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Li doping effect on properties and phase transfomations of $KNbO_3$

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Abstract

Dielectric permittivity and infrared reflectivity spectra of Li doped $KNbO_3$ single crystals have been studied for the first time for $K_{1-x}Li_xNbO_3$ with $x = 0.015$, 0.02, 0.065. It was found that Li admixture results in occurrence of dielectric relaxation with the relaxation parameters very close to those in Li doped $KTaO_3$. The relaxation was attributed to $\pi/2$ dipole reorientation of Li^+ ⟨1 0 0⟩ off-centers substituted for K^+, which appear to be present in both paraelectric cubic phase and in ferroelectric phase down to low-temperatures. Besides, Li doping is accompanied by an increase of the cubic-tetragonal phase transition temperature, a decrease of tetragonal-orthorhombic-rhombohedral phase transition temperatures and TO soft mode stiffening at room temperature.

Keywords: Impurities; Spectroscopy; Ferroelectric properties; Perovskites

1. Introduction

Doping with Li, which substitutes K in the $KTaO_3$ (KTO) quantum paraelectric and forms Li^+ off-center ions with large (∼1.2 Å) displacement along ⟨1 0 0⟩ directions has been the subject of extensive studies for a long period of time (see, e.g.[1–5] and references therein). Such doping crucially modifies KTO properties, leading to the appearance of a large dielectric relaxation polarization and various low-temperature multi-scale dipole ordering effects, varying from polar glass to long-range ordered polar state, depending on Li concentration. At the same time, Li doping effect in related ferroelectric $KNbO_3$ (KNO) is not known. Presumably, some physical–chemical aspects of $KNbO_3$–$LiNbO_3$ system using ceramic species have been reported only in Ref.[6] It was found that at low Li concentration $K_{1-x}Li_xNbO_3$ (KLN) has perovskite-type structure with stability limit $x_s \sim 10$–15% mol and Li admixture decreased dielectric permittivity and piezoelectric response.

At the same time, serious fundamental scientific and technological reasons appeared for studies of KLN. First, potassium niobate, similarly to $BaTiO_3$, is a well-known model ferroelectric, obeying three cubic-tetragonal-orthorhombic-rhombohedral phase transitions (PT) of the first-order at 703 K^h, 495 K^h and 221 K^c, respectively (c, denotes cooling; h, heating run), keeping orthorhombic symmetry from 223 to 495 K.[7] It has the largest effective nonlinear optical coefficient among the commonly used inorganic crystals. Therefore, it is normally used for frequency doubling in low and medium power lasers such as diode lasers, diode pumped solid state lasers and Nd:YAG and Ti:Sapphire lasers. It is also an efficient crystal for low threshold and high efficient optical parametric oscillators (OPO) and generators (OPG). However, heating over 483 K and cooling below 233 K can destroy the crystal as well as its careless treatment. Temperature instability leads to domain structure appearance and instable frequency doubling output, which limits KNO applicability for practice. We believe that Li doping can sufficiently modify these properties, and improve KNO crystals stability. Secondly, recent findings demonstrated that related lead-free (K,Na)NbO_3–$LiTaO_3$ materials show very promising piezoelectric properties ($d_{33}$is up to ∼230 p CN^{-1}).[8] KLN is the limit case of $K_{1-x}Li_xTa_{1-y}Nb_yO_3$ solid solution, known

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by their unusual properties and phase transitions as well as by their prospective applications in electrically controlled holographic and compositionally graded pyroelectric devices.[9,10] We report on the first synthesis and studies of the KLN crystals extending investigations of Li doping effect on properties and phase transformations of the classical ferroelectric assuming that in KLN, small Li^+ ions (ion radius of 0.68 Å) also substitute for K^+ (1.64 Å[11]) lattice sites and form strong reorientable ⟨1 0 0⟩ off-center dipoles. It was intended: (i) to perform the growth of KLN single crystals; (ii) to study the ability Li^+ related dipole ⟨1 0 0⟩ centers to modify phase transitions of KNO, and maybe even suppress some of these transitions and (iii) to reveal the presence (*or absence*) of Li^+ related dielectric relaxation in paraelectric cubic as well as in ferroelectric phases, and at low-temperatures. The main attention was paid to Li doping effect on cubic-tetragonal-rhombic phase transitions.

