Thermally-induced phase transformations in KNNS-BNKZ lead-free piezoceramics

DOI:

[10.1016/j.jeurceramsoc.2019.10.009](https://doi.org/10.1016/j.jeurceramsoc.2019.10.009)

Document Version

Accepted author manuscript

[Link to publication record in Manchester Research Explorer](#)

Citation for published version (APA):

Tangsrirakul, J., Tang, C. C., Hall, D. A., & Day, S. J. (2019). Thermally-induced phase transformations in KNNS-BNKZ lead-free piezoceramics. *Journal of the European Ceramic Society*.
<https://doi.org/10.1016/j.jeurceramsoc.2019.10.009>

Published in:

Journal of the European Ceramic Society

Citing this paper

Please note that where the full-text provided on Manchester Research Explorer is the Author Accepted Manuscript or Proof version this may differ from the final Published version. If citing, it is advised that you check and use the publisher's definitive version.

General rights

Copyright and moral rights for the publications made accessible in the Research Explorer are retained by the authors and/or other copyright owners and it is a condition of accessing publications that users recognise and abide by the legal requirements associated with these rights.

Takedown policy

If you believe that this document breaches copyright please refer to the University of Manchester's Takedown Procedures [<http://man.ac.uk/04Y6Bo>] or contact uml.scholarlycommunications@manchester.ac.uk providing relevant details, so we can investigate your claim.

Thermally-induced phase transformations in KNNS-BNKZ lead-free piezoceramics

J. Tansritrakul^{1,2}, C.C. Tang³, S.J. Day³ and D. A. Hall¹

¹*School of Materials, University of Manchester, Manchester M13 9PL, UK.*

²*Faculty of Science and Technology, Thammasat University, Pathum Thani 12120, Thailand*

³*Diamond Light Source, Harwell Science and Innovation Campus, Didcot, Oxfordshire OX11 0DE, UK*

Abstract

Promising piezoelectric properties have been reported in potassium sodium niobate-based ceramics by introducing $\text{Bi}_{0.5}(\text{Na}_{0.82}\text{K}_{0.18})_{0.5}\text{ZrO}_3$ (BNKZ) into $\text{K}_{0.48}\text{Na}_{0.52}\text{Nb}_{0.95}\text{Sb}_{0.05}\text{O}_3$ (KNNS) solid solutions in order to control the polymorphic phase transformation temperatures. In the present study, synchrotron x-ray powder diffraction (SXPd) was employed in combination with dielectric and ferroelectric measurements in order to clarify the influence of BNKZ on the phase transition temperatures of (1-x)KNNS-(x)BNKZ ceramics (with x = 0 to 0.05). The results, presented in terms of temperature-dependent SXPd patterns, dielectric permittivity and thermal depolarisation characteristics, confirmed that polymorphic phase transformation temperatures all shifted in a systematic manner with increasing BNKZ content. Broadening of the phase transition regions was also observed with increasing BNKZ content, leading to improvements in thermal stability of the ferroelectric properties. Microstructural examination of the KNNS-BNKZ ceramics revealed the presence of core-shell microstructures; this was correlated with the presence of weak shoulders on the diffraction peaks.

Keywords: polymorphic phase transformation; synchrotron x-ray diffraction; core-shell microstructure; potassium sodium niobate; temperature dependence.

1. Introduction

Piezoelectric materials have been used in a wide range of applications such as medical ultrasonic imaging, piezoelectric printheads and automotive fuel injectors.[1] Lead zirconate titanate (PZT) ceramics are the common piezoelectric materials in commercial products since the near-vertical morphotropic phase boundary (MPB) between ferroelectric rhombohedral and tetragonal (R-T) phases leads to excellent piezoelectric properties combined with good temperature stability.[2, 3] However, the major drawback of PZT is the presence of Pb, which causes health and environmental concerns.[1, 4] Therefore, one of the current active topics in piezoelectric materials research is the search for new lead-free materials that could be suitable as replacements for PZT in practical devices.

Presently, several different types of lead-free perovskite solid solutions and complex perovskite compounds have been investigated, including (Ba,Ca)(Zr,Ti)O₃ (BCZT), (Na,Bi)TiO₃ (NBT) and (K,Na)NbO₃ (KNN).[1, 2, 5, 6, 7] Methods for improving the piezoelectric properties of such materials by controlling phase coexistence have also been studied; two common approaches involve compositional control of MPBs or polymorphic phase transformations (PPTs), often leading to the coexistence of different crystalline phases.[1, 8, 9] Lidjici [10] reported the coexistence of R-T phases in the binary system (1-x)Bi_{0.5}Na_{0.5}TiO₃-(x)BaTiO₃ (BNT-BT), yielding piezoelectric coefficients $d_{33} = 150$ pC N⁻¹ and $k_t = 51\%$ for the composition with $x = 0.065$. An MPB region was also observed in (1-x)Bi_{0.5}Na_{0.5}TiO₃-(x)Bi_{0.5}K_{0.5}TiO₃ (NBT-KBT) ceramics for $x = 0.16$ to 0.20 , which exhibited the maximum piezoelectric properties in this region.[11, 12, 13] Furthermore, the occurrence of MPBs in numerous binary and ternary lead-free piezoelectric systems has been reported in many other publications.[14, 15, 16, 17, 18, 19, 20]

For KNN-based ceramics, compositional modifications have been employed as a means to shift the phase transformation temperatures towards room temperature and hence to enhance their

piezoelectric properties. Many studies have investigated the substitution of perovskite compounds such as BiScO₃, CaTiO₃, LiSbO₃, BaTiO₃ or LiNbO₃ in KNN in order to reduce the orthorhombic-tetragonal (O-T) phase transition temperature, T_{O-T} . [1, 9, 21, 22, 23, 24, 25, 26] Zang reported that T_{O-T} for the 0.948(K_{0.5}Na_{0.5})NbO₃–0.052LiSbO₃ solid solution occurred at ~35°C and led to a d_{33} value ~265 pC N⁻¹. [24] Similarly, improvements in piezoelectric properties were also obtained by the addition of (x)Ba(Ti_{0.95}Zr_{0.05})O₃ to (1-x)(K_{0.5}Na_{0.5})NbO₃ ceramic (0.04 ≤ x ≤ 0.06), attributed to the occurrence of mixed O-T phases at room temperature. [21] Moreover, the coexistence of rhombohedral-tetragonal (R-T) at room temperature was also achieved by doping Sb⁵⁺ into 0.96[(K_{0.48}Na_{0.52})_{0.95}Li_{0.05}NbO₃]-0.04[BaZrO₃] ceramic or KNLN_{1-x}S_x-BZ which lead to the shifting of T_{O-T} and T_{R-O} towards to room temperature. [27] As a result, the enhancement of piezoelectric properties was observed where x ≥ 0.07 due to the presence of R-T mixed phases. In addition, Rubio-Marcos et al. [28] showed that both intrinsic (structural distortion) and extrinsic (increase of grain size) contributions play a significant role on the improvement of piezoelectric properties in (K_{0.44}Na_{0.52}Li_{0.04})[(Nb_{0.86}Ta_{0.10}Sb_{0.04})_{1-x}Zr_{5x/4}]O₃ ceramic.

