

Combined effects of Li content and sintering temperature on polymorphic phase boundary and electrical properties of Li/Ta co-doped (Na, K)NbO₃ lead-free piezoceramics

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Abstract Crystallographic structure, phase transition and electrical properties of lead-free (Na_{0.535}K_{0.485})_{1-x}Li_x(Nb_{0.942}Ta_{0.058})O₃ ($x = 0.042$ – 0.098) (NKL_xNT) piezoelectric ceramics were investigated. The experimental results show that both Li content and sintering temperature strongly affect the orthorhombic–tetragonal polymorphic phase boundary (PPB), which results in remarkable differences of the piezoelectric property and its temperature stability in the NKL_xNT ceramics. Chemical analysis indicates that sodium volatilizes more seriously than potassium and lithium with increasing sintering temperature. Due to the comprehensively optimized effects of Li content and sintering temperature, an enhanced piezoelectric constant d_{33} (276 pC/N) was obtained at room temperature in the ceramics with $x = 0.074$ sintered at 1000°C. In the same composition, a further high d_{33} up to 354 pC/N was obtained at 43°C, which is close to its T_{0-t} temperature. Furthermore, better temperature stability can be obtained when $x = 0.082$ sintered at 1000°C, whose piezoelectric constant d_{33} (236 pC/N) keeps almost constant from room temperature to 100°C. Such a temperature-independent piezoelectric property is available in the NKL_xNT ceramics with high Li content because its T_{0-t} was moved below room temperature.

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1 Introduction

Conventional lead-based piezoelectric ceramics such as Pb(Zr_xTi_{1-x})O₃ (PZT) are widely used in sensors and actuators due to their excellent piezoelectric properties [1]. However, because of high toxicity of Pb element, environmental and safety concerns with respect to the utilization, recycling, and disposal of lead-based piezoelectric ceramics have induced a new surge in developing lead-free piezoelectric ceramics [2–9].

Recently, much attention for lead-free piezoelectric ceramics has mainly focused on (Na, K)NbO₃ (NKN)-based ceramics because the excellent piezoelectric properties are discovered in textured Li-, Ta-, and Sb-modified (Na,K)NbO₃ ceramics by Y. Saito et al. [2]. In NKN-based ceramics, recent studies revealed that the orthorhombic–tetragonal polymorphic phase boundary (PPB) strongly affects its piezoelectric properties [8, 9], and a coexistence of the orthorhombic and tetragonal phases, i.e. a PPB, near room temperature, rather than the formation of the morphotropic phase boundary (MPB) similar to that observed in the PZT system [10], would be helpful to obtain enhanced piezoelectric properties. Meanwhile, according to previous work [9], although high d_{33} value can be obtained using Sb ion on the pentavalent sites of the perovskite lattice, it is preferable to avoid the use of toxic Sb element for health and environmental reasons. Therefore, the piezoelectric properties of Li- and Ta-modified NKN ceramics are themselves sufficient to arouse keen interest in further developing alkali niobate tantalates as a viable lead-free alternative piezoelectric ceramics.

Among reported Li- and Ta-modified NKN ceramics, owing to the shift of the T_{0-t} to near-room temperature, the enhancement of piezoelectric properties can be obtained [11].

However, associated with a PPB, an issue of property instability against temperature increases the difficulty for applications [8]. Besides this issue, there are also several points of limitations existing. Firstly, these ceramics contain a large amount of Ta element (≥ 10 mol%), and adding large amounts of Ta to NKN ceramics will limit the applications of these materials because the price of Ta_2O_5 is much more high than that of Nb_2O_5 . Secondly, in order to improve stability, while maintaining high piezoelectric properties, it is desirable to shift the T_{0-t} out of the application temperature range (usually -50 – 200°C), but unfortunately, in Li- and Ta-modified NKN ceramics as usual, further shifting of the T_{0-t} downward below room temperature cannot be achieved owing to solubility limitations (6–8%), where excessive additions lead to undesirable second phases, thus deteriorating their properties [12]. Finally, the sintering temperature of these ceramics is usually higher than 1070°C , and this high sintering temperature accelerates the volatilization of Na_2O [13], so that impurity phase such as $\text{K}_3\text{Li}_2\text{Nb}_5\text{O}_{15}$ [12], which prevents parts of Li from entering the perovskite lattice, can be more easily formed. Actually, low sintering temperature is favorable for increasing Li doping amount, and this is confirmed by our recent work [14].

