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Short communication

Thermal expansion behavior and polarization properties of lead-free ferroelectric potassium lithium tantalate niobate single crystals

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Abstract

Lead-free ferroelectric niobium-rich potassium lithium tantalate niobate $K_{0.95}Li_{0.05}Ta_{1-x}Nb_xO_3$ (KLTN) single crystals were grown by the top-seeded melt method. Thermal expansion properties of $K_{0.95}Li_{0.05}Ta_{1-x}Nb_xO_3$ ($x=0.78$, 0.69, 0.60, and 0.52) single crystals were investigated in the temperature range of 140 K–800 K using a dilatometer. According to the thermal expansion data, phase transition temperatures of all compositions were determined, and temperature dependence of local polarization was calculated. In addition, the results were discussed in combination with the composition and crystallographic orientation.

Keywords: C. Thermal expansion; D. Perovskites; Phase transitions

1. Introduction

Potassium tantalate niobate, $K(Ta,Nb)O_3$ (KTN), solid solution system has attracted considerable attention, owing to the rich diversity of electrical and optical properties and possible applications in various technological devices [1]. So far, most research work about KTN system is focusing on the tantalum-rich KTN side and mainly for their quadratic electrooptic effect [2], quantum ferroelectric behavior of $KTaO_3$ [3], photorefractive and holographic application of cubic KTN single crystal [4]. There are few investigations on niobium-rich KTN single crystals perhaps due to the difficulties in the high quality crystal growth. However, systematical characterization of room temperature ferroelectric KTN-series single crystals is very important and interesting. Large linear electro-optical effect [5], impressive piezoelectric performance [6], phase transitions [7] and polarization mechanism [8] of KTN family demand new investigations which facilitate further research work and accelerate commercial applications of KTN-series materials.

With slight lithium implantation, niobium-rich $K_{0.95}Li_{0.05}Ta_{1-x}Nb_xO_3$ ($x=0.78$, 0.69, 0.60, and 0.52) (KLTN) room temperature ferroelectric single crystals were grown using the top-seeded melt growth method. Their piezoelectric, ferroelectric, pyroelectric and linear electro-optical performances make KLTN solid solution a promising material for various electro-mechanical-optical coupled applications [9]. Thermal expansion that is related to square of the polarization in general can be used to investigate phase transition, anisotropic behavior and local polarization in material [10]. When temperature is above ferroelectric–paraelectric transition point, the deviation from its linear behavior of thermal strain can be used for many studies. For the relaxor-like behavior, local polarization exists even above the transition temperature while it disappears or is immeasurable above certain temperatures, namely Burns temperature [11]. Wang et al. [12] reported thermal properties of high Ta and cubic KTN system, but the results of high Nb, room temperature ferroelectrics KTN are scares.

In this work, we studied thermal expansion properties of Nb-rich KLTN solid solution single crystals. Thermal strain and thermal expansion coefficients were measured. The phase

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transition behaviors according to thermal expansion were determined from the abrupt discontinuity of experimental data. Local polarization behavior was also analyzed from the thermal expansion data. In order to qualitatively analyze the relation between thermal properties and Nb concentration, four $K_{0.95}Li_{0.05}Ta_{1-x}Nb_xO_3$ compositions with different Nb