Although the temperature-stability of functional properties is generally degraded in materials with PPTs, novel modifications of KNN-based ceramics have yielded piezoelectric properties that are said to be comparable to those of PZT. [29] Promising piezoelectric properties in (1-x)K_{0.48}Na_{0.52}Nb_{0.95}Sb_{0.05}O₃–(x)Bi_{0.5}(Na_{0.82}K_{0.18})_{0.5}ZrO₃ (KNNS–BNKZ) ceramics are attributed to the coexistence of R-T phases at room temperature. [30] However, the precise nature of phase coexistence in KNNS–BNKZ ceramics and the influence of the polymorphic phase transformations on their temperature-dependent functional properties have yet to be clarified. [30, 31] Therefore, the influence of BNKZ content on the thermal evolution of structure and functional properties of (1-x)KNNS–(x)BNKZ ceramics were investigated in the present study.

2. Experimental methods

The conventional solid state reaction method was used to prepare $(1-x)(\text{K}_{0.48}\text{Na}_{0.52}\text{Nb}_{0.95}\text{Sb}_{0.05})-(x)(\text{Bi}_{0.5}(\text{Na}_{0.82}\text{K}_{0.18})_{0.5}\text{ZrO}_3)$ ceramics ($0 \leq x \leq 0.05$), denoted as 0BNKZ to 5BNKZ in this work. The precursor powders of K_2CO_3 (99.0%), Na_2CO_3 (99.8%), Nb_2O_5 (99.0%), Sb_2O_3 (98.0%), Bi_2O_3 (99.0%) and ZrO_2 (99.0%) were milled in isopropanol for 24 hours and then dried in an oven at 85°C for 24 hours. Note that K_2CO_3 and Na_2CO_3 powders were dried overnight before weighing due to their moisture sensitivity.[32] Then, the mixed powders were calcined at 850°C for 6 hours followed by milling after calcination for 24 hours. Next, the resulting powders were mixed with 2 wt% polyethylene glycol (m.w. = 1500) as a lubricant/binder before uniaxial pressing at 25 MPa into a disc shape with diameter of ~ 8 mm and thickness of ~ 1 mm. The green samples, covered by a layer of calcined powder, were sintered in an alumina crucible at temperatures of 1120, 1140, 1150 and 1170°C for 0BNKZ, 1BNKZ, 2BNKZ to 4BNKZ and 5BNKZ, respectively, for 3 hours after binder burnout at 500°C for 1 hour.

For microstructural studies, the 0BNKZ to 5BNKZ ceramics were mounted in acrylic resin. Then, the cross-sections of all specimens were ground sequentially using silicon carbide papers of grade P400 to P1200 and polished with 6, 1, and $0.25\ \mu\text{m}$ diamond paste, then finally with SiO_2 suspension for 1 hour in the final polishing step. Subsequently, the polished samples were coated with carbon prior to observing the microstructure using a field-emission scanning electron microscope (FEGSEM), Philips XL30, in backscattered electron (BSE) imaging mode. Also, micro-chemical analysis was carried out using energy-dispersive x-ray spectroscopy (EDS). The average grain size was calculated by the linear intercept method.[33]

For electrical measurements, silver electrodes (Gwent Group type C2000107P3) were applied on the parallel surfaces of the samples, ground to ~ 1 mm in thickness, and then fired at 550°C for 30 min. The temperature-dependent dielectric properties were measured over a range of temperature between 50°C and 450°C using a HP4284A impedance analyser at a frequency of 100 kHz. The ferroelectric P-E hysteresis behaviour was measured as a function of temperature from 25°C to 150°C .

Four cycles of a sinusoidal electric field with amplitude of 4 kV mm⁻¹ and frequency of 2 Hz were applied to the samples immersed in silicone oil. Further details of the P-E loop measurement system used in this experiment are given in previous work.[34] In addition, the depolarisation temperature (T_d) was investigated by using a HP34401A multimeter in combination with a current amplifier [34] to determine the remnant polarisation of a poled sample as a function of temperature from 25°C to 350°C. Note that all samples were poled prior to measurement by applying an AC field with amplitude of 4 kV mm⁻¹ at room temperature.

Since phase coexistence in (1-x)KNNS-(x)BNKZ ceramics has been reported in the literature[30], an in-situ temperature-dependent high resolution Synchrotron X-ray Powder Diffraction (SXPd) study was carried out on beamline I11 at the Diamond Light Source, UK, with a photon energy of 15 keV ($\lambda = 0.825711 \text{ \AA}$), calibrated using NIST SRM640c Si standard).[35] Sample preparation for SXPd measurements involved the packing of crushed ceramic powders into borosilicate glass capillaries of diameter 0.3 mm, which were mounted on a magnetic spinner. The temperature-dependent SXPd patterns were collected by using a wide-angle position sensitive detector (PSD), covering the angular range from 10° to 90° 2 θ , in conjunction with a LN₂ Cryostream (Oxford Cryosystems) to control the temperature from -143 to 227 °C and a Cyberstar hot air blower to provide higher temperatures up to 450°C. Phase identification at different temperatures was achieved by means of a full-pattern refinement method with a Pseudo-Voigt peak-shape function using Topas software (version 5, Bruker).[36]

3 Results and Discussion

3.1. Microstructure

Figure 1 shows the polished cross-section microstructures for the KNNS-BNKZ ceramics observed by using SEM in BSE mode. Chemically homogeneous grains with average size of $3.9 \pm 1.9 \text{ }\mu\text{m}$ were observed only for the unmodified KNNS, while the addition of BNKZ had a dramatic effect on microstructure. Chemical heterogeneity in the form of core-shell microstructures was evident in all

