

Phase transition and domain variation contributions to piezoelectric properties of alkaline niobate based lead-free systems

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Abstract The intrinsic correlation and mechanism between electrical properties and phase transitions in alkaline niobate based lead-free piezoelectric ceramics were explored by taking typical $(\text{Na}_{0.52}\text{K}_{0.48-x})(\text{Nb}_{0.95-x}\text{Ta}_{0.05})\text{O}_3-x\text{LiSbO}_3$ compositions as a case study. The diffuseness of the phase transition leads to two-phase coexistence promoting piezoelectric activity and simultaneously induces remarkable temperature sensitivity, based on the variation of orthorhombic and tetragonal domains. The polymorphism, not a morphotropism of the phase boundary was considered as a structural root for these kinds of compositions. The refinement of compositions within two-phase coexistence zone compromises two opposite effects, although the composition range is narrow, suggesting the property sensitivity to the composition and a processing solution to the property optimization as well.

1 Introduction

The morphotropic phase boundary (MPB) between two orthorhombic ferroelectric phases is formed in $(\text{Na}_{0.5}\text{K}_{0.5})\text{NbO}_3$ (NKN) [1], near which the material exhibits good dielectric, piezoelectric and electromechanical properties together with high Curie temperatures (T_c , ~ 420 °C).

Moreover, there exists a polymorphic phase transition (PPT) between orthorhombic and tetragonal phases at ~ 200 °C in pure NKN, which made a difference between MPB NKN and other MPB piezoelectric systems, such as $\text{Pb}(\text{Zr}, \text{Ti})\text{O}_3$ (PZT). The reason is that the poled NKN samples may suffer from the loss of part of oriented domains or polarization vectors when heated or cooled across PPT. The same problems were transplanted into the (Li, Ta, Sb) modified NKN compositions because enhanced piezoelectric and electromechanical properties in these compositions are predominantly attributed to the two-phase coexistence which is actually developed by shifting the PPT in pure NKN downwards to near room temperature (T_R) through the addition of Li, Ta and/or Sb [2–4]. Although the mechanism of the enhancement of piezoelectric properties looks similar in conventional Pb-based perovskite compositions and NKN based lead-free compositions, yet the sensitivity of electrical properties to temperature is extremely different. The (Li, Ta, Sb) modified NKN compositions exhibit poling processing, composition and temperature dependences of piezoelectric properties [5–7]. Additionally, it was reported that piezoelectric properties of these kinds of compositions appear better close to the tetragonal side within the two-phase coexistence zone [8]. Although this phenomenon is probably related to particular domain structures as reported in PZT systems [9], yet it can be also correlated to the phase and domain change with temperature or composition, particularly in the compositions with a PPT near T_R .

Therefore, a procedure to further optimize piezoelectric properties was sought in this paper by exploring the correlations between the electrical properties and the phase transition behavior. The diffuseness of the PPT, the origin of two-phase coexistence, and the mechanism of temperature characteristics were discussed. Typical lead-free compositions $(\text{Na}_{0.52}\text{K}_{0.48-x})(\text{Nb}_{0.95-x}\text{Ta}_{0.05})\text{O}_3-x\text{LiSbO}_3$

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(NKNT-xLS) were taken for a case study. These compositions were reported by Ming et al. [10] to show excellent overall properties.

2 Experimental

A conventional solid-state synthesis method was employed to manufacture lead-free NKNT-xLS ($0.0405 \leq x \leq 0.0495$) ceramics. The processing details can be referred to elsewhere [11]. The specimens were sintered in air at 1,060–1,120 °C for 3 h. Lead-free silver paste was coated and then fired on both sides of the sintered samples at 550 °C for 30 min. The samples were poled at 110 °C in a silicone oil bath with a dc electric field of 2 kV/mm for 15 min and the electrical field was maintained during cooling to T_R .

The crystal structure was examined by an X-ray diffractometer (XRD, D/Mzx-rB, Rigaku, Japan) using a Cu $K\alpha$ radiation. The XRD data was fitted by Rietveld method to calculate the lattice parameters. Dielectric properties were measured as a function of temperature by an LCR meter (Agilent E4980A, USA) during heating at a rate of 2 °C/min. The piezoelectric strain constant d_{33} was measured by a Belincourt-meter (YE2730A, Sinocera, Yangzhou, China). The planar electromechanical coupling factor k_p and the mechanical quality factor Q_m were determined by a resonance-antiresonance method with an impedance analyzer (PV70A, Beijing Band ERA Co., Ltd, China).

