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Co-Doping Effect of BiGaO₃ and (Bi,Na,K,Li)ZrO₃ on **Multi-Phase Structure and Piezoelectric Properties of** (K,Na)NbO₃ Lead-Free Ceramics

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Abstract: The phase boundary structure of (K,Na)NbO₃ piezoelectric ceramic was modified by doping with Bi(Na,K,Li)ZrO₃ and BiGaO₃ through normal solid-state sintering. Rietveld refinements by X-ray diffraction revealed that the Bi(Na,K,Li)ZrO₃/BiGaO₃ co-doping in (K,Na)NbO₃ led to a multi-phase structure at room-temperature, effectively moving the rhombohedral-orthorhombic (R-O) and orthorhombic-tetragonal (O-T) polymorphic phase transition temperatures close to the room temperature region. Increased levels of doping also generated a structural transition, i.e., triphasic R-O-T to diphasic R-T (T-rich) and finally to R-T (R-rich), contributing to shrinkage of the O phase as well as the increase of R phase fraction. A sensitive influence of the BiGaO₃ doping (0.001 mole fraction level) on the structural properties such as the phase and microstructure was shown, resulting from the effect of the super-tetragonal structure of BiGaO₃. The d_{33} property was strongly dependent on the phase and its volume fraction, in addition to the grain sizes. Eventually, enhanced and balanced properties of the piezoelectric coefficient and Curie temperature ($d_{33} = 309 \text{ pC/N}, T_{C} = 343 \text{ °C}$) were obtained when the doped ceramic had a T-rich (86%) R-T structure.

Keywords: lead-free piezoelectric ceramics; potassium-sodium niobate (KNN); phase boundary structure; phase fraction

1. Introduction

The recent great improvement of the piezoelectric coefficient d_{33} of polycrystalline (K,Na)NbO₃ (KNN) lead-free ceramics has been made through the advent of emerging rhombohedral-tetragonal (R-T) [1–7] and rhombohedral-orthorhombic-tetragonal (R-O-T) phase boundaries [8–10]. This progress has spurred further research, concerning elaborate control of the phase boundary structure, of KNN to develop viable and environmentally friendly lead-free piezoceramics. In order that two intrinsic polymorphic phase transitions of KNN—i.e., the R-O transition ($T_{\text{R-O}}$, -123 °C) and the O-T transition (T_{O-T}, 200 °C)—can concurrently move to room temperature, complicated compositional manipulation by means of two or more dopants is used to construct novel phase boundaries. Various dopant materials, including special ions (usually, Li⁺, Sb⁵⁺ and Ta⁵⁺) and/or ABO₃-type perovskite compounds with different valence states of A- and B-sites, have been employed to tune the discrete $T_{\text{R-O}}$ and $T_{\text{O-T}}$ values. Relevant research activity, especially to construct the R-O-T and R-T multi-phase structures, has led to surprisingly high room-temperature piezoelectric coefficient d_{33} values ranging from 360 to 570 pC/N. The highest d_{33} value (570 pC/N) reported to date was achieved by constructing an R-T phase boundary by doping with Sb⁵⁺, BaZrO₃ and (Bi,K)HfO₃ [1]. This work also showed that sophisticated control of material compositions as well as proper choices of dopant material is critical

to enhancing the piezoelectric performance. Nevertheless, this marked progress in d_{33} has been unavoidably achieved at the expense of Curie temperature $T_{\rm C}$, similar to the case of conventional lead zirconium titanate [Pb(Zr,Ti)O₃ (PZT)] ceramics. It was unfortunate that the resulting ceramics had relatively low $T_{\rm C}$ values, typically less than 200 °C.