BNKZ-containing compositions, as shown in Figure 1(b)-(d).[37, 38] For the 1BNKZ composition, there are some ultra-large grains surrounded by fine grains, causing the average grain size to drop to $1.4 \pm 0.6 \mu\text{m}$. However, as the BNKZ content increased from 2BNKZ to 4BNKZ, the average grain size increased slightly from $1.8 \pm 0.4 \mu\text{m}$ to $2.6 \pm 0.4 \mu\text{m}$. The increase of grain size with increasing BNKZ content is possibly due to liquid phase formation due to the presence of bismuth oxide, together with the associated eutectic reactions.[39] In contrast, the average grain size of the 5BNKZ composition was significantly lower, at less than $1 \mu\text{m}$. Similarly, Xing [39] also found a sudden decrease of grain size in $(1-x)\text{K}_{0.48}\text{Na}_{0.52}\text{Nb}_{0.95}\text{Sb}_{0.05}\text{O}_3 - (x)(\text{Bi}_{0.5}\text{Na}_{0.5})_{0.9}(\text{Li}_{0.5}\text{Ce}_{0.5})_{0.1}\text{ZrO}_3$ ceramics for $x > 0.045$ because the addition of excess $(\text{Bi}_{0.5}\text{Na}_{0.5})_{0.9}(\text{Li}_{0.5}\text{Ce}_{0.5})_{0.1}\text{ZrO}_3$ inhibited grain growth. Although Wang and Zhen [40, 41] found that the occurrence of core-shell microstructure caused a decrease of piezoelectric properties in KNN-based ceramics, there are some contradictory reports of promising piezoelectric properties in core-shell microstructured ceramics for $\text{Bi}_{1/2}\text{Na}_{1/2}\text{TiO}_3\text{-SrTiO}_3$ or $(\text{K}_{0.51}\text{Na}_{0.47}\text{Li}_{0.02})(\text{Nb}_{0.8}\text{Ta}_{0.2})\text{O}_3\text{-CaZrO}_3$ solid solutions.[38, 42] This suggests that the role of core-shell microstructure on piezoelectric properties is still unclear and requires further investigation to clarify the mechanisms that control functional properties in such materials.

Figure 1. Polished cross-sections illustrating SEM images (BSE mode) of (a) 0BNKZ with homogeneous microstructure and (b)-(d) 1BNKZ, 3BNKZ and 5BNKZ with chemically heterogeneous core-shell type microstructures.

An investigation of chemical heterogeneity in the core-shell microstructure of the 3BNKZ ceramic was conducted using EDS, as illustrated Figure 2. The results obtained for four different areas in the microstructure, labelled as *core*, *shell*, *region 1* and *region 2*, are shown. The EDS results reveal that the amount of K in the core is slightly higher than that of Na, but lower in the shell, as shown in Figure 2(a). Similarly, Zhou [43] reported the occurrence of K^+ vacancies in the shell regions for core-shell structured $(K_{0.48(1-x)}Na_{0.52})_{0.95}Li_{0.05}Nb_{0.95}Sb_{0.05}O_3$ ceramics. The origin of chemical heterogeneity in KNN-based piezoceramics has been discussed recently by Thong et al. [44] According to the difference of diffusion couple reaction rate between Na_2CO_3/Nb_2O_5 and K_2CO_3/Nb_2O_5 , chemical heterogeneity can originate in the KNN calcined powder in which $NaNbO_3$ grains can growth larger than those of

KNbO₃. Consequently, the A-site chemical heterogeneity occurred in the KNN sintered ceramic, consistent with the EDS results presented in Figure 2(a). However, for the other elements, no obvious differences in concentrations were observed between core and shell regions.

Furthermore, the chemical compositions of regions 1 and 2, shown in Figure 2(a), were investigated by EDS. The results reveal that region 1 contains high K and Nb concentrations, with low amounts of Na, Sb, Bi and Zr, which corresponds to the EDS results of secondary phase in KNN-ZrO₂ reported by Malicet al.[45] Hence, it can be assumed that region 1 is possibly the secondary phase of K_{2.75}Nb_{5.45}O₁₅ that was observed by the high-resolution SXPD as mentioned in previous work.[31] On the other hand, the feature in region 2 is possibly associated with the segregation of Sb, Bi and Zr inside the core-shell grains which could not be detected by diffraction.

Figure 2. (a) EDS analysis of core, shell, region 1 and region 2 in (b) BSE image for 3BNKZ ceramic showing K-enrichment and K-deficiency in core and shell regions, respectively. In addition, the secondary phase of K_{2.75}Nb_{5.45}O₁₅ and the segregation of Sb, Bi and Zr are identified in regions 1 and 2, respectively.

3.2. Thermally-induced phase transformations

Surface plots of the pseudo-cubic {200}_p diffraction profiles as a function of temperature from -143°C to 227°C for the KNNS-BNKZ ceramics are shown in Figure 3; these plots illustrate the

1 effects of BNKZ on the phase transition temperatures, using the results of high-resolution SXPD
2 measurements. For 0BNKZ, two polymorphic phase transformations occur upon heating from -143°C
3 to 227°C; the single peak of the rhombohedral (R) phase is present at -143°C, transforming into
4 characteristic doublets associated with orthorhombic (O) and tetragonal (T) phases at temperatures
5 around -100°C and 100°C, respectively, as shown in Figure 3(a).

6 On introducing BNKZ into the KNNS solid solution, the two polymorphic phase
7 transformations are still observed for the 1BNKZ composition but the transition temperatures differ
8 from those of the unmodified KNNS ceramic. Furthermore, there is a weak shoulder that becomes
9 apparent, especially in the tetragonal phase field, at lower 2θ values for both $(002)_T$ and $(020)_T$
10 reflections, indicated by the arrows in Figure 3(b). With increasing BNKZ composition, it was found
11 that the orthorhombic phase region disappears for the 3BNKZ composition, while only two phases,
12 tetragonal and rhombohedral, are observed over this range of temperature. It is assumed that T_{R-O}
13 and T_{O-T} are shifted with increasing BNKZ content and merge at room temperature. Consequently, the
14 orthorhombic phase region is not apparent for the 3BNKZ ceramic. On the other hand, only broad
15 peaks are present for the 5BNKZ composition over the full temperature range, which is possibly
16 related to its microstructure, which exhibits the smallest grain size of less than 1 μm , as illustrated in
17 Figure 1(d).

Figure 3. Changes in $\{200\}_p$ diffractions peak profiles for (a) 0BNKZ, (b) 1BNKZ, (c) 3BNKZ and (d) 5BNKZ ceramics upon heating from -143°C to 227°C showing modification of the thermally-induced phase transformations with increasing BNKZ content ($\lambda = 0.825711 \text{ \AA}$).

