

# Electric field induced phase instability in typical (Na,K)(Nb,Sb)O<sub>3</sub>-LiTaO<sub>3</sub> ceramics near orthorhombic and tetragonal phase boundary

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(Received 16 July 2012; accepted 14 August 2012; published online 31 August 2012)

The Li, Ta, and Sb modified (Na,K)NbO<sub>3</sub> ceramics were reported to exhibit excellent piezoelectric properties typically in the vicinity of orthorhombic (O) and tetragonal (T) phase boundaries. *Ex-* and *in-situ* synchrotron x-ray diffraction measurements have provided a direct evidence of the electric-field induced phase instability owing to reversible phase transition between monoclinic (M<sub>c</sub>) phase and T phase. A low-symmetry M<sub>c</sub> phase was irreversibly produced from the initial O phase after the electric field was applied. Experimental results suggested that the M<sub>c</sub>-T phase coexistence and reversible M<sub>c</sub>-T phase transition (phase instability) may be responsible for enhanced piezoelectric activity in these compositions. © 2012 American Institute of Physics.

[<http://dx.doi.org/10.1063/1.4748320>]

Excellent piezoelectric properties have been reported in the Li, Ta, and Sb modified (Na,K)NbO<sub>3</sub> (NKN) lead-free ceramics since 2004.<sup>1-3</sup> The most interesting thing is that the optimum electrical properties basically appear in the vicinity of the orthorhombic (O) and tetragonal (T) phase coexistence zone or polymorphic phase boundary (PPB),<sup>2</sup> as compared to conventional Pb-based piezoelectric ceramics. After the work of Saito,<sup>1</sup> a lot of attempts have been devoted to further improvement of the piezoelectric properties. Recently, Zuo *et al.* published their work on the compositional optimization of this system.<sup>2</sup> Both the piezoelectric constant  $d_{33}$  and electromechanical coupling factor  $k_p$  rapidly increased with increasing the LiTaO<sub>3</sub> (LT) content  $x$  and reached their optimum values ( $d_{33} = 395$  pC/N and  $k_p = 52\%$ ) in (Na,K)(Nb,Sb)O<sub>3</sub>- $x$ LiTaO<sub>3</sub> (NKNS- $x$ LT,  $x = 0.0375$ , and 8 mol. % Sb was fixed) within the O-T phase boundary (see Fig. 1). Questions, which were frequently asked for Pb-based piezoelectric ceramics, have arisen concerning what is the mechanism for the high piezoelectric activity in these lead-free compositions, particularly for O-T PPB compositions.

Extrinsic contributions to piezoelectric properties have been recently addressed for NKN based lead-free ceramics in Ref. 4, where it was pointed out that the enhanced piezoelectric response should be due to lower polarization anisotropy induced by the miniaturized nanodomain structures. In comparison to extrinsic contributions, the intrinsic mechanism was ascribed to the flattening of the free energy profile induced by the phase instability by means of phenomenological calculations,<sup>5-8</sup> which actually is concerned with the common feature of the phase transition and would probably suit for piezoelectric compositions with an O-T polymorphic phase transition.<sup>9</sup> Like PbZrO<sub>3</sub>-PbTiO<sub>3</sub> (PZT), the reason for the optimum piezoelectric properties close to the O-T PPB in

NKN-based ceramics could be also simply understood by means of an increase in the multiplicity of polarization states (six in T phase and twelve in O phase). This kind of understanding was advanced afterwards owing to the finding of intermediate phases in Pb-based piezoelectric compositions, particularly the monoclinic (M) phase in PZT suggested by Noheda *et al.*<sup>10</sup> Ge *et al.*<sup>11</sup> recently recognized that an M symmetry should exist in LiNbO<sub>3</sub> modified NKN ceramics, which acts as a structural bridge and facilitates the polarization rotation. Fu *et al.*<sup>12</sup> found a low-symmetry intermediate phase (possibly O phase) in quasi-ternary BaZrO<sub>3</sub>-NKNS-LT ceramics with rhombohedral (R)-T phase coexistence. Modified polarization rotation path of R-O-T was ascribed to the enhanced piezoelectric properties. Unfortunately, these studies basically rely on the zero-field macro- and microscopic electrical properties. *In-situ* measurements, for example, x-ray diffraction on ceramics being applied by an electric field, might help find what is really happening. As

