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Enhancement of electromechanical properties in lead–free $(1-x)K_{0.5}Na_{0.5}O_3$–$xBaZrO_3$ piezoceramics

Trang An Duong[1], Hoang Thien Khoi Nguyen[1], Sang-Sub Lee[1], Chang Won Ahn[2], Byeong Woo Kim[3], Jae–Shin Lee[1], and Hyoung–Su Han[1,+]

Abstract

This study analyzes the phase transition behavior and electrical properties of lead-free $(1–x)K_{0.5}Na_{0.5}NbO_3$–$xBaZrO_3$ (KNN–100xBZ) piezoelectric ceramics. The stabilized crystal structures in $BaZrO_3$-modified KNN ceramics is clarified to be pseudocubic. The polymorphic phase transition from the orthorhombic to pseudocubic phases can be observed with KNN–6BZ ceramics considering the optimized piezoelectric constant (d_{33}). Electromechanical strain behaviors are discussed. Accordingly, the enhancement of strain value at x = 0.08 (composition) may originate from the coexistence of ferroelectric domains and polar nanoregions. A schematic of domains for KNN, KNN–8BZ, and KNN–15BZ ceramics has been proposed to describe the relationship between the stabilized relaxor and changes in electrical properties.

Keywords : Lead-free, Piezoceramics, Relaxor, PNRs, Phase transition.

1. INTRODUCTION

Lead-based piezoceramics with efficient electrical properties, e.g., $Pb(Zr_{0.52}Ti_{0.48})O_3$ (PZT), $Pb(Mg_{1/3}Nb_{2/3})O_3$–$PbTiO_3$ (PMN–PT) [1], and $(Pb,La)(Zr,Ti)O_3$ (PLZT) [2], are widely applied to electronic and electrical devices. However, these materials contain lead (>60%) as a classifiable toxicity, which severely affects human and environment [3]. In recent times, several scientists focused on the development of lead-free piezoceramics to replace lead-based materials [4-6].

Among lead-free piezoelectric materials, $K_{0.5}Na_{0.5}NbO_3$ (KNN) and its compounds are promising candidates owing to their excellent dielectric and piezoelectric properties [7,8]. Several studies have been carried out to improve electrical properties for KNN-based materials based on concept of polymorphic phase transition (PPT) [9]. Although electrical properties of KNN-based materials can be improved based the PPT concept, temperature sensitivity issue remains a challenge. To overcome this problem, there are several methods, such as texturing, stabilization of a single tetragonal phase, and formation of a morphotropic phase boundary (MPB) like that of PZT [10,11]. Although texturing in ceramics can exhibit high piezoelectric performance and excellent temperature stability [12,13], it requires complex synthesis process with a high cost. In the case of the stabilization of a single tetragonal phase, thermal sensitivity improves, while piezoelectric properties degrade [14,15]. Hence, the MPB concept with thermal stability and a high piezoelectric property would be the most promising approach.

To form MPB, two phases, c tetragonal (T) phase and rhombohedral (R) phase, are required to be stabilized simultaneously [16]. Several candidates can help stabilization T phase at room temperature in the KNN–based system [17-20], while the R phase at room temperature is relatively rare. The reason for this is that the R phase is inherently stabilized at a low temperature (around -120 °C) in KNN ceramics. It implies that the R phase in KNN would be difficult to stabilize near room temperature. Nevertheless, few studies have claimed that the modification of zirconium-based compounds (especially $BaZrO_3$) in KNN ceramics can help stabilize the R phase near room temperature [21,22]. In 2009, Wang *et al* first reported the induced R phases by modifying $BaZrO_3$ (BZ) [21] and other $AZrO_3$ [22] in KNN ceramics. Then, several studies have reported the formation of

[1] School of Materials Science and Engineering, University of Ulsan, 12, Techno saneop-ro 55 beon-gil, Nam-gu, Ulsan 44776, Republic of Korea
[2] Department of Physics and EHSRC, University of Ulsan, 93, Daehak-ro, Nam-gu, Ulsan 44610, Republic of Korea
[3] Department of Electrical Engineering, University of Ulsan, 93, Daehak-ro, Nam-gu, Ulsan 44610, Republic of Korea
[+] Corresponding author: hsejs@ulsan.ac.kr
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MPB (comprising R and T phases) in KNN-based ceramics using zirconium-based compounds [23,24]. On the other hand, it has been recently suggested that relaxor behavior relating to the phase boundary between an orthorhombic or tetragonal phase and cubic phase (pseudocubic) phase in KNN-based ceramics can help enhance electrical properties [25-28]. Accordingly, this implies that the identity of stabilized phase in KNN-based ceramics is still a highly controversial issue. Furthermore, the investigation on electromechanical strain behaviors with temperature stability in KNN-based ceramics remains a challenge.