In this work, we prepared Li- and Ta-modified NKN lead-free ceramics, i.e. $(\text{Na}_{0.535}\text{K}_{0.485})_{1-x}\text{Li}_x(\text{Nb}_{0.942}\text{Ta}_{0.058})\text{O}_3$ (NKL_xNT), by the conventional solid-state sintering method, where no undesirable second phases are observed even for Li doping amount up to 0.098. In the NKL_xNT ceramics with Li content $x = 0.082$ sintered at 1000°C , because its T_{0-t} temperature is moved below room temperature, we obtained a relatively high piezoelectric constant d_{33} (236 pC/N), which is nearly temperature-independent from room temperature to 100°C . It should be noted here that the Ta content is fixed at 0.058 because a small amounts of Ta are beneficial to improve sintering behavior and cannot increase the sintering temperature excessively. Meanwhile, through optimizing the added amounts of sodium and potassium, Na:K ratio is fixed at 0.535:0.485. Our investigations of this study are mainly focused on the combined effects of Li content and sintering temperature on the crystallographic structure, phase transition and electrical properties of NKL_xNT ceramics.

2 Experimental

$(\text{Na}_{0.535}\text{K}_{0.485})_{1-x}\text{Li}_x(\text{Nb}_{0.942}\text{Ta}_{0.058})\text{O}_3$ ceramics, where $x = 0.042$ – 0.098 , were prepared by a conventional ceramic fabrication method using reagent grade Na_2CO_3 , K_2CO_3 , Li_2CO_3 , Nb_2O_5 , and Ta_2O_5 as starting materials. For each composition, the starting materials were weighed according to the stoichiometric formula and ball milled for 24 h in ethanol using ZrO_2 balls. After separating the balls, the slurries were dried and calcined at 750°C for 5 h, and then ball

milled again for 24 h and dried. Without any special treatment, the powders were subsequently pre-pressed to pellets 15 mm in diameter, followed by a cold isostatic pressing (CIP) under 200 MPa. Using a heating rate of $10^\circ\text{C}/\text{min}$, sintering was carried out at 980 – 1060°C for 2 h in air. Bulk densities of sintered pellets were measured using the Archimedes method. X-ray diffraction (XRD) characterization of the ceramics was performed using $\text{Cu } K\alpha_1$ radiation ($\lambda = 1.5406 \text{ \AA}$) filter through Ni foil. Inductively Coupled Plasma (ICP) method was used to detect sodium, potassium and lithium contents in the final ceramic bodies, and the distribution of chemical elements in microscale regions were analyzed using Energy Dispersive Spectrometer (EDS) after the sample surfaces were polished to a mirror-like face.

For electrical characterization, ceramic samples were polished and painted with silver paste on both sides. Dielectric constants at 100 kHz of the ceramics were measured as a function of temperature using an Agilent 4294A precision impedance analyzer. For piezoelectric and electromechanical measurements, the ceramic samples were poled at 120°C for 30 min under an electric field of 3 kV/mm in silicone oil. The piezoelectric constant d_{33} was measured using a quasi-static piezoelectric constant testing meter (ZJ-3A, Institute of Acoustics, Chinese Academy of Science, Beijing, China). The planar mode electromechanical coupling factor k_p was determined by a resonance and antiresonance methods performed on the basis of IEEE standards using an impedance analyzer (Agilent 4294A). The polarization–electric field (P – E) hysteresis loop was measured by a Radiant Precision workstation based on a standard Sawyer–Tower circuit at room temperature.

3 Results and discussion

Figure 1 shows the bulk densities of the NKL_xNT ceramics with $x = 0.042$, 0.066, 0.074 and 0.090 sintered at different temperatures. Ranging over different x values in the NKL_xNT ceramics (some compositions are not shown in Fig. 1), the sintering temperatures corresponding to the highest bulk density are 1040°C , 1000°C and 980°C , respectively for the Li contents $x = 0.042$, $x = 0.050$ – 0.082 and $x = 0.090$ – 0.098 . High Li content x is in favor of obtaining the highest bulk density at low sintering temperatures. Actually, Li_2O itself is a good sintering aid on the purpose of reducing sintering temperature for the preparation of piezoelectric ceramics [15, 16]. For each composition, the bulk density, after reaching the peak value, decreases gradually with increasing sintering temperature owing to the volatilization of alkali metal ions [17].