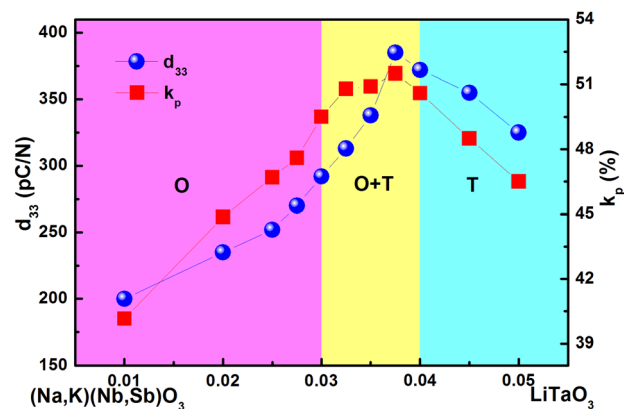


FIG. 1. Piezoelectric and electromechanical properties of (Na,K)(Nb,Sb)O<sub>3</sub>-LiTaO<sub>3</sub> ceramics (8 mol. % Sb is fixed) in different phase zones as determined at room temperature using a conventional powder x-ray diffractometer (see Ref. 2).

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far as the literature survey is concerned, how the phase structure evolves under the action of electric field, and whether/how it relates to the final piezoelectric properties were not yet addressed for NKN-based ceramics particularly in the vicinity of O-T phase boundary.

In the present work, *ex-* and *in-situ* synchrotron x-ray diffraction measurements were carried out on unpoled and poled (Na,K)(Nb,Sb)O<sub>3</sub>-LiTaO<sub>3</sub> (NKNS-LT) ceramics. Experimental evidences of the electric field induced irreversible O-M<sub>c</sub> phase transition and reversible M<sub>c</sub>-T phase transition (phase instability) were provided. These results were correlated to the dielectric and piezoelectric properties to address the question whether the applied electric field has induced additional lattice distortion. Is it permanent or temporal?

NKNS-xLT ceramic samples ( $x = 0.01-0.05$ ; 8 mol. % Sb, 52 mol. % Na, and 48 mol. % K) were manufactured by a conventional solid-state reaction method as described elsewhere.<sup>2</sup> The sintered ceramic disks were ground and polished, and then carefully annealed in air at 550 °C for 3 h to eliminate the strains. Silver electrodes were applied to two major surfaces and fired at 550 °C for 30 min. The samples were poled under a dc field of 3 kV/mm at 110 °C for 15 min for the measurement of dielectric and piezoelectric properties. Dielectric constant ( $\epsilon/\epsilon_0$ ) at 1 kHz of unpoled and poled samples was measured using an Agilent 4194 (Hewlett-Packard, Palo Alto, CA). Unipolar 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). Meanwhile, conductive adhesives were screened on two major polished surfaces and dried at 120 °C. These samples were poled under the same conditions mentioned above. For *ex-situ* x-ray diffraction measurements, the electrodes of poled samples were removed by alcohol. In addition, gold electrodes were sputtered onto both well-polished sides of some ceramic disks

for *in-situ* x-ray diffraction measurement. *Ex-situ* and *in-situ* high-resolution synchrotron x-ray diffraction measurements were performed using beamline 14B1 ( $\lambda = 1.2378 \text{ \AA}$ ) at the Shanghai Synchrotron Radiation Facility (SSRF). The beam size at the sample position is about  $0.3 \times 0.3 \text{ mm}$ . The grain size of the samples for the synchrotron radiation is about 2–5  $\mu\text{m}$ . Therefore, the collected diffraction data would disclose the statistical average structure information.