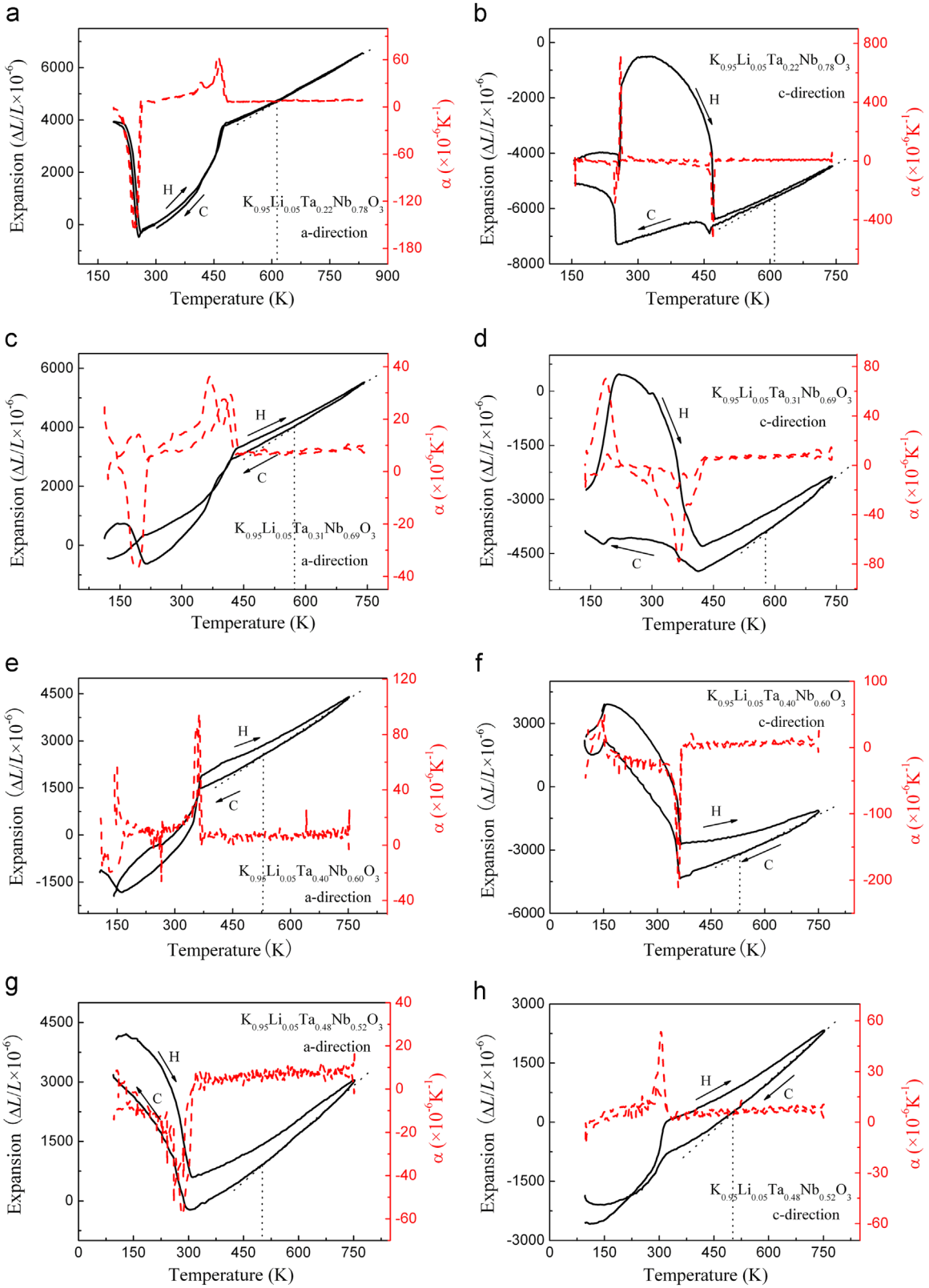

Fig. 1. Crystallographic orientation dependent thermal strain ($\Delta L/L_0$) and thermal expansion coefficients (α) of $K_{0.95}Li_{0.05}Ta_{1-x}Nb_xO_3$ crystals as a function of temperature: (a) *a*-direction for $x=0.78$; (b) *c*-direction for $x=0.78$; (c) *a*-direction for $x=0.69$; (d) *c*-direction for $x=0.69$; (e) *a*-direction for $x=0.60$; (f) *c*-direction for $x=0.60$; (g) *a*-direction for $x=0.52$ and (h) *c*-direction for $x=0.52$.

concentrations (x=0.78, 0.69, 0.60, and 0.52) were used in the experiments.

2. Experimental

$K_{0.95}Li_{0.05}Ta_{1-x}Nb_xO_3$ single crystals used in these investigations were grown using the top-seeded melt growth technique. By varying the Ta-to-Nb ratio, $K_{0.95}Li_{0.05}Ta_{1-x}Nb_xO_3$ solid solution exhibited a composition controlled phase transition temperature T_c between 13 K (x=0) and 700 K (x=1). Thus the crystal composition can be determined by using dielectric measurement data [13]. Four samples of $K_{0.95}Li_{0.05}Ta_{1-x}Nb_xO_3$, x=0.78, 0.69, 0.60, and 0.52, were cut to rectangular bar. Before thermal expansion measurements, all samples were poled along the [001] direction at 500 K, at an electric field of 350 V/mm, for 30 min. The samples were then slowly cooled down to room temperature under electric field.