Perovskite oxides containing Bi³⁺ ion, such as BiMO₃ or (Bi,M)ZrO₃, are of special interest in lead-free piezo-/ferroelectrics and multiferroic materials [11,12]. This is because the Bi^{3+} ion has a stereochemically active 6s² lone pair, which results in structural distortion of the prototypical cubic phase owing to ion-off centering in its perovskite compounds, as is the case for the Pb^{2+} ion in lead-based piezoelectrics. When used as doping agents for modifying KNN, these perovskites are deemed highly promising because they can improve d_{33} without great sacrifice to $T_{\rm C}$, unlike the case of the Sb⁵⁺ ion, which results in a typically large decrease in T_C [12,13]. In particular, the (Bi,M)ZrO₃ (M: alkali metals) material system has been intensively investigated because the dopants of $(Bi,M)^{2+}$ and Zr^{4+} ions are known to play effective roles in decreasing T_{O-T} and increasing T_{R-O} , which are necessary for the formation of R-O-T or R-T phase boundaries [14,15]. Meanwhile, our recent investigation concerning the effects of different alkali metals in the (Bi,M)ZrO₃ system has shown that these oxides were highly effective at forming R-O-T or R-T phase boundaries in KNN; the highest piezoelectricity was obtained when M was a combination of Na, K and Li [16]. Among the simple Bi MO_3 family, the compound BiGaO₃ can be a suitable candidate co-dopant for further control of phase boundary structure, because theoretical studies have indicated that it should have a high piezoelectric and ferroelectric performance with large spontaneous polarization. Compared to other members of the simple BiMO₃ family, moreover, this compound has been predicted to have huge tetragonal distortion; the *a* lattice constant is 3.64 Å and the c/a ratio is 1.3 [17,18]. Doping with this material is thus of concern with respect to both the structural modification and piezoelectricity of KNN.

In this work, the two Bi-containing perovskite oxides, $Bi_{0.5}(Li_{0.7}Na_{0.2}K_{0.1})_{0.5}ZrO_3$ (BNKLZ) and BiGaO₃ (BG), were introduced as dopant materials to modify KNN ceramics. In consideration of practical applications, the use of toxic Sb and high-cost Ta were avoided, although these materials are in common use and are useful doping elements for KNN ceramics. KNN-BNKLZ-BG ternary ceramics were prepared using conventional solid-state sintering. Particular attention was paid to the effects of super-tetragonal BG on the phase, microstructure and piezoelectric properties of KNN. Room-temperature phase structure, including constituent phases and their quantities, was accurately identified by Rietveld refinement method based on X-ray diffraction (XRD).

2. Materials and Methods

(1 - x - y)KNN-*x*BNKLZ-*y*BG (x = 0.035/0.045, y = 0-0.005) ternary ceramics were prepared using the conventional solid-state powder method. Here, the K/Na molar ratio was 0.48/0.52. The BNKLZ concentrations (x = 0.035 and 0.045) were selected based on our previous study [16], because these concentrations were expected to form the R-O-T or the R-T phase coexistence, allowing us to study the effect of BiGaO₃ doping on the formation of multi-phase structure with different ratios of R, O and T phases.

The starting powders were K₂CO₃ (\geq 99.0%, 150 µm, Sigma-Aldrich, St. Louis, MO, USA), Na₂CO₃ (\geq 99.5%, 10 µm, Sigma-Aldrich, St. Louis, MO, USA), Li₂CO₃ (99.997%, 20 µm, Sigma-Aldrich, St. Louis, MO, USA), Nb₂O₅ (99.9%, 2 µm, Sigma-Aldrich, St. Louis, MO, USA), Bi₂O₃ (99.9%, 10 µm, Sigma-Aldrich, St. Louis, MO, USA), ZrO₂ (99.0%, 5 µm, Sigma-Aldrich, St. Louis, MO, USA), and Ga₂O₃ (\geq 99.99%, 10 µm, Sigma-Aldrich, St. Louis, MO, USA). Stoichiometric powder mixtures with different concentrations of *x* and *y* were homogenized in ethanol for 24 h using a roller mill machine operating at 70 rpm; samples were then dried at 120 °C for 24 h. All treatments of these powders, including weighing and drying, were carefully performed in a glove box filled with Ar gas. Calcination was then carried out at 850 °C for 6 h. The calcined powders were mixed with poly-vinyl alcohol (PVA) as a binder and axially compacted into disks 10 mm in diameter. After burning off the PVA at 650 °C, conventional pressureless sintering was carried out at 1100 °C for 3 h in air. The sintered ceramics were ground to a thickness of 1 mm.

