



Short communication

## Strain effects of temperature and electric field induced phase instability in (Na,K)(Nb,Sb)O<sub>3</sub>-LiTaO<sub>3</sub> lead-free ceramics



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## ABSTRACT

The temperature and electric field induced phase instability were found to produce distinctly different temperature-dependences of small- and high-field strains in the proximity of orthorhombic (O) to tetragonal (T) polymorphic phase transition of (Na,K)(Nb,Sb)O<sub>3</sub>-LiTaO<sub>3</sub> lead-free ceramics. As evidenced by means of in-situ and ex-situ synchrotron x-ray diffraction and quantitative analyses, both O-T phase coexistence and intermediate monoclinic (M<sub>c</sub>) phase were believed to promote intrinsic piezoelectric strains. Further increase of high-field strains with temperature was ascribed to enhanced contributions from field-induced reversible M<sub>c</sub>-T phase transition, plus little extrinsic contribution from non-180° domain switching which was unexpectedly hindered near the phase boundary.

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## 1. Introduction

Lead-free piezoelectric materials have attracted a lot of attention in recent years, particularly for Na<sub>0.5</sub>K<sub>0.5</sub>NbO<sub>3</sub> (NKN) based solid-solution ceramics owing to their excellent piezoelectric and electromechanical properties [1]. High-performance NKN based ceramics are chemically designed close to a phase boundary between ferroelectric phases of different crystallographic symmetries, such as rhombohedral (R) and orthorhombic (O), R and tetragonal (T), or O and T phases [1–4], by adjusting their polymorphic phase transition (PPT) temperatures. However, the diffuseness feature of PPT has made these ferroelectric phases coexist in a relatively wide temperature range, thus inducing an obvious temperature dependence of piezoelectric properties.

It is known that the achievable high-field strain is one of the most important characteristics for actuator ceramics, which commonly relies on both intrinsic and extrinsic contributions. The intrinsic piezoelectric contribution could be significantly enhanced in the proximity of morphotropic phase boundary (MPB) in Pb(Zr,Ti)O<sub>3</sub> based ceramics or close to the polymorphic phase boundary (PPB) in NKN based lead-free ceramics [5–7]. Landau-Ginzburg-Devonshire phenomenological model suggests that the enhancement of piezoelectric effects near PPB or MPB should be due to the flattening of a free energy profile [8,9]. In addition, the domain switching and field induced phase transition would also

make a large difference in the evolution of high-field strains, particularly how the domain switching behaves would be a critical issue as the composition gets close to the phase boundary. These questions are important especially for NKN-based lead-free piezoelectric ceramics since their phase coexistence states could change with increasing temperature. Moreover, the performance of ferroelectric devices when operated over a wide temperature range is subject to considerable changes resulting from the temperature dependence of strain characteristics of the functional materials. In some cases, the electric field induced phase transformation could make a significant contribution to strains. Large strains (>0.4%) were reported in a few relaxor ferroelectric ceramics as a result of the field-induced reversible ergodic relaxor-ferroelectric phase transformation [10,11], yet exhibiting an extremely large strain hysteresis. Furthermore, the enhancement of high-field strains in these relaxors concurrently accompanied a rapid drop of quasi-static piezoelectric effect.

In this work, a special emphasis was placed on the evolution of phase structures with both temperature and electric field near O-T PPB of NKN-based ceramics and its effect on the temperature dependence of small- and high-field strains by means of high-resolution synchrotron x-ray diffraction (XRD). Although the diffuseness of this kind of phase transition was believed to help improve the temperature stability of strains to a certain degree [12], the relevant physical mechanisms are still unclear. Particularly, how all contributing mechanisms of strains behave with varying temperature and electric field needs to be clearly addressed.

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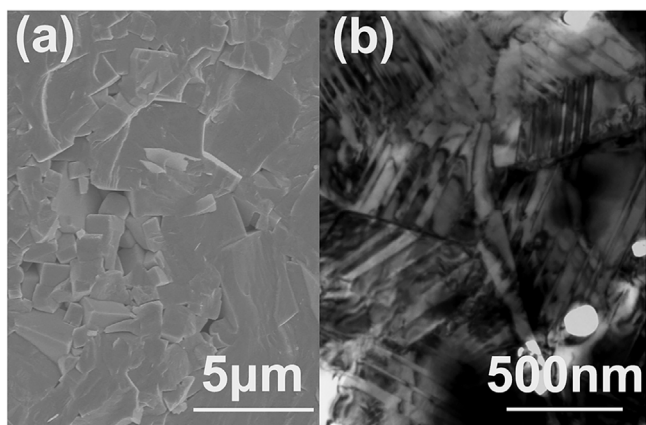


Fig. 1. (a) SEM micrograph on the fractured surface and (b) bright-field image for NKNS-3LT sample at room temperature.

