

High piezoelectric activity in (Na,K)NbO₃ based lead-free piezoelectric ceramics: Contribution of nanodomains

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The origin of high piezoelectric response in (Na_{0.52}K_{0.48-x})(Nb_{0.92-x}Sb_{0.08})O_{3-x}LiTaO₃ lead-free ceramics was investigated by looking into the composition-dependent domain morphology by means of transmission electron microscopy. Nanodomains of alternate orthorhombic and tetragonal domains with a width of 20–50 nm were surprisingly observed but only for compositions near polymorphic phase coexistence zone. The formation of nanodomain morphology was considered to result from the reduction of the domain wall energy owing to the vanishing of the polar anisotropy, which ultimately induced enhanced piezoelectric properties. The result indicated that nanodomains are not proprietary features of traditional Pb-based piezoelectric ceramics with a morphotropic phase boundary. © 2011 American Institute of Physics. [doi:10.1063/1.3624704]

Excellent piezoelectric responses have been observed near an orthorhombic-tetragonal (O-T) phase boundary for Li, Ta, and/Sb modified (Na,K)NbO₃ (NKN) lead-free piezoelectric ceramics. However, the origin of high piezoelectric activity in these lead-free compositions has been rarely investigated, compared to Pb-based counterparts.¹ In this respect, a lot of research work was focused mainly on Pb-based piezoelectric ceramics such as PbZrO₃-PbTiO₃ (PZT) which have a rhombohedral-tetragonal morphotropic phase boundary (MPB). In terms of an average structure information, additional reflections were found in Pb-based MPB piezoelectric compositions by means of high-resolution synchrotron x-ray diffraction.^{2,3} It was believed that these possible intermediate phases (monoclinic phase or O phase) would cause the instability of the polarization state and thus could provide an easy path of polarization rotation.^{4,5} By comparison, real structure models would be probably derived from transmission electron microscopy (TEM) studies.^{6–8} It was, however, found that the appearance of intensity in diffraction patterns formerly linked to a monoclinic phase should be directly correlated to a miniaturization of the average domain structure of PZT ceramics in the presence of nanodomains.⁷ In addition, it was considered that extrinsic piezoelectric effect in morphotropic PZT should be closely connected to the existence of nanodomains.⁹

Although the domain structure of NKN based piezoelectric ceramics was analyzed by various ways,^{10–13} yet these work was basically done on single crystals or polycrystalline ceramics of pure NKN with quite large grains, such that real domain structures of normally sintered NKN based ceramics cannot be disclosed. Most importantly, why piezoelectric properties can be effectively enhanced in these NKN based ceramics as the composition gets close to the phase coexistence zone were rarely discussed from the domain structure point of view.

In our work, we presented the composition-dependent ferroelectric domain structures of Li, Ta, and Sb modified NKN lead-free piezoelectric ceramics. Particularly, the influence of phase coexistence on the domain structure was studied, which is crucial for the understanding of macroscopic properties. Nanodomains were found out and considered to contribute to the high piezoelectric activity of NKN-based lead-free ceramics.

(Na_{0.52}K_{0.48-x})(Nb_{0.92-x}Sb_{0.08})O_{3-x}LiTaO₃ (NKNS-xLT) (0.01 ≤ x ≤ 0.045) samples were prepared by a conventional solid state process, as described in Ref. 14. The phase structure of each specimen was determined by an x-ray diffractometer (D/MAX2500VL/PC, Rigaku) with a temperature-controlling furnace. The phase transition temperature was achieved by measuring the dielectric constant versus temperature curves using an LCR meter (E4980A, Agilent, Santa Clara, CA). The piezoelectric coefficient d₃₃ and electromechanical properties k_p were measured by a Belincourt meter (YE2730A, Sinocera, China) and an impedance analyzer (PV70A, Beijing Band ERA Co. Ltd., China), respectively. Specimens for TEM studies were prepared from bulk ceramics by mechanically polishing to ~20 μm and then ion-milling on a Gatan Dual Ion Mill unit (Model 600) at 5 kV. The domain morphology was observed on TEM (Phillips CM-20, Hillsboro, OR) operated at 200 kV with a charge coupled device camera. Convergent beam electron diffraction (CBED) patterns were recorded at 120 kV.