In order to perform calibration and take into account thermal expansion of the measuring system, reference samples of fused silica were used. Samples with length and size close to those of the reference fused silica were placed inside a fused silica holder. Thermal expansion was measured with a linear voltage differential transformer (LVDT) dilatometer (Series 6500, theta industries, Inc., NY). The measurements were performed over 140 K and 800 K with heating and cooling rate of 2 °C/min [14]. Also, crystallographic orientation dependent thermal expansion measurements of KLTN crystals along the a- and c-direction were carried out. The LVDT has an advantage over other transformers as it gives a linear output for every unit displacement. Moreover, different from dielectric measurement, thermal expansion is related to DC frequency displacement response rather than high frequency dielectric response.

3. Results and discussion

3.1. Thermal expansion

The relationship of strain, thermal expansion and local polarization can be described by the equations below:

$$\alpha = \frac{\Delta L}{L_0}\frac{1}{\Delta T} \quad (1)$$

$$x_{ij} = \frac{\Delta L}{L_0} = Q_{ijkk}P_k{}^2 \quad (2)$$

where α is thermal expansion coefficient, $\Delta L/L_0$ and x_{ij} are thermal expansion strain, ΔT is small temperature change, Q_{ijkk} is quadratic electrostrictive coefficient and P_k represents polarization. Electrostrictive coefficients Q_{ijkk} are determined in paraelectric phase and considered constant for most of perovskite structure materials [15].

Crystallographic orientation dependent thermal strain and thermal expansion coefficient of $K_{0.95}Li_{0.05}Ta_{1-x}Nb_xO_3$ crystals as a function of temperature are presented in Fig. 1. The abrupt discontinuities of thermal strain at the phase transition for all compositions were clearly observed. Thermal strain and thermal expansion coefficient of KLTN crystals at room temperature are small, with a sharp change near phase transition temperature. From different thermal strain behaviors in Fig. 1, the almost zero polarization state temperature (T_0) can be defined. Below the zero polarization state temperature, thermal strain starts to deviate from the linear relationship. Thermal expansion coefficient, phase transition temperature and T_0 are summarized in Table 1. The values of T_0 are in the range from 500 K to 600 K and increase with Nb content. T_0 is much higher than ferroelectric–paraelectric transition temperature, and the difference between maxima transition temperature T_m and T_0 was found to decrease with increasing Nb concentration. Phase transition temperature (T_{O-T}) between ferroelectric tetragonal to orthorhombic phases can also be determined from thermal expansion strain below T_m for x=0.78, 0.69 and 0.60 compositions.

Fig. 2 shows thermal strains parallel and perpendicular to ferroelectric c-direction of $K_{0.95}Li_{0.05}Ta_{0.22}Nb_{0.78}O_3$ single crystal. For all four $K_{0.95}Li_{0.05}Ta_{1-x}Nb_xO_3$ crystal compositions, x=0.78, 0.69, 0.60, and 0.52, phase transition

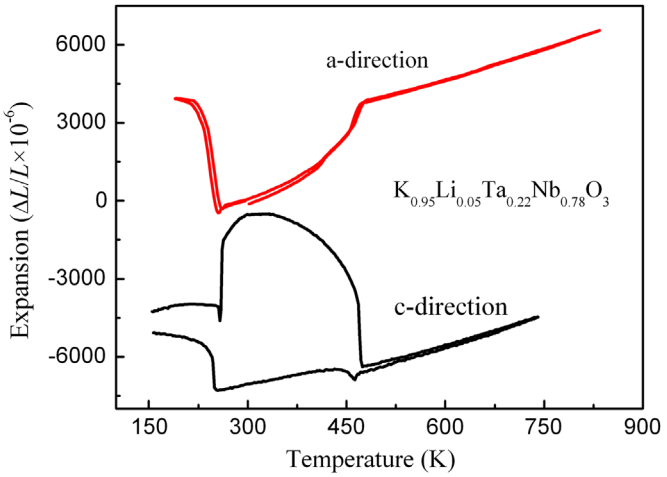

Fig. 2. Thermal expansion ($\Delta L/L_0$) results along the a- and c-direction for $K_{0.95}Li_{0.05}Ta_{0.22}Nb_{0.78}O_3$.

