

Electric field induced intermediate phase and polarization rotation path in alkaline niobate based piezoceramics close to the rhombohedral and tetragonal phase boundary

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High resolution synchrotron x-ray and dielectric measurements on unpoled and poled (Na,K)(Nb,Sb)O₃-LiTaO₃-xBaZrO₃ lead-free ceramics close to the rhombohedral-tetragonal (R-T) phase boundary have suggested an additional lattice distortion induced by poling field. This intermediate phase (IP) is consistent with the orthorhombic (O) symmetry but lower symmetries cannot be discarded. As a result, a modified polarization rotation path along R-IP-T in poled ceramics would be responsible for their high piezoelectric activity owing to the effect of the IP bridging the R and T phases. Simultaneously, the electric field induced phase transition would probably contribute to the observed large piezoelectric strains. © 2012 American Institute of Physics. [<http://dx.doi.org/10.1063/1.3696071>]

The ferroelectric (Na,K)NbO₃ (NKN) based lead-free system has been extensively studied in recent years because of its excellent electromechanical properties close to the polymorphic phase boundary (PPB) between the orthorhombic (O) and tetragonal (T) regions¹⁻³ or between rhombohedral (R) and O regions.^{4,5} As far as the phase composition is concerned, the PPB in NKN based compositions is clearly different from the traditional morphotropic phase boundary (MPB) in Pb-based materials⁶⁻⁸ or lead-free (Bi_{0.5}Na_{0.5})-TiO₃-BaTiO₃ (Refs. 9 and 10) that separates T symmetry from R symmetry. In addition, the electric-field induced strain was usually very small (<0.1% under 2 kV/mm) in previously reported NKN based random ceramics although they could show appropriate piezoelectric properties ($d_{33} \approx 250-400$ pC/N).^{2,3} A good progress has been made on quasi-ternary (Na,K)(Nb,Sb)O₃-LiTaO₃-xBaZrO₃ (NKNS-LT-xBZ) lead-free ceramics with R-T phase coexistence.¹¹ The superior piezoelectric activity (piezoelectric constant $d_{33} = 365$ pC/N and electromechanical coupling factor $k_p = 45\%$) was obtained in the vicinity of the R-T phase coexistence zone ($x = 0.025$). Moreover, NKNS-LT-0.025BZ ceramics exhibited large electric-field induced strains ($S_{\max} = 0.21\%$ under 4 kV/mm) as compared to a few typical piezoelectric materials^{2,3,12} (see Fig. 1). Questions have arisen concerning what is the origin of high piezoelectric activity in these lead-free compositions, and why it is accompanied by large strains.

The origin of ultra-high piezoelectric response in Pb-based complex perovskite oxides has ever been puzzling for long time. Traditionally, it was explained by the coexistence of the 14 (six in T phase and eight in R phase) possible

equivalent polarization vectors.⁷ Later on, some intermediate phases were observed around MPB Pb-based perovskite compositions,¹³⁻¹⁸ particularly the monoclinic (M) phase in Pb(Zr,Ti)O₃ (PZT) suggested by Noheda *et al.*¹⁹ The finding of these intermediate phases provided a perspective to view the R-T (or T-R) phase transition and the mechanism of high piezoelectric response in Pb-based piezoelectric materials. Theoretically, relevant studies might include first-principle study by Fu and Cohen²⁰ and higher-order Devonshire theory by Vanderbilt and Cohen.²¹ Moreover, high strains in PZT related systems were generally believed to be due to the highly polarizable Pb ions and the existence of MPB.²² However, this understanding requires a reassessment particularly because of the discovery of intermediate phases in MPB compositions. A considerable volume change might be observed as electric field can induce inter-ferroelectric (ferroelectric-ferroelectric) phase transformations.^{23,24}

In the present work, experimental evidences of the electric field induced intermediate phase in R-T phase coexisted NKN based ceramics are presented by means of high-resolution synchrotron radiation source and dielectric spectroscopy on unpoled and poled NKNS-LT-xBZ disk ceramics (or powders), generating a modified phase diagram. These experiments were originally designed to address the question whether the poling process in the phase coexistence zone would simply change the domain orientation, or whether it would induce an additional permanent lattice distortion.

NKNS-LT-xBZ ($x = 0.01, 0.025, \text{ and } 0.05$) ceramic samples were prepared by a conventional solid state route. The detailed experimental procedure was reported elsewhere.¹¹ The two major surfaces of as-sintered disk samples were ground and polished, followed by a careful annealing treatment in air at 550 °C for 3 h to eliminate the strains.