3 Results and discussion

An orthorhombic-tetragonal phase transition in NKNT-xLS compositions was identified near room temperature approximately at $x = 0.04$ – 0.045 [10], a couple of compositions only close to the two-phase coexistence zone were thus synthesized in this study to look into the response of the structure and properties to the variation of the composition. Depending on the XRD results, the lattice parameters of these compositions were calculated although the calculation is difficult to be done for a composition within a two-phase zone where there should be two sets of lattices, particularly for alkaline niobate based systems whose phase boundary lies between orthorhombic and tetragonal phases. It is known that the orthorhombic phase in this system is usually characterized by two split peaks of (200)/(002) at lower angle and (020) at higher angle because $a \approx c > b$, and the tetragonal phase is characterized by splitting of peaks, (002) at lower angle and (200)/(020) at higher angle because $c > a = b$. To date there have not yet been reports on separating these diffraction peaks in this system as done in PZT systems [12], because diffraction peaks of {200} plane for tetragonal and orthorhombic phases are close to each

other and even partly overlapped. Therefore, it is very hard to identify the coexistence of orthorhombic and tetragonal phases directly from diffraction peaks. The calculation for lattice parameters was done from a pseudo-cubic primitive cell as shown in Fig. 1, supposed that all compositions are purely tetragonal. Because of the mixture of two phases in nature, the lattice constants do not change linearly in the range of $x = 0.0405$ – 0.0465 as a single phase behaviors, then have a jump at $x = 0.048$, and finally start to decrease ($a = b$; c gets smaller) after $x = 0.048$. The inset of Fig. 1 indicates the relation of lattice parameters with composition for orthorhombic-tetragonal phase-coexisted solid solution systems. The change of calculated lattice parameters with x suggests that compositions studied lie in a two-phase coexistence zone ($0.0405 < x < 0.0465$) and become purely tetragonal starting at $x = 0.048$. For the same reason, if purely orthorhombic phases are supposed for synthesized compositions, the conclusion should be the same. Of course, the following dielectric measurements could provide another support to the above judgment.

Figure 2 shows the dielectric constant at 10 kHz measured at different temperatures during heating for unpoled NKNT-xLS ceramics. It can be seen that the PPT below T_C was slowly moved downwards owing to the addition of LS, as clearly seen from gentle peaks in the dielectric constant versus temperature curves (also see inset of Fig. 2). These small peaks get flatter as the PPT is moved below T_R . For NKNT-0.0405LS ceramics, the PPT can be estimated to be at 60 °C (a bit higher than room temperature). This implies that the crystal structure of this composition should be made of more orthorhombic phase and less tetragonal phase at T_R . The actual PPT temperature for this composition should be slightly lower than 60 °C owing to a

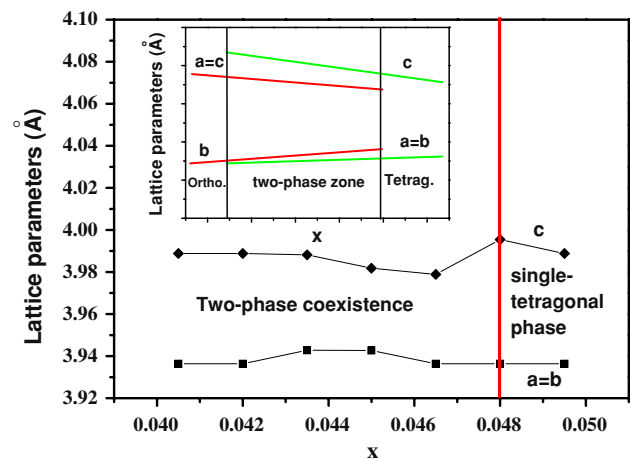


Fig. 1 Lattice parameters of NKNT-xLS ceramics with different x as indicated (Inset indicates the change of lattice parameters in an orthorhombic and tetragonal phase-coexisted system)