2. Experimental

$K_{1-x}Li_xNbO_3$ single crystals with $x = 0.015$, 0.02 and 0.065 (KLN-1.5, KLN-2 and KLN-6.5) were grown by spontaneous crystallization from slowly cooled flux. The batch consisted of Nb_2O_5, with approximately 15% excess of K_2CO_3 and certain amount of ultra-high purity Li_2CO_3. Obtained crystals were transparent with resistivity exceeding $10^{10}\,\Omega\,cm$. The Li content inside the experimental specimens was determined by atomic absorption spectroscopy analysis using a VARIAN AAS Spectrometer AA-30. X-ray diffraction analysis confirms the perovskite structure for all KLN-1.5, KLN-2 and KLN-6.5 crystals. Specimens for dielectric permittivity experiments were fabricated as thin platelet capacitors with surfaces oriented normal to the [1 0 0] principal axis of the paraelectric cubic phase. The complex dielectric permittivity was studied in the 100 Hz–1 MHz frequency range and 10–800 K temperature interval using HP 4192A impedance analyzer. Complementary unpolarized far-infrared reflectivity was measured at RT with a Bruker IFS 113v spectrometer in the range 20–2000 cm^{-1} and fitted using the factorized form of the dielectric function.[12]

3. Results and discussion

All crystal compositions under study reveal very weak dielectric permittivity dispersion, which is caused by the presence of ferroelectric domains in the ferroelectric phases and an increase of the conductivity in the paraelectric cubic phase. In each case the presence of three characteristic $\varepsilon'(T)$ maxima and temperature hysteresis evidenced three first-order phase transitions inherent to parent KNO. Fig. 1a presents the dielectric permittivity for KLN-1.5 taken on cooling for the temperature range of cubic-tetragonal-rhombohedral PT and respective PT temperatures for KNO.[7] It is seen that Li admixture leads to an increase of the cubic-tetragonal transition temperature and a decrease of the tetragonal-orthorhombic one, i.e. a broadening of the temperature region of stability of the tetragonal phase. The magnitudes of the $\varepsilon'(T)$ maxima appeared to be larger than those in KNO in the vicinity of the cubic-tetragonal PT (∼4500) and nearly the same as at the tetragonal-orthorhombic PT.[13] Fig. 1b presents dielectric permittivity for KLN-1.5 in the orthorhombic-rhombohedral transition region. It is seen that Li admixture decreases the temperature of this transition. The same PT shifts were found in KLN-2 and KLN-6.5 with magnitude of shifts increasing with Li concentration. Therefore, maxima of $\varepsilon'(T)$ appear in KLN-6.5 at ∼740 K^c and 747 K^h for cubic-tetragonal and 425 K^c, 453 K^h for tetragonal-orthorhombic phase transitions. Fig. 2a represents the dielectric relaxation, which is found in KLT-1.5 at low-temperatures. It is observed that the $\tan\delta(T)$ maximum shifts to higher temperatures with frequency. We found that the relaxation obeys satisfactorily the Arrhenius law $\tau = \tau_0 \exp(U/kT)$ with $\tau_0 \approx 2 \times 10^{-13}$ s and $U \approx 94.7$ meV (∼1100 K), which is very close to the Li^+ relaxation parameters in $KTaO_3$. Fig. 2b presents the unpolarized IR reflectance spectrum of KLN-2 taken at RT and fitted by a factorized oscillator model. Reflectance spectrum of the parent cubic paraelectric phase contains three characteristic restrahlen bands for perovskites in the region ∼60–600 cm^{-1}. They can be split by symmetry change due to phase transitions.[14] As a result, KLN-2 at room temperature is in the orthorhombic phase and has three IR active irreducible representations A_1, B_1, B_2. Therefore, the

