Composition and Temperature Dependence of Structure and Piezoelectricity in (1−x)(K1−yNa)yNbO3−x(Bi1/2Na1/2)ZrO3 Lead-Free Ceramics

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Lead-free piezoceramics with the composition (1−x)(K1−yNa)yNbO3−x(Bi1/2Na1/2)ZrO3 (KNN−xBNZ) were prepared using a conventional solid-state route. X-ray diffraction, Raman spectroscopy, and dielectric measurements as a function of temperature indicated the coexistence of rhombohedral (R) and tetragonal (T) phase, typical of a morphotropic phase boundary (MPB) as the BNZ concentration increased and by adjusting the K/Na ratio. High remnant polarization (P_r = 24 μC/cm²), piezoelectric coefficient (d_33 = 320 pC/N), effective piezocoefficient (d_31 = 420 pm/V), coupling coefficient (κ_p = 48%), and high strain (S = 0.168%) were obtained at room temperature, but significant deterioration of P_r, d_31, and κ_p were observed by increasing from room temperature to 160°C (17.5 μC/cm², 338 pm/V, and 32%, respectively) associated with a transition to a purely T phase. Despite these compositions showing promise for room-temperature applications, the deterioration in properties as a function of increasing temperature poses challenges for device design and remains to be resolved.

Keywords: lead-free ceramics; piezoelectric materials/properties; potassium-sodium niobate/KNN

I. Introduction

Piezoelectric materials have been extensively investigated because of their widespread applications ranging from medical, environmental, and industrial process monitoring to robotics, energy harvesting, and high-frequency communication systems. Most commonly used materials are based on lead zirconate titanate Pb(Zr,Ti)O3 (PZT) due to their high piezoelectric performance. However, regulations against hazardous substances such as lead in electric and electronic equipment have stimulated research in lead-free piezoceramics over the last two decades. Potassium-sodium niobate (K,Na)NbO3 (KNN) is one of the leading candidates to replace PZT and has been extensively investigated due to its moderately large piezoelectric coefficient (d_33) and high Curie temperature (T_C) since its discovery in the 1950s. In particular, research on KNN accelerated when Saito et al. (2004) reported giant d_33 ~ 416 pC/N, comparable to those of PZTs, in textured (Li,Ta,Sb)-modified KNN. However, disadvantages such as obtaining well-densified ceramics due to the high volatility of the alkaline components and low piezoelectric properties in polycrystalline ceramics have prevented KNN being commercialized. In general, dopants in KNN enhance piezoelectricity (d_33 > 200 pC/N) by pushing the orthorhombic (O) to tetragonal (T) transition boundaries closer to room temperature. This effect is well documented for dopants such as LiSbO3, LiTaO3, Bi0.5Na0.5TiO3, and BaTiO3. But coexistence of rhombohedral (R) and O phases has been reported for dopants with the general formula A[ZrO2 (A=Ba, Sr, or Ca) or BiMoO5 (M=Fe, Sc, Co)]. Compositions which rely on R-O coexistence generally, however, exhibit d_33 < 230 pC/N that are significantly lower than the compositions which utilize O-T phase boundary to optimize d_33.

Recently, PZT-like morphotropic phase boundary (MPBs) (R-T) have been reported in KNN-based ceramics by integrating compositions which were previously used to optimize the O-T and O-R phase boundaries. In 2011, Zuo et al. reported R-T phase coexistence in (Li,Ta,Sb) and BaZrO3 multimodified KNN lead-free ceramics and obtained a high d_33 = 365 pC/N. For similar compositions, Wu et al. obtained d_33 ~ 425 pC/N. But more recently, Sb together with (Bi,M)NO3 (M=Na, K, Li, Ag, N=Zr, Hf, Sn) have been used to enhance d_33 and electromechanical strain (S) with d_33 and S improved to >400 pC/N and 0.46% at 3 kV/cm, respectively. Despite promising d_33 and S values there are still a number of concerns. For Sb doping, T_C is reported to decrease alarmingly and de-poling may jeopardize some applications. More importantly, however, to our knowledge, the temperature dependence of the piezoelectric properties is rarely reported. It is likely that the supposed MPB in many KNN-based compositions is not temperature independent and therefore phase coexistence and high d_33/S are not maintained during high-temperature applications or at high field cyclic loading in which temperature is likely to increase. Given the above concerns, this contribution presents the composition and temperature dependence of the piezoelectric properties (1−x)(K1−yNa)yNbO3−x(Bi1/2Na1/2)ZrO3 (KNN−xBNZ) lead-free ceramics in which LiSbO3 dopants have been excluded to maintain a high T_C.