The crystal structures of the unpoled samples were characterized by an X-ray diffractometer (XRD; D/Max-2500; Rigaku, Tokyo, Japan) using Cu K α radiation at a power of 40 kV and 15 mA and a scan speed of 1°/min. Rietveld refinement of XRD patterns was performed to accurately determine the phases and their quantitative volume fractions using Rigaku's PDXL software with the Whole Pattern Powder Fitting (WPPF) method; the system was connected to the Inorganic Crystal Structure Database (ICSD; FIZ Karlsruhe, Germany). Initial models used for refinement were three KNbO₃ crystal structures, i.e., orthorhombic (*Amm2*; JCPDS 01-071-0946; ICSD code 9533), rhombohedral (*R3m*; JCPDS 01-071-0947; ICSD code 9534), and tetragonal (*P4mm*; JCPDS 01-071-0948; ICSD code 9535); their crystal structure parameters were acquired from the ICSD.

The morphology of the sintered samples was studied using a field-emission scanning electron microscope (FE SEM; Sirion; FEI, Eindhoven, The Netherlands) with an operating voltage of 20 kV equipped with an energy-dispersive X-ray spectrometer (EDXS). The values of grain boundary length, together with the grain size, were estimated to investigate the effect of the grain boundary area on the piezoelectric response for all sintered ceramics. Quantitative measurements were carried out using automatic image analysis software (Matrox imaging library 10) for SEM images taken from each sample; the number of analyzed images was ~4–8 per sample, measurement area per image ~475 μ m², and the total number of grains ~400 to several thousand.

For the electrical measurements of the sintered ceramics, both sides of the disks were polished and painted with a silver paste, after which disks were fired at 650 °C for 10 min. The samples were then poled in silicon oil at room temperature. After optimization through pre-tests for poling over time and in an electric field, poling field and time were set at 40 kV/mm and 10 min, respectively. Dielectric constant (ε_r) measurements were conducted for the unpoled samples between 30 and 500 °C using an impedance analyzer (SI 1260; Solartron; Farnborough, UK) combined with a dielectric interface (SI 1287; Solartron; Farnborough, UK). Using a piezo- d_{33} meter (ZJ-6B; IACAS; Beijing, China), the longitudinal piezoelectric coefficients (d_{33}) were measured at room temperature for the poled samples.

3. Results

Figure 1 shows the room-temperature XRD patterns of the (1 - x - y)KNN-*x*BNKLZ-*y*BG ternary ceramics (x = 0.035/0.045, y = 0-0.005). All the ceramics were found to have a pure perovskite structure without second phases, showing that BNKLZ and BG dopants diffused into the KNN lattice to form homogeneous solid solutions in the investigated concentration ranges. Meanwhile, there was a dramatic change of phase structure with the variation of the BNKLZ and BG concentrations, as observed by the expanded XRD patterns in the 2θ range of $44-47^{\circ}$. This structural change is particularly notable because it was induced by doping with only a small amount of BG (0.001–0.005 in mole fraction) at each BNKLZ concentration (x). The features of peak shape around 2θ of 45.5° also suggested that the doped ceramics retained multiphase structure at/near room temperature, rather than single phase (R, O and T).

To characterize the exact structural nature of the KNN-BNKLZ-BG ceramics, Rietveld refinements were carried out for the corresponding XRD patterns. To ensure the reliability of the refinement results, the fitting quality of the powder patterns was checked by means of two parameters, i.e., the goodness-of-fit indicator *S* and the reliability factor R_{wp} . In addition to the involved phase and its volume fraction, the cell parameters of each ferroelectric phase (R, O and T) obtained from the KNN-*x*BNKLZ-*y*BG (x = 0.045, y = 0-0.005) are presented in Table 1. The typical refinement profiles including the measured and calculated diffraction profiles are well matched, which is confirmed by their difference profiles, shown at the bottom of each figure; the smoother solid line indicates the more accurate results. The low-reliability factor value R_{wp} (8.3–8.8%) and the goodness-of-fit indicator *S* close to 1 (Table 1) suggest the high degree of reliability of the refinement results; a comparison with values reported from other studies [19–22] also proved the high reliability of our results. In the Rietveld analysis results, the constituent phases and their volume fractions are presented as a function of *x* and