Table 1
Parameters derived from the thermal expansion measurement of the $K_{0.95}Li_{0.05}Ta_{1-x}Nb_xO_3$ single crystals.

Composition	T_m (K)	T_0 (K)	T_0-T_m (K)	T_{O-T} (K)	α, c-direction ($\times 10^{-6}$ K^{-1})	P_d@RT (μC/cm^2)	P_s@RT (μC/cm^2)[a]
$K_{0.95}Li_{0.05}Ta_{0.22}Nb_{0.78}O_3$	465	613	148	244	3.22	27.5	8
$K_{0.95}Li_{0.05}Ta_{0.31}Nb_{0.69}O_3$	417	573	156	192	4.27	23.1	5
$K_{0.95}Li_{0.05}Ta_{0.40}Nb_{0.60}O_3$	358	529	171	148	4.83	21.8	4
$K_{0.95}Li_{0.05}Ta_{0.48}Nb_{0.52}O_3$	305	499	194	–	3.37	5.8	–

[a]From pyroelectric measurements.

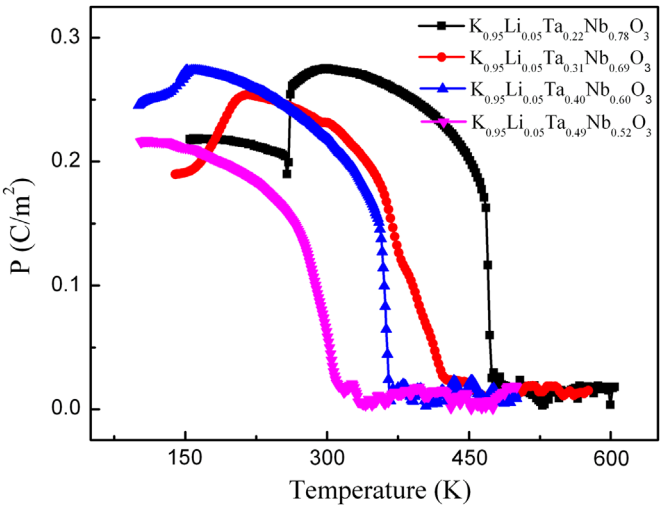

Fig. 3. Calculated total polarization (P_d) as a function of temperature for the KLTN single crystals.

temperatures exactly match as both the *a*- and *c*-direction expansion measurements results.

3.2. Polarization properties

Local polarization P_d was obtained at various temperatures by analyzing the strain deviation from high temperature linear behavior and using Eq. (2). However, due to the much larger strain along the poled *c*-direction, we put more emphasis on these data rather than that perpendicular to the *c*-axis. To estimate P_d, the expression $\Delta L/L_0 = Q_{11}P^2$ has been used to calculate the total P, i.e. $((P^2)^{1/2})$. Using the typical values of perovskite structure, $Q_{11} = 9.5 \times 10^{-2}$ m^4/C^2 and $Q_{12} = -3.1 \times 10^{-2}$ m^4/C^2 [16], for $K_{0.95}Li_{0.05}Ta_{1-x}Nb_xO_3$ crystals, $x = 0.78$, 0.69, 0.60, and 0.52, P_d values were calculated and are shown in Fig. 3. The spontaneous polarization, P_s, determined from pyroelectric measurement is also shown in Table 1. The results indicate that the value of the local polarization increases with increasing Nb concentration in the compositions and the abrupt discontinuity of polarization curve points out the nature of the transition.