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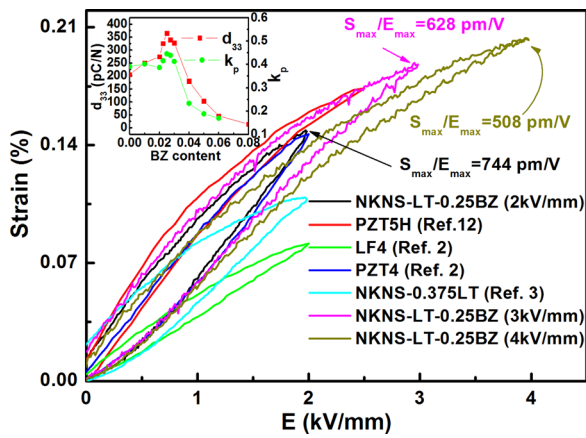


FIG. 1. (Color online) Strain versus electric-field curves for various types of piezoelectric ceramics (inset shows the d_{33} and k_p values as a function of BZ content).

Conductive adhesives were screened on two major polished surfaces and dried at 120°C . Sample disks were poled under a dc field of 2.5 kV/mm at 110°C for 15 min and then field cooled to room temperature. Dielectric constant (ϵ_r) and loss tangent ($\tan\delta$) of poled samples was measured as a function of temperature by means of an LCR meter (E4980A, Agilent, Santa Clara, CA). Strain versus electric field curves were measured by a ferroelectric test system (Precision LC, Radiant Technologies Inc., Albuquerque, NM) connected with a laser interferometric vibrometer (SP-S 120, SIOS Meßtechnik GmbH, Germany). The piezoelectric coefficient d_{33} and electromechanical properties k_p were measured by a Belincourt meter (YE2730A, Sinocera, Yangzhou, China) and an impedance analyzer (PV70A, Beijing Band ERA Co. Ltd., Beijing, China), respectively. For x-ray diffraction measurements, the electrodes of poled samples were then removed chemically by alcohol. In addition, some of as-sintered samples were crushed and ground in an agate mortar under acetone for the powder x-ray diffraction measurement. High-resolution x-ray diffraction of both the powders and disks were taken at Shanghai Synchrotron Radiation Facility using beam line 14B1 ($\lambda = 1.2378\text{ \AA}$).

Figure 2 shows the powder x-ray diffraction patterns of unpoled NKNS-LT-xBZ ($x = 0.01, 0.025, \text{ and } 0.05$) ceramics. The fitting analysis of the diffraction peak profiles was carried out by using pseudo-Voigt peak shape function. The symmetry of the samples can be well established from the peak splitting and the relative intensity of these reflection lines. It can be clearly seen that a transition from LT-rich T phase to BZ-rich R phase occurs with changing the BZ content x . For the composition with $x = 0.01$, the peak profiles can be well resolved in terms of T symmetry, as they are characterized by a single symmetric Bragg peak at pseudocubic (222) position and two doublets at pseudocubic (200) and (220) peaks with weaker reflections on the lower- and higher-angle sides, respectively. All reflection peaks become broad as the BZ content x increases to 0.025. It is easy to deduce that the undoped sample with $x = 0.025$ consists of a mixture of T and R phases. By comparison, a distinct R symmetry can be detected in the composition with $x = 0.05$, as featured by the (222) splitting reflections and a single symmetric (200) peak. It is worth to mention that any intermediate phase in these compositions lying at R-T phase boundary was not detected. The results seem different from those in conventional Pb-based piezoelectric materials where additional reflections representing neither T nor R symmetry, but M (or O) symmetry, can be observed near room temperature.^{18,19}

Figures 3(a)–3(c) show high-resolution synchrotron x-ray diffraction results for unpoled and poled NKNS-LT-xBZ ceramic disks. It can be seen that both the peak intensity and the position of the diffraction profiles have been obviously changed after electric poling. The change of the domain orientation after poling might cause a considerable effect on the peak intensity ratios between (002) and (200) reflections for the T phase (Fig. 3(a)), and between (111) and (11-1) reflections for the R phase (Fig. 3(c)). The possible change of the domain orientation can also be disclosed from the increased (202)/(220) peak intensity ratio in the T phase composition ($x = 0.01$). The change of both (002)/(200) and (202)/(220) intensity ratios shows similar tendency for the compositions near R-T phase boundary.