Figure 2a shows the XRD patterns of the NKL_xNT ceramics with $x = 0.074$ sintered at 980 – 1040°C . The enlarged XRD patterns of the ceramics in the ranges of 2θ

from 30° to 33° and from 44° to 47° are shown in Fig. 2b and c, respectively. As shown in Fig. 2b, only one peak can be seen when the ceramics were sintered at $980\text{--}1000^\circ\text{C}$, while a shoulder peak is attached onto its right side when sintered above 1020°C . Meanwhile, according to Fig. 2c, when the sintering temperature exceeds 1020°C , the (002) and (200) peaks apparently split. All these characteristics demonstrate the coexistence of orthorhombic and tetragonal phases in the ceramics sintered at $980\text{--}1000^\circ\text{C}$, while the tetragonal phase becomes dominant when sintered above 1020°C . In our previous studies [13, 18], this kind of temperature dependence of phase structure transition behavior was also found, and we attributed it to the different extents of the volatilization of alkali metal ions during sintering at different temperatures. In this study, we detected sodium, potassium and lithium contents of the NKL_xNT ceramics

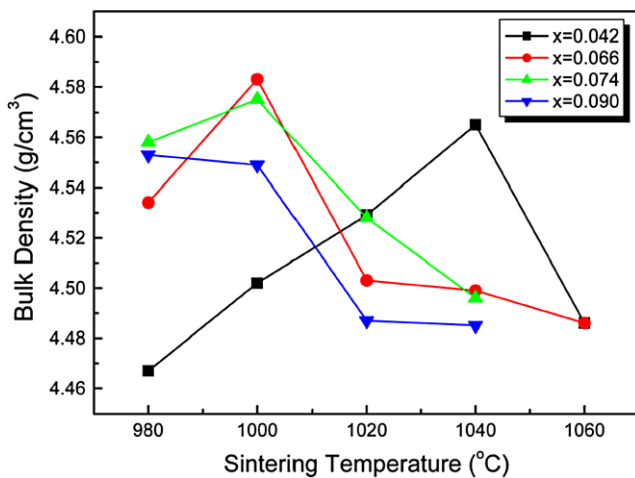
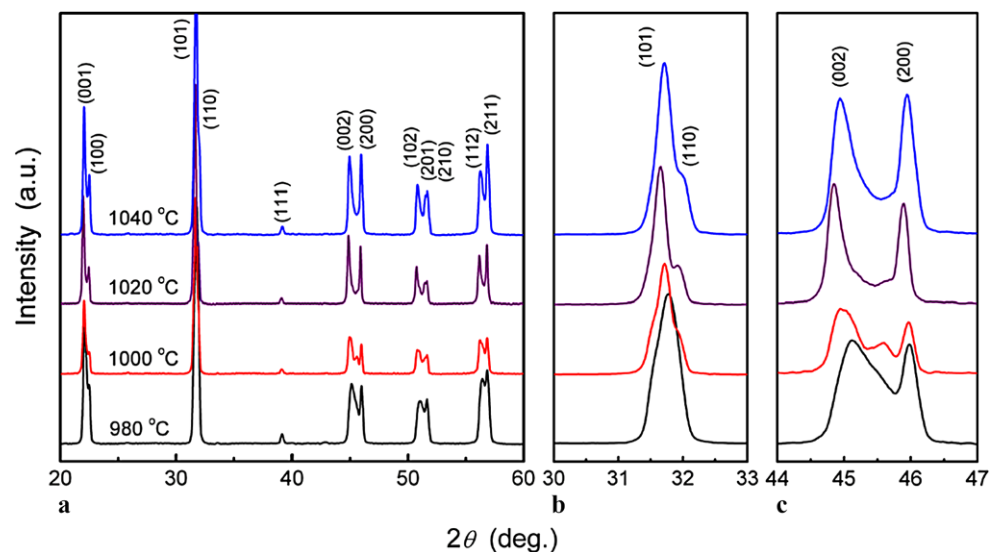


Fig. 1 Bulk densities of the NKL_xNT ceramics with $x = 0.042, 0.066, 0.074$ and 0.090 sintered at different temperatures

Fig. 2 X-ray diffraction patterns of the NKL_xNT ceramics with $x = 0.074$ sintered at $980\text{--}1040^\circ\text{C}$ in the ranges of 2θ **a** from 20° to 60° , **b** from 30° to 33° , and **c** from 44° to 47°



with $x = 0.074$ sintered at $980\text{--}1060^\circ\text{C}$ using ICP method. The results of chemical analysis are shown in Table 1.