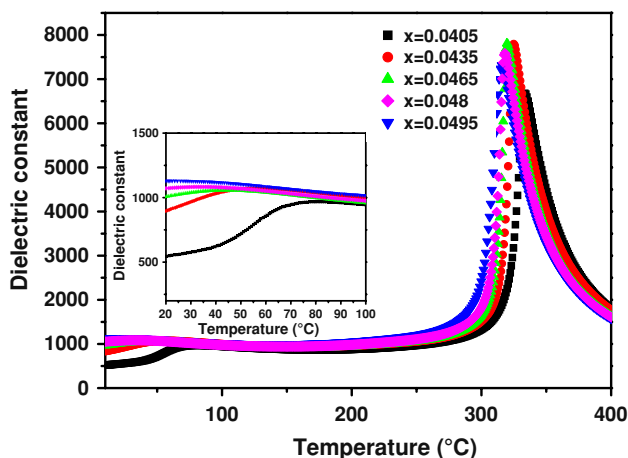


Fig. 2 Dielectric constant 10 kHz as a function of temperature for NKNT-xLS ceramics as indicated (*Inset* is the locally magnified plots near PPT)

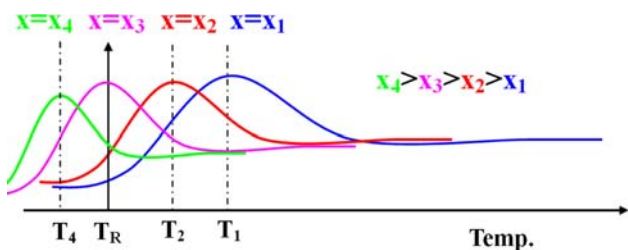


Fig. 3 Schematic diagram showing how the PPT changes with temperature and composition for NKNT-xLS compositions; note that T_1 , T_2 , T_R , and T_4 are the central temperatures of the PPT for compositions with $x = x_1, x_2, x_3$, and x_4 , respectively

thermal hysteretic effect because the dielectric constant was measured during heating. These results further confirm that the PPT of the studied compositions lies near T_R , that is to say, these compositions lie near a two-phase coexistence zone.

Figure 3 schematically depicts how the phase transition behavior responds to temperature or composition. It can be easily observed that the PPT is diffuse within a broad temperature range, meaning that the transition from orthorhombic to tetragonal phases is continuous and gradual. The diffuseness of the PPT could result in two-phase coexistence at a certain temperature possibly as a result of the inhomogeneity of the compositional distribution (or two-phase mixture). For compositions with different x , the central temperatures of their PPT are different. Supposed that the samples are composed of 50% orthorhombic and 50% tetragonal phases at the central temperature, for example, $x = x_3$, the compositions with $x < x_3$ (x_1 and x_2) at T_R should be composed of more orthorhombic phases and less tetragonal phases. On the contrary, the compositions with $x > x_3$ (x_4) should be composed of less orthorhombic phases and

more tetragonal phases. Therefore, with continuously changing the composition (x), the materials will undergo a transition from a single orthorhombic phases to a mixture of orthorhombic and tetragonal phases and finally to a single tetragonal phase. Within the two-phase zone, the percentage of tetragonal phases increases with increasing x . The boundary or the polymorphic phase boundary (PPB) between single orthorhombic phases and single tetragonal phases owing to the composition change is thus analogous to a traditional MPB in a sense of the two-phase coexistence. The two-phase coexistence could lead to the increased number of spontaneous polarization vectors in a certain composition, leading to enhanced piezoelectric activities.

It was previously reported that the Q_m value in some alkaline niobate based compositions is usually larger at the orthorhombic side than that at the tetragonal side [13], although the mechanism is still not clearly known at present. However, it is understandable that the minimum values should exist in compositions near the two-phase coexistence because the increased number of domains in PPB compositions with the two-phase coexistence tends to ease the domain motion under an external electric field, thus inducing a soft characteristic. Therefore, the Q_m values become smaller as the composition within two-phase coexistence zone is far away from the single orthorhombic phase side, as shown in Fig. 4. On the other hand, as the materials become a pure tetragonal phase after $x = 0.048$ as confirmed above. The Q_m value does not increase with x but continues to slightly decrease owing to the decreased tetragonality in this zone (the c value decreases after $x = 0.048$ in Fig. 1). This conclusion fits another two systems as well. As often observed in lead based perovskite systems such as $\text{Pb}(\text{Mg}_{1/3}\text{Nb}_{2/3})\text{-PbTiO}_3$ ceramics, the increased tetragonality with adding more PT tends to increase the coercive field and vice versa. This is because the increase of tetragonality tends to promote the formation of 90° domains (predominantly in tetragonal phases) which are more difficultly switched than non- 90° domains. Moreover, in $(\text{Na}_{0.52}\text{K}_{0.48-y})(\text{Nb}_{0.93-y}\text{Sb}_{0.07})\text{O}_3\text{-yLiTaO}_3$ (NKNS-yLT) compositions [14], Q_m slightly increases with the increase of y at the tetragonal side because the addition of LT tends to stabilize the ferroelectric phase by increasing the tetragonality of the system. In addition, other electrical properties exhibit strong compositional dependence as well even within two-phase coexistence zone. They first increase with x , reaching the best values approximately at $x = 0.0465$, and then declines with a further increase of x . It is apparent that the best piezoelectric properties do not appear in the compositions close to the orthorhombic side or in the middle of two-phase coexistence zone, but rather close to the side of single tetragonal phase.