## 2. Experimental

$(\text{Na}_{0.52}\text{K}_{0.45}\text{Li}_{0.03})(\text{Nb}_{0.89}\text{Sb}_{0.08}\text{Ta}_{0.03})\text{O}_3$  (NKNS-3LT) ceramics were prepared via a solid-state reaction method. The detailed experimental procedure for preparing NKNS-3LT ceramics could be referred elsewhere [13]. The sample density was evaluated by the Archimedes method. The microstructure was analyzed by using a scanning electron microscope (SEM, JEOL JSM-6490LV, Tokyo, Japan). The domain morphology was observed by using a transmission electron microscope (TEM, Phillips CM-20, Hillsboro, OR) operated at 200 kV with a charge coupled device camera. Silver paste was fired at 550 °C for 30 min on both major surfaces as electrodes for dielectric, ferroelectric and piezoelectric measurements. Dielectric permittivity ( $\epsilon_r$ ) at 1 kHz of unpoled samples was measured as a function of temperature by an LCR meter (Agilent E4980A, Santa Clara, CA). The bipolar and unipolar strain versus electric field (S-E) curves at 1 Hz were measured as a function of temperature by using a ferroelectric test system (Precision LC, Radiant Technologies Inc., Albuquerque, NM) connected with a laser interferometric vibrometer (SP-S 120E, SIOS Meßtechnik GmbH, Ilmenau, Germany). Small-signal piezoelectric coefficient  $d_{33}$  was obtained by the Rayleigh analysis by making a linear extrapolation of  $d_{33}(E) \propto E$  relation up to zero field, and thus the obtained  $d_{33}$  value reflects the true intrinsic contribution [14]. Gold electrodes were sputtered onto both well-polished sides of the ceramic disk for high-resolution XRD measurements at Shanghai Synchrotron Radiation Facility (SSRF) using beam line 14B1 ( $\lambda = 1.2378 \text{ \AA}$ ) successively on virgin, poling and poled disk samples at different temperatures.

## 3. Results and discussion

Fig. 1(a) shows the SEM image on the fractured surface for the NKNS-3LT sample sintered at 1100 °C for 3 h. It can be seen that the sample was well densified (>95% theoretical density) with cubic grain morphology. In addition, 60° and 120° domains can be clearly identified in Fig. 1(b) for the NKNS-3LT sample at room temperature, which are typical characteristics for an O ferroelectric phase [13].

Fig. 2(a and b) show unipolar (non-first cycle) and bipolar (first cycle: black line and non-first cycle: red line) S-E curves of NKNS-3LT samples at different temperatures, respectively. It is obvious that both strain loops varied drastically with increasing temperature from 25 °C to 90 °C. Various strain values including the poling strain  $S_{\text{pol}}$ , positive strain  $S_{\text{pos}}$ , and negative strain  $S_{\text{neg}}$  could be derived from these strain loops, as shown in Fig. 2(c). The maximum  $S_{\text{pos}}$  was achieved at 58 °C where  $S_{\text{neg}}$  reached almost the mini-