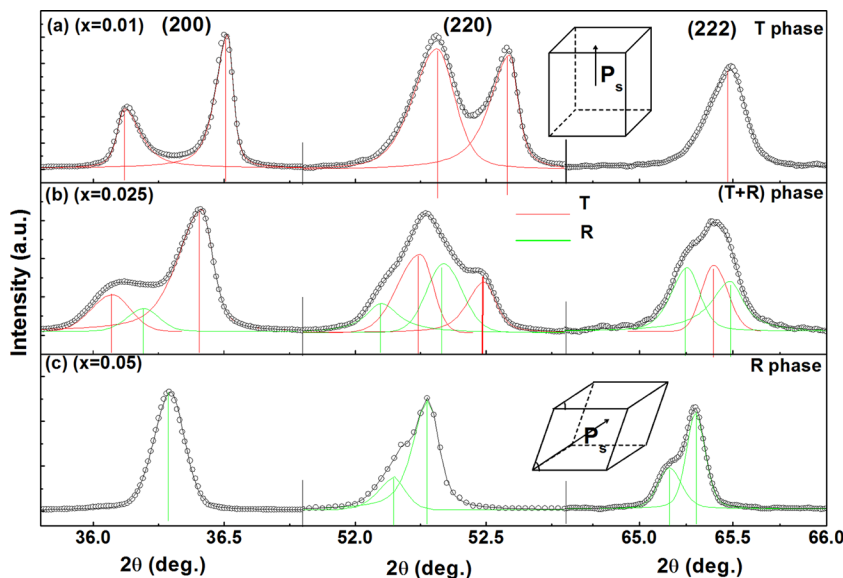


FIG. 2. (Color online) Powder x-ray diffraction patterns on pseudocubic (200), (220), and (222) reflections for unpoled NKNS-LT-xBZ ceramics ($x = 0.01, 0.025, \text{ and } 0.05$).

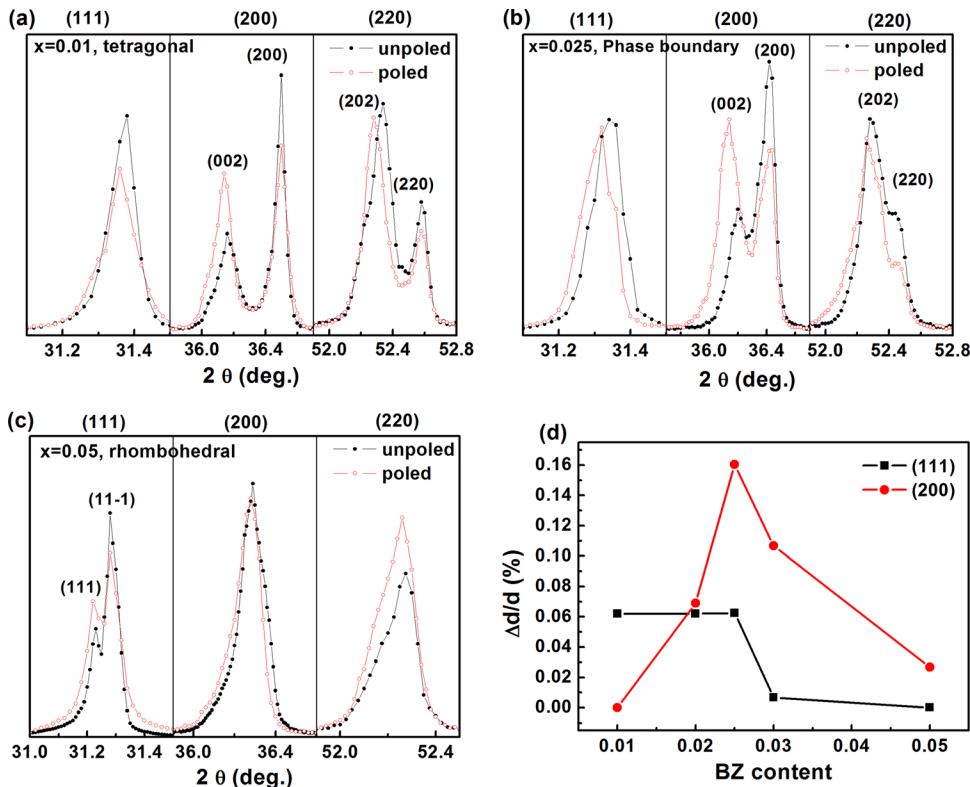


FIG. 3. (Color online) X-ray diffraction patterns on (111), (200), and (220) pseudocubic reflections for unpoled and poled NKNS-LT-xBZ ceramics with (a) $x=0.01$, (b) $x=0.025$, and (c) $x=0.05$; (d) the variation of d spacing ($\Delta d/d$) before and after poling.