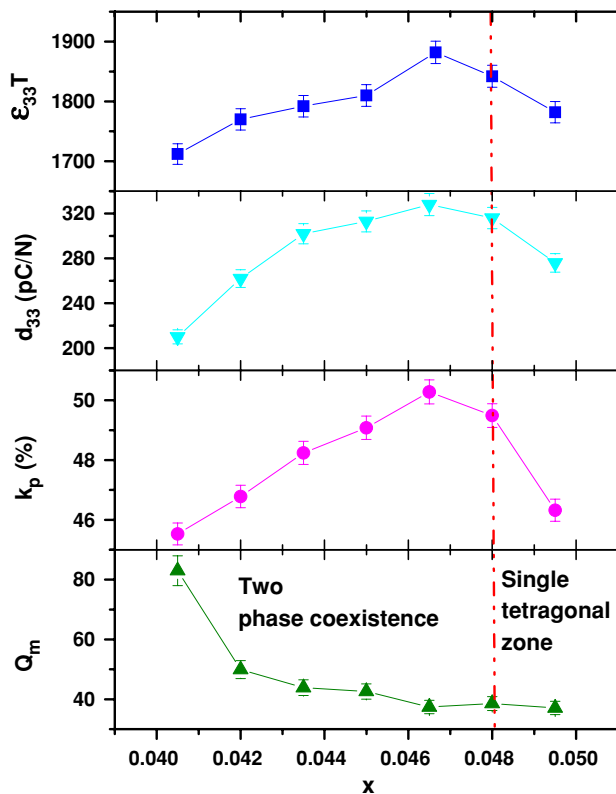


Fig. 4 Various electrical properties of poled NKNT-xLS ceramics as a function of the LS content x

All samples in this study were poled under a dc field of 2 kV/mm at 110 °C. This poling temperature is actually higher than the PPT temperatures of any samples such that all compositions should exhibit a tetragonal structure when being poled. Thus, the compositions lying in the two-phase coexistence zone may undergo a phase transition during cooling when the poling time is over. Owing to the phase transition, part of tetragonal phases with oriented domains will transform to orthorhombic phases with non-oriented domains. Of course, the domains in the orthorhombic phases could be also oriented to a certain degree because the electrical loading is maintained during the total period of cooling. The higher the content of the orthorhombic phase is, the larger the effect from domain variation is. So, the best piezoelectric properties appear at $x = 0.0465$, which is rather close to the side of single tetragonal phases. When x is slightly larger than 0.0465, the piezoelectric properties of the materials start to slowly decrease, because the contribution of two-phase coexistence to piezoelectric properties becomes very small and the materials become nearly a single phase. Further increase of x up to 0.0495 causes the piezoelectric properties to drop quickly because the composition with $x = 0.0495$ lies in single tetragonal phase zone. The variation of tetragonal and orthorhombic domains with temperature in NKN based ceramics may have caused not only the effect of electric poling conditions

(for example, temperature), but also the compositional dependence even within two-phase coexistence zone. That is to say, it is possible to further enhance piezoelectric properties of the materials by optimizing the composition design even within a narrow composition range, particularly refining the composition selection near the side of more tetragonal phases.

4 Conclusion

The correlation of the phase transition and the property optimization was explored for alkaline niobate based piezoelectric compositions. The diffuseness of the phase transition was thought of as the origin of the two-phase coexistence. The optimum electrical properties appear in NKNT-xLS compositions with a room-temperature PPT in which a compromise between the contribution of two-phase coexistence to the domain orientation and the loss of oriented domains after poling owing to the phase transition can be reached. This finding is supposed to fit any of NKN based lead-free piezoelectric systems which own a PPT near T_R .

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