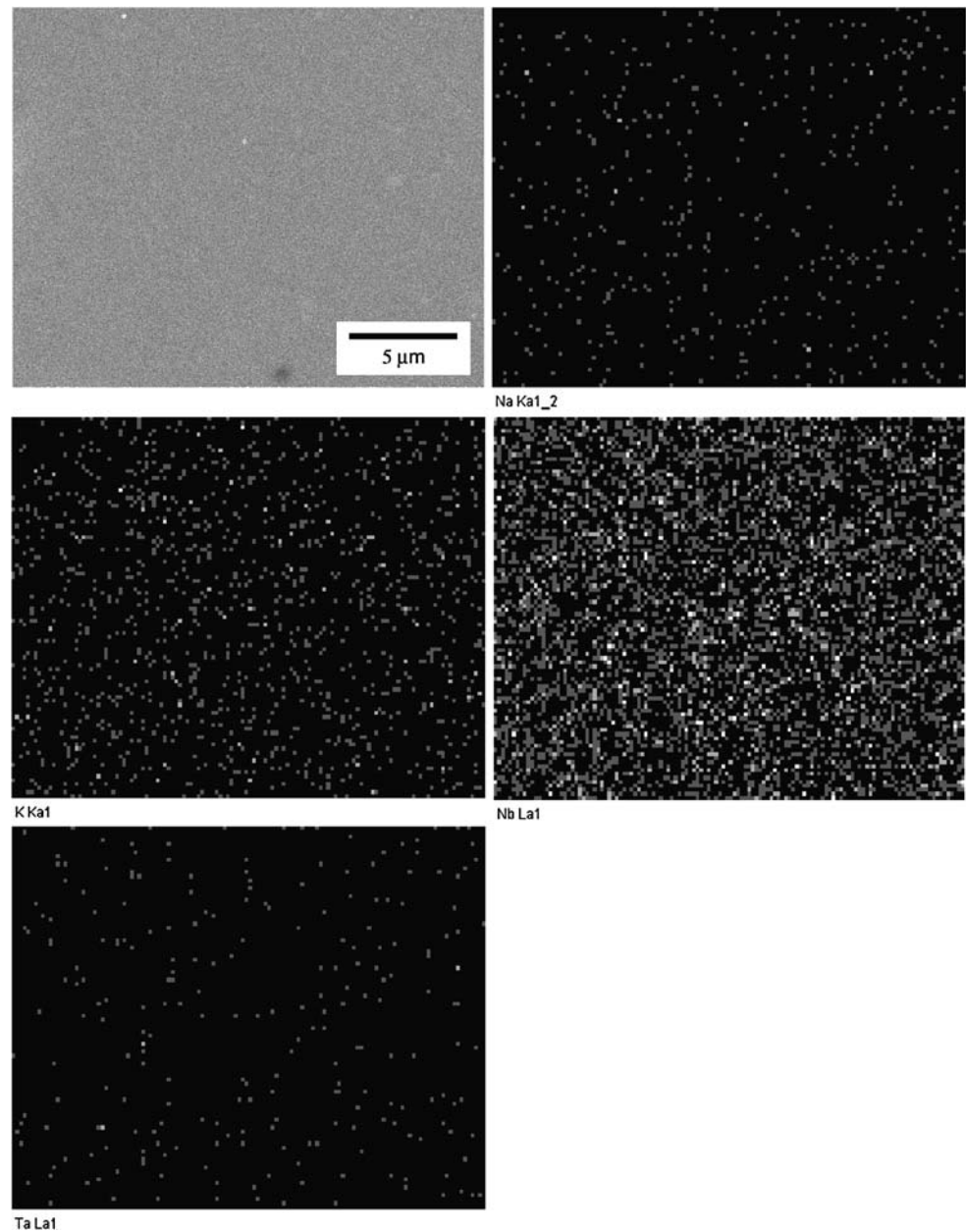
As can be seen from Table 1, when the sintering temperature is 980°C , the volatilization of alkali metal ions is slight compared with calculated values according to the stoichiometric composition. However, when the sintering temperature was over 1000°C , extents of the volatilization of alkali metal ions different from the results listed in Table 1 are observed. Especially, with increasing sintering temperature, sodium volatilizes more seriously than potassium and lithium. In addition, as a selected sample, the distribution of chemical elements of the NKL_xNT ceramics with $x = 0.074$ sintered at 1000°C is shown in Fig. 3. Although lithium cannot be analyzed by EDS, the homogeneous distribution of sodium, potassium, niobium and tantalum, as shown in Fig. 3, indicates that lithium should be also distributed homogeneously in the ceramic bodies.