Therefore, this study investigated the effect of modified BZ on crystal structures, phase transition behaviors, and electrical properties in KNN ceramics. Furthermore, we have successfully demonstrated the modeling for enhanced electromechanical strain properties in BZ-modified KNN ceramics by comparing virgin strain curves (e.g., poling strain curves) between pure KNN and BZ-modified KNN ceramics.

2. EXPERIMENTAL

Lead-free piezoelectric $(1–x)(Na_{0.5}K_{0.5})NbO_3$–$xBaZrO_3$ (KNN-100*x*BZ; $x = 0.03$, 0.06, 0.08, 0.10, and 0.15) ceramics were prepared using a conventional solid-state reaction method. High-purity carbonate powders, e.g., Na_2CO_3 (99%), K_2CO_3 (99%), and $BaCO_3$ (99.95%), and oxide powders, e.g., Nb_2O_5 (99.9%) and ZrO_2 (98%), were used as raw materials. After being mixed in stoichiometric proportions based on the conventional ball–milling method in ethanol using Zirconia balls, the mixtures were dried and calcined at 850 °C for 3 h to form uniform solid solutions. The calcined powders were mixed with polyvinyl alcohol (PVA) as a binder, pressed into green body discs of diameter 12 mm under a uniaxial pressure of 200 MPa, and sintered at 1110–1220 °C for 3 h.

The crystal structures of all the samples were characterized by means of X–ray diffractometry (XRD, RAD III, Rigaku, Japan), and microstructures were observed using field-emission scanning electron microscopy (FE–SEM, JEOL JSM–65OFF, Japan). The silver paste was applied to both sides of each specimen and baked at 700 °C for 30 min to form an electrode on the samples for electrical measurements. The temperature-dependent dielectric constant and dielectric loss were recorded using a high-temperature electric prober system (KEYSIGHT–E4980AL Precision LCR Meter, USA). The piezoelectric constant (d_{33}) was measured using a quasistatic piezoelectric d_{33}/d_{31} meter (ZJ–6B; Institute of Acoustics, Chinese Academy of Sciences, Beijing, China). Electric-field-induced strain (*S*) curves and polarization (*P*) curves of the electric field (*E*) were measured at 1 Hz using aixPES (aixACCT Systems GmbH, Germany).

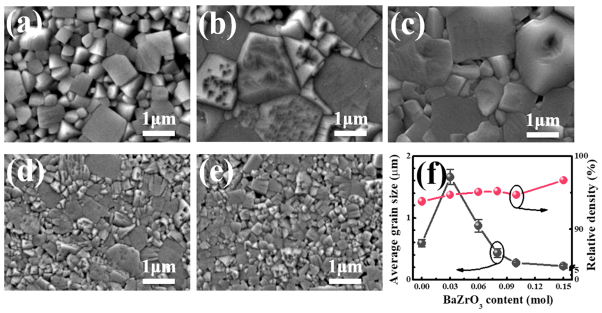

Fig. 1. Polished and thermally etched surface images of KNN-100*x*BZ ceramics: (a) $x = 0$, (b) $x = 0.03$, (c) $x = 0.06$, (d) $x = 0.08$, (e) $x = 0.10$, and (f) the calculated average grain size and relative density values of KNN-100*x*BZ ceramics as a function of BZ content.

3. RESULTS AND DISCUSSIONS

Fig. 1 shows the polished and thermally etched surface images of KNN-100*x*BZ ceramics. All the samples exhibited dense microstructures with very small numbers of holes and inhomogeneous grain distributions. We obtained that the relative density of KNN-100*x*BZ ceramics monotonically improved with an increase in the BZ content. This result indicates the improved sinterability of KNN ceramics by modifying BZ, which is compared in Fig. 1. The average grain size increased from 0.61 ± 0.02 mm for pure KNN to the highest value of 1.67 ± 0.04 mm for KNN–3BZ. It is suggested that low concentrations of BZ can be well diffused into KNN lattices to form a new homogeneous solid solution, responsible for grain growth [29,30]. However, the average grain size has drastically decreased with a further increase in the BZ content. This implies that excess particles of BZ at high concentrations may remain near the grain boundary and restrain the grain growth [31-33].