Figure 1 shows the composition-property-temperature phase diagram of NKNS-xLT solid solution ceramics. It can be seen that the O-T polymorphic phase transition (PPT) temperatures decrease monotonously with increasing the LT content. At x = 0.03–0.04, the PPT temperature is approximately moved to room temperature (T_R) such that O and T phases can coexist. At the same time, the maximum piezoelectric and electromechanical properties were obtained near phase coexistence zone. This kind of phase boundary was named as the polymorphic phase boundary (PPB), rather than the classical MPB in Pb-based ferroelectrics.¹⁴ It was

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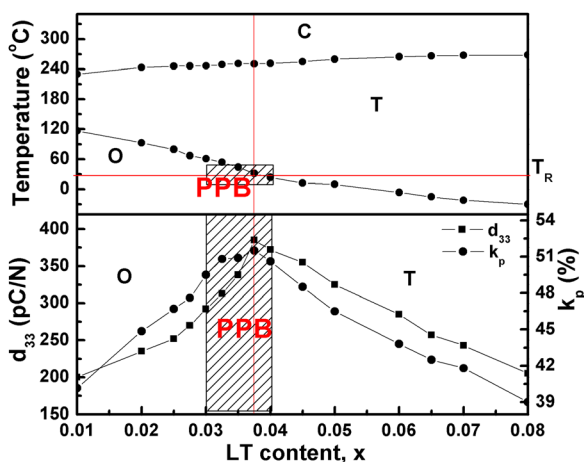


FIG. 1. (Color online) Composition-property-temperature phase diagram of NKNS-xLT solid solution ceramics.

generally believed that the more polarization vectors from coexisted ferroelectric phases positively contribute to the final piezoelectric properties. However, it is still not clear what the more fundamental reason for enhanced piezoelectric properties is for PPB NKN based compositions. By comparison, much more work has been done on MPB Pb-based counterparts.

The domain morphology of representative NKNS-xLT ceramic samples with different phase structures was analyzed by TEM, as shown in Fig. 2. As the composition lies in a single O phase zone ($x=0.02$), one can see complicated ferroelectric domain morphology with irregularly shaped domain boundaries (Fig. 2(a)). As x increases to 0.045, the composition owns a pure T symmetry. Typical 90° domain morphology with parallel strips was observed as shown in Fig. 2(c), which can be described as the alternation of broad and narrow sub-micron sized domains.⁸ It is worthy to note from Fig. 2(b) that as $x=0.0375$, there exist lots of nanodomains with a width of a few nanometers that were arranged within microdomains. In order to identify the local structure information, the $\langle 001 \rangle$ zone axis CBED patterns obtained from the adjacent nanodomains within individual micron domain (Fig. 2(b)) were indicated in Figs. 2(d) and 2(e). It can be seen that the mirror plane is parallel to the $\langle 110 \rangle$ direction in Fig. 2(d) and to the $\langle 100 \rangle$ direction in Fig. 2(e).

For O phases with 2 mm symmetry, the mirror plane in CBED patterns observed along pseudocubic $[001]$ incidence should be parallel to the $\langle 110 \rangle$ direction, but it should be parallel to the $\langle 100 \rangle$ direction for T phases with 4 mm symmetry.¹⁵ Therefore, one can conclude that O and T phases have coexisted within the adjacent nanodomains for $x=0.0375$ samples. In this composition, about 30% of grains in the TEM specimen display nanodomain structure and this feature occupies about 75% within an individual grain. The other compositions in the PPB region are expected to show the similar coexistence of two phases, though the fraction of grains exhibiting two phase coexistence is expected to be less than that in the composition of $x=0.0375$.

To look into the details of nanodomains (Fig. 2(b)), domain structures obtained from the $[001]$ incidence were further analyzed, as shown in Fig. 3. The width of nanodomains is in the range of 20–50 nm. It is found that domain walls intersect each other at either 90° angle between two nanodomains inside two adjacent sub-micron domains or 45° angle between nano- and sub-micron domains. For an O symmetry, there are twelve possible spontaneous polarizations (P_s) in all $[110]$ directions. However, the T symmetry provides six possible P_s in all directions. The adjacent polarization vectors arranged via “head to tail” are limited to the $\{100\}$ planes for 90° O domains and the $\{110\}$ planes for 90° T domains, respectively.¹⁰ Therefore, the domain walls in Fig. 3(a) are in (100) and (010) directions for O phases and in (110) directions for T phases along the $[001]$ zone axis, which can be clearly seen in the sketch of domain evolution shown in Fig. 3(b). It is indicated that the corresponding projection traces of nanodomain walls are approximately along $[010]$ and $[100]$ for O phases and along $[1\bar{1}0]$ for T phases in $[001]$ zone axis. The sub-micron domains are assembled by T nanodomains with the same (110) domain walls. With increasing the volume fraction of T phases (as x increases), these T nanodomains connect each other and finally form the sub-micron domain with (110) walls as can be observed in a single T phase.