Since the sintering temperature can apparently affect the volatilization of alkali metal ions, and then the phase structure transition behavior, it is achievable for the NKL_xNT ceramics with different Li contents to figure out a corresponding right sintering temperature where the orthorhombic and tetragonal phases can coexist. The phase structure of the NKL_xNT ceramics with various Li contents x sintered at different temperatures is shown in Table 2. For a given sintering temperature, with increasing Li content x , the phase structure changes from the orthorhombic to the tetragonal, across a region where the coexistence of the orthorhombic and tetragonal phases occurs. Meanwhile, when the Li content x is high, the coexistence of the orthorhombic and the tetragonal phases will occur at a relative low sintering temperature.

Picking out the NKL_xNT ceramics with different Li content x sintered at 1000°C , the lattice parameters were calculated by fitting the XRD profiles, as shown in Fig. 4. The

Table 1 ICP chemical analysis results of Na, K, and Li elements in the NKL_xNT ceramics with $x = 0.074$ sintered at 980–1060°C

Element	Before sintering	After sintering at different temperatures (°C)				
		980	1000	1020	1040	1060
Na (mg/g)	64.91	64.88	62.67	62.55	60.95	60.73
K (mg/g)	100.069	100.02	99.98	98.98	98.92	99.16
Li (mg/g)	2.927	2.919	2.903	2.894	2.79	2.756

Fig. 3 Distribution of chemical elements of the NKL_xNT ceramics with $x = 0.074$ sintered at 1000°C

ceramics show the orthorhombic symmetry when $x \leq 0.066$, but change to the tetragonal phases when $x \geq 0.082$. Apparently, there is a transition zone between the orthorhombic and the tetragonal phases in the range of $0.066 < x < 0.082$.

Figure 5 shows the piezoelectric constant d_{33} and the planar electromechanical coefficient k_p of the NKL_xNT ceramics sintered at 1000 and 1020°C. As can be seen from Fig. 5, d_{33} and k_p show a strong dependence on the Li con-

Table 2 The phase structure of the NKL_xNT ceramics with various Li contents x sintered at different temperatures

Sintering temperature (°C)	Li content x							
	0.042	0.050	0.058	0.066	0.074	0.082	0.090	0.098
	Phase structure							
980	<i>O</i>	<i>O</i>	<i>O</i>	<i>O</i>	<i>O-T</i>	<i>O-T</i>	<i>T</i>	<i>T</i>
1000	<i>O</i>	<i>O</i>	<i>O</i>	<i>O</i>	<i>O-T</i>	<i>T</i>	<i>T</i>	<i>T</i>
1020	<i>O</i>	<i>O</i>	<i>O</i>	<i>O-T</i>	<i>T</i>	<i>T</i>	<i>T</i>	<i>T</i>
1040	<i>O</i>	<i>O</i>	<i>O-T</i>	<i>T</i>	<i>T</i>	<i>T</i>	<i>T</i>	<i>T</i>
1060	<i>O</i>	<i>O-T</i>	<i>T</i>	<i>T</i>	<i>T</i>	<i>T</i>	<i>T</i>	<i>T</i>

Notes: *O*: Orthorhombic phase, *T*: Tetragonal phase, *O-T*: Coexistence of the orthorhombic and the tetragonal phases

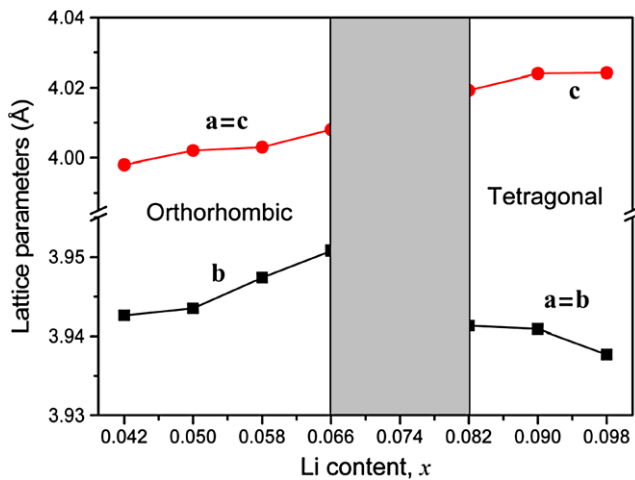


Fig. 4 Lattice parameters of the NKL_xNT ceramics sintered at 1000°C as a function of Li content x

