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Short communication

Structure and dielectric properties of niobium-rich potassium lithium tantalate niobate single crystals

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Abstract

The structure and lattice parameters of high quality niobium-rich potassium lithium tantalate niobate $(K_{0.95}Li_{0.05})(Ta_{1-x}Nb_x)O_3$ ($x=0.44$–0.66) single crystals were determined by the X-ray powder diffraction technique. Dielectric properties were studied in the temperature range from 20 to 500 K. The transition temperatures were determined, and the Curie temperatures adjusted between 330 K and 480 K through the suitable selection of Ta-to-Nb ratio. The degree of relaxation (γ) has been estimated using the modified Curie–Weiss law. The $(K_{0.95}Li_{0.05})(Ta_{1-x}Nb_x)O_3$ single crystals have also shown strong dc electric field dependent dielectric behavior, and high dielectric tunability (~43%) for $x=0.44$.

Keywords: B. X-ray methods; C. Dielectric properties; D. Perovskites

1. Introduction

The KTN system is a well-known solid solution with good dielectric and optical properties, and is one of the earliest found photorefractive materials, and the photorefractive and electro-optical properties have been widely studied [1–3]. So far most reports about potassium tantalum niobate $KTa_{1-x}Nb_xO_3$ (KTN) single crystals are available for tantalum-rich compositions. Potassium tantalum $KTaO_3$ and potassium niobate $KNbO_3$ single crystals both exhibit the ABO_3 perovskite structure, but have widely separated Curie points; $KTaO_3$ single crystal is a quantum ferroelectric below about 13 K [4], and the Curie temperature of ferroelectric $KNbO_3$ single crystal is about 700 K [5]. The lattice parameters of $KTaO_3$ (~4.0026 Å) and $KNbO_3$ (~4.0226 Å) in the cubic phase differ only slightly [6]. Based on this, and the isomorphic nature of tantalum and niobium compounds, single crystals of a range of compositions in the solid-solution $KTa_{1-x}Nb_xO_3$ system are grown. According to the phase diagram, KTN single crystals have four different crystallographic states; from low to high temperature , they go through from rhombohedra, orthorhombic, tetragonal to cubic phases. The Curie temperature is adjusted between 13 K and 700 K through the suitable selection of Ta-to-Nb ratio. Below $x\approx0.05$, the Curie temperature obeys $T_c=276(x-0.008)^{1/2}$ K [7]; above $x\approx0.05$, the Curie temperature follows the relation $T_c=676x+32$ K [8]; and when x is in between, KTN crystals show weak diffuse phase transition characteristics.

However, niobium-rich KTN single crystal compositions are difficult to be grown, and the electrical properties have rarely been reported. To facilitate good single crystal growth, we added 5% of lithium on A-site to grow high quality niobium-rich potassium lithium tantalate niobate $(K_{0.95}Li_{0.05})(Ta_{1-x}Nb_x)O_3$ (abbreviated as KLTN) single crystals. Recently, the good pyroelectric, piezoelectric, ferroelectric and electro-optic properties of KLTN single crystals have been investigated [9–12]. In this paper we will report the structure and dielectric properties of lead-free ferroelectric KLTN single crystals.

2. Experimental

High purity starting materials K_2CO_3, Li_2CO_3, Ta_2O_5 and Nb_2O_5 powders were prepared according to the composition

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selected in the phase diagram [13]. The top-seeded melt growth method was employed to grow KLTN single crystals. During the growth, the rotation rate of the seed rod was set to 10 rpm, and the pulling speed was 0.5 mm/h. After finishing the growth process, the annealing step was followed. The temperature rate of annealing & cooling was kept very low and it was set at about 20°C/h. After 6–7 days of entire growth run, high quality single crystals of KLTN were obtained.

After cutting, polishing, and stress releasing (thermal annealing), good samples with different sizes and aspect ratios desirable for various experimentations were prepared. The structure and lattice parameters of KLTN single crystals were determined by an X-ray diffractometer (D/max-rB 12 kW). Dielectric properties along [001] crystallographic direction were measured as a function of temperature and at different frequencies using an HP4284 LCR meter. Dielectric tunability was determined by measuring dielectric constant of the sample under an applied electric field using a voltage source (Trek 610, Trek Inc.) and a high voltage blocking circuit, which effectively separates the LCR meter from the voltage (0–2 kV) applied to the sample.