II. Experimental Procedure

The KNN-xBNZ ceramics with compositions of (1−x) (K1−yNa)yNbO3−x(Bi1/2Na1/2)ZrO3 (x = 0, 0.02, 0.03, 0.04, 0.045, 0.05, 0.06, 0.08, and y = 0.6) and (x = 0.045, and y = 0.4, 0.45, 0.49, 0.53, 0.56, 0.6, 0.65, and 0.7) were prepared using a conventional solid-state reaction. Raw materials, including Na2CO3 (99.9%, Fisher Scientific), K2CO3...
(99.7%, Fisher Scientific), Nb$_2$O$_5$ (99.5%, Sigma-Aldrich), ZrO$_2$ (99%, Sigma-Aldrich), and Bi$_2$O$_3$ (99.9%, Sigma-Aldrich) were batched stoichiometrically according to the nominal compositions and ball-milled in isopropanol for 24 h. The dried mixed powders were calcined at 850°C for 6 h to synthesize the compound and then ball milled in isopropanol for 12 h. The calcined powders were mixed with a polyvinyl alcohol (PVA) binder solution, granulated and pressed into pellets with 10 mm in diameter. Following binder burnout at 550°C, the pellets were sintered in a sealed crucible with sacrificial powders at 1150°C-1230°C for 3-6 h. The density of the sintered samples was measured by the Archimedes method. The relative density of all studied samples was higher than 95%. The phase structure of the sintered samples was studied using a Bruker D2 Phaser X-ray powder diffraction (XRD) and in situ XRD performed for selected samples using a Siemens D5000 HTXRD in the temperature range 30°C-350°C. Ceramic morphology and microstructure was examined using an FEI Inspect F scanning electron microscope (SEM). Raman spectra were acquired from 150°C to 350°C using a Renishaw inVia Raman microscope. For electrical tests, sintered samples were electroded using fire-on silver paste, followed by the samples being poled in silicon oil at room temperature with an applied electric field of 30-40 kV/cm. Piezoelectric coefficient ($d_{33}$) was measured using a Piezotest PM300 $d_{33}$ meter. Polarization hysteresis and strain-electric field behavior were determined using an aixACCT TF 2000 ferroelectric tester at a frequency of 1 Hz from room temperature to 160°C. The displacement data were synchronously captured by a laser interferometer. The temperature-dependent dielectric permittivity from 25°C to 600°C was measured using an Agilent 4184A multifrequency precision LCR meter. The planar electromechanical coupling factor ($k_p$) was determined from the resonance and antiresonance frequencies, which were measured using an Agilent 4294A Impedance/Gain-phase analyzer according to IEEE standards on piezoelectricity. 51,52

III. Results and Discussion

(1) Compositional Evolution of Structure–Property Relations

The room-temperature XRD patterns of KN$_y$N-xBNZ in the 20 range of 20°–70° are shown in Fig. 1. All peaks for 12 h. The calcined powders were mixed with a polyvinyl alcohol (PVA) binder solution, granulated and pressed into pellets with 10 mm in diameter. Following binder burnout at 550°C, the pellets were sintered in a sealed crucible with sacrificial powders at 1150°C-1230°C for 3-6 h.

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Fig. 1. Room temperature XRD patterns of KN$_y$N-xBNZ (a) KN0.6N-xBNZ and (b) KN$_y$N-0.045BNZ; amplified XRD patterns simulated by Gaussian for (c) KN0.06N-0.02BNZ (d) KN0.06N-0.045BNZ (e) KN0.06N-0.08BNZ.