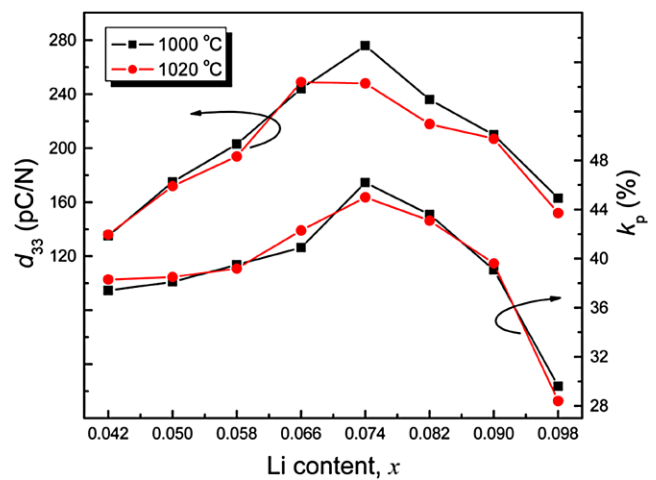


Fig. 5 Piezoelectric constant d_{33} and planar electromechanical coefficient k_p of the NKL_xNT ceramics sintered at 1000 and 1020°C

tent x , and the NKL_xNT ceramics possess relatively good performances in the range of $0.066 < x < 0.082$. Moreover, within the same x range, the sintering temperature can effectively affect the d_{33} value. For example, the maximum d_{33} values— 249 pC/N and 236 pC/N —are obtained for $x = 0.066$ sintered at 1020°C and $x = 0.082$ sintered at 1000°C , respectively. Particularly, through comprehensively optimized effects of Li content and sintering temperature, a maximum d_{33} value of 276 pC/N was obtained for $x = 0.074$ sintered at 1000°C , and this value is fairly high for the Li- and Ta-modified NKN ceramics with Sb doping [19]. The highest d_{33} value should be attributed to the coexistence of the orthorhombic and tetragonal phases near room temperature, as shown in Table 2 and Fig. 4. Relatively similar to the variation behavior of d_{33} , k_p reaches its maximum value of 46.2% for $x = 0.074$ sintered at 1000°C . In addition, maximum k_p values— 42.3% and 43.6% —are obtained for $x = 0.066$ sintered at 1020°C and $x = 0.082$ sintered at 1000°C , respectively.

Figure 6 shows the piezoelectric constant d_{33} values of several specimens as a function of measuring temperature. For $x = 0.074$ sintered at 1000°C , the highest d_{33} value of

276 pC/N is obtained at room temperature, even though a d_{33} value of 354 pC/N is obtained when the measuring temperature shifts to 43°C , but it shows a strong temperature dependence from room temperature to 100°C . Moreover, this temperature dependence characterization of d_{33} value is also observed for ceramics with $x = 0.066$ and 0.074 sintered at 1020°C . However, for the $x = 0.082$ composition sintered at 1000°C , in spite of its relatively low d_{33} value of 236 pC/N as compared with some specimens in this study, exhibits nearly temperature-independent properties from room temperature to 100°C . The d_{33} value of 236 pC/N is higher than 200 pC/N reported recently by Zhang et al. in CaTiO_3 -modified $\text{K}_{0.5}\text{Na}_{0.5}\text{NbO}_3$ -based lead-free ceramics [20], which also exhibits nearly temperature-independent properties. Actually, Zhang et al. obtained a tetragonal phase at room temperature in $\text{K}_{0.5}\text{Na}_{0.5}\text{NbO}_3$ -based ceramics modified by CaTiO_3 [20], i.e., T_{o-t} shifts downward to below room temperature. From this point of view, we present an easier way to obtain tetragonal phase at room temperature in NKN-based ceramics in the condition of high Li doping amount and low temperature sintering.