**Table 1**

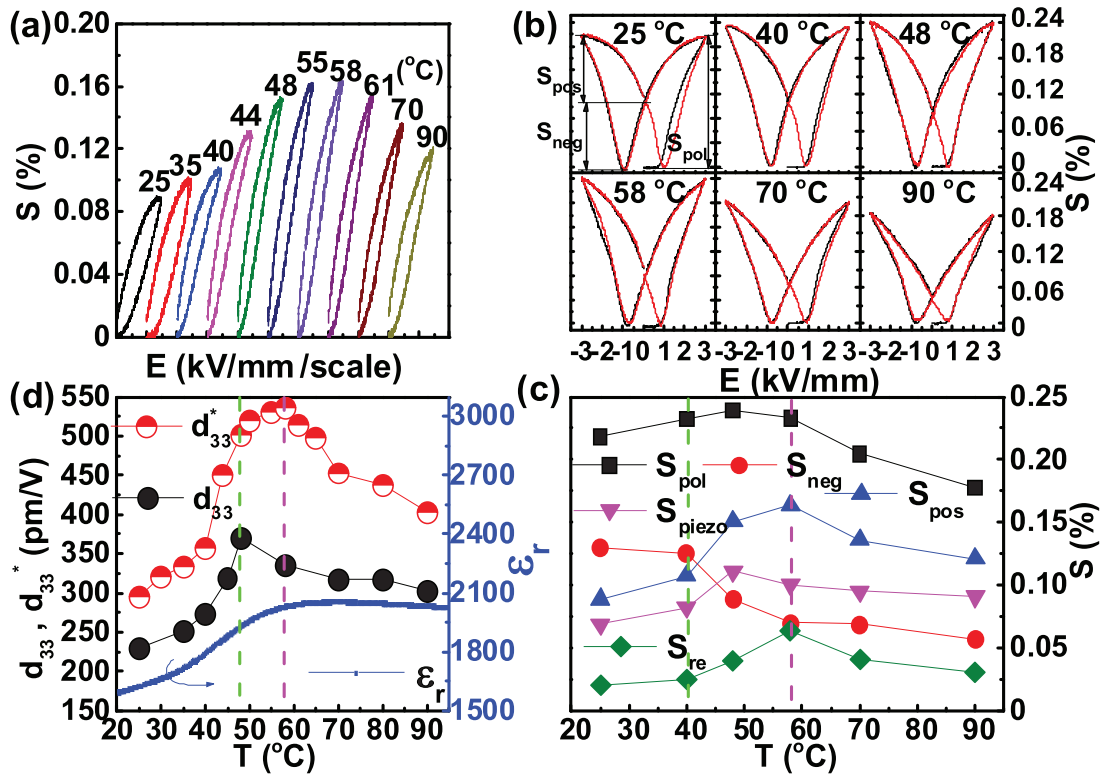
Identification of the phase structure of NKNS-3LT ceramic samples at various temperatures and under different electric field conditions.

| Phases | Virgin | Poling             | Poled              |
|--------|--------|--------------------|--------------------|
| 25 °C  | O      | O + M <sub>C</sub> | O + M <sub>C</sub> |
| 40 °C  | O      | O + M <sub>C</sub> | O + M <sub>C</sub> |
| 48 °C  | O + T  | M <sub>C</sub>     | M <sub>C</sub> + T |
| 58 °C  | T      | M <sub>C</sub>     | T                  |
| 70 °C  | T      | T                  | T                  |