In addition to the change of the peak intensity induced by domain orientation, the diffraction patterns for poled NKNS-LT-xBZ samples also show explicit changes in the peak positions with respect to unpoled ones. These changes are generally considered to be the result of the elongation of the unit cell. No peak shift was observed for the (002) diffraction lines of T phases (Fig. 3(a)) and the (111) diffraction lines of R phases (Fig. 3(c)), indicating that any elongation along respective spontaneous polarization directions was absent after the electric field was applied. However, the electric poling does produce a notable peak shift of the (111) and (202) reflection lines in the T phase case ($x=0.01$), which corresponds to a significant change of the d spacing (plane spacing). In the R phase zone, the peak position of (200) and (220) reflections also exhibits some changes although they are extremely slight compared to those of (111) and (202) reflections in the T-side compositions. These results clearly indicate that the elongation of the unit cell after poling does not take place along the spontaneous polarization directions in either T or R phases, but through an additional phase distortion. This phenomenon looks similar to that in Pb-based piezoelectric materials.¹³ Particularly in the case of the composition with $x=0.025$ (Fig. 3(b)), it should be located at the R-T phase boundary before poling at room temperature, but seems to transform into a low symmetry phase after poling. This is manifested by a high-angle-side shoulder in the (111) reflection and doublet (200) reflections with a stronger peak intensity at lower angle. Further evidence for symmetry lowering is obtained from the microstrain values along different directions as shown in Fig. 3(d). It can be seen that larger $\Delta d/d$ values appear along [111] direction for the T phase and along [200] for the R phase. The maximum strains either along [111] or [200] direction appear in $x=0.025$ compositions. It is usually believed that the significant increase in the

microstrain $\Delta d/d$ is an important feature of the phase transition,²⁵ which might be associated with the electric field induced intermediate phase in the present study. The field induced features described above are consistent with the orthorhombic symmetry, but a unit cell with concrete lattice parameters needs to be extracted to present clear evidence that the induced phase is orthorhombic. Unfortunately, it is not possible to do so for poled ceramics.

To further confirm the existence of an intermediate phase between R and T phases, the temperature dependence of the dielectric constant and loss of the NKNS-LT-0.025BZ sample is shown in Figure 4. Compared to unpoled samples, three distinct dielectric anomalies can be distinguished in poled samples, which correspond to the phase transitions from ferroelectric R to ferroelectric IP/O, then to ferroelectric T and finally to paraelectric cubic phase during heating. Therefore,

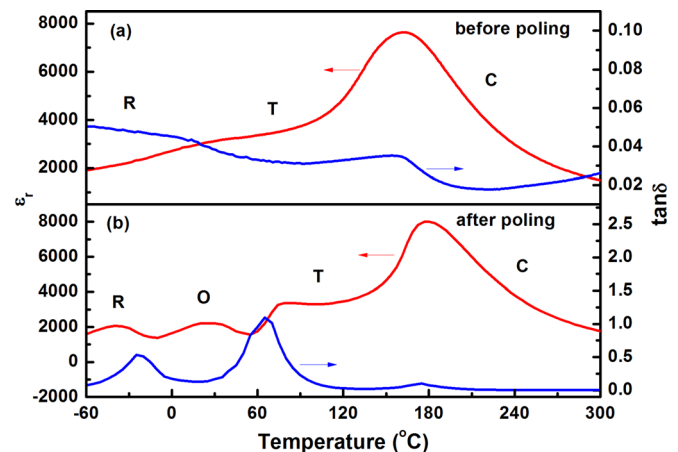


FIG. 4. (Color online) Dielectric constant and loss tangent of unpoled and poled NKNS-LT-0.025BZ ceramics at 1 MHz as a function of temperature.