Fig. 2. Rietveld refinement analysis of KN0.6N-0.045BNZ using the GSAS+EXPGUI package. Two phases R3c + P4 mm were used. $R_p = 6.2\%$, $R_{wp} = 9.7\%$ and $\chi^2 = 1.88$.

Fig. 3. Room temperature Raman spectra of KN$_y$N-xBNZ (a) KN0.6N-xBNZ, inset shows the Raman amplified peaks around 600 cm$^{-1}$ simulated by Gaussian and (b) KN$_y$N-0.045BNZ.

Fig. 4. Room temperature Raman spectra of KN$_y$N-xBNZ (a) KN0.6N-xBNZ, inset shows the Raman amplified peaks around 600 cm$^{-1}$ simulated by Gaussian and (b) KN$_y$N-0.045BNZ.
could be attributed to perovskite phases, indicating that a stable solid solution was formed in the studied range. Diffraction peaks shifted to a lower and higher diffraction angle with increasing BNZ and Na concentration, respectively, consistent with differences in relative ionic radius of the dopant/substituent ions with the matrix composition.

Splitting of (200) peak at ~20° = 45° was used to determine the likely symmetry of compositions. In the expanded XRD patterns [Fig. 1(a)], O phase was dominant in KN0.6N-xBNZ with x ≤ 0.02, but R, O and T phases coexisted for compositions of 0.03 ≤ x ≤ 0.04. As x increased further, ceramics with 0.045 ≤ x ≤ 0.05 showed mixed R and T

**Fig. 4.** High electric field bipolar polarization hysteresis and strain loops for KNyN-xBNZ (a) KN0.6N-xBNZ and (b) KNyN-0.045BNZ.

**Fig. 5.** Ferroelectric and strain properties of KNyN-xBNZ (a) P_r and E_C as a function of BNZ, (b) P_r and E_C as a function of Na, (c) S and d_{33} as a function of BNZ, (d) S and d_{33} as a function of Na.
Fig. 6. Dielectric and piezoelectric properties of KNyN-xBNZ (a) $\varepsilon_r$ and tan$\delta$ as a function of BNZ, (b) $\varepsilon_r$ and tan$\delta$ as a function of Na, (c) $d_{33}$ and $k_p$ as a function of BNZ, (d) $d_{33}$ and $k_p$ as a function of Na.

Fig. 7. Temperature dependence of $\varepsilon_r$ and tan$\delta$ for KNyN-xBNZ (a) KN0.6N-xBNZ, (b) KNyN-0.045BNZ, (c) $T_C$ and $T_{O/R-T}$ as a function of BNZ, (d) $T_C$ and $T_{O/R-T}$ as a function of Na.
Fig. 8. In situ temperature dependence of Raman spectra for KN0.6N-0.045BNZ (a) −150°C–0°C, (b) 20°C–350°C, (c) v1 peak shift as a function of temperature.

For x > 0.05, a single peak emerged, suggesting that R phase dominated. For compositions in which x was maintained at 0.045 (KNN-N-0.045BNZ), the splitting of (200)/(002) peaks gradually disappeared as y increased, suggesting the coexistence of R and T for a wide variation in Na/K ratio, Fig. 1(b). To confirm the phase evolution in KNN-xBNZ as a function of composition, simulations were performed, Fig. 1(c-e), which are consistent with experimental data and also the interpretation by Wang et al.43,44 Rietveld refinement analysis of the MPB composition KNO.6N-0.045BNZ was also performed using the GSAS+EXPGUI package,53,54 where a two phases refinement (R3c + P4 mm) was used, as shown in Fig. 2. A good agreement between the observed and calculated patterns was obtained with R_p = 6.2%, R_m = 9.7% and chi-squared (χ^2) = 1.88, indicating the coexistence of R (R3c, 32.5%) and T (P4 mm, 67.5%) phases in the MPB composition.