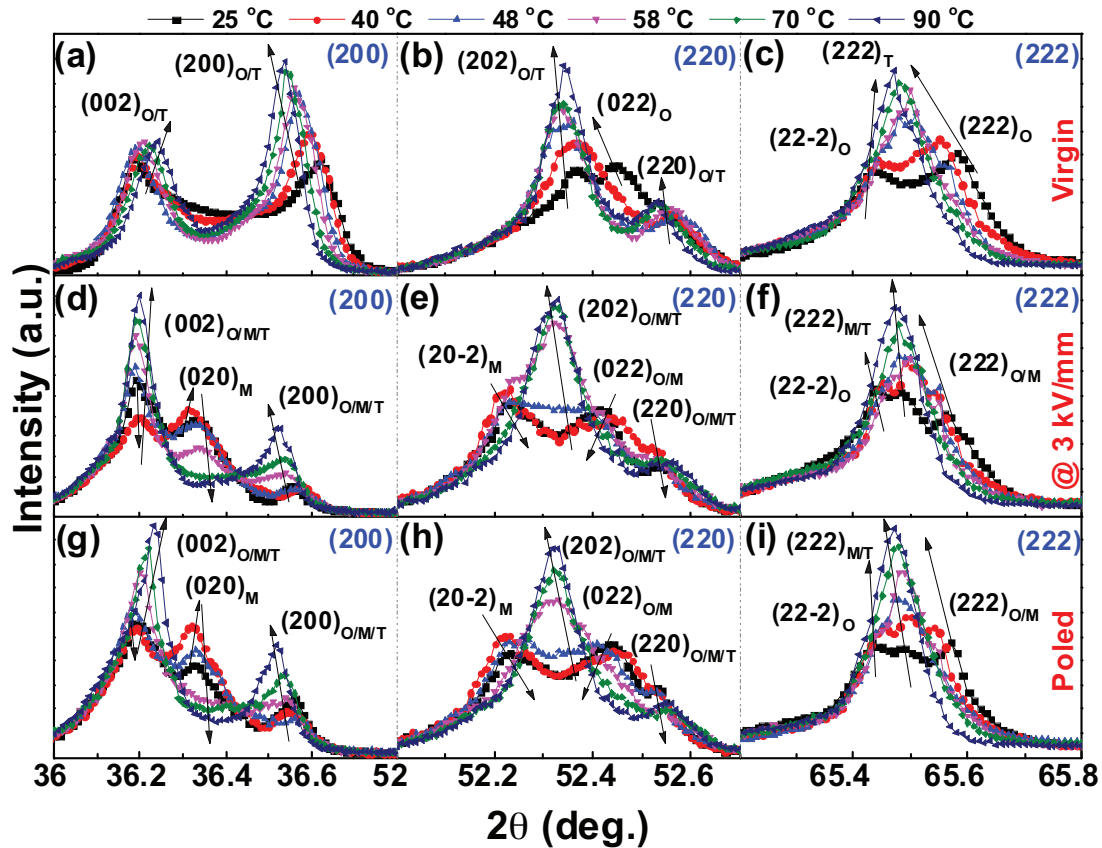
um. The small-signal  $d_{33}$  was measured at different temperatures in comparison with high-field strain coefficient (normalized strain,  $d_{33}^* = S_{\text{pos}}/E_{\text{max}}$  from Fig. 2(a)), as shown in Fig. 2(d). It can be seen that the intrinsic piezoelectric effect could be maximized at 48 °C, however high-field strain coefficient ( $d_{33}^*$ ) reached its maximum at 58 °C. Nevertheless, both of these strain maxima were found to appear in the proximity of O and T phase coexistence zone, as can be clearly from the  $\epsilon_r$ -T curve in Fig. 2(d). The diffuseness of PPT provides a solid structural fundament for O and T phase coexistence in a relatively wide temperature range. A complete  $\epsilon_r$ -T curve has already been reported in Ref. [15] where a flat dielectric hump was believed to result from O-T PPT. It is known that high-field strains should be concerned with various contributions including intrinsic and extrinsic ones. The achievable  $S_{\text{pos}}$  should be a sum of the piezoelectric strain  $S_{\text{piezo}}$  and all other reversible strains ( $S_{\text{re}}$ ) from non-180° domain switching ( $S_{\text{rd}}$ ) and from reversible ferroelectric to ferroelectric phase transition ( $S_{\text{rp}}$ ) ( $S_{\text{pos}} = S_{\text{piezo}} + S_{\text{rd}} + S_{\text{rp}}$ ). Both  $S_{\text{piezo}}$  and  $S_{\text{re}}$  with changing temperature are shown in Fig. 2(c) where  $S_{\text{piezo}}$  was roughly estimated by using the small-signal  $d_{33}$  and the applied electric field. It can be found that  $S_{\text{re}}$  increased with increasing temperature and reached its maximum at 58 °C. Therefore, this should be responsible for the maximum  $S_{\text{pos}}$  at 58 °C because intrinsic piezoelectric contribution started to decay after 48 °C.

In order to further make clear the underlying mechanism for the evolution of electric field induced strains with increasing temperature, the evolution of (200), (220) and (222) diffraction lines at different temperatures for NKNS-3LT samples with a virgin state, a poling state (3 kV/mm) and a poled state (electrically cycled under 3 kV/mm at the corresponding temperature) are shown in Fig. 3(a)–3(c), 3(d)–3(f) and 3(g)–3(i), respectively. For virgin samples, a typical O phase was identified because of the (200) and (222) doublets and the (220) triplet before 40 °C, and then a pure T phase was observed according to the (200) doublet and the single (222) peak after 58 °C. At 48 °C (in the range of 40–58 °C), a mixture of O and T phases can be clearly identified. Under an electric field of 3 kV/mm, additional diffraction lines corresponding to a low-symmetry monoclinic (M<sub>C</sub>) phase apart from initial O phases were observed (Fig. 3(d–f)) as  $T \leq 40$  °C. As  $70$  °C >  $T \geq 48$  °C, a pure M<sub>C</sub> was identified because of the presence of the (002)<sub>M</sub>, (020)<sub>M</sub> and (200)<sub>M</sub> triplet and the (22-2)<sub>M</sub> and (222)<sub>M</sub> doublet. After the electric field was released, the coexistence of O and M<sub>C</sub> phases could be recognized in the poled sample. A pure T phase appeared as temperature was higher than 58 °C. At 48 °C, O phases have been completely transformed into the M<sub>C</sub> phase such that a mixture of M<sub>C</sub> and T phases was observed. It can be seen that the variation of temperature and external electric field has produced an obvious influence on the phase structure of NKNS-3LT samples.