In addition, the 2D contour maps of the $\{200\}_p$ reflection for all of the KNNS-BNKZ ceramics are illustrated in Figure 4. It is evident that T_{O-T} gradually decreases, while T_{R-O} slightly increases with increasing BNKZ content. As a result, the orthorhombic phase region becomes more contracted and disappears for 3BNKZ, giving rise to the R-T mixed phase region at room temperature, as seen in Figure 3(c) and Figure 4(d). Furthermore, another effect of introducing BNKZ into the KNNS solid solution is the broadening of the mixed phase region near T_{R-O} and T_{O-T} as the BNKZ content increases. Many publications [30, 46] have identified the shifting of T_{O-T} and T_{R-O} on the basis of temperature-dependent dielectric permittivity measurements. However, in the present work, the high-resolution

- 1 SXP measurements are used in combination with dielectric studies to confirm the shifting and
- 2 broadening of T_{O-T} and T_{R-O} directly.

3
4 *Figure 4. Contour plots of the $\{200\}_p$ diffractions peaks on heating from -143 to 227 °C, showing the*
5 *shifting and broadening of T_{O-T} and T_{R-O} transformation regions for (a)0BNKZ, (b)1BNKZ, (c)2BNKZ,*
6 *(d)3BNKZ, (e)4BNKZ and (f)5BNKZ ceramics ($\lambda = 0.825711 \text{ \AA}$).*

7
8 Some additional high temperature measurements up to 450°C, in excess of the Curie point
9 (T_c), were carried out in order to extend the study into the cubic (C) phase field. Figure 5 shows the
10 $(200)_c$ peak profiles together with temperature-dependent lattice parameters for 0BNKZ and 2BNKZ
11 compositions at temperatures above T_c , from 300°C to 450°C. Note that the lattice parameters were
12 derived from full-pattern refinement with cubic space group $Pm3m$. The data presented in Figure 5(a)
13 represents a single cubic phase for the 0BNKZ composition, with a gradual increase of the lattice
14 parameter being apparent due to thermal expansion.[38] In contrast, the high temperature SXP
15 profiles for the 2BNKZ composition reveal the presence of a persistent shoulder in all reflections which
16 indicates the existence of a second cubic phase, as illustrated in Figure 5(b). Correspondingly, this

1 persistent peak is consistent with the occurrence of the weak shoulders that were also identified in
2 Figure 3(b-c).

3
4 Figure 5. Surface plots of the (200)_c peak profiles (left) with temperature-dependent lattice parameters
5 (right) within the cubic phase field for (a) 0BNKZ and (b) 2BNKZ compositions ($\lambda = 0.825711$ Å). The
6 noticeable deviation of the *a*_{core} data in (b) is due to the weak intensity contributions of the second
7 cubic phase.

8
9 The presence of the weak shoulder at low 2θ values in the SXPD profiles can be attributed to
10 the occurrence of core-shell microstructures, in which there are variations in chemical composition
11 between core and shell regions; K-rich in the core and K-deficient in the shell, as mentioned earlier in
12 section 3.1. In previous work, Tellier reported that the unit cell size of K_xNa_{1-x}NbO₃ ceramics increased
13 with increasing K content because the effective ionic radius of K⁺ (~1.64 Å) is larger than that of Na⁺
14 (~1.39 Å). [47] Therefore, it can be assumed that the occurrence of the weak shoulder at low 2θ, or

high d -spacing, is possibly generated by the cubic phase of the K-rich core. On the other hand, the presence of the major peak is attributed to the cubic reflection of the K-deficient shell. It can be concluded that the observed weak shoulder in Figure 5(b) is associated with the core, while the major peak is attributed to the shell.

3.3. Identification of crystal structure at different temperatures

Figure 6 shows the $\{200\}_p$ profiles from full-pattern refinements for the KNNS-BNKZ ceramics at certain temperatures of -140°C , 20°C , 227°C and 350°C . It is observed that the best-fit refinements for 0BNKZ at these temperatures are rhombohedral $R3mR$ (R), orthorhombic $Amm2$ (O), tetragonal $P4mm$ (T) and cubic $Pm3m$ (C), respectively. The evolution of lattice parameters and phase fractions as a function of temperature upon heating from -153°C to 227°C for the unmodified KNNS ceramic are also illustrated in Figure 8(a) and (c), respectively.

Figure 6. $\{200\}_p$ diffraction peak profiles illustrating the measured (black circles), calculated (red line) and difference (grey line) curves from full-pattern refinements at -140°C , 20°C , 227°C and 350°C for (a) 0BNKZ (b) 1BNKZ, (c) 3BNKZ and (d) 5BNKZ with individual best-fit phase identifications ($\lambda = 0.825711 \text{ \AA}$).

Since the introduction of BNKZ into KNNS ceramics caused the occurrence of core-shell microstructure as well as the weak shoulder in the SXPD profiles, as described previously, full-pattern

refinement for the 1BNKZ composition at -140°C is best fitted with coexisting rhombohedral models, referred to as *core-shell rhombohedral*. It was found that the lowest R_{wp} from the full-pattern refinement of 1BNKZ at -140°C with a single rhombohedral model was 7.70%, while the core-shell rhombohedral model shows an improved fit with R_{wp} of 5.57%. Additionally, the improvement of the calculated curve was also evident when fitting with core-shell rhombohedral model, as shown in Figure 7. This implies that the stable phase formation for the 1BNKZ ceramic at -140°C comprises core-shell rhombohedral (R_{core} - R_{shell}).

Figure 7. Comparison of full-pattern refinements for 1BNKZ composition at -140°C with single rhombohedral and core-shell rhombohedral models showing the improvements of the calculated (red) and difference (grey) curves in core-shell rhombohedral model ($\lambda = 0.825711 \text{ \AA}$).

With increasing temperature, it was found that the crystal structure of the 1BNKZ ceramic transforms to core-shell orthorhombic (O_{core} - O_{shell}), core-shell tetragonal (T_{core} - T_{shell}) and core-shell cubic (C_{core} - C_{shell}) at 20°C, 227°C and 350°C, respectively, as observed in Figure 6(b). The evolution of core-shell lattice parameters and phase fractions for the 1BNKZ ceramic from -153°C to 227°C is

illustrated in Figure 8(b) and (d), showing a broader transition temperature region in comparison with 0BNKZ. Note that the lattice parameters of each phase in the transition region were extrapolated individually from the trend of each phase in the single phase field.

Figure 8. Thermal evolution of (a),(b) lattice parameters and (c),(d) phase fractions of rhombohedral (R), orthorhombic (O) and tetragonal (T) phases for 0BNKZ and 1BNKZ compositions showing the widening of the phase transition range. Note that the uncertainties in lattice parameters and phase fractions are typically less than 0.002% and 1%, respectively.