To further confirm phase evolution as a function of composition, room-temperature Raman spectra of KNOyN-xBNZ ceramics were obtained as shown in Fig. 3. Among the full Raman active mode of KNN, v1, v2, and v3 are stretching modes, v5 and v6 are bending modes of the NbO6 octahedra.55 The strongest peak around 600 cm−1 is related to the v1 mode; whereas the left and right weaker peaks are assigned to the v2 and v3 mode, respectively, as indicated by the simulated data shown in the inset of Fig. 3(a). With increasing BNZ content, the v1 and v2 peaks were found to shift to lower wave number as shown in Fig. 3(a). On the other hand, the v1 and v2 peaks shift to higher wave number with an increase in Na content as shown in Fig. 3(b). The peak shift to a lower/highest frequency is due to an increase/decrease in binding strength caused by the expansion/shrinkage of the distance between Nb5+ and its coordinated oxygen, resulting in the corresponding variation in crystal cell volume.55,56 However, the clear but gradual symmetry changes observed by XRD were not apparent in the Raman spectra, as evidenced by the absence of the appearance of new symmetry related modes. Raman, however, is not only sensitive to the macroscopic symmetry but is influenced strongly by local distortions to the lattice. It is postulated that within the KNNyN-xBNZ system there are compositional regions dominated by “pseudosymmetry” in a manner discussed for La-doped BiFeO3 compositions by Khesro et al.57 and Bi1-x(K1-xNa)x)2TiO3 by Levin and co-workers.58 In these compositions, there are local perturbations in the average macroscopic symmetry more commonly associated with adjacent phases within the phase diagram, for example, short-range antipolar order in the paraelectric phase for La-doped BiFeO3. We propose a similar model for KNNyN-xBNZ based on the absence of new symmetry modes in Raman and the gradual changes in peak splitting in XRD but extensive transmission electron microscopy (TEM) work is required before this can be proved conclusively.

The SEM images for the surface of KNNyN-xBNZ ceramics (not shown) revealed that the grain size of KN0.6N-xBNZ decreased with increasing BNZ content, from ~5 μm for x = 0 and to ~1 μm for x = 0.08 but the grain size of KNYyN-0.045BNZ was insensitive to the K/Na ratio.

The high electric field bipolar polarization hysteresis and strain loops for KNYyN-xBNZ as a function of BNZ and Na content are shown in Fig. 4, from which the remnant polarization (P_r) coercive field (E_c) and average electric field induced strain (S) as a function of BNZ and Na content can be obtained, Fig. 5. The normalized strain coefficient d33, representing the average strain per unit of electric field, is calculated by, d33 = S_{max}/E_{max}, where E_{max} is the maximum electric field value, and S_{max} is the average value of the corresponding maximum strain. As shown in Fig. 5(a and b), with increasing BNZ and Na concentration in KN0.6N-xBNZ, P_r increased and then decreased after reaching a peak value, at which point the lowest E_c was obtained. The highest value of P_r = 24 μC/cm2 and lowest value of E_c = 10.5 kV/cm was achieved for x = 0.045, y = 0.6 at the MPB.55,57 The S and d33 values increased with increasing BNZ and Na content, reaching maximum values of 0.163%, 408 pm/V at x = 0.045, y = 0.6 and 0.168%, 420 pm/V at x = 0.045, y = 0.56, respectively, above which they reduced. Fig. 5(c and d), d33 is dominated by extrinsic effects, mainly domain wall motion, which the coexistence of R and T phases encourages at the MPB.55,57

The dielectric and piezoelectric properties of KNNyN-xBNZ as a function of BNZ and Na content are shown in Fig. 6. The room-temperature permittivity (ε_r) of KN0.6N-xBNZ increases with BNZ concentration, whereas it initially increases and then decreases as a function of Na/K ratio. Fig. 6(a and b). tanδ initially decreased with BNZ and Na concentration but then became stable for a broad range of compositions, Fig. 6(a and b). d33 and k_p both increased significantly with increasing BNZ and Na concentration as shown in Fig. 6(c and d), reaching a maxima of 310 pC/N and 48% for x = 0.045, y = 0.06, and 320 pC/N and 50% for x = 0.045, y = 0.056, respectively, and then decreasing for BNZ > 0.05 and Na > 0.6. As with d33, d33 is optimized at the MPB, largely through extrinsic
contributions. The facile rotation of the polarization vector between states of similar free energy facilitated by phase coexistence, allows the domain walls to displace reversibly, resulting in a strong extrinsic contribution to the piezoelectric properties.\(^{61,64}\)

