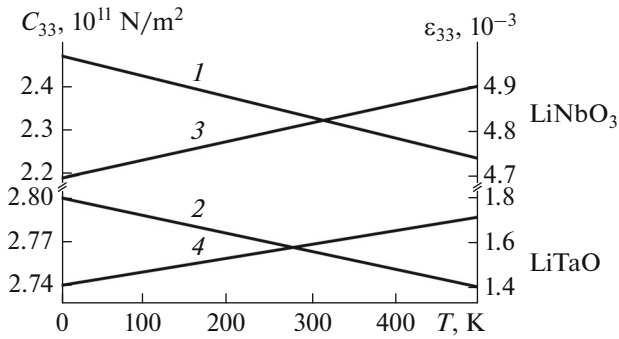
Fig. 1. Temperature dependences of (*1, 2*) elastic constants C_{33} and (*3, 4*) relative deformations ε_{33} in lithium niobate and tantalate.
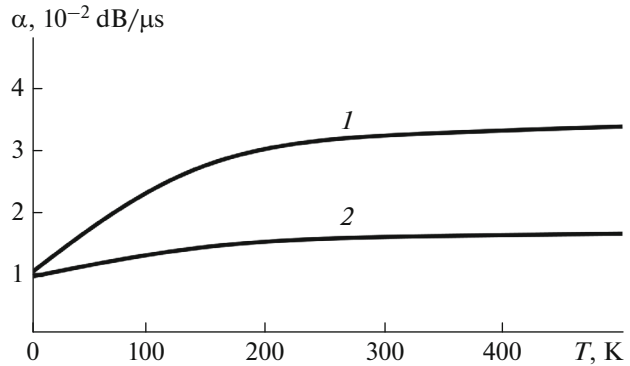

Fig. 2. Temperature dependences of attenuation α of a longitudinal acoustic wave along axis (333) ($f = 300$ MHz) in (*1*) lithium niobate and (*2*) tantalate.

and Ta–O bonds tend to increase at larger displacements of Nb or Ta cations. Therefore, according to this model, the difference in the covalency of Nb–O and Ta–O bonds leads to differences in Nb–O and Ta–O interionic interactions, resulting in unusual ferroelectric, optic, and elastic properties of lithium niobate and tantalate.

Since the validity of the proposed model has yet to be confirmed experimentally, we attempted to determine the effect structural JT ions of the second order have on the elastic properties of pure lithium niobate and tantalate in a wide range of temperatures by measuring the velocities and attenuation of longitudinal and transversal ultrasonic waves in the interval of 100–300 MHz.

EXPERIMENTAL

Ultrasonic waves were chosen because their characteristics reveal most clearly the effect JT ions have on the parameters of the structural phase transition and ordering among JT ions [11, 12]. For example, the values of elastic moduli ($C_{11}-C_{12}$), C_{33}, and C_{44} characterize the distances between a JT ion and the closest O ion in an octahedral environment and the angles of JT ion–O–JT ion deformation, while C_B (the bulk modulus) characterizes the changes in unit cell volume.

The values of elastic moduli $C_{ij} = \rho V_B^2$, deformations $\varepsilon = Ng/C_{ij}$, and JT energies E_{JT} were determined from the acoustic wave velocities. $E_{JT} = Ng^2 Q/C_{ij}$, where N is the number of JT ions in unit volume, g is the electron–lattice interaction constant [13], and Q is the quadrupole operator. The results from calculating the temperature dependence of C_{ij} values based on the measured velocities of high-frequency (up to 800 MHz) acoustic waves showed that moduli C_{33} in lithium niobate and tantalate increase with a reduction in temperature, while moduli C_{44} decrease slightly at lower temperatures (Fig. 1).

According to our current understanding of the nature of JT ordering [14], this increase in C_{33} correlates with the increasing displacement of Nb^{5+} or Ta^{5+} ions from the initial symmetric position in NbO_6 and TaO_6 unit cells and the corresponding enhancement of ordering among cells along axis $\overline{C}$. Since the energy states of JT complexes NbO_6 and TaO_6 depend on local lattice deformations, macroscopic lattice vibrations caused by acoustic waves should be maximized if acoustic waves produce lattice deformations corresponding to one of the vibrational modes (specifically, NbO_6 or TaO_6 complexes). In the case under consideration, these are the t_{2g} vibrations along axis $\overline{C}$.

RESULTS AND DISCUSSION

The attenuation (α) along axis $\overline{C}$ was much weaker in both samples than those along axes X and Y. The suppression of attenuation of ultrasonic waves along $\overline{C}$ observed at lower temperatures (Fig. 2) could be due to an increase in the degree of ordering among oxygen octahedral and an increase in the acoustic Q-factor of samples.

In our view, the suppression of attenuation observed for most acoustic modes at lower temperatures is another manifestation of the JT effect energetics, since $\alpha_{JT} \sim (\omega\tau_{JT})^{-1}$, where τ_{JT} is the JT relaxation time in the adiabatic propagation of elastic waves. The value of τ_{JT} increases with a reduction in temperature, which is also typical of other JT systems [13]. The values of α for $LiNbO_3$ were higher than those for $LiTaO_3$ over the range of measurements (500–4.2 K), in agreement with the ratio of elastic moduli.

The JT energies (Fig. 3) in lithium niobate were ~2.5 times higher than those in lithium tantalate, which agrees with the results from theoretical calculations [10]. The greatest contribution to the JT energy came not from dipole–dipole interaction, but from elastic deformations. This conclusion is based on the
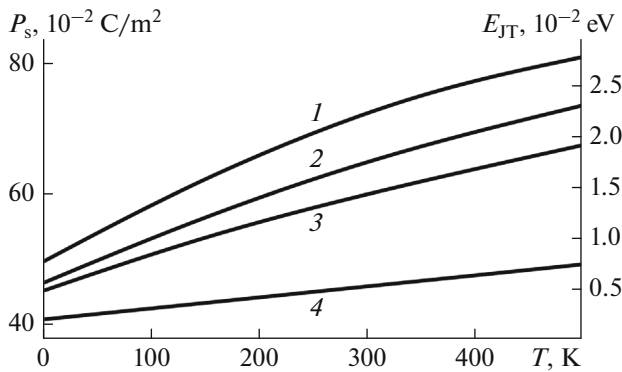
Fig. 3. Temperature dependences of spontaneous polarization P_s (*1, 2*) and JT energy E_{JT} (*3, 4*) in lithium niobate and tantalate.

ratio between C_{33} moduli and elastic deformations. Large elastic JT deformations and their ratio in lithium niobate and tantalate could account for the observed differences in polarization of these materials in the ferroelectric phase.

Examining the temperature behavior of the elastic properties of single crystals of lithium niobate and tantalate by analyzing the propagation of high-frequency acoustic waves in them allowed us to obtain new data on the nature of influence of JT ions Nb^{5+} and Ta^{5+} on the elastic and ferroelectric properties of these materials. The differences found in the low-temperature dependences of elastic moduli, attenuation, JT energies, and deformations (with their predominant and sharp variation along the trigonal axis) confirmed the results from earlier theoretical calculations.

CONCLUSIONS

Our results on the temperature dependences of elastic characteristics of single crystals of lithium niobate and tantalate lend credibility to the theory that the nature of structural phase transitions to ferroelectric phase *R3C* is determined by a two-stage process: the displacement of second-order JT ions Nb^{5+} and Ta^{5+} from the initial centrosymmetric position in oxygen octahedra and the ordering of the latter along axis $\overline{C}$. In both processes, the shaping of unusual ferroelec-

tric and elastic characteristics is much more apparent at lower temperatures.

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