Although the identification of phase formation at room temperature described in previous work indicated the occurrence of O-T coexisting phases in the 1BNKZ composition[31], the contour plots of the thermally-induced SXPD profiles (Figure 4) in the present results revealed contradictory results. The coexistence of R-O was observed clearly in the temperature range of -73°C to -43°C, whereas the O-T mixed phase occurred for temperatures between 87°C and 117°C, as seen in the

figure. Hence, phase formation for the 1BNKZ composition at room temperature ($\sim 20^\circ\text{C}$) is more correctly assigned to core-shell orthorhombic ($O_{\text{core}}-O_{\text{shell}}$) instead of coexisting O-T phases. This suggests that the identification of coexisting phases at room temperature is not always straightforward. Therefore, the additional analysis of temperature-dependent diffraction profiles should be considered in order to make more accurate identification of mixed phases at room temperature.

Furthermore, the phase identification for the 3BNKZ ceramic becomes more complicated due to the broadening of the phase transitions with increasing BNKZ content. Figure 6(c) shows that the core-shell rhombohedral ($R_{\text{core}}-R_{\text{shell}}$) structure is still observed for 3BNKZ at a temperature of -140°C , while the coexistence of rhombohedral-tetragonal (R-T), core-shell tetragonal ($T_{\text{core}}-T_{\text{shell}}$) and core-shell cubic ($C_{\text{core}}-C_{\text{shell}}$) phases are found at temperatures of 20°C , 227°C and 350°C , respectively. Full-pattern refinements of the 5BNKZ data were also attempted, although the SXPD profiles of this composition show diffuse diffraction peaks. It was found that 5BNKZ at -140°C possibly comprises R-T coexisting phases, not core-shell rhombohedral as observed in other compositions, since a lower R_{wp} value was obtained by full-pattern refinement with the R-T model (7.46%) compared with the core-shell rhombohedral model (7.77%). This is possibly due to the broadening of the R-T phase coexistence region, which occurs at 20°C in 3BNKZ, with increasing BNKZ content. Furthermore, the coexistence of rhombohedral and cubic phases (R-C) is observed at 20°C , whereas core-shell cubic ($C_{\text{core}}-C_{\text{shell}}$) was identified at 227°C and 350°C for 5BNKZ, as shown in Figure 6(d).

3.4. Temperature-dependent dielectric properties

The phase transformation temperatures in KNNS-BNKZ ceramics were investigated by temperature-dependent dielectric permittivity and loss tangent measurements over the temperature range from 50°C to 450°C , as shown in Figure 9. Note that only two phase transition temperatures, $T_{\text{O-T}}$ and T_{C} , could be observed from the ϵ_r -T plots. It is apparent that T_{C} reduces gradually from $\sim 300^\circ\text{C}$ to $\sim 200^\circ\text{C}$, while $T_{\text{O-T}}$ decreases slightly from $\sim 125^\circ\text{C}$ to below 50°C as the BNKZ content changes from

0BNKZ to 4BNKZ. Moreover, the change of dielectric permittivity as a function of temperature at both T_{O-T} and T_c becomes more diffuse as BNKZ content increases, which correlates well with the SXPD results described in section 3.2 above. However, the orthorhombic phase may not completely disappear for 3BNKZ to 4BNKZ composition as found in the SXPD result, since the presence of subtle change at T_{O-T} for temperature-dependent dielectric permittivity as well as polarisation is still observed as seen in Figure 9 and Figure 12, respectively. The inset plots in Figure 9 show the results for 5BNKZ, which exhibited a diffuse phase transition due to the fine-grained microstructure shown in Figure 1(d). For $\tan\delta$, the highest loss values near room temperature were found for the 0BNKZ composition because of its low relative density (<90%) as described previously.[31]

Figure 9. ϵ_r - T and $\tan\delta$ - T plots for KNNS-BNKZ ceramics, measured at 100 kHz, showing the decrease of orthorhombic-tetragonal (T_{O-T}) and tetragonal-cubic (T_c) phase transition temperatures with increasing BNKZ content.

A comparison of the contour maps of the $\{200\}_p$ XRD peak profiles, dielectric permittivity and loss tangent in the temperature range from 50°C to 200°C for 0BNKZ and 4BNKZ is presented in Figure 10(a) and (b) respectively, in order to study the relationship between the O-T structural phase transformation and dielectric properties. It was found that the abrupt change of dielectric permittivity for 0BNKZ starts at ~100°C and reached a peak at ~125°C, while the crystal structure fully transforms to tetragonal beyond 125°C. The increase in dielectric permittivity at T_{O-T} is derived from both intrinsic

(lattice distortion, ionic polarization) and extrinsic (domain wall motion, localised domain switching) contributions.[48, 49] In contrast, the $\tan\delta$ values reduced gradually over the same temperature range, indicating that the domain walls are generally less mobile in the tetragonal phase region, as reported by Peng et al.[50] However, the T_{O-T} was not observed in this range of temperature in 4BNKZ but the sudden increase of dielectric permittivity was observed from $\sim 150^\circ\text{C}$ to $\sim 200^\circ\text{C}$ due to approaching the tetragonal-cubic phase transformation at T_c , as shown in Figure 10(b).

Figure 10. Comparison between diffraction data, represented as contour maps of $\{200\}_p$ peak profiles, dielectric permittivity (red squares) and loss tangent (black circles) measured at 100 kHz for (a) 0BNKZ and (b) 4BNKZ upon heating from 50 to 200 °C.

3.5. Temperature-dependent ferroelectric properties

Figure 11(a) and (b) illustrate the effect of temperature on the ferroelectric P-E hysteresis loops for 1BNKZ and 5BNKZ ceramics respectively, measured at a frequency of 2 Hz with an electric field amplitude of 4 kV mm⁻¹. The changes in remnant polarisation (P_r) and coercive field (E_c) as a function of temperature from 25°C to 150°C for all BNKZ-containing compositions are illustrated in Figure 11(c) and (d), respectively. It is apparent that P_r and E_c decrease gradually with increasing temperature. For 1BNKZ, P_r decreases from 0.18 to 0.08 C m⁻² (~54%) as temperature increases to 150°C, while the percentage of P_r degradation for 2BNKZ to 5BNKZ compositions is lower which implies more thermal stability. Jin [51] suggested that the thermal degradation in P_r and E_c is due primarily to

a reduction in spontaneous polarisation within the domains, which are more easily switched under an electric field. These effects can be correlated with the reduction in tetragonality (for example), due to the thermally-dependent lattice parameters, as shown in Figure 8.