(2) Evolution of Structure–Property Relations as a Function of Temperature

The temperature dependence of dielectric permittivity and loss for KNyN-xBNZ with different BNZ concentration and K/Na ratio is given in Fig. 7. It is well-known that KNN exhibits two dielectric peaks above room temperature, corresponding to the ferroelectric O-T phase transition at \(\approx 176^\circ\)C \((T_{O-T})\) and the T-cubic \((C)\) phase transition at \(\approx 381^\circ\)C (Curie temperature, \(T_C\)). With increasing BNZ concentration, the maximum \(\varepsilon_r\) at \(T_C\) (\(\varepsilon_{max}\)) increased and \(T_C\) decreased continuously, meanwhile, \(T_{O-T}\) decreased and merged with the ferroelectric R-O phase transition \((T_{R-O})\), resulting in coexistence of R and T phases at room temperature, Fig. 7(a,c), which is consistent with the XRD results (Fig. 1) and previous reports.\(^{43-50}\) However, \(T_C\) remained at \(\approx 310^\circ\)C and \(T_{R-T}\) increased with increasing Na concentration, suggesting the K/Na ratio had little effect on the ferroelectric-paraelectric phase transition of KNyN-xBNZ and that its major influence is on lower temperature transitions. We note also that broad relaxor-like peaks are observed in all compositions if the BNZ concentrations exceeds, \(x = 0.08\). Relaxor behavior, however, is not the focus of this study and we note only that KNyN-xBNZ follows trends typically observed in ferroelectric to relaxor compositional transitions with a transformation from a clearly defined macroscopic symmetry.
(x = 0) to pseudosymmetry (x > 0.08) that is associated with loss of long range ferroelectric order through chemical disorder that induces local competition/frustration between phases of similar free energy.

To clarify the structural evolution of KNyN-xBNZ as a function of temperature, in situ temperature dependence of Raman and XRD measurements for the selected MPB composition KN0.6N-0.045BNZ were performed, the results from which are plotted in Figs. 8 and 9. As shown in Fig. 8, the general trend is that the \( v_1 \) peak shifted to lower wave number and broadens, accompanied by a gradual fading of the \( v_2 \) peak. More specifically, the \( v_1 \) peak [Fig. 8(c)] revealed a gradual shift in frequency (wave number) up to 70°C–100°C after which there was a sharp change in frequency, coincident with the broad peaks in \( e_r \) at the same temperature range in Fig. 7.

In situ high-temperature XRD data for KN0.6N-0.045BNZ is shown in Fig. 9 which focused on evolution of splitting of the \{200\} peaks. Phase coexistence was apparent at room temperature as shown by broad multiple peaks that gradually disappeared to become a single peak at high temperatures in the cubic phase. To confirm the phase evolution as a function of temperature, simulations were performed, Fig. 9(c–k). As temperature increased, the coexistence of R-T phases remained up to 70°C–100°C, after which the phase structure total transformed to a T and then C phase above \( T_C \), consistent with experimental \( e_r \) and Raman spectroscopy data as function of temperature.

The in situ temperature dependence of high electric field bipolar polarization hysteresis and strain loops for two MPB compositions (KN0.49N-0.045BNZ and KN0.6N-0.045BNZ) are shown in Fig. 10, from which the \( P_r \) and \( d_{33} \) as a function of temperature were obtained, Fig. 11. As temperature increased, \( P_r \) and \( d_{33} \) for both MPB compositions decreased linearly, coincident with a similar temperature dependence of \( k_p \), as shown in the inset of Fig. 11. The piezoelectric effect in ferroelectric ceramics is attributed to both intrinsic (lattice deformation) and extrinsic (domain wall motion) contributions. Normally, \( P_r \) reflects intrinsic contribution, and \( d_{33} \) and \( k_p \) contain both components.\(^{40,48}\) However, detailed knowledge of the domain morphology is required to fully appreciate how the extrinsic contributions is likely to vary as a function of temperature and composition and extensive transmission electron or piezoforce microscopy is required. Nonetheless, the data presented in this contribution clearly illustrates that KNN-BNZ suffers from extreme temperature
dependence which may inhibit its usage in high drive applications and high-temperature applications despite the attractive values of $k_p$ and $d_{33}$ at room temperature.