3. Results and discussion

3.1. Structure of KLTN single crystals

The X-ray diffraction patterns of KLTN single crystals on random orientations at room temperature are shown in Fig. 1(a). The patterns indicate a pure perovskite phase without any trace of pyrochlore structure. The splitting peaks observed for the diffraction peaks (002) and (200) demonstrate that the KLTN crystals are in the tetragonal phase with 4 mm point group, revealed by the relative intensities and shapes of these two peaks [inset of Fig. 1(a)].

Based on the observed diffraction angles of the peaks in the patterns, the lattice parameters were calculated, as listed in Table 1. As the cation radius of tantalum $r(Ta^{5+})$ is larger than that of niobium $r(Nb^{5+})$, the lattice parameters a and b decrease (c increases) with the increase of niobium concentration. The evolution of the lattice parameters is also described in Fig. 1(b). From linear fitting of the lattice parameters, it can be assumed that the intersection of the red line (linear fitting of c) and the black line (linear fitting of a and b) will be $x \approx 0.35$, which is consistent with Ref. [8] that when $x \approx 0.35$,, the Curie temperature is around room temperature.

3.2. Dielectric behaviors

$KTa_{1-x}Nb_xO_3$ ($x > 0.35$) single crystals undergo rhombohedral, orthorhombic, tetragonal ferroelectric states and finally to cubic paraelectric state at the transition temperature, T_C, while heating from low to high temperature up to ~500 K. The transition temperature from rhombohedral to orthorhombic phase is designated as T_{R-O}, orthorhombic to tetragonal as T_{O-T} and finally tetragonal to cubic as T_C.

Fig. 2 shows dielectric behaviors of unpoled KLTN samples along [0 0 1] crystallographic direction at different frequencies in the heating runs, and dielectric constant and loss tangent as solid lines and dashed lines, respectively.

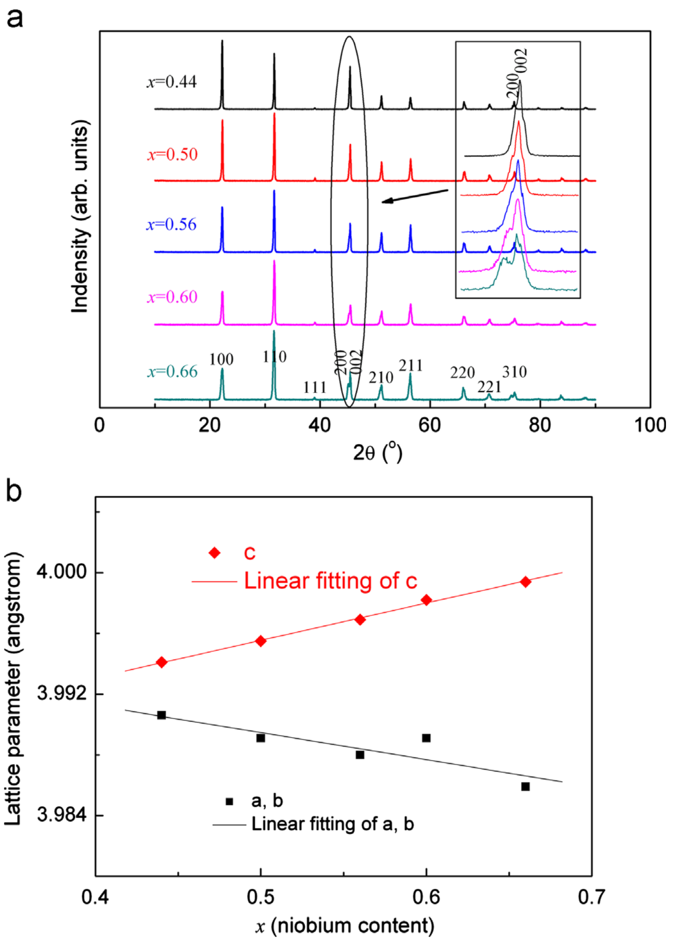

Fig. 1. (a) X-ray powder diffraction of the $K_{0.95}Li_{0.05}Ta_{1-x}Nb_xO_3$ single crystals on random orientations at room temperature, and (b) The lattice parameters (a, b, c) and linear fit. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

Table 1
The lattice parameters, dielectric constant, loss tangent and transition temperatures of $K_{0.95}Li_{0.05}Ta_{1-x}Nb_xO_3$ single crystals.

x	$a=b$ (Å)	c (Å)	T_{R-O}(K)	T_{O-T}(K)	T_C(K)	ε_{33RT}	tan δ_{RT}	ε_{33para}	tan δ_{para}
0.44	3.9906	3.9941	50	80	330	6, 390	0.080	8, 200	0.045
0.50	3.9891	3.9955	50	90	370	3, 910	0.582	6, 100	0.056
0.56	3.9880	3.9969	65	130	420	6, 470	0.428	12, 000	0.054
0.60	3.9891	3.9982	80	140	445	586	0.509	1, 700	0.051
0.66	3.9859	3.9994	120	270	480	858	0.083	2, 600	0.134