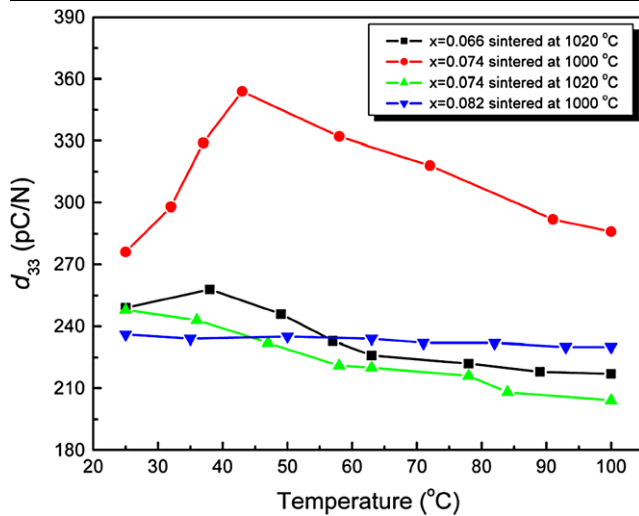


Fig. 6 Temperature dependence of piezoelectric constant d_{33} of NKL_xNT ceramics with $x = 0.066$ sintered at 1020°C , $x = 0.074$ sintered at 1000 and 1020°C , and $x = 0.082$ sintered at 1000°C

Figure 7 shows the temperature dependence of dielectric constant of NKL_xNT ceramics with $x = 0.058, 0.066, 0.074, 0.082$ and 0.090 sintered at 1000°C , the measuring frequency being 100 kHz . As shown in Fig. 7, the temperature dependence of dielectric constant of the NKL_xNT ceramics shows two phase transitions, i.e., a Curie temperature T_c and a polymorphic orthorhombic–tetragonal phase transition temperature T_{o-t} . The corresponding T_c and T_{o-t} for $x = 0.058$ are 425°C and 125°C , respectively. With increasing Li content x , the T_c slightly shifts to higher temperatures while T_{o-t} shifts to lower temperatures. Moreover, the T_{o-t} shifts downward to below room temperature when the x value is higher than 0.082 , which can be clearly seen by the inset in Fig. 7, and this is in agreement with the analysis results shown in Table 2. For the $x = 0.082$ composition sintered at 1000°C , due to its T_{o-t} shifts downward to below room temperature, the d_{33} value, as shown in Fig. 6, is nearly temperature-independent from room temperature to 100°C . According to the combined results of Figs. 6 and 7, the orthorhombic–tetragonal polymorphic phase transition temperature T_{o-t} is crucial to affect the property of temperature stability. If the T_{o-t} shifts downward to near room temperature, it is in favor of obtaining higher piezoelectric constant, but the temperature stability is poor. While the T_{o-t} shifts downward to a lower than room temperature, a good property of temperature stability can be obtained. The NKL_xNT ceramics with $x = 0.082$ possess a good temperature stability and a high T_c of 445°C , which is a potential Pb-free candidate for the replacement of PZT ceramics.

In order to study the effect of Li content on the ferroelectric properties, the P – E hysteresis loops of the NKL_xNT ceramics as a function of x were measured at room temperature. Figure 8a shows the P – E hysteresis loops of NKL_xNT

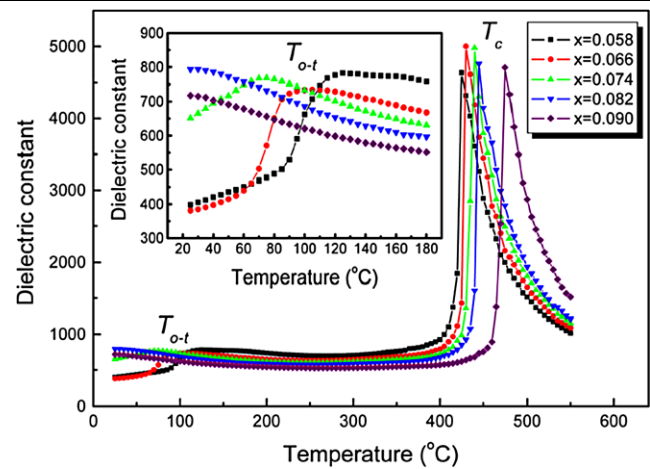


Fig. 7 Temperature dependence of dielectric constant of NKL_xNT ceramics with $x = 0.058, 0.066, 0.074, 0.082$ and 0.090 sintered at 1000°C . Measurement was performed at 100 kHz under the heating process. The inset shows an expanded view from room temperature to 180°C