Fig. 2 shows XRD patterns for BZ–modified KNN ceramics. Peaks in 2θ ranges of 30.3°–32.5°, 43.7°–46.5°, and 55.2°–57.4° are investigated to clarify changes in crystal structure for all compositions. As shown in Fig. 2(b), two distinct peaks as (202) and (020) are observed in pure KNN and KNN–3BZ ceramics that correspond to a single orthorhombic structure. For KNN-6BZ ceramics, the split peaks began transitioning into (200) peak. At KNN-8BZ ceramics, the peaks are merged into a single (200) peak corresponding to a rhombohedral or a cubic structure.

In fact, (*h*00), (*hh*0), and (*hhh*) reflections of cubic symmetry

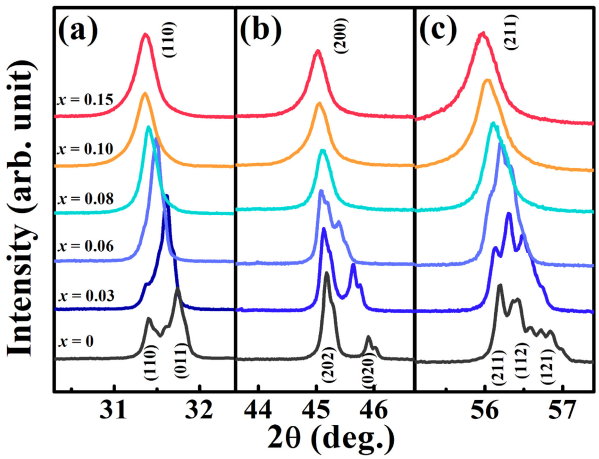

Fig. 2. X-ray diffraction patterns of KNN-100*x*BZ ceramics as a function of the BZ content in the 2θ ranges of (a) 30.3°–32.5°, (b) 43.7°–46.5°, and (c) 55.2°–57.4°.

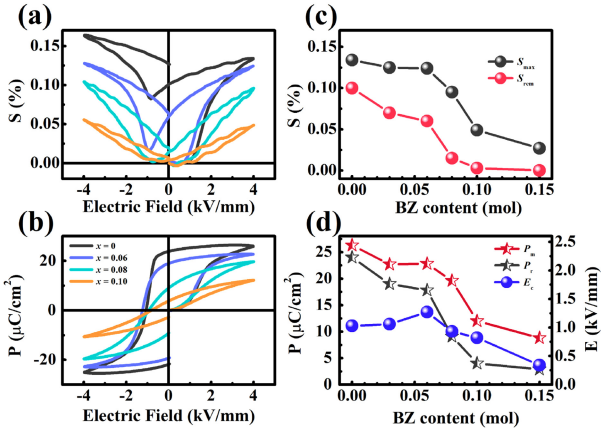

Fig. 4. (a) Bipolar strain (*S*–*E*) and (b) polarization (*P*–*E*) curves and extracted parameters such as (c) S_{max}, S_{rem} and (d) P_{max}, P_r, E_c for KNN-100*x*BZ ceramics as a function of the BZ content.

are reflected as single peaks based on the perpendicularity. Meanwhile, a rhombohedral symmetry ($\alpha = \beta = \gamma \neq 90°$) indicates split peaks at (*hh*0) and (*hhh*) reflections [34, 35]. Accordingly, KNN-8BZ ceramics can be identified as a cubic structure by detecting single (110) peaks in Fig. 2 (a) and single (211) peaks in Fig. 2 (c).

Fig. 3 shows the temperature-dependent dielectric properties of KNN–100*x*BZ ceramics. Curie temperature (T_C) and temperature with regard to an orthorhombic to a tetragonal phase transition (T_{O-T}) were decreased with an increase in the BZ content. T_C monotonically reduced from 400 °C for pure KNN to 60 °C for KNN-15BZ ceramics, while T_{O-T} reduced from 200 °C for KNN to near room temperature for KNN-8BZ ceramics. We observed sharp phase transitions (first-order phase transition behaviors) in pure KNN, KNN-3BZ, and KNN-6BZ ceramics that these features can be categorized as normal ferroelectrics.

On the other hand, frequency-dependent dielectric behaviors with a broad phase transition as a function of the applied frequency were observed in KNN-8BZ ceramics, and became stronger dispersion with further increasing BZ content. BZ modification in KNN ceramics significantly affects dielectric properties and is responsible for ferroelectrics to relaxor phase transition.