Figure 11. Temperature-dependent P-E loops from 25 °C to 150 °C for (a) 1BNKZ and (b) 5BNKZ ceramics with thermal degradation of (c) remnant polarisation and (d) coercive field for KNNS-BNKZ ceramics.

Although Ochoa [49] reported that the saturation and remnant polarisation values of $(K_{0.44}Na_{0.52}Li_{0.04})(Nb_{0.86}Ta_{0.10}Sb_{0.06})O_3$ ceramic reach a peak at T_{O-T} due to the enhancement of polarisation orientations in the coexisting O-T phases, such an increase of polarisation at T_{O-T} was not observed in the present study. However, a marked reduction in E_c , from 1.53 kV mm⁻¹ (at 90°C) to 1.30 kV mm⁻¹ (at 120°C), was evident for 1BNKZ, as shown in Figure 11(d). According to the results reported in section 3.2, the broadening of the phase transformation ranges was observed with increasing BNKZ content. In other words, the 1BNKZ composition, which exhibits the narrowest phase transformation

region, also shows the strongest reductions in P_r and E_c with increasing temperature. Therefore, it can be assumed that the broadening of phase transformation regions can play a significant role in the improvement of thermal stabilisation of P_r and E_c for KNNS-BNKZ ceramics.

3.6. Thermal depolarisation

The influence of BNKZ content on the depolarisation behaviour of KNNS ceramics was studied in the temperature range between 50°C and 300°C, as shown in Figure 12. For BNT-based ceramics, the depolarisation temperature (T_d) was defined by Anton [52] as the temperature at which the steepest decrease of remnant polarisation occurs as a function of temperature, due to the occurrence of polymorphic phase transformations. In the present results, it was found that there are two depolarisation regions for the 1BNKZ ceramic; the first occurs at ~110°C and the second at ~285°C, corresponding to the T_{O-T} and T_c values observed in the ϵ_r -T plots (Figure 9). With increasing BNKZ content, gradual reductions in T_c and T_{O-T} , similar to those observed by the SXPD and dielectric measurements, are also confirmed by the depolarisation study.

Figure 12. Thermal depolarisation for 1BNKZ to 5BNKZ ceramics showing the decrease of depolarisation temperature with increasing BNKZ content.

4 Conclusions

Investigations on thermally-induced phase transformations and functional properties of KNNS-BNKZ ceramics were presented in this work. The introduction of BNKZ into KNNS solid solutions leads to the formation of core-shell microstructures due to chemical heterogeneity, which has a strong influence on crystal structure. This indicates that the enhancement of piezoelectric properties for KNNS-BNKZ ceramic is possibly due to the contributions of both intrinsic and extrinsic factors. Temperature-dependent SXPD measurements were employed to clarify the effect of BNKZ on the polymorphic phase transformations. Persistent low-angle shoulders, which were observed in all diffraction peak profiles even after transformation to the cubic phase, are attributed to differences in potassium content between core and shell regions. As a result, the coexistence of core-shell rhombohedral, orthorhombic, tetragonal and cubic phases was identified for different temperatures and compositions. Furthermore, the shifting of T_{O-T} and T_{R-O} toward room temperature, due to the addition of BNKZ and Sb into KNN ceramics, as mentioned in previous literature[30], was also confirmed in the present study by high resolution SXPD, leading to the occurrence of O-T or R-T mixed phases at room temperature with increasing BNKZ content. Additionally, reductions in T_{O-T} and T_c with increasing BNKZ content were verified by measurements of the temperature-dependent dielectric properties and thermal depolarisation behaviour. Temperature-dependent ferroelectric measurements demonstrated thermal degradation in P_r and E_c values, but improvement of thermal stability due to broadening of the phase transformation regions with increasing BNKZ content in KNNS ceramics.

Acknowledgements

We would like to thank Diamond Light Source for access to beamline I11 (proposal number EE13116) that contributed to the results presented here. Also, JT thanks Thammasat University for financial support in the form of a PhD scholarship at the University of Manchester.

References

1. Rodel J, Jo W, Seifert KTP, Anton EM, Granzow T, Damjanovic D. Perspective on the Development of Lead-free Piezoceramics. *J Am Ceram Soc.* 2009;92:1153-77.
2. Panda PK, Sahoo B. PZT to Lead Free Piezo Ceramics: A Review. *Ferroelectrics.* 2015;474:128-43.
3. Guo R, Cross LE, Park SE, Noheda B, Cox DE, Shirane G. Origin of the High Piezoelectric Response in $\text{PbZr}_{1-x}\text{Ti}_x\text{O}_3$. *Physical Review Letters.* 2000;84:5423-6.
4. Ringgaard E, Wurlitzer T. Lead-free piezoceramics based on alkali niobates. *Journal of the European Ceramic Society.* 2005;25:2701-6.
5. Rodel J, Webber KG, Dittmer R, Jo W, Kimura M, Damjanovic D. Transferring lead-free piezoelectric ceramics into application. *Journal of the European Ceramic Society.* 2015;35:1659-81.
6. Takenaka T. *Lead-Free Piezoelectric Ceramics.* San Diego: Elsevier Academic Press Inc; 2013.
7. Rigoberto L-J, Federico G, María-Elena V-C. *Lead-Free Ferroelectric Ceramics with Perovskite Structure: InTech;* 2011.
8. Shrout TR, Zhang SJ. Lead-free piezoelectric ceramics: Alternatives for PZT? *Journal of Electroceramics.* 2007;19:111-24.
9. Li JF, Wang K, Zhu FY, Cheng LQ, Yao FZ. (K,Na)NbO₃-Based Lead-Free Piezoceramics: Fundamental Aspects, Processing Technologies, and Remaining Challenges. *J Am Ceram Soc.* 2013;96:3677-96.
10. Lidjici H, Lagoun B, Berrahal M, Rguitti M, Hentatti MA, Khemakhem H. XRD, Raman and electrical studies on the $(1-x)(\text{Na}_{0.5}\text{Bi}_{0.5})\text{TiO}_3$ - $x\text{BaTiO}_3$ lead free ceramics. *J Alloy Compd.* 2015;618:643-8.
11. Moosavi A, Bahrevar MA, Aghaei AR, Ramos P, Alguero M, Amorin H. High-field electromechanical response of $\text{Bi}_{0.5}\text{Na}_{0.5}\text{TiO}_3$ - $\text{Bi}_{0.5}\text{K}_{0.5}\text{TiO}_3$ across its morphotropic phase boundary. *J Phys D-Appl Phys.* 2014;47.
12. Otoničar M, Škapin SD, Spreitzer M, Suvorov D. Compositional range and electrical properties of the morphotropic phase boundary in the $\text{Na}_{0.5}\text{Bi}_{0.5}\text{TiO}_3$ - $\text{K}_{0.5}\text{Bi}_{0.5}\text{TiO}_3$ system. *Journal of the European Ceramic Society.* 2010;30:971-9.
13. Atsushi S, Tatsuya C, Youichi M, Etsuo O. Dielectric and Piezoelectric Properties of $(\text{Bi}_{0.5}\text{Na}_{0.5})\text{TiO}_3$ - $(\text{Bi}_{0.5}\text{K}_{0.5})\text{TiO}_3$ Systems. *Japanese Journal of Applied Physics.* 1999;38:5564.
14. Pal V, Thakur OP, Dwivedi RK. Investigation of MPB region in lead free BLNT-BCT system through XRD and Raman spectroscopy. *J Phys D-Appl Phys.* 2015;48.
15. Pan Z, Wang Q, Chen J, Liu C, Fan LL, Liu LJ, Fang L, Xing XR. Enhanced Piezoelectric Properties of Tetragonal $(\text{Bi}_{1/2}\text{K}_{1/2})\text{TiO}_3$ Lead-Free Ceramics by Substitution of Pure Bi-Based $\text{Bi}(\text{Mg}_{2/3}\text{Nb}_{1/3})\text{O}_3$. *J Am Ceram Soc.* 2015;98:104-8.
16. Martin-Arias L, Castro A, Alguero M. Ferroelectric phases and relaxor states in the novel lead-free $(1-x)\text{Bi}_{1/2}\text{K}_{1/2}\text{TiO}_3$ - $x\text{BiScO}_3$ system ($0 \leq x \leq 0.3$). *J Mater Sci.* 2012;47:3729-40.