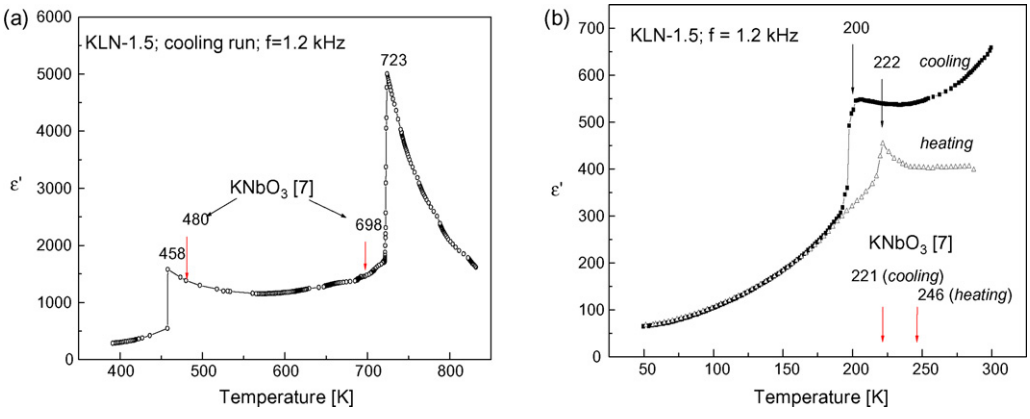

Fig. 1. (a) Dielectric permittivity for KLN-1.5 in the region cubic-tetragonal-orthorhombic phase transitions; arrows show the phase transition temperatures for $KNbO_3$ (cooling run) and (b) permittivity in the region of orthorhombic-rhombohedral phase transition.

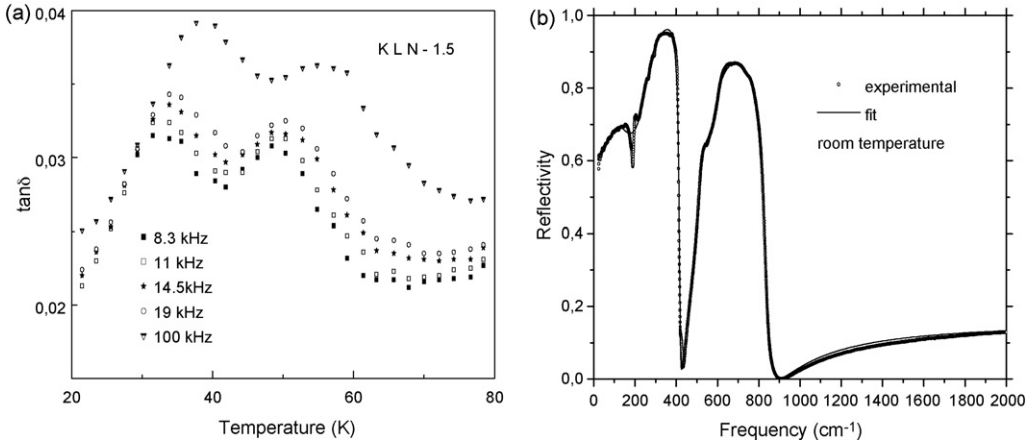

Fig. 2. (a) Low-temperature part of dielectric losses for KLN-1.5 and (b) IR reflectivity and fit by factorized oscillator model for KLT-2.

number of Infrared active modes at RT can be higher than three. In comparison with pure KNO the reflectivity of KLN-2 in the range of soft mode is much lower (KNO ∼85%; KLN ∼62%). This leads to two important suggestions: (i) Li admixture stiffens the TO soft mode in KNO at RT and (ii) TO lattice modes provide contribution into low-frequency permittivity yield only $\varepsilon' \sim 70$ (from IR) in contrast with $\varepsilon' \sim 290$ is observed in dielectric permittivity experiment, which clearly indicates presence of relaxation contribution connected with Li^+ related dielectric relaxation.

4. Conclusion

It is shown that Li doping of KNO crystals leads to a decrease of the dielectric permittivity at room temperature due to TO soft mode stiffening. The increase of the magnitude of the low-frequency permittivity temperature maximum at the cubic-tetragonal phase transition is connected with Li^+ related dielectric relaxation contribution. Like in KTO, Li^+ ions in KNO form ⟨1 0 0⟩ reorientable dipole off-centers, not only in paraelectric, but also in ferroelectric phases at low-temperatures. Relaxation parameters obtained at low-temperatures in the orthorhombic phase appeared to be very close to those in KTO, which means that FE ordering of KNO does not strongly influence Li^+ relaxation characteristics. Moderately doped KLN, similarly as the parent KNO, evidences three characteristic first-order phase transitions. Li admixture appreciably influences the temperature of the phase transitions: temperature of the cubic-tetragonal ferroelectric PT increases and temperature of the tetragonal-orthorhombic PT decreases (increase of the temperature range of stability of the tetragonal phase), temperature of the orthorhombic-rhombohedral PT decreases as well. These shifts increase with increasing Li content.

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