The Role of Adding $\text{Bi}_{0.5}\text{A}_{0.5}\text{ZrO}_3$ in Affecting Orthorhombic-Tetragonal Phase Transition

Temperature and Electrical Properties in Potassium Sodium Niobate Ceramics

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Abstract: By studying the alone and synergetic effects of Zr^{4+} and Bi^{3+} on potassium sodium niobate ((K, Na)NbO₃, KNN) ceramics, we revealed how $\text{Bi}_{0.5}\text{A}_{0.5}\text{ZrO}_3$ (A = K, Na, Ag, and (Na_{0.82}K_{0.18})) reduces the orthorhombic-tetragonal phase transition temperature ($T_{\text{O-T}}$) of KNN ceramics. Investigations into the alone effects reveal that aliovalent substitutions on K^+/Na^+ (Nb^{5+}) with Bi^{3+} (Zr^{4+}) inevitably destroy long-range ordering (LRO) and thus worsen piezo/ferroelectric properties. Despite this, Zr^{4+} can replace Nb^{5+} within a high content, remain an orthorhombic (O) phase, and slightly increase $T_{\text{O-T}}$. Although substituting on K^+/Na^+ with Bi^{3+} decreases $T_{\text{O-T}}$, it already significantly destroyed LRO before shifting $T_{\text{O-T}}$ to room temperature. Then, investigations into the synergetic effects show that Zr^{4+} acts as a buffer, Bi^{3+} is an accelerator, and A^+ is a stabilizer. The buffer can exist in KNN ceramics within a high content and neutralizes the charges caused by the accelerator that concentrates on decreasing $T_{\text{O-T}}$, and the stabilizer compensates for the stability of the perovskite phase. Their synergetic effects explain why $\text{Bi}_{0.5}\text{A}_{0.5}\text{ZrO}_3$ can gradually reduce the $T_{\text{O-T}}$ of KNN ceramics without significantly destroying LRO. Therefore, this work helps understand how

$\text{Bi}_{0.5}\text{A}_{0.5}\text{ZrO}_3$ decreases $T_{\text{O-T}}$ and further design the phase boundary for KNN ceramics.

Keywords: KNN ceramics; $\text{Bi}_{0.5}\text{A}_{0.5}\text{ZrO}_3$; Orthorhombic-tetragonal phase transition temperature; Alone effect; Synergetic effect

1. Introduction

Developing high-performance lead-free piezoceramics is accelerated to replace lead-based counterparts used in kinds of electronic devices and achieve sustainable development [1, 2]. As one of the lead-free candidates, KNN-based ceramics are the most eye-catching because of their continuously enhanced piezoelectric properties [2-5]. Notably, their piezoelectric coefficient (d_{33}) values have recently risen to the level of some commercial lead-based piezoceramics [6-9]. The significantly increased d_{33} values hinge on the multiphase coexistence constructed by the addition of indispensable additives [3, 10]. These additives shift the phase transition temperatures of KNN ceramics, including the rhombohedral-orthorhombic phase transition temperature ($T_{\text{R-O}}$) and $T_{\text{O-T}}$ to room temperature, and then form a multiphase coexistence at room temperature [11, 12]. Specifically, when decreasing $T_{\text{O-T}}$ to room temperature, most researchers claim d_{33} values to be higher than 400 pC/N [10]. Numerous references have demonstrated that $\text{Bi}_{0.5}\text{A}_{0.5}\text{ZrO}_3$ ($\text{A} = \text{Na}, \text{K}, \text{Ag}, \text{ and } (\text{Na}_{0.82}\text{K}_{0.18})$)—the most widely doped additive in KNN ceramics—rapidly decreased $T_{\text{O-T}}$ to room temperature and then significantly improved d_{33} values [10]. However, understanding how $\text{Bi}_{0.5}\text{A}_{0.5}\text{ZrO}_3$ decreases $T_{\text{O-T}}$ goes much slowly compared to the rapidly increased d_{33} values.