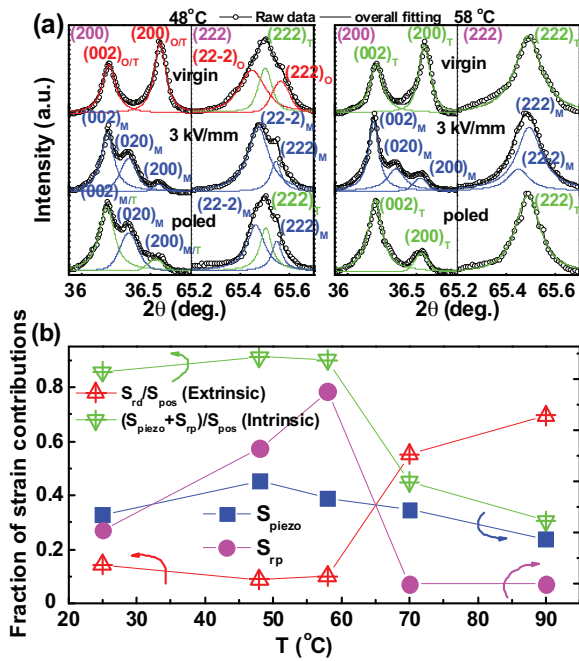
The phase structures of NKNS-3LT samples with different poling states at various temperatures were summarized in Table 1. It can be seen that the O and T phases could coexist before poling in a certain temperature range (40–58 °C). The application of an electric field has irreversibly induced the O to M<sub>C</sub> phase transition. By comparison, the M<sub>C</sub>-T phase transition proved to be reversible, starting from 48 °C and ending at 58 °C. On the one hand, the O and T phase coexistence at the virgin state and the appearance of inter-



**Fig. 2.** (a) Unipolar and (b) bipolar S-E curves under an electric field of 3 kV/mm at various temperatures as indicated during heating, (c) temperature dependence of various strain values  $S_{pol}$ ,  $S_{pos}$ ,  $S_{neg}$ , and  $S_{re}$  as defined in the text, and (d) temperature-dependent dielectric permittivity at 1 kHz for the virgin NKNS-3LT sample, and both  $d_{33}^*$  and  $d_{33}$  values measured at different temperatures.



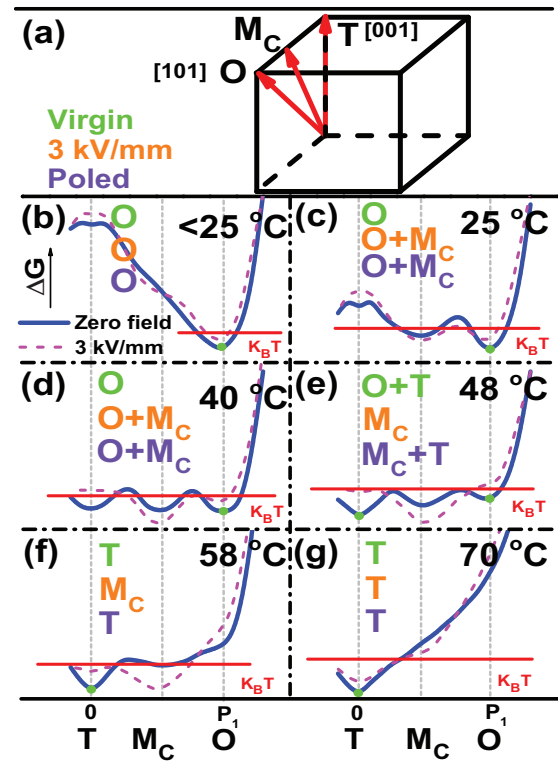
**Fig. 3.** The evolution of (200), (220) and (222) reflections at various temperatures for the (a–c) virgin state, and (d–f) poling state and (g–i) poled state of NKNS-3LT ceramics, respectively.