IV. Conclusion

In this work, KNN based lead-free ceramics with the composition $(1-x)(K,Na)NbO_3-xBi_2Ti_2O_7$ were successfully prepared by a conventional solid-state route. With the increase in BNZ content, the phase structure of KNN gradually transformed from O to mixed R-T and then R phase, indicating the MPB is not temperature independent unlike MPB, there is a dramatic decrease in properties with temperature. Transformation from O to mixed R-T and then R phase, Eur. Ceram. Soc. 31, 7209-7213 (2005) for funding and supporting this work. AK and FH acknowledge Abdul Wall Khan Mardan & NED University of Engineering and Technology for funding respectively.

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References

1. B. Jaffe, W. R. Cook, and H. Jaffe, Piezoelectric Ceramics, Academic Press, London, New York City, New York, 1971.
2. G. H. Haertling, “Ferroelectric Ceramics: History and Technology,” J. Am. Ceram. Soc. 79, 823–831 (1996).
3. D. Damjanovic, “Ferroelectric, Dielectric and Piezoelectric Properties of Ferroelectric Thin Films and Ceramics,” Rep. Prog. Phys. 61, 1267–324 (1998).
4. T. R. Shroft and S. Zhang, “Lead-Free Piezoelectric Ceramics: Alternatives for PZT,” J. Electroceram. 19, 113–26 (2007).
5. G. J. Luo, L. E. Cross, S. -E. Park, B. Noheda, D. E. Cox, and G. Shirane, “Origin of the High Piezoelectricity in PbZr$_x$Ti$_{1-x}$O$_3$, Phys. Rev. Lett. 84, 5423–6 (2000).
6. EU-Directive 2002/96/EC, “Waste Electrical and Electronic Equipment (WEEE),” Off. J. Eur. Union. 46, 24–38 (2003).
7. EU-Directive 2002/95/EC, “Restriction of the Use of Certain Hazardous Substances in Electrical and Electronic Equipment (RoHS),” Off. J. Eur. Union. 46, 19–23 (2003).
8. J. Rödel, K. G. Webber, R. Dittmer, W. Jo, M. Kimura, and D. Damjanovic, “Transferring Lead-Free Piezoelectric Ceramics Into Application,” J. Eur. Ceram. Soc. 28, 1649–1659 (2008).
9. D. M. Daeder, D. Damjanovic, and N. Setter, “Lead Free Piezoelectric Materials,” J. Electroceram. 13, 385–92 (2004).
10. J. Rödel, W. Jo, K. T. P. Seifert, E. M. Anton, T. Granzow, and D. Damjanovic, “Perspective on the Development of Lead-Free Piezocermics,” J. Am. Ceram. Soc. 92, 1153–77 (2009).
11. A. Safari and M. Abazari, “Lead-Free Piezoelectric Ceramics and Thin Films,” IEEE Trans. Ultrason. Ferroelectr. Freq. Control. 57, 2165–76 (2010).
12. T. Takenaka and H. Nagata, “Current Status and Prospects of Lead-Free Piezoelectric Ceramics,” J. Eur. Ceram. Soc. 25, 7693–700 (2005).
13. D. Q. Xiao, J. G. Wu, L. Wu, J. G. Zhu, P. Yu, et al., “Investigation on the Composition Design and Properties Study of Perovskite Lead Free Piezoelectric Ceramics,” J. Mater. Sci., 19, 5408–19 (2009).
14. K. P. Rana, “Review: Environmental Friendly Lead-Free Piezoelectric Materials,” J. Mater. Sci. 44, 5049–62 (2009).