y, as shown in Figure 3. Overall, the ceramics in the investigated *x* and *y* ranges had a multiphase coexistence, i.e., triphasic R-O-T or diphasic R-T, which is the result of ferroelectric R, O, and T phases in different ratios. It should be noted that the shrinkage of the O phase is obviously due to the BNKLZ and BG doping. At *x* = 0.035, the ceramics exhibited a triphasic R-O-T structure with a fair proportion of O phase (13–19%). As *y* increased, the volume fraction of the O phase slightly decreased, together with an increase in the proportion of R or T phases. When *x* increased to 0.045, the O phase was greatly suppressed but still remained at a small proportion for the ceramics with *x* = 0 and 0.001. Accordingly, the R-O-T structure was maintained up to *y* = 0.001. Notably, when *y* increased to 0.002, the O phase disappeared, leading to a two-phase coexistence comprising R and T phases. The mole fractions of the BNKLZ and BG dopants, required for the formation of R-T coexistence without O phase, were 0.045 and 0.002, respectively. In the R-T region, the highest amount of T phase (86%) appeared at *y* = 0.002, but the R phase became enriched with a further increase *y* from 0.002 to 0.005.



Figure 1. Room-temperature XRD patterns of KNN-*x*BNKLZ-*y*BG ternary ceramics (y = 0-0.005) in the 2 θ range of 20–60°: (**a**) x = 0.035; (**b**) x = 0.045. Amplified XRD patterns ($2\theta = 44-47^{\circ}$) are also presented.

Mole Fraction of BiGaO ₃ (<i>y</i>)	Phase Structure	Cell Parameters				Phase	R _{wp}	s
		a (Å)	b (Å)	c (Å)	$\alpha (= \gamma = \beta) (^{\circ})$	Fraction (%)	(%)	3
0	R-O-T	3.9813 3.9635 3.9723	3.9813 5.664 3.9723	3.9813 5.656 4.0164	89.820 90 90	15.5 (R3m) 12 (Amm2) 72.5 (P4mm)	8.28	1.0044
0.001	R-O-T	3.9808 3.9630 3.9721	3.9808 5.655 3.9721	3.9808 5.6770 4.0152	89.815 90 90	11 (R3m) 8.5 (Amm2) 80.5 (P4mm)	8.48	1.0204
0.002	R-T	3.9811 3.9720	3.9811 3.9720	3.9811 4.0151	89.806 90	14 (R3m) 86 (P4mm)	8.77	1.0483
0.003	R-T	3.9978 3.97124	3.9978 3.97124	3.9978 4.0107	89.548 90	25.9 (R3m) 74.1 (P4mm)	8.72	1.0305
0.004	R-T	3.9895 3.9733	3.9895 3.9733	3.9895 4.0080	89.91 90	43.2 (R3m) 56.8 (P4mm)	8.82	1.0315
0.005	R-T	3.9966 3.9792	3.9966 3.9792	3.9966 4.0147	89.99 90	54.5 (R3m) 46.5 (P4mm)	8.72	1.0192

Table 1. Results of Rietveld refinement for powder samples with KNN-0.045BNKLZ-yBG (y = 0-0.005).



Figure 2. Rietveld refinement of XRD patterns for KNN-0.045BNKLZ-*y*BG ternary ceramics (y = 0-0.005).



Figure 3. Quantitative phase fraction data (R, O, and T phases) identified by Rietveld refinements for KNN-*x*BNKLZ-*y*BG ternary ceramics (y = 0-0.005): (**a**) x = 0.035; (**b**) x = 0.045.