17. Morozov MI, Einarsrud MA, Grande T. Polarization and strain response in $\text{Bi}_{0.5}\text{K}_{0.5}\text{TiO}_3\text{-BiFeO}_3$ ceramics. *Applied Physics Letters*. 2012;101.
18. Cheng RF, Xu ZJ, Chu RQ, Hao JG, Du J, Li GR. Structure and electrical properties of $\text{Bi}_{1/2}\text{Na}_{1/2}\text{TiO}_3$ -based lead-free piezoelectric ceramics. *RSC Adv*. 2015;5:41646-52.
19. Cheng RF, Xu ZJ, Chu RQ, Hao JG, Du J, Ji WB, Li GR. Large piezoelectric effect in $\text{Bi}_{1/2}\text{Na}_{1/2}\text{TiO}_3$ -based lead-free piezoceramics. *Ceram Int*. 2015;41:8119-27.
20. Zhou CR, Liu XY, Li WZ, Yuan CL. Dielectric and piezoelectric properties of $\text{Bi}_{0.5}\text{Na}_{0.5}\text{TiO}_3\text{-Bi}_{0.5}\text{K}_{0.5}\text{TiO}_3\text{-BiCrO}_3$ lead-free piezoelectric ceramics. *J Alloy Compd*. 2009;478:381-5.
21. Li XH, Jiang M, Liu J, Zhu JL, Zhu XH, Li LH, Zhou Y, Zhu JG, Xiao DQ. Phase transitions and electrical properties of $(1-x)(\text{K}_{0.5}\text{Na}_{0.5})\text{NbO}_3\text{-xBiScO}_3$ lead-free piezoelectric ceramics with a CuO sintering aid. *Phys Status Solidi A-Appl Mat*. 2009;206:2622-6.
22. Wu J, Xiao D, Wang Y, Wu W, Zhang B, Zhu J. Improved temperature stability of CaTiO_3 -modified $[(\text{K}_{0.5}\text{Na}_{0.5})_{0.96}\text{Li}_{0.04}](\text{Nb}_{0.91}\text{Sb}_{0.05}\text{Ta}_{0.04})\text{O}_3$ lead-free piezoelectric ceramics. *Journal of Applied Physics*. 2008;104:024102.
23. Lin D, Kwok KW, Chan HLW. Microstructure, dielectric and piezoelectric properties of $(\text{K}_{0.5}\text{Na}_{0.5})\text{NbO}_3\text{-Ba}(\text{Ti}_{0.95}\text{Zr}_{0.05})\text{O}_3$ lead-free ceramics with CuO sintering aid. *Appl Phys A-Mater Sci Process*. 2007;88:359-63.
24. Zhang S, Xia R, Shrout TR, Zang G, Wang J. Piezoelectric properties in perovskite $0.948(\text{K}_{0.5}\text{Na}_{0.5})\text{NbO}_3\text{-}0.052\text{LiSbO}_3$ lead-free ceramics. *Journal of Applied Physics*. 2006;100:104108.
25. Park H-Y, Ahn C-W, Song H-C, Lee J-H, Nahm S, Uchino K, Lee H-G, Lee H-J. Microstructure and piezoelectric properties of $0.95(\text{Na}_{0.5}\text{K}_{0.5})\text{NbO}_3\text{-}0.05\text{BaTiO}_3$ ceramics. *Applied Physics Letters*. 2006;89:062906.
26. Gong YQ, Yang G, Li XJ, Gong LJ, Li L, Peng JF, Zheng XJ. Piezoelectric properties and aging mechanism of $\text{K}_{0.5}\text{Na}_{0.5}\text{Nb}_{(1-y)}\text{Sb}_y\text{O}_3$ piezoceramics prepared by low temperature solvothermal method. *J Mater Sci-Mater Electron*. 2012;23:1910-5.
27. Rubio-Marcos F, López-Juárez R, Rojas-Hernandez RE, del Campo A, Razo-Pérez N, Fernandez JF. Lead-Free Piezoceramics: Revealing the Role of the Rhombohedral–Tetragonal Phase Coexistence in Enhancement of the Piezoelectric Properties. *ACS Applied Materials & Interfaces*. 2015;7:23080-8.
28. Rubio-Marcos F, Fernandez JF, Ochoa DA, García JE, Rojas-Hernandez RE, Castro M, Ramajo L. Understanding the piezoelectric properties in potassium-sodium niobate-based lead-free piezoceramics: Interrelationship between intrinsic and extrinsic factors. *Journal of the European Ceramic Society*. 2017;37:3501-9.
29. Wang K, Yao FZ, Jo W, Gobeljic D, Shvartsman VV, Lupascu DC, Li JF, Rodel J. Temperature-Insensitive $(\text{K,Na})\text{NbO}_3$ -Based Lead-Free Piezoactuator Ceramics. *Adv Funct Mater*. 2013;23:4079-86.
30. Wang XP, Wu JG, Xiao DQ, Zhu JG, Cheng XJ, Zheng T, Zhang BY, Lou XJ, Wang XJ. Giant Piezoelectricity in Potassium-Sodium Niobate Lead-Free Ceramics. *J Am Chem Soc*. 2014;136:2905-10.
31. Tangsritrakul J, Hall DA. Structural and functional characterisation of KNNS–BNKZ lead-free piezoceramics. *Advances in Applied Ceramics*. 2018;117:42-8.
32. Bomlai P, Wichianrat P, Muensit S, Milne SJ. Effect of calcination conditions and excess alkali carbonate on the phase formation and particle morphology of $\text{Na}_{0.5}\text{K}_{0.5}\text{NbO}_3$ powders. *J Am Ceram Soc*. 2007;90:1650-5.
33. Mendelson MI. Average grain size in polycrystalline ceramics *J Am Ceram Soc*. 1969;52:443.
34. Stewart M, Cain MG, Hall DA. *Ferroelectric Hysteresis Measurement & Analysis*. Teddington: National Physical Laboratory, 1999.
35. Thompson SP, Parker JE, Potter J, Hill TP, Birt A, Cobb TM, Yuan F, Tang CC. Beamline I11 at Diamond: A new instrument for high resolution powder diffraction. *Review of Scientific Instruments*. 2009;80:075107.