15. G. G. Wu, D. Q. Xiao, and J. G. Zhu, “Potassium-Sodium Niobate Lead-Free Piezoelectric Materials: Past, Present, and Future of Phase Boundaries,” Chem. Rev., 115, 2559–95 (2015).
16. F. Li, K. Wang, F. Y. Zhu, L. Q. Cheng, and F. Z. Yao, “(K,Na)NbO$_3$ Based Lead-Free Piezoelectric Ceramics,” Phys. Status Solidi RRL 8, 438–42 (2015).
17. Y. Saito, H. Takao, T. Tami, T. Nonoyama, K. Takatorii, et al., “Lead-Free Piezocermics,” Nature, 432, 84–7 (2004).
18. E. Cross, J. G. Wu, D. Q. Xiao, and L. Q. Cheng, “Fundamental Aspects of Processing Technologies, and Remaining Challenges,” J. Am. Ceram. Soc. 96, 3677–96 (2013).
19. E. Leger and D. M. Dillon, “Piezoelectric and Dielectric Properties of Ceramics in the System Potassium Sodium Niobate,” J. Am. Ceram. Soc. 42, 438–42 (1959).
20. Y. Saito, H. Takao, T. Tami, T. Nonoyama, K. Takatorii, et al., “Lead-Free Piezocermics,” Nature, 432, 84–7 (2004).
21. E. Cross, J. G. Wu, D. Q. Xiao, and L. Q. Cheng, “Fundamental Aspects of Processing Technologies, and Remaining Challenges,” J. Am. Ceram. Soc. 96, 3677–96 (2013).
22. T. Zheng, J. G. Wu, D. Q. Xiao, J. G. Zhu, X. J. Wang, and J. G. Cheng, et al., “Lead-Free Piezocermics in Potassium-Sodium Niobate Lead-Free Ceramics,” J. Am. Chem. Soc., 136, 2905–10 (2015).
23. X. P. Wang, T. Zheng, J. G. Wu, D. Q. Xiao, J. G. Zhu, et al., “Characteristics of Giant Piezoelectricity Around the Rhombohedral–Tetragonal Phase Transition Boundary in (K,Na)NbO$_3$-Based Ceramics With Different Additives,” J. Mater. Chem. A, 3, 15951–61 (2015).
24. R. P. Wang, H. Bando, T. Katsumata, Y. Inaguma, and M. Itoh, “Tuning the Orthorhombic-Rhombohedral Phase Transition Temperature in Sodium Potassium Niobate by Incorporating Barium Zirconate,” Phys. Status Solidi RRL 3, 142–4 (2009).
25. Y. B. Zhang, J. G. Wu, X. P. Wang, X. J. Cheng, J. G. Zhu, and D. Q. Xiao, “Rhombohedral–Orthorhombic Phase Coexistence and Electrical Properties of Na$_{0.5}$K$_{0.5}$NbO$_3$-Sb$_2$O$_3$ Lead-Free Piezoelectric Ceramics,” J. Appl. Phys. 101, 074111, 6pp (2007).
26. R. Zhang, D. Lv, J. F. Yu, Y. Liu, and L. Li, “Phase Transition and Electrical Properties of Lead Free Na$_{0.5}$K$_{0.5}$NbO$_3$:BaTiO$_3$ Ceramics,” J. Alloys Compd, 476, 1383–9 (2009).
27. R. Guo, L. E. Cross, S. -E. Park, B. Noheda, D. E. Cox, and G. Shirane, “Origin of the High Piezoelectricity in PbZr$_x$Ti$_{1-x}$O$_3$, Phys. Rev. Lett. 84, 5423–6 (2000).
28. H. Du, W. Zhou, F. Luo, D. Zhu, S. Qu, et al., “Lead-Free Piezoelectric Ceramics,” J. Electroceram. 94, 186–90 (2015).
49. Y. Y. Wang, L. Hu, Q. L. Zhang, and H. Yang, “Phase Transition Characteristics and Associated Piezoelectricity of Potassium-Sodium Niobate Lead-Free Ceramics,” *Dalton Trans.*, **44**, 13688–99 (2015).
50. Z. Wang, D. Q. Xiao, J. G. Wu, M. Xiao, F. X. Li, and J. G. Zhu, “New Lead-Free (Na_{0.5}K_{0.5})NbO_3–X(Bi_{0.5}Na_{0.5})ZrO_3 Ceramics With High Piezoelectricity,” *J. Am. Ceram. Soc.*, **97**, 688–90 (2014).