Combining the results of dielectric and pyroelectric measurements [12], three phase transition temperatures T_{R-O}, T_{O-T} and T_C are determined, and increase with niobium concentration. The Curie temperatures adjust between 330 K and 480 K through an appropriate Nb/Ta ratio, according to the function $T_c = 676x + 32$ K [5]. However, for T_{R-O} and T_{O-T}, the obvious changing law was not found. Table 1 also summarizes the values of dielectric constant and loss at room temperature (ε_{33RT}, tanδ_{RT}) and in the paraelectric phase (ε_{33para}, tanδ_{para}).

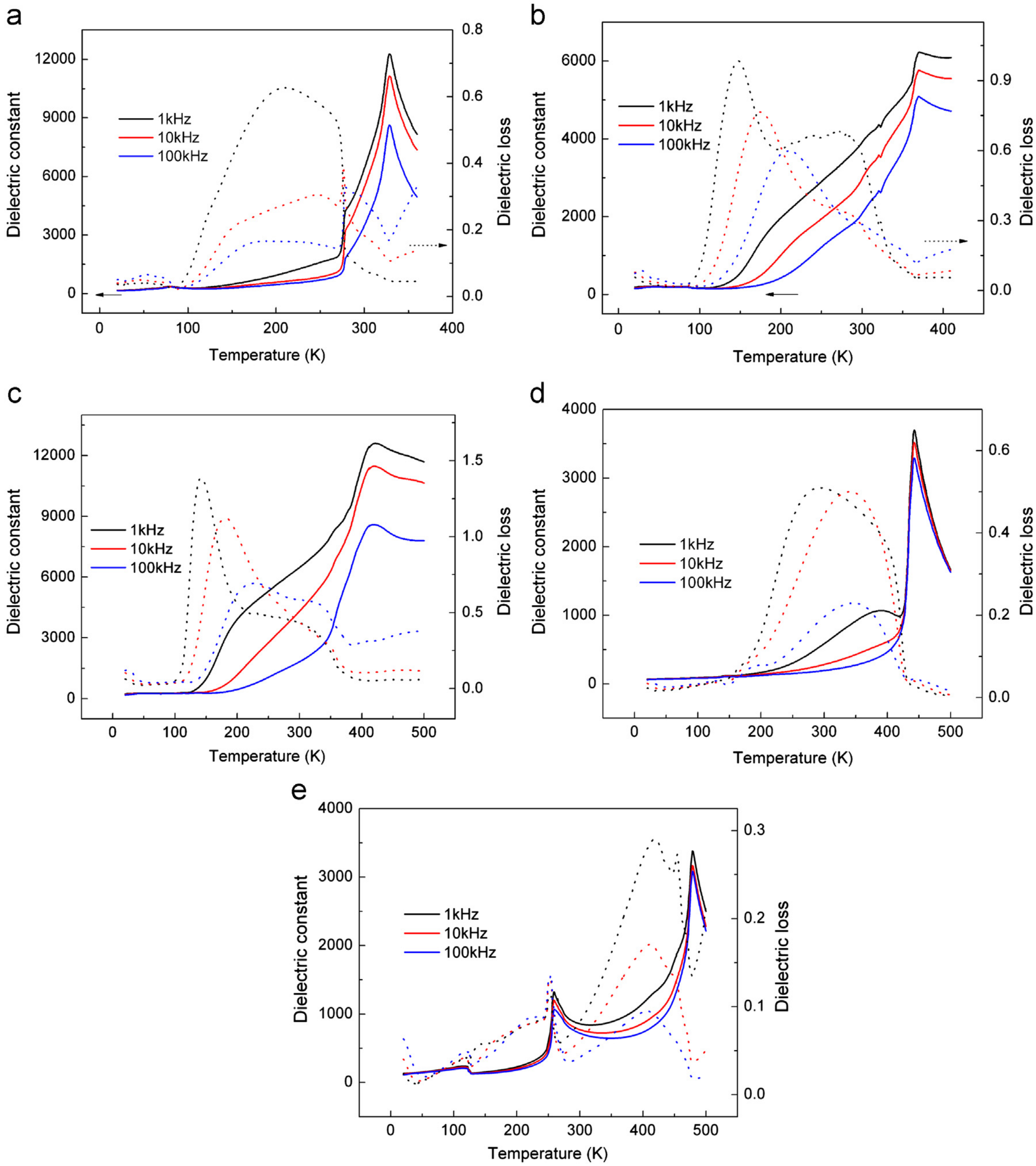

Fig. 2. Dielectric constant and loss of $K_{0.95}Li_{0.05}Ta_{1-x}Nb_xO_3$ single crystals along [001] crystallographic direction as a function of temperature at different frequencies in the heating runs: (a) $x=0.44$, (b) $x=0.50$, (c) $x=0.56$, (d) $x=0.60$, and (e) $x=0.66$.