Electromechanical strain (*S*–*E*) and polarization (*P*–*E*) curves for KNN-100*x*BZ ceramics as a function of BZ content are compared in Fig. 4. At BZ content $x < 0.08$, typical ferroelectric features such as butterfly-shaped *S*–*E* curves and square-shaped *P*–*E* curves were observed. On the other hand, the significantly reduced remnant polarization (P_r) and the negligible remanent strain (S_{rem}) can be observed for KNN-10BZ and KNN-15BZ ceramics. In the case of coercive field (E_c), first, it was monotonically increased and drastically decreased with an increase in the BZ content. The highest maximum strain (S_{max}) was obtained at KNN-8BZ ceramics with a drastic decrease in P_r and remanent strain (S_{rem}). Changes in those results are strongly related to the appearance of relaxor features in KNN–100*x*BZ ceramics [28,36]. It will be discussed in detail with a phase diagram (in Fig. 5) and a schematic modeling for strain mechanism (in Fig. 6).

Fig. 5 shows a phase diagram based on crystallographic changes and electrical properties for KNN-100*x*BZ ceramics as a function of the BZ content. The piezoelectric constant (d_{33}) slightly increased with an increase in the BZ content up to 6 mol% and then drastically declined with a further increase in the BZ content. The highest value of d_{33} of 130 pC/N was obtained in

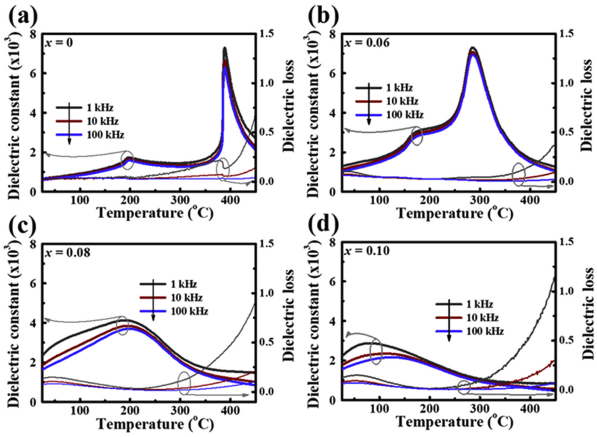

Fig. 3. Temperature–dependent dielectric constant for KNN–100*x*BZ ceramics as a function of BZ content.

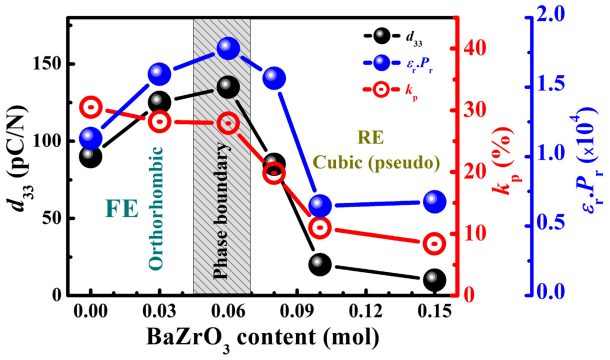

Fig. 5. Compositional phase diagram of KNN–100xBZ ceramics with changes in piezoelectric constant (d_{33}), electromechanical coupling factor (k_p), and $\varepsilon_r \cdot P_r$ as a function of the BZ content.

KNN-6BZ ceramics, which may be related to the PPT concept with the coexistence of orthorhombic and cubic phases.

Several studies reported that these enhanced electrical properties in KNN-based ceramics originated from the coexistence of two phases corresponding to the polymorphic phase boundary [19,37]. In the case of the electromechanical coupling factor (k_p) for KNN-100xBZ ceramics, first, we observed a slight reduction of up to 6 mol% of BZ and then a drastic degradation with a further increase in the BZ content. Moreover, it is suggested that the BZ modification in KNN-based ceramics causes the dissociation of long-range-ordered ferroelectricity based on compositional disorder and lattice distortion [38-40]. Therefore, the destabilization of ferroelectrics with the stabilization of relaxor (cubic phase) is responsible for the drastic degradation of k_p and d_{33} for $x \geq 0.08$ composition. Moreover, changes in d_{33} for KNN-100xBZ ceramics are strongly influenced by the product of the dielectric constant (ε_r) and remanent polarization (P_r) [41], as expressed by the following equation:

$$d_{33} = 2Q\varepsilon_r P_r \ , \qquad (1)$$

where Q is the electrostrictive coefficient of materials. As a result, the corresponding trend of d_{33} and $\varepsilon_r \times P_r$ graphs in Fig. 5 indicates that piezoelectric constant is well related to dielectric and ferroelectric properties.

For better understanding of the improved electromechanical strain properties in KNN-8BZ ceramics, schematic modeling of electromechanical strain behaviors of three different states was proposed (Fig. 6). In principle, the proposed schematic modeling includes normal ferroelectrics with ferroelectric domains (FDs) for pure KNN ceramics, a relaxor state with polar nanoregions (PNRs) for KNN-15BZ ceramics, and an intermediate state with the coexistence of relaxor and ferroelectrics for KNN-8BZ ceramics.