Figure 2 shows the variation of (200), (220), and (222) pseudocubic reflections for NKNS-xLT ceramics before and after electric poling by means of high-resolution synchrotron x-ray diffraction. As seen from Fig. 2(a), the unpoled NKNS-0.02LT and NKNS-0.03LT samples could be undoubtedly identified as an O phase because of the presence of the (200) and (222) doublets and the (220) triplet,<sup>13</sup> while the  $x = 0.045$  sample exhibits a single T phase with a clear splitting of the (200) reflections and a single (222) peak. For compositions with  $x = 0.03-0.0375$ , the phase structure becomes more complex and can be regarded as neither O phase nor T phase but the mixture of them. None of M symmetries could be obviously detected for unpoled NKNS-xLT samples. Therefore, the O-T phase coexistence zone occurs in the range of  $0.03 < x < 0.0375$  in fresh samples. By comparison, both the peak intensity and the position of the diffraction profiles show obvious changes after electric poling as shown in Fig. 2(b). It can be seen that the intensity ratio of lower to higher-angle diffraction peaks for all reflections increased, suggesting that electric poling has induced considerable domain orientation along the electric field direction. In addition, the peak profiles for the  $x = 0.03$  poled sample could be well resolved in terms of a distinct M<sub>c</sub> phase with space group P<sub>m</sub>. Therefore, it can be deduced that the initial O phase was irreversibly transformed into a low-symmetry M<sub>c</sub> phase after poling since an M<sub>c</sub> symmetry stands there after removal of electric fields. The existence of an irreversible O to M<sub>c</sub> phase transition induced by the application of an electric field

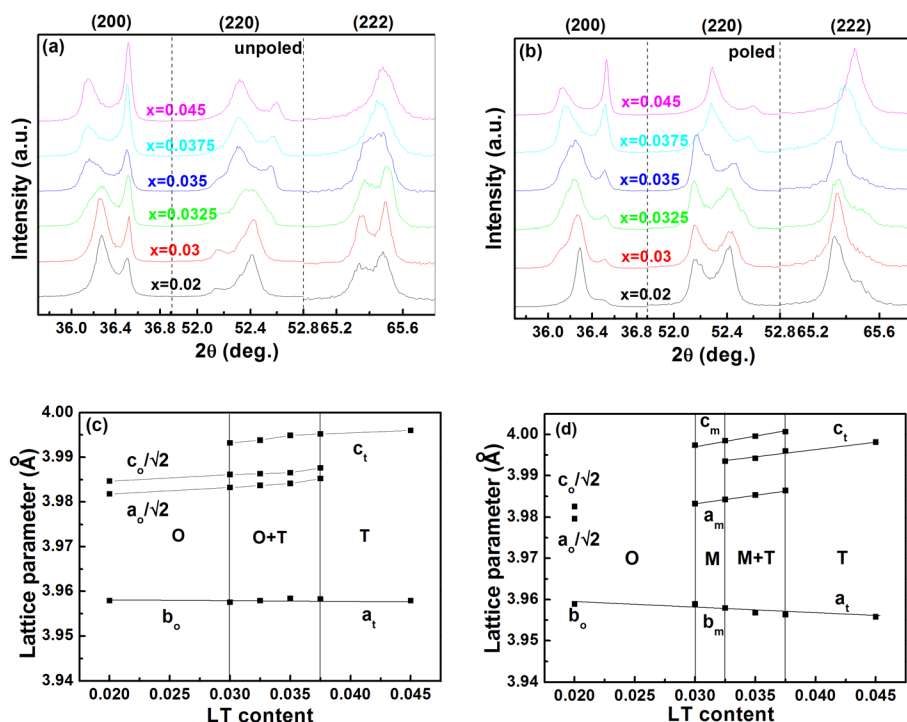


FIG. 2. Synchrotron x-ray diffraction patterns on (200), (220), and (222) pseudocubic reflections for (a) unpoled and (b) poled NKNS-xLT ceramics as indicated; the lattice parameters and phase structures (c) before and (d) after electric poling.