The microstructural evolution of KNN-BNKLZ-BG ceramics is shown in Figure 4. The values of grain size and grain boundary length, measured from the SEM images, are presented in this figure.

Overall, the grain structure exhibited an obvious compositional sensitivity to BG; the grain size (or grain boundary length) sensitively changed with the addition of a small amount of BG (i.e., 0.001 mole fraction level). The grain size first increased until y = 0.002; in this region, the ceramics typically showed a bimodal grain size distribution and the smaller grains filled gaps among larger grains. Then, the grain size dramatically decreased between y = 0.003-0.004. Those behaviors were commonly observed for two BNKLZ compositions. For the KNN-based ceramics doped with Bi-containing perovskite oxides, it has been generally shown that the grain size dramatically decreased owing to a slight increase (usually by about 0.01 mole fraction) of the amount of dopants at certain doping levels [23–27]. The origin of this sudden decrease in grain size is attributed to the effects of the solubility limits of low-melting-point Bi³⁺ ion or BiMO₃ dopant in KNN and aggregation at grain boundaries. The grain size behavior observed in this work, including a dramatic decrease in grain size, was consistent with those reported in previous studies [23–27]. The only notable difference was that the BG doping induced more compositional sensitivity (i.e., 0.001 mole fraction level) to the grain structure evolution, which is likely owing to the effects of the super-tetragonal structure of BG [17]. The resulting ceramics had densities ranging from 4.23 to 4.31 g/cm³ (greater than 94% of the theoretical density), as determined based on the Archimedes method.



Figure 4. SEM images of KNN-*x*BNKLZ-*y*BG ternary ceramics (y = 0-0.005): (**a**) x = 0.035; (**b**) x = 0.045. The values of average grain size and grain boundary length are provided in this figure.

Figure 5 shows the piezoelectric d_{33} properties obtained from the poled ceramics. Regarding the effect of BNKLZ, the d_{33} values obtained from the ceramics with x = 0.045 were higher than those from ceramics with x = 0.035. It can also be seen that, as the BG content increased, the d_{33} value first increased and then reached its maximum; this was followed by its decrease, and this behavior was common regardless of the BNKLZ concentration (x). The observed d_{33} behavior could be explained by

the well-established grain size effect in lead-based piezoceramics; as the increased grain boundaries generally constrain the domain wall motion, the decreased grain sizes induced the decline of d_{33} .



Figure 5. Variation of piezoelectric coefficient d_{33} for KNN-*x*BNKLZ-*y*BG material system (x = 0.035/0.045, y = 0-0.005).

On the other hand, the comparison of the d_{33} behavior with the phase fraction outcomes (Figure 3) also suggested that the d_{33} property was dominated by the involved phase and its volume fraction. The volume fractions of O phase for the ceramics with x = 0.045 decreased compared to those for ceramics with x = 0.035, whereas the T phase fractions for the ceramics with x = 0.045 were higher than those for the ceramics with x = 0.035. It can also be seen that, as the BG content increased, the T phase increased and then decreased; in the R-T region, the R phase was enriched. Eventually, the measured d_{33} values became higher with the increase of the T phase fraction, while the R and O phases induced poor piezoelectric performance. The maximum value (309 pC/N) was obtained when the phase boundary structure comprised of 14% of R phase and 86% of T phase without O phase. Hence, the variation trend of d_{33} with the increase of the BG content, i.e., an initial increase followed by a dramatic decrease, could be fully explained by both properties, i.e., phase and grain size (Figures 4 and 5).

We also ascribed the dramatic decline of d_{33} observed in the R-T region to the decreased grain sizes (Figure 4b), as well as to the decreased T phase fraction (or increased R phase fraction). Besides this, the decreased tetragonality (c/a) with an increase in BG content (y) might be a further contribution to the decline of d_{33} , as shown in Figure 6.



Figure 6. Variation of tetragonality (c/a) and T phase fraction for ceramics (y = 0.002-0.005) with R-T phase coexistence in KNN-0.045BNKLZ-*y*BG material system. Tetragonality (c/a) is obtained from cell parameters in Table 1.