It is also of much interest to know why the sub-micron domains can be divided into nanoscale domains via introducing the O phase in T phase matrix. It was found that the free energy profile can be flattened in the phase transition region.¹⁶ Therefore, the polarization anisotropy between two

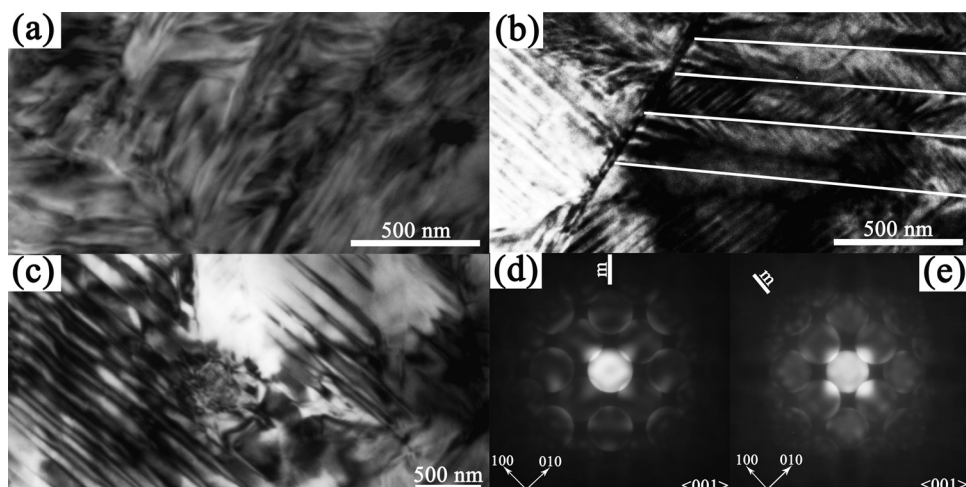


FIG. 2. Bright-field images for various NKNS-xLT compositions: (a) $x=0.02$, (b) $x=0.0375$, (c) $x=0.045$, and (d) and (e) $\langle 001 \rangle$ zone axis CBED patterns for the sample with $x=0.0375$.

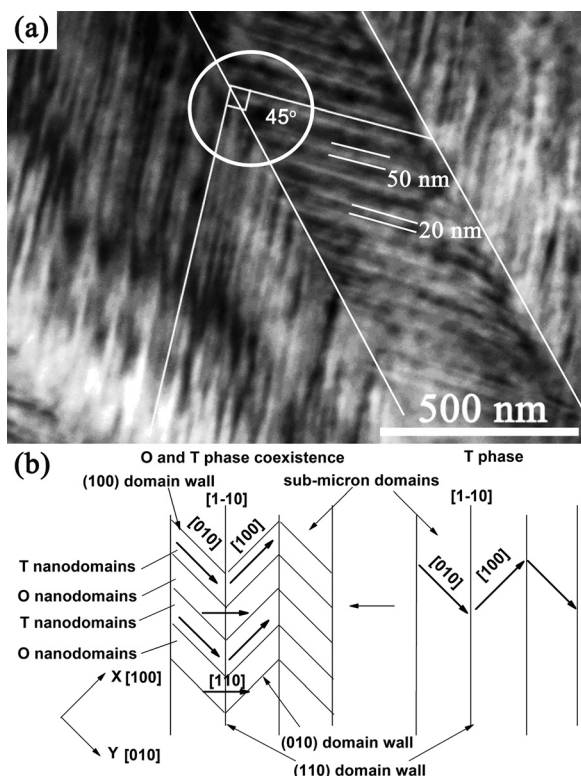


FIG. 3. (a) Bright-field image of NKNS-0.0375LT ceramic sample and (b) the sketch of domain morphology evolution from single T phase to coexisted O and T phases.

polar phases can be vanished in the PPB region, resulting in a decrease of the free energy difference between O and T phases. (In fact, charged domain walls exist unavoidably in the ferroelectrics with local distribution, particularly for nanodomain structure. As a result, the polarization anisotropy in a real system cannot be absolutely zero but should still be lowest in PPB region.) The domain wall then can be considered as the layer that separates two domains with different but crystallographically equivalent directions of the polarization vector.¹⁷ As a result, the domain wall energy decreases as the composition is getting close to the phase boundary. According to the classical theory of ferroelectric domains, the domain size is proportional to the square root of domain wall energy, since domain size is determined by a balance between the energy of domain wall and the energies of electric and elastic fields caused by the spontaneous polarization and strain.¹⁸ Therefore, the domain size tends to be minimized such that nanodomains would be gradually formed as NKNS-xLT compositions move close to the PPB. Because the energy of nanodomain walls is inherently lower, they would be more easily reoriented under the applied electric field, ultimately resulting in the high piezoelectric response in NKNS-xLT systems. This typical nanodomain

morphology was actually observed in conventional MPB PZT based piezoelectric ceramics.^{7–9} The coexistence of two ferroelectric phases tend to produce nanodomains irrespective of the property of the phase boundary (morphotropism or polymorphism).

In summary, the domain morphology of Li, Ta, and Sb modified NKN based lead-free piezoelectric ceramics was analyzed by transmission electron microscopy. The coexistence of O and T phases within adjacent domains was confirmed by means of CBED patterns. Nanodomains of alternate O and T phase domains with a width of 20–50 nm were observed only for compositions in the vicinity of PPB, and induced by the reduction of the domain wall energy owing to the vanishing of the polar anisotropy between O and T phases. The existence of nanodomains was believed to be closely related to the high piezoelectric response in PPB NKN based piezoelectric compositions.

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