suggests that a new O- $M_c$  phase boundary should exist close to  $x = 0.03$  in poled NKNS-xLT phase diagram. With further increasing the LT content, it can be seen that the fraction of the  $M_c$  phase gradually increases. An abrupt change of the (200) and (220) reflections between  $x = 0.035$  and  $x = 0.0375$  indicates that the phase structure has probably changed from  $M_c$ -rich phase zone into T-rich phase zone (Fig. 2(b)). The room-temperature phase diagram and lattice parameters for unpoled and poled NKNS-xLT samples are shown in Figs. 2(c) and 2(d), respectively. It is clear that the initial O-T phase boundary in unpoled samples transformed into the O- $M_c$  and  $M_c$ -T phase boundaries after electric poling. Particularly, there is a clear phase coexistence zone close to the  $M_c$ -T phase boundary. Interestingly, it is found that the variation of the lattice constants from  $b_o$  ( $b_m$ ) to  $a_t$  is continuous across the phase boundary either before or after poling, meaning that the polar axis changes from [101] to [001] via the (010) plane during the process of O-T phase transition. This further indicates that the electric field induced phase is an  $M_c$  phase according to the universal phase diagram by Vanderbilt and Cohen.<sup>14</sup>

The dielectric constants  $\epsilon_{up}$  and  $\epsilon_p$  of unpoled and poled NKNS-xLT ceramics are shown in Fig. 3. As can be seen, the dielectric constant of unpoled samples exhibited a slight decrease with increasing the LT content in the O phase zone ( $x \leq 0.03$ ). However, a drastic increase was observed as  $x$  changes within the O-T PPB ( $x = 0.03$ – $0.0375$ ). The observed increase in the dielectric constant could be a consequence of the phase structure transformation from O to T phases. Although similar tendency was observed in poled samples, the onset composition corresponding to the increase of the dielectric constant shifted to  $x = 0.02$ . As a result, the corresponding composition range was enlarged into  $x = 0.02$ – $0.04$  after poling, which is just located in the O- $M_c$ -T phase transition zone (Fig. 2(d)). It is worthy of note that the dielectric constant for most of compositions shows an obvious increase after poling, as characterized by  $\epsilon_p/\epsilon_{up}$ . The maximum  $\epsilon_p/\epsilon_{up}$  value is located at  $x = 0.0375$ , probably owing to the  $M_c$ -T phase coexistence.

The electric field induced phase transition would probably produce a large piezoelectric strain due to the volume effect during the phase transition. However, as can be seen from Fig. 4(a), unipolar strains of all compositions are significantly

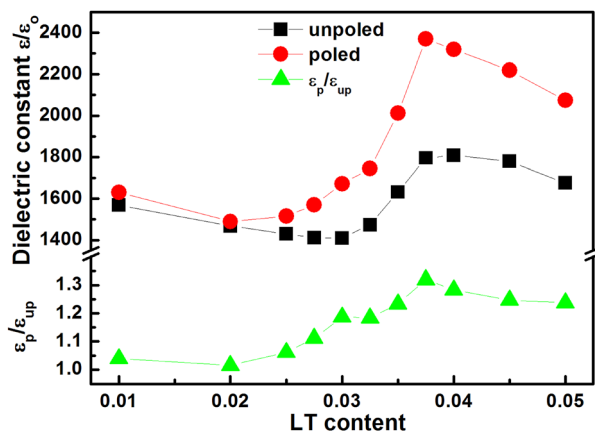


FIG. 3. Dielectric constants at 1 kHz of unpoled and poled NKNS-xLT ceramics as a function of the LT content.