KLTN single crystals also show strong orientation dependent dielectric properties and the typical value of dielectric constant of $K_{0.95}Li_{0.05}Ta_{0.40}Nb_{0.44}O_3$ single crystal along [100] crystallographic direction (ε_{11}) at room temperature is ~7600. For dielectric constant of $K_{0.95}Li_{0.05}Ta_{0.40}Nb_{0.44}O_3$ single crystal along [100] and [001] crystallographic directions, the values of ε_{11} are more than 10 times of dielectric constant along [001] crystallographic direction.

Dielectric loss displays an abnormal behavior in the ferroelectric phase. For $x=0.50$, 0.56 and 0.60, the values of dielectric loss at room temperature are around 0.5, and for the other two compositions, low values are found (~0.08). However, when the samples are in the paraelectric phase, the loss could decrease to a lower level.

3.3. Relaxor behavior

To describe “the diffuseness of the phase transition” of relaxor ferroelectrics, a modified Curie–Weiss law is adapted as [14]:

$$\frac{1}{\varepsilon}-\frac{1}{\varepsilon_m}=\frac{(T-T_m)^\gamma}{c'} \tag{1}$$

where c' is modified Curie–Weiss constant; ε_m is dielectric constant at Curie temperature; and γ is relaxor factor, $1\leq\gamma\leq2$,

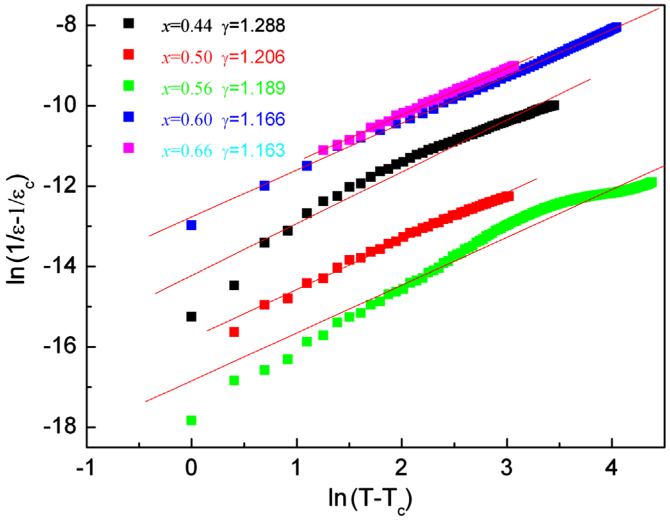

Fig. 3. Relaxor factors of the $K_{0.95}Li_{0.05}Ta_{1-x}Nb_xO_3$ single crystals.

when $\gamma=1$, the material is a kind of normal ferroelectric, when $\gamma=2$, it is a typical relaxor ferroelectric.

Relaxor factors of KLTN single crystals are shown in Fig. 3, and continuously decrease from 1.288 to 1.163 with the increase of niobium content. Thus, KLTN single crystal compositions have weak diffuse transition characteristics.

3.4. Tunability

Dielectric tunability was determined by finding the change in dielectric constant with an applied dc bias compared to those dielectric values under zero field at a given temperature, using [15,16]:

$$\text{tunability}(\%) = \frac{\varepsilon(E_0) - \varepsilon(E)}{\varepsilon(E_0)} \times 100\% \qquad (2)$$

where $E_0=0$ V/mm and E is the electric field at which we calculate the tunability.

The figure of merit (K factor) for tunable dielectric materials is defined as [13]

$$K\ \text{factor} = \frac{\varepsilon(E_0) - \varepsilon(E)}{\varepsilon(E_0)}(1/\tan\delta) \qquad (3)$$

$K_{0.95}Li_{0.05}Ta_{0.56}Nb_{0.44}O_3$ single crystal was employed for dielectric tunability measurement. The capacitance and loss were measured at four temperatures, which are 370 K, 400 K, 430 K and 450 K. At each equilibrium temperature, the electric field was applied in the following consecutive cycles, including (1) increasing from 0 to 200 V/mm, and (2) decreasing from 200 V/mm to 0. The dc field dependence of dielectric constant and loss at different temperatures is shown in Fig. 4.