**Fig. 4.** (a) The (200) and (222) diffraction peaks at 48 °C and 58 °C for virgin, poling and poled states of NKNS-3LT samples shown representatively and fitted by using PeakFit software as indicated, and (b) fraction of intrinsic and extrinsic strain contributions and absolute strain values ( $S_{\text{piezo}}$  and  $S_{\text{rp}}$ ) changing with measuring temperature.

mediate  $M_c$  phase at poling and poled states could well account for the maximum  $d_{33}$  value at 48 °C because of enhanced polarization orientation ability [16,17]. Moreover, the field induced  $M_c$  phase was believed to have a large lattice distortion, which might also help increase the intrinsic piezoelectric contribution [18]. On the other hand, reversible  $M_c$ -T phase transition should contribute to the enhancement of high-field strains with temperature owing to its volume effect. In addition, the intensity ratio of lower to higher angle diffraction peaks for most of reflections was found to vary obviously as the electric field was being applied or had been released, suggesting that electric poling might induce considerable domain orientation along the electric field direction as well.

In order to quantitatively resolve all reversible strain contributions such as  $S_{\text{piezo}}$ ,  $S_{\text{rp}}$  and  $S_{\text{rd}}$ , the XRD peaks were fitted by using PeakFit software to ascertain the position and intensity of diffraction lines belonging to different phases, as shown in Fig. 4(a) using XRD data at 48 °C and 58 °C as examples.  $S_{\text{piezo}}$  was derived from the lattice deformation of the (222) reflection using the equation  $S_{\text{piezo}} = S_L = (d_{3\text{kV/mm}} - d_{\text{poled}}) / d_{\text{poled}}$  ( $d$ : interplanar spacing) based on the theoretical calculation result that the maximum value of the intrinsic component of the piezoelectric coefficient should be along with the nonpolar direction of the ferroelectric phase [19]. It was found that the lattice strain from the (222) reflection is maximal in the present study. The  $S_{\text{rp}}$  value resulting from the field-induced inter-ferroelectric phase transformation was calculated from the volumetric change between the initial and resultant phase by considering unit cell volumes and fraction of each phase. For example,  $S_{\text{rp}}(48^\circ\text{C}) = 1/3 * \{F_M' * V_M' - (F_M * V_M + F_T * V_T)\} / (F_M * V_M + F_T * V_T)$  in which  $F_M'$ ,  $F_M$ , and  $F_T$ , and  $V_M'$ ,  $V_M$ , and  $V_T$  are the phase fractions and unit cell volumes of the  $M_c$  (3 kV/mm),  $M_c$  (poled) and T (poled) phases, respectively. Moreover,  $S_{\text{rd}}$  was calculated from the relationship between the variation of the volume fraction (f) of domains along the electric field direction and the  $S_{\text{neg}}$  value (Fig. 2) according to the equation:  $S_{\text{rd}} = S_{\text{neg}} * (f_{3\text{kV/mm}} - f_{\text{poled}}) / (f_{\text{poled}} - f_{\text{virgin}})$  [20]. As shown in Fig. 4(b), the fraction of all intrinsic strain contributions only slightly increased with increasing temperature



**Fig. 5.** (a) Sketch of the relationship of spontaneous polarization between T, O and  $M_c$  phases, and (b)–(g) the cross section of the free energy profiles along O-( $M_c$ )-T path (polarization vector  $[P_1, 0, 1]$ ) for NKNS-3LT ceramics on heating at 0 and 3 kV/mm. The horizontal red segments indicate the average thermal activation energy ( $K_B T$ ). (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