ceramics with $x = 0.050, 0.058, 0.074, 0.082$, and 0.098 sintered at 1000°C , while the variations of the remnant polarization P_r and coercive field E_c with x are shown in Fig. 8b. A large remnant polarization ($P_r = 36.6\ \mu\text{C}/\text{cm}^2$) and low coercive field ($E_c = 1.47\ \text{kV}/\text{mm}$) are obtained when Li content x is 0.050 . With increasing Li content x , the remnant polarization P_r decreases while coercive field E_c approximately increases. Meanwhile, as shown in Fig. 8a, when $x > 0.074$, although the P – E loops become non-typical, we consider that these P – E loops without saturation are different from those with a round shape due to significant current leakage [21]. The present two P – E loops without saturation should not be induced by the loss derived from leakage currents, because the dielectric loss (at 1 kHz) of all NKL_xNT ceramics is lower than 0.05 . In addition to a strong coercive field obtained in the compositions with $x > 0.074$, as shown in Fig. 8b, these P – E loops without saturation should be attributed to the weakening ferroelectricity of the ceramics induced by high Li content doping. In other words, the decrease in P_r suggests that increasing x would weaken the ferroelectricity of the ceramics.

4 Conclusions

Lead-free $(\text{Na}_{0.535}\text{K}_{0.485})_{1-x}\text{Li}_x(\text{Nb}_{0.942}\text{Ta}_{0.058})\text{O}_3$ piezoelectric ceramics are prepared by the conventional solid-state reaction and normal sintering processes. The combined effects of Li content and sintering temperature on the crystallographic structure, phase transition and electrical properties, were studied. Through modifying composition and optimizing sintering temperature, the room temperature piezoelectric constant d_{33} is enhanced to $276\ \text{pC}/\text{N}$ for the ceramics with $x = 0.074$ sintered at 1000°C , and the d_{33} value

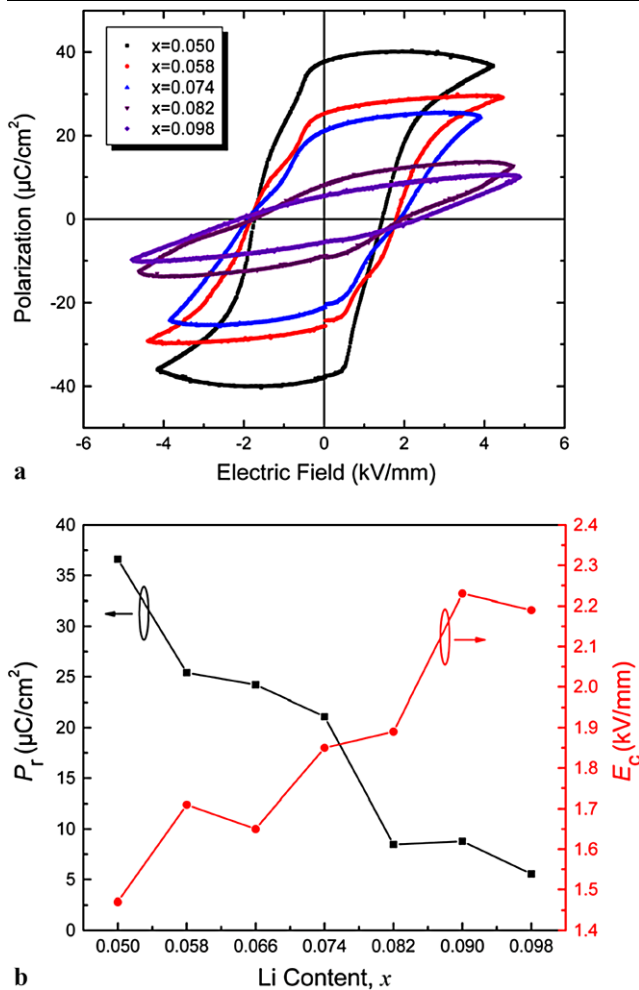


Fig. 8 **a** P - E hysteresis loops of NKL_{*x*}NT ceramics with $x = 0.050, 0.058, 0.074, 0.082$ and 0.098 sintered at 1000°C . **b** Remnant polarization and coercive field of the NKL_{*x*}NT ceramics sintered at 1000°C as a function of x

even increases to 354 pC/N when the measuring temperature shifts to 43°C , which is close to its $T_{\text{o-t}}$ temperature. Furthermore, a relatively high piezoelectric constant d_{33} (236 pC/N), which is nearly temperature-independent

from room temperature to 100°C , is obtained for the ceramics with $x = 0.082$ sintered at 1000°C because its $T_{\text{o-t}}$ temperature is moved below room temperature. The present NKL_{*x*}NT ceramics with $x = 0.082$ are considered to be a very promising lead-free piezoelectric material for practical applications because of its low sintering temperature and good piezoelectric property stability.

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