36. Coelho AA. TOPAS and TOPAS-Academic: an optimization program integrating computer algebra and crystallographic objects written in C++. *Journal of Applied Crystallography*. 2018;51:210-8.
37. Liu ZY, Fan HQ, Li MM. High temperature stable dielectric properties of $(\text{K}_{0.5}\text{Na}_{0.5})_{(0.985)}\text{Bi}_{0.015}\text{Nb}_{0.99}\text{Cu}_{0.01}\text{O}_3$ ceramics with core-shell microstructures. *J Mater Chem C*. 2015;3:5851-8.
38. Acosta M, Schmitt LA, Molina-Luna L, Scherrer MC, Brilz M, Webber KG, Deluca M, Kleebe H-J, Rödel J, Donner W. Core–Shell Lead–Free Piezoelectric Ceramics: Current Status and Advanced Characterization of the $\text{Bi}_{1/2}\text{Na}_{1/2}\text{TiO}_3$ – SrTiO_3 System. *J Am Ceram Soc*. 2015;98:3405-22.
39. Xing J, Tan Z, Jiang L, Chen Q, Wu J, Zhang W, Xiao D, Zhu J. Phase structure and piezoelectric properties of $(1-x)\text{K}_{0.48}\text{Na}_{0.52}\text{Nb}_{0.95}\text{Sb}_{0.05}\text{O}_3$ - $x(\text{Bi}_{0.5}\text{Na}_{0.5})_{0.9}(\text{Li}_{0.5}\text{Ce}_{0.5})_{0.1}\text{ZrO}_3$ lead-free piezoelectric ceramics. *Journal of Applied Physics*. 2016;119:034101.
40. Wang Y, Damjanovic D, Klein N, Hollenstein E, Setter N. Compositional Inhomogeneity in Li- and Ta-Modified (K,Na)NbO₃ Ceramics. *J Am Ceram Soc*. 2007;90:3485-9.
41. Zhen Y, Li J-F. Abnormal Grain Growth and New Core–Shell Structure in (K,Na)NbO₃-Based Lead-Free Piezoelectric Ceramics. *J Am Ceram Soc*. 2007;90:3496-502.
42. Choi SY, Jeong SJ, Lee DS, Kim MS, Lee JS, Cho JH, Kim BI, Ikuhara Y. Gigantic Electrostrain in Duplex Structured Alkaline Niobates. *Chem Mat*. 2012;24:3363-9.
43. Zhou M, Lu XM, Yang DY, He J, Huang FZ, Mei F, Ren XM, Xu XY, Li Y, Zhu JS. Induced core-shell structure and the electric properties of $(\text{K}_{0.48}\text{Na}_{0.52})_{0.95}\text{Li}_{0.05}\text{Nb}_{0.95}\text{Sb}_{0.05}\text{O}_3$ ceramics. *Phys Chem Chem Phys*. 2017;19:1868-74.
44. Thong H-C, Zhao C, Zhu Z-X, Chen X, Li J-F, Wang K. The impact of chemical heterogeneity in lead-free (K, Na)NbO₃ piezoelectric perovskite: Ferroelectric phase coexistence. *Acta Materialia*. 2019;166:551-9.
45. Malic B, Bernard J, Bencan A, Kosec M. Influence of zirconia addition on the microstructure of $\text{K}_{0.5}\text{Na}_{0.5}\text{NbO}_3$ ceramics. *Journal of the European Ceramic Society*. 2008;28:1191-6.
46. Zuo R, Fu J, Lv D, Liu Y. Antimony Tuned Rhombohedral-Orthorhombic Phase Transition and Enhanced Piezoelectric Properties in Sodium Potassium Niobate. *J Am Ceram Soc*. 2010;93:2783-7.
47. Tellier J, Malic B, Dkhil B, Jenko D, Cilensek J, Kosec M. Crystal structure and phase transitions of sodium potassium niobate perovskites. *Solid State Sciences*. 2009;11:320-4.
48. Damjanovic D. A morphotropic phase boundary system based on polarization rotation and polarization extension. *Applied Physics Letters*. 2010;97:062906.
49. Ochoa DA, Esteves G, Jones JL, Rubio-Marcos F, Fernández JF, García JE. Extrinsic response enhancement at the polymorphic phase boundary in piezoelectric materials. *Appl Phys Lett*. 2016;108:142901.
50. Peng B, Yue Z, Li L. Evaluation of domain wall motion during polymorphic phase transition in (K, Na)NbO₃-based piezoelectric ceramics by nonlinear response measurements. *Journal of Applied Physics*. 2011;109:054107.
51. Jin L, Li F, Zhang SJ. Decoding the Fingerprint of Ferroelectric Loops: Comprehension of the Material Properties and Structures. *J Am Ceram Soc*. 2014;97:1-27.
52. Anton E-M, Jo W, Damjanovic D, Rödel J. Determination of depolarization temperature of $(\text{Bi}_{1/2}\text{Na}_{1/2})\text{TiO}_3$ -based lead-free piezoceramics. *Journal of Applied Physics*. 2011;110:094108.