up to 58 °C and then rapidly decayed with further increasing temperature. By comparison, the fraction of extrinsic contributions mainly from reversible non-180° domain switching was slightly decreased in the temperature range of the O-T phase coexistence (see Table 1), and then increased drastically as temperature was above 70 °C. At higher temperatures, the enhancement of  $S_{\text{rd}}$  should be easily understood because domain switching became easier. If one checked the absolute strain contribution, it can be found that the calculated  $S_{\text{piezo}}$  reached its maximum value at 48 °C as expected, keeping a good consistency with the experimental results in Fig. 2(d). By comparison, the calculated  $S_{\text{rp}}$  was found to continuously increase with increasing temperature and reached its maximum at 58 °C although  $S_{\text{piezo}}$  started to decline after 48 °C. The calculated results indicated that the enhancement of high-field strains at 58 °C should be mainly ascribed to a large volume effect from reversible  $M_c$ -T phase transition ( $S_{\text{rp}}$ ) instead of reversible domain switching ( $S_{\text{rd}}$ ). This observation contradicted the basic premise of the martensitic-theory-based explanation which emphasizes on enhanced domain wall motion as the primary factor for the anomalous piezoelectric response in MPB piezoelectrics. The hindrance to the domain switching at the phase coexistence zone was believed to correlate to the field induced phase transformation [21].

The sketch of the relationship between T, O and  $M_c$  phases is shown in Fig. 5(a). The unit cell of  $M_c$  phase (space group  $P_m$ ) is primitive with a polarization vector constrained in (010) plane. The O and T symmetry can be regarded as the limit cases of the  $M_c$  symmetry because the polar vector is fixed along  $(101)_c$  and  $(001)_c$ , respectively. As PPB is approached, a stronger competition between different phases makes the crystal structure unstable under a weak external stimulus such as variation of temperature or electric field.

Fig. 5(b)–(g) sketched the cross section of the free energy profiles of NKNS-3LT ceramics along O-(M<sub>c</sub>)-T path [8,9]. The free energy of M<sub>c</sub> should be decided by the change of the free energy of both O and T phases. It is known that the thermal activation energy ( $K_B T$ ), which increases linearly on heating, should be the main driving force for the phase transition if it is large enough to overcome the barrier. As temperature is below 25 °C, O is the only stable phase. However, both M<sub>c</sub> and T are too unstable to be induced even under a high field because of their high free energies. Upon heating, the free energy of the T phase decreases while the free energy of the O phase increases gradually. Simultaneously, the thermal activation energy increases and the potential barriers between different phases drastically change accordingly. Only when part of  $K_B T$  is large enough to overcome the potential barrier of O phase at ~48 °C (it would also overcome the potential barrier of M<sub>c</sub> phase) (Fig. 5(e)), T phase with a lower potential well would be stabilized. Part of O phases would be still maintained because of part of lower  $K_B T$ . As a result, the coexistence of O and T phases was observed at zero field under this circumstance. Although the increase of temperature does not completely stabilize M<sub>c</sub> phase, yet the metastable M<sub>c</sub> phase would exist stably when an external electric field was applied. Because external electric field is usually anisotropic and prone to stabilize the phase with spontaneous polarization axes close to the direction of the electric field. Namely, the free energy of M<sub>c</sub> phase would be decreased, as indicated by the magenta dash lines, and then the M<sub>c</sub> phase would be favored by external electric fields basically owing to its far more polarization vectors than O and T phases. The induced M<sub>c</sub> phase cannot turn back to the initial O phase even if the electric field was released because the  $K_B T$  is relatively low. However, it can reverse back to the initial T phase as the potential well of T phase is the lowest (Fig. 5(e and f)). At 58 °C, T phase becomes the only stable one at zero field while the M<sub>c</sub> is the only stable phase under high electric field, resulting in reversible T-M<sub>c</sub> phase transformation during electric field cycle. Above 70 °C, only T phase can be stable even under a strong external electric field. The above analyses indicated that both external electric field and temperature variation could induce remarkable phase instability, thus causing a phase structural transition through changing free energy states of different phases around PPB of NKNS-3LT ceramics.

#### 4. Conclusions

In summary, strain effects of the temperature and electric field induced phase structural instability close to the O-T PPB of NKNS-3LT lead-free ferroelectric ceramics were quantitatively resolved by means of high-resolution synchrotron x-ray diffraction. Both experimental and calculated results indicated that small-signal piezoelectric strain was maximized at 48 °C because of temperature-induced O-T phase coexistence and electric field induced intermediate M<sub>c</sub> phase. The appearance of the maximum high-field strain at 58 °C should be ascribed to a reversible field induced M<sub>c</sub>-T phase transition instead of non-180° domain switching, which was however not favored in the temperature range of O-T phase coexistence. In combination with the analysis of free energy profiles, these results would help well understand the underlying mechanisms for the evolution law of high-field strains with temperature and the temperature-sensitive piezoelectric response for NKN-based lead-free ferroelectric ceramics near PPBs.

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