At the initial state (i), all the compositions regardless of FDs and/or PNRs are randomly organized, which results in no microscopic polarization (corresponding to the zero point in strain curves). In the case of pure KNN ceramics shown in Fig. 6(a), the FDs can be aligned toward the applied electric field direction, which was expressed as state (ii) [42]. The most important feature in this state is accompanied by a huge strain—poling strain (S_{pol}). Once the domains are aligned, they no longer revert to initial state even if the applied electric field is removed, which corresponds to state (iii). Thus, huge remanent strain (S_{rem}) and polarization remain in normal ferroelectric materials. Therefore, usable strain corresponding to unipolar strain (S_{uni}) can be obtained in pure KNN ceramics as normal ferroelectrics. In fact, S_{uni} can be expressed by the difference of S_{pol}–S_{rem} [43,44].

In contrast, it is suggested that KNN–15BZ ceramics is expressed as a relaxor state with dynamic PNRs (Fig. 6(c)). In this case, all the PNRs can easily align along the electric field direction. However, it is impossible to induce long-range-ordered or macroscopic ferroelectric domains owing to insufficient interaction among PNRs (their size and numbers). Therefore, low S_{pol} was obtained in KNN-15BZ ceramics. When the applied electric field is removed (E = 0, as state (iii)), the aligned PNRs rapidly revert to the initial state (state (i)) as a randomized configuration, thereby resulting in negligible S_{rem}.

As we explained previously, the coexistence of PNRs and FDs was suggested in KNN-8BZ ceramics (Fig. 6(b)). Once a

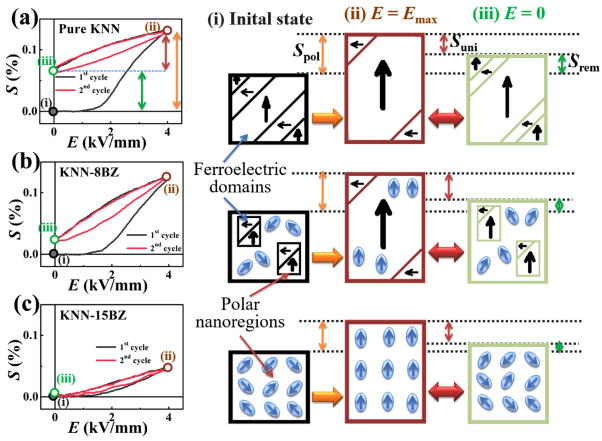

Fig. 6. Modeling of electromechanical strain of three different states: (a) normal ferroelectrics (pure KNN ceramics), (b) an intermediate state with coexistence of PNRs and ferroelectric domains (KNN-8BZ ceramics), and (c) relaxor state with PNRs (KNN-15BZ ceramics).

significant electric field is applied (corresponding to state (ii)), PNRs and FDs are sequentially reoriented along the applied electric field direction. In this case, it is expected that most relaxor regions (nonpolar phase) are reversibly transformed into the long-range-ordered ferroelectric domains. Therefore, S_{pol} (corresponding to S_{max}) of KNN-8BZ ceramics is compared with that of pure KNN ceramics. PNRs with FDs play an important role in reducing the energy barrier related to the domain switching in KNN-8BZ ceramics as "accelerators" [45]. The most important feature of KNN-8BZ ceramics is that S_{rem} drastically reduces as state (iii). When the applied electric field is removed, induced ferroelectric domains mostly revert to the initial state. This result implies that the reversible transition from relaxor to ferroelectric domains is responsible for the optimized S_{pol} and minimized S_{rem} in KNN-8BZ ceramics. Based on the relationship of $S_{uni} \approx S_{pol}$-S_{rem}, significantly enhanced electromechanical strain is obtained in KNN-8BZ ceramics.

4. CONCLUSIONS

Lead-free KNN–100*x*BZ piezoelectric ceramics were successfully prepared using a conventional solid-state reaction method. According to single peaks at (110) and (211) reflections in XRD pattern, the stabilized crystal structures in $BaZrO_3$-modified KNN ceramics can be identified as the cubic (pseudocubic) phase. The polymorphic phase transition from the ferroelectric orthorhombic phase to the relaxor cubic phase was observed in KNN–6BZ ceramics with the optimized piezoelectric constant d_{33}. Moreover, we found and suggested that the enhanced electromechanical strain in KNN–8BZ ceramics is originated from the coexistence of FDs and PNRs. Furthermore, to explain the enhanced electromechanical strain properties, a schematic related to domain structures of KNN–100*x*BZ ceramics was successfully illustrated using virgin unipolar strain curves as a function of electric field.

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