4. Conclusion

Thermal expansion properties of $K_{0.95}Li_{0.05}Ta_{1-x}Nb_xO_3$ (KLTN), $x = 0.78$, 0.69, 0.60, and 0.52, single crystals were studied over 140 K–800 K. It was found that thermal expansion exhibited a linear relation with temperature above T_m, and showed deviation below T_0, ranging from 500 K to 600 K, depending on Nb concentrations. T_0 was higher than ferroelectric–paraelectric transition temperature in all compositions. The temperature difference between T_m and T_0 decreased with the decrease of Nb concentration. Total local polarization calculated from the thermal expansion data increased with increasing Nb content. The results suggested possible contributions to the polarization from other sources in the crystals, which could be related to a small inhomogeneous composition distribution on the micro to nanoscale.

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References

[1] D. Fluck, R. Gutmann, P. Günter, R.J. Irmsc, Optical waveguides in $KTa_{1-x}Nb_xO_3$ produced by He ion implantation, Applied Physics 70 (1991) 5147–5149.
[2] S. Riehemann, D. Sabbert, S. Loheide, Holographic double-exposure interferometry with tetragonal $KTa_{1-x}Nb_xO_3$: Fe crystals, Optical Materials 4 (1995) 437–440.
[3] U.T. Höchli, L.A. Boatner, Quantum ferroelectricity in $K_{1-x}Na_xTaO_3$ and $KTa_{1-y}Nb_yO_3$, Physical Review B 20 (1979) 266–275.
[4] F.S. Chen, A Laser-Induced, Inhomogeneity of refractive indices in KTN, Journal of Applied Physics 38 (1967) 3418–3420.
[5] W. Haas, R. Johannes, Linear electrooptic effect in KTN crystals, Applied Optics 6 (1967) 2007–2009.
[6] J. Li, Y. Li, Z.X. Zhou, R.Y. Guo, A.S. Bhalla, Electrical properties of lead-free niobium rich piezoelectric $(K_{0.95}Li_{0.05})(Ta_{1-x}Nb_x)O_3$ single crystals, Integrated Ferroelectrics 130 (2011) 65–72.
[7] D. Rytz, A. Chatelain, Elastic properties in quantum ferroelectric $KTa_{1-x}Nb_xO_3$, Physical Review B. 27 (1983) 6830–6840.
[8] J. Toulouse, X.P. Wang, L.A. Knauss, L.A. Boatner, Dielectric nonlinearity and spontaneous polarization of $KTa_{1-x}Nb_xO_3$ in the different transition range, Physical Review B 43 (1991) 8297–8302.
[9] Y. Li, J. Li, Z.X. Zhou, R.Y. Guo, A.S. Bhalla, Frequency dependent electro-optic properties of potassium lithium tantalate niobate single crystal, Ferroelectrics 425 (2011) 82–89.
[10] A.S. Bhalla, R.Y. Guo, L.E. Cross, G. Burns, F.H. Dacol, Measurements of strain and the optical indices in the ferroelectric $Ba_{0.4}Sr_{0.6}Nb_2O_6$: polarization effects, Physical Review B 36 (1987) 2030–2035.
[11] G. Burns, F.H. Dacol, Crystalline ferroelectrics with glassy polarization behavior, Physical Review B 28 (1983) 2527–2530.
[12] X.P. Wang, J.Y. Wang, H.J. Zhang, Thermal properties of cubic $KTa_{1-x}Nb_xO_3$ crystals, Journal of Applied Physics (2008) 103033513.
[13] Y. Li, J. Li, Z.X. Zhou, R.Y. Guo, A.S. Bhalla, Low-frequency-dependent electro-optic properties of potassium lithium tantalate niobate single crystals, Europhysics Letter 102 (2013) 37004.
[14] M. Unruan, A. Prasatkhetragarn, Y. Laosiritaworn, R.Y. Guo, A. S. Bhalla, Thermal expansion behavior and estimated total polarizations of lead zirconate titanate–lead nickel niobate ceramics, Materials Letters 64 (2010) 1960–1963.
[15] R. Wongmaneerung, R.Y. Guo, A.S. Bhalla, R. Yimnirun, S. Ananta, Thermal expansion properties of PMN–PT ceramics, Journal of Alloys and Compounds 461 (2008) 565–569.
[16] K. Uchino, S. Nomura, L.E. Cross, R.E. Newnham, Electrostrictive effects in potassium tantalate niobate, Ferroelectrics 38 (1981) 825–828.