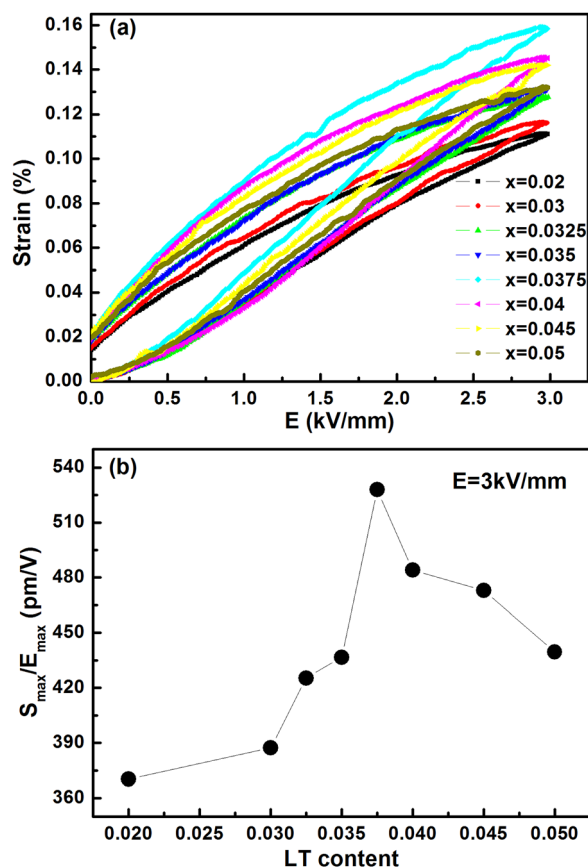


FIG. 4. (a) Unipolar strains versus electric field hysteresis loops and (b)  $S_{max}/E_{max}$  of NKNS-xLT ceramics as indicated.

lower than those of NKN-based ceramics with R and T phase coexistence.<sup>12</sup> The possible reason could be attributed to the small difference in the lattice distortion between  $M_c$  and O/T phases in this study. The O phase was usually described as the limiting case of the  $M_c$  phase with  $a_m = c_m$ .<sup>15</sup> With increasing the LT content, a sharp increase in  $S_{max}/E_{max}$  was observed from  $x = 0.03$  to  $x = 0.0375$  and the maximum  $S_{max}/E_{max}$  value up to 530 pm/V was found at  $x = 0.0375$  (Fig. 4(b)). It seems that the optimum dielectric and piezoelectric properties do not appear in the  $x = 0.03$  sample (O- $M_c$  phase boundary), but in the  $x = 0.0375$  sample which lies in the T-rich side of  $M_c$ -T phase boundary (for poled samples). The mechanism of this behavior needs to be addressed by further looking into more details from *in-situ* x-ray diffraction.

*In-situ* x-ray diffraction on (200) and (220) peak profiles of NKNS-xLT ceramics ( $x = 0.0375$  and  $0.045$ ) as a function of electric field is shown in Fig. 5. As the applied electric field is zero, the peak profiles of the  $x = 0.0375$  sample can be appropriately resolved in terms of T symmetry, as they are characterized by two doublets at pseudocubic (200) (Fig. 5(a)) and (220) peaks (Fig. 5(b)) with weaker reflections on the lower- and higher-angle sides, respectively. However, it is evident that as soon as the electric field is larger than a certain value, additional reflections can be found in both (200) and (220) peak profiles, which can be resolved in terms of an  $M_c$  symmetry characterized by its unique feature with an obvious (200) triplet. As we discussed in Figs. 2(a) and 2(c), the  $x = 0.0375$  unpoled sample should lie close to the T-rich side of the O-T phase boundary. Therefore, it is evident that the  $M_c$  phase can be induced at the phase coexistence zone