As the Curie temperature is 330 K, $K_{0.95}Li_{0.05}Ta_{0.56}Nb_{0.44}O_3$ single crystal is in paraelectric state at those four temperatures. As the temperature is farther away from the Curie point, the dielectric tunability continuously increases. At the beginning of every equilibrium temperature, the tunability increases sharply with the increase of applied electric field, and then becomes roughly stable. The maximum value of dielectric tunability that occurred at 370 K is about 43%, while the electric field is 160 V/mm.

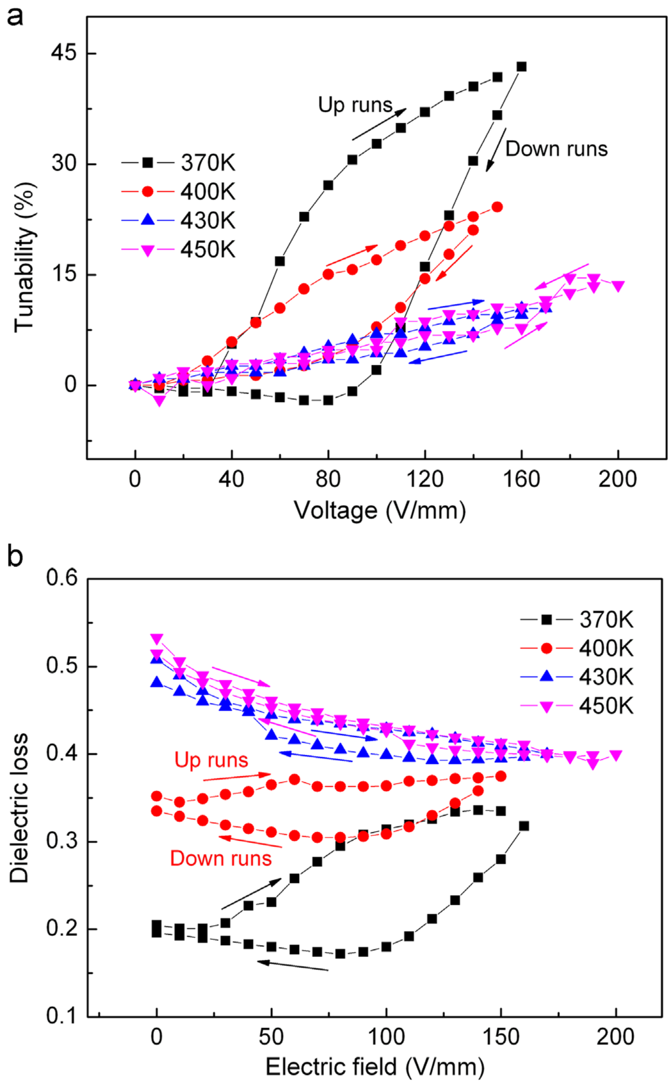

Fig. 4. (a) Dielectric tunability of $K_{0.95}Li_{0.05}Ta_{0.56}Nb_{0.44}O_3$ single crystal along [001] crystallographic direction, (b) dielectric loss of $K_{0.95}Li_{0.05}Ta_{0.56}Nb_{0.44}O_3$ single crystal along [001] direction as a function of electric field.

When $T=370$ K and $T=400$ K, dielectric loss increases to a stable value (designated as A) with the increase of electric field; When $T=430$ K and $T=450$ K, dielectric loss decreases to a stable value (designated as B) with the increase of electric field; the interesting thing is that these two stable values A and B are almost the same (~0.4). In other words, after loading voltage at different temperatures, dielectric loss approaches the same value. As the value of dielectric loss is relatively large, K factor was calculated to be 1.36.

4. Conclusion

The Li-doped $KTa_{1-x}Nb_xO_3$, i.e. $(K_{0.95}Li_{0.05})(Ta_{1-x}Nb_x)O_3$, with $x=0.44-0.66$ single crystals were grown using the top-seeded melt growth method. The lattice parameters a and b decrease (c increases) with the increase of niobium concentration. All transition temperatures increase with niobium content and the Curie temperatures adjust between 330 K and 480 K through an appropriate Ta/Nb ratio. Relaxor factors were determined by the modified Curie-Weiss law, and show weak diffuseness of phase transition. High dielectric tunability (~43%) is very attractive for $x=0.44$; however, the figure of merit (*K* factor) was calculated to be 1.36 due to relatively high dielectric loss with dc bias. Further studies on the performance improvements are in progress and the results will be reported in the forthcoming publications.

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