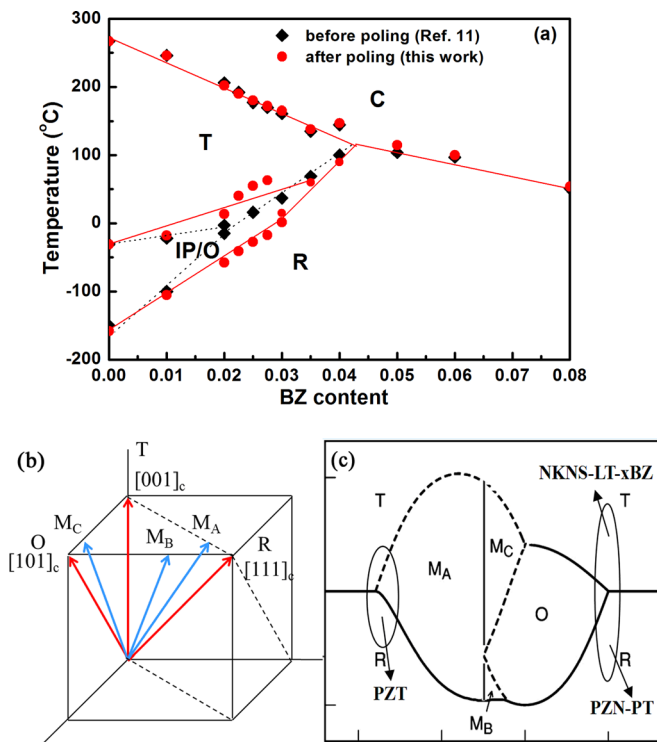


FIG. 5. (Color online) (a) Phase diagrams of poled and unpoled NKNS-LT-xBZ ceramics, (b) sketch of the relationship between T, O, R, and three M phases, and (c) sketch of the universal phase diagram for ferroelectric perovskites as proposed by Vanderbilt and Cohen (see Ref. 21).

the phase diagram of NKNS-LT-xBZ systems can be modified after poling, as shown in Figure 5(a). It can be seen that the initial R-T phase coexistence around room temperature does not occur any more after poling, and that the IP/O phase becomes stable at zero field for compositions with $0.02 < x < 0.03$. As a result, an irreversible R(T)-IP/O phase transition occurs at zero-field after poling. It seems that that the IP/O phase zone in the NKNS-LT-xBZ phase diagram was enlarged owing to the application of external electric field. The enlarged IP/O phase zone was also observed in $\text{Pb}(\text{Zn}_{1/3}\text{Nb}_{2/3})\text{O}_3\text{-PbTiO}_3$ (PZN-PT) single crystals.¹⁴ For PZN-PT, the field induced O phase can follow a polarization path to T symmetry via an intermediate M phase with increasing the electric field. Therefore, we cannot exclude the possibility of M symmetry existing in NKNS-LT-xBZ system. However, this can be easily understood by comparing the relationship between R, O, T and three different types of M phases (three types of ferroelectric M phases (M_A , M_B , and M_C)) have been suggested by Vanderbilt and Cohen by using higher-order Devonshire theory²¹), as schematically shown in Figure 5(b). The spontaneous polarization vector should be confined to the (1-10) (or (10-1)) plane for the M_A (or M_B) phase (space group C_m) with a doublet unit cell, which is rotated by 45° with respect to the pseudocubic c axis. As a result, the polarization vector direction would lie anywhere between T and R polar directions (M_A) or between R and O polar directions (M_B). For M_C phase (space group P_m), the unit cell is primitive with a polarization vector constrained in the (010) plane. From these viewpoints, O symmetry can be regarded as the limit case of the M_B or M_C symmetry as the polar vector is fixed along $\langle 101 \rangle_c$. Therefore, this O symmetry should be easily rotated to M symmetry

with electric field. As far as the symmetry of the intermediate phase is concerned, it is found that there is a striking similarity between lead-free NKNS-LT-xBZ and Pb-based PZN-PT system. It is of great interest to view the universal phase diagram for ferroelectric perovskites proposed by Vanderbilt and Cohen,²¹ as shown in Figure 5(c). Similar to PZN-PT, the phase boundary in NKNS-LT-xBZ should probably lie close to the right-hand side of a triple point connecting R, IP/O, and T phase zone. From the phase diagram, one can easily understand why not M phase but IP/O phase in our study can be induced by external electric field. The electric field induced IP/O phase acting as a bridge between R and T phases could greatly make the polarization rotation easier, thus leading to a high piezoelectric activity. On the other hand, the possible phase transitions (R-IP/O and/or IP/O-T) created by poling field would contribute to large strains observed during polarization switching, because big volume change between different phases would be involved, apart from the direct piezoelectric effect. Nevertheless, it is better to carry out *in-situ* synchrotron x-ray measurements on samples applied by electric field in order to clarify how the phase composition changes as a function of electric field. This work is currently underway.

In summary, the origin of high piezoelectric activity in NKNS-LT-xBZ piezoelectric ceramics was explored by means of high resolution synchrotron radiation source and dielectric spectroscopy. The coexistence of R and T ferroelectric phases was identified near room temperature for powder samples (or unpoled samples), to be similar to that of widely-used PZT ceramics. An intermediate phase, possibly with O symmetry, was observed in a narrow composition range for poled counterpart bulk samples. If the O symmetry was confirmed, this would be consistent with the initial low-temperature O phase zone being enlarged by external electric field. The electric-field induced phase transition and modified polarization rotation path of R-O-T were ascribed to high piezoelectric performances in niobate based lead-free ceramics.

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