51. Standards Committee of the IEEE Ultrasonics, Ferroelectrics and Frequency Control Society, “IEEE Standard on Piezoelectricity.” American National Standards Institute, New York City, New York, 1987.

52. S. Zhang, E. F. Alberta, R. E. Eitel, C. A. Randall, and T. R. Shrout, “Elastic, Piezoelectric, and Dielectric Characterization of Modified BiScO_3–PbTiO_3 Ceramics,” *IEEE Trans. Ultrasonics, Ferroelectr. Freq. Control*, **52**, 2131–9 (2005).

53. C. Larson and R. B. Von Dreele, “General Structure Analysis System (GSAS),” *Los Alamos National Laboratory Report LAUR*, Los Alamos, 2004.

54. H. Toby, “EXPGUI, a Graphical User Interface for GSAS,” *J. Appl. Cryst.*, **34**, 210–3 (2001).

55. K. Kakimoto, K. Akao, Y. Guo, and H. Ohsato, “Raman Scattering Study of Piezoelectric (Na_{0.5}K_{0.5})NbO_3–LiNbO_3 Ceramics,” *Jpn. J. Appl. Phys.*, **44**, 7064–7 (2005).

56. Z. Y. Liu, H. Q. Fan, and M. M. Li, “High Temperature Stable Dielectric Properties of (K_{0.5}Na_{0.5})_{0.985}Bi_{0.015}Nb_{0.99}Cu_{0.01}O_3 Ceramics With Core-Shell Microstructures,” *J. Mater. Chem. C*, **3**, 5851–8 (2015).

57. A. Khesro, R. Boston, I. Sterianou, D. C. Sinclair, and I. M. Reaney, “Phase Transitions, Domain Structure, and Pseudosymmetry in La- and Ti-Doped BiFeO_3,” *J. Appl. Phys.*, **119**, 054101, 8pp (2016).
58. I. Levin, and I. M. Reaney, “Nano- and Mesoscale Structure of Na_{1/2}Bi_{1/2}TiO_3: A TEM Perspective,” *Adv. Funct. Mater.*, **22**, 3445–52 (2012).
59. I. Levin, I. M. Reaney, E. -M. Anton, W. Jo, J. Rodel, et al., “Local Structure, Pseudosymmetry, and Phase Transitions in Na_{1/2}Bi_{1/2}TiO_3–K_{1/2}Bi_{1/2}TiO_3 Ceramics,” *Phys. Rev. B*, **87**, 024113, 11pp (2013).

60. C. A. Randall, N. Kim, J. Kucera, W. Cao, and T. R. Shrout, “Intrinsic and Extrinsic Size Effects in Fine-Grained Morphotropic-Phase-Boundary Lead Zirconate Titanate Ceramics,” *J. Am. Ceram. Soc.*, **81**, 677–88 (1998).
61. D. Wang, M. Cao, and S. Zhang, “Investigation of Ternary System Pb(HfO_2–PbTiO_3–Pb(Mg_{1/3}Nb_{2/3})O_3 With Morphotropic Phase Boundary Compositions,” *J. Am. Ceram. Soc.*, **95**, 3220–8 (2012).
62. F. Chen, Y. H. Li, G. Y. Gao, F. Z. Yao, K. Wang, et al., “Intergranular Stress Induced Phase Transition in CaZrO_3 Modified KNN-Based Lead-Free Piezoelectrics,” *J. Am. Ceram. Soc.*, **98**, 1372–6 (2015).
63. Y. Qin, J. Zhang, Y. Tan, W. Yao, C. Wang, and S. Zhang, “Domain Configuration and Piezoelectric Properties of (K_{0.2}Na_{0.8})_{0.4}Li_{0.6}(Nb_{0.38}Ta_{0.22}) O_3 Ceramics,” *J. Eur. Ceram. Soc.*, **34**, 4177–84 (2014).
64. S. Zhang, R. Xia, L. Lebrun, D. Anderson, and T. R. Shrout, “Piezoelectric Materials for High Power, High Temperature Applications,” *Mater. Lett.*, **59**, 3471–5 (2005).