In KNN-based ceramics, there have been only a few studies on the correlation between the multi-phase structure (e.g., coexisting phases and their volume fraction) and the piezoelectricity. As for the O-T phase coexistence, Ahn et al. and Rubio-Marcos et al. emphasized the need to construct a T-rich structure for piezoelectric enhancement [28,29]. Rubio-Marcos et al. also reported that a higher T phase fraction for the R-T phase coexistence was beneficial to the piezoelectric enhancement [30]. According to Lv et al., this enhancement is attributed to larger degrees of lattice distortion and induced internal stress produced by T phase rather than by R phase [31]. Recent in-situ synchrotron XRD investigations revealed that the enhanced piezoelectricity for a T-rich R-T phase coexistence was attributed to the more positive role of the irreversible tetragonal-electric induced phase transition compared to the rhombohedral-electric induced phase transition with a certain degree of reversibility [32,33]. Our findings are in good agreement with these previous investigations; the T phase was beneficial, whereas the R and O phases were detrimental to the piezoelectricity of KNN for states with coexisting phases or phase boundaries.

The effect of the addition of dopants on the $T_{\rm C}$ of KNN was investigated by temperature-dependent dielectric constant ($\varepsilon_{\rm r}$ –T) measurements between 30 and 500 °C (Figure 7). It was noted that the $T_{\rm C}$ value gradually decreased with increasing the BG content (y) from 0 to 0.005; from 351 to 319 °C ($\Delta T_{\rm C} \approx 32$ °C) at x = 0.035 and from 346 to 298 °C ($\Delta T_{\rm C} \approx 48$ °C) at x = 0.045. Promisingly, the overall $T_{\rm C}$ values were maintained at high levels above 300 °C without showing a serious doping-induced loss. In this work, the ceramic with the highest d_{33} (309 pC/N) exhibited a relatively high $T_{\rm C}$ value of 343 °C. As a result, the BG was found to be a very effective dopant to develop balanced properties of d_{33} and $T_{\rm C}$ without losing $T_{\rm C}$. In addition, one can see that there was a transition from the normal phase to diffuse ferroelectric phase (i.e., diffused phase transitions) with increasing the BG content, as usually observed in doped KNN-based ceramics.



Figure 7. Temperature dependence of dielectric constant ε_r measured at 100 kHz in temperature range of 30 to 500 °C for KNN-*x*BNKLZ-*y*BG material system (y = 0-0.005): (**a**) x = 0.035; (**b**) x = 0.045. Variations of T_C are also given as a function of y.

4. Conclusions

In this work, KNN piezoelectric ceramics co-doped with BNKLZ and BG have been prepared using conventional solid-state sintering method, and the effect of both dopants on the phase boundary structure and piezoelectric properties has been investigated. Rietveld refinements by XRD revealed that BNKLZ/BG co-doping effectively modified a room-temperature phase boundary structure of KNN by moving discrete T_{R-O} and T_{O-T} values toward the room temperature region. Initially produced R-O-T structure was changed to R-T structure via shrinkage of O phase, with an increase in the dopant concentrations. Due to the removal of the O phase from the R-O-T structure, the doping levels required to form the R-T structure were 0.045 for BNKLZ and 0.002 for BG, based on the mole fraction. In particular, a high compositional sensitivity of BG doping (0.001 mole fraction level) to the phase, microstructure, and piezoelectric properties was notable, resulting from the effect of

the super-tetragonal structure of BG. The d_{33} values not only exhibited a strong correlation with the grain size property, but also were clearly dominated by the phase structure. Overall, the d_{33} values for ceramics with R-T phase coexistence were higher than those for ceramics with R-O-T phase coexistence. In the R-T region, the richer the T phase was, the higher the d_{33} value was. Enhanced piezoelectric coefficient and high Curie temperature ($d_{33} = 309 \text{ pC/N}$, $T_C = 343 \text{ °C}$) were obtained from the ceramic with a T-rich (86%) R-T structure, promisingly showing balanced properties without serious doping-induced loss of T_C .

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