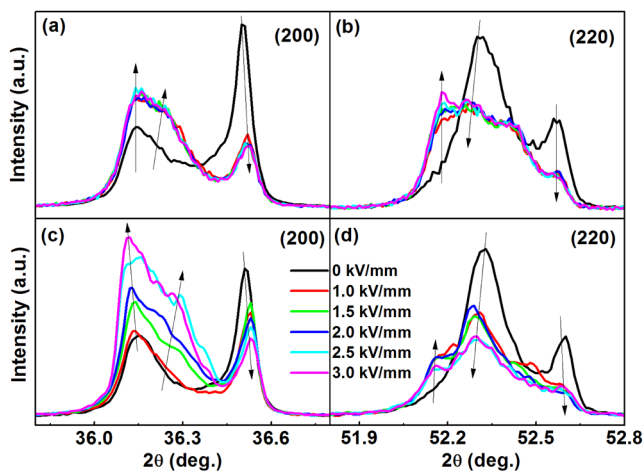


FIG. 5. Evolution of (a) (200) and (b) (220) pseudocubic reflections for the  $x = 0.0375$  sample, and (c) (200) and (d) (220) pseudocubic reflections for the  $x = 0.045$  sample under different external fields.

by an electric field, however, it is still not clear whether the transition from T phase to  $M_c$  phase is reversible or irreversible. By comparison, the  $x = 0.45$  unpoled sample is located at the single T phase zone close to the phase boundary. It can be seen from Fig. 5(b) that the T phase also can gradually transform into the  $M_c$  phase with increasing an electric field, as characterized by the transformation from  $(002)_t$  and  $(200)_t/(020)_t$  doublet into  $(002)_m$ ,  $(200)_m$ , and  $(020)_m$  triplet. However, the induced  $M_c$  phase from the high-field T phase cannot be maintained after removal of the field, as shown in Fig. 2(b). This means that the electric field induced T- $M_c$  phase transition is reversible. Similar phase transition behavior has been also observed in  $\text{Pb}(\text{Zn}_{1/3}\text{Nb}_{2/3})\text{O}_3\text{-PbTiO}_3$ ,<sup>16</sup> in which the transformation occurs from R to M is irreversible but the transition from M to T is reversible owing to the application of an electric field. Therefore, the initial O and T phase coexistence in fresh NKNS-xLT samples changes into the  $M_c$  and T phase coexistence owing to the excitation of external electric fields. Compared with the O- $M_c$  boundary at  $x = 0.03$ , this kind of reversible phase transformation tends to cause the phase instability such that the free energy profile in the  $M_c$ -T phase coexistence becomes shallow and flat. Such phase instability was also found in complex relaxor ferroelectrics, which is, however, induced by the polar nanoregions.<sup>17</sup> Theoretical and experimental studies have suggested that the phase instability and the enhanced piezoelectric response be closely related.<sup>7,8,16,18</sup> The phase instability in this study would be mainly ascribed to the reversibility of the  $M_c$ -T phase transition, in addition to the two-phase coexistence itself. The reversible phase transition means the

proximity of the free energy of these two phases and thus significantly lowers their polarization anisotropy, which would largely contribute to large dielectric and piezoelectric responses.

In summary, the mechanism for high piezoelectric response in NKNS-LT lead-free ceramics especially in the vicinity of O-T phase boundary was explored by means of *ex-* and *in-situ* synchrotron x-ray diffraction. The applied electric field would irreversibly change an initial O phase into a low-symmetry  $M_c$  phase such that the O-T phase coexistence in fresh samples was transformed into the  $M_c$ -T phase coexistence in poled counterparts. The enhancement of piezoelectric properties was mainly attributed to the  $M_c$ -T phase coexistence and the phase instability owing to the reversible  $M_c$ -T phase transition as confirmed by comparing *ex-* and *in-situ* x-ray diffraction results.

The authors would like to thank Shanghai Synchrotron Radiation Source for use of the synchrotron radiation facilities. Financial support from the Natural Science Foundation Anhui Province (Grant No. 1108085J14), the National Natural Science Foundation of China (Grant No. 50972035), the National Key Basic Research Program of China (2012CB825700), and the Ministry of Education of China, Zhejiang University-Helmholtz cooperation fund is gratefully acknowledged.

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