We recently proved that the high electronegativity of Bi^{3+} is crucial for $\text{Bi}_{0.5}\text{A}_{0.5}\text{ZrO}_3$ to decrease $T_{\text{O-T}}$

[13]. The high electronegativity of Bi^{3+} causes a higher covalent bond percentage in Bi-O bonds than K/Na-O bonds [3]. Furthermore, theoretical calculations have proved that the high hybridization between the Pb 6s and O 2p orbitals induces high covalent Pb-O bonds and thus stabilizes the T phase in PbTiO_3 [14-16]. This explanation can extend to Bi-O bonds because Pb and Bi have the same extranuclear electron arrangement in 6s orbit (Pb: $6s^2 6p^2$ and Bi: $6s^2 6p^3$) [17, 18]. Besides, the $T_{\text{O-T}}$ of KNN-based ceramics was reported to increase when replacing $(\text{Bi}_{0.5}\text{Na}_{0.5})^{2+}$ with other ions (e.g., Sr^{2+} , Ca^{2+} , Ba^{2+}) that have a lower electronegativity than Bi^{3+} , further proving the foregoing analysis [13, 19, 20]. In principle, aliovalent substitutions on A-site ($\text{K}^{+}/\text{Na}^{+}$) with Bi^{3+} shall destroy long-range ordering (LRO) and hinder grain growth [21]. However, $\text{Bi}_{0.5}\text{A}_{0.5}\text{ZrO}_3$ can continuously reduce $T_{\text{O-T}}$ without significantly destroying LRO and even promote the grain growth to some degree [3, 10]. Therefore, besides the high electronegativity of Bi^{3+} , Zr^{4+} and A^{+} also contribute to the decreased $T_{\text{O-T}}$ in some unknown ways. Although certain references studied the effects of ZrO_2 on KNN ceramics, they used ZrO_2 as the oxide aid instead of substituting B-site (Nb^{5+}) [22, 23]. Therefore, investigations into the alone and synergetic effects of Zr^{4+} and Bi^{3+} on KNN ceramics are crucial to fully understand how $\text{Bi}_{0.5}\text{A}_{0.5}\text{ZrO}_3$ decreases $T_{\text{O-T}}$.

To study the alone effects of Zr^{4+} and Bi^{3+} on KNN ceramics, we designed $\text{K}_{0.48}\text{Na}_{0.52}\text{Nb}_{(1-4x)/5}\text{Zr}_x\text{O}_3$ (abbreviated as KNN-Zr), $(\text{K}_{0.48}\text{Na}_{0.52})_{1-3y}\text{Bi}_y\text{Nb}_{0.955}\text{Sb}_{0.045}\text{O}_3$ (abbreviated as KNNS-Bi), and $(\text{K}_{0.48}\text{Na}_{0.52})_{1-3z}\text{Bi}_z\text{NbO}_3$ (abbreviated as KNN-Bi) ceramics, respectively. Logically, we only needed KNN-Bi ceramics to study the alone effects of Bi^{3+} . Here we also prepared KNNS-Bi ceramics because of the consideration, that is, can doping Bi^{3+} alone also reduce $T_{\text{O-T}}$ of KNNS ceramics to room temperature? If yes, high d_{33} values are expected in KNNS-Bi ceramics like the situation of KNNS-

BNZ ceramics [24], indicating that Zr^{4+} and A^{+} are dispensable. Otherwise, KNN-Bi and KNNS-Bi ceramics shall show a similar tendency of T_{O-T} , suggesting the importance of Zr^{4+} and A^{+} . Our results demonstrate the latter. We first studied the alone effects of Zr^{4+} and Bi^{3+} on the phase structure, grain growth, ferroelectric domains, and electrical properties. Our results show that aliovalent substitutions on K^{+}/Na^{+} (Nb^{5+}) with Bi^{3+} (Zr^{4+}) inevitably destroy LRO and worsen piezo/ferroelectric properties because of forming local random electric fields. Despite this, Zr^{4+} can replace Nb^{5+} within a high content, remain an O phase, and slightly increase T_{O-T} . However, Bi^{3+} can but substitute K^{+}/Na^{+} at a very low content only and thus decrease T_{O-T} . Then, we revealed the synergetic effects of Zr^{4+} , Bi^{3+} , and A^{+} on T_{O-T} . We found that Zr^{4+} acts as a buffer, Bi^{3+} is an accelerator, and A^{+} is a stabilizer. The buffer can exist in KNN ceramics within a high content and compensates for the charges caused by the accelerator that concentrates on decreasing T_{O-T} , and the stabilizer compensates for the stability of the perovskite phase. Their synergetic effects explain why $Bi_{0.5}A_{0.5}ZrO_3$ continuously reduces T_{O-T} of KNN ceramics without significantly destroying LRO.

2. Experimental procedure

The process of the material preparations and characterizations is described in Supplementary Material.

3. Results and discussion

We collected the room-temperature composition-dependent XRD patterns to show the variations of phase structure (Figures 1(a, d)). All compositions exhibit the typical perovskite structure, and some compositions have an undesired secondary phase that is indexed to be the $K_6Nb_{10.8}O_{30}$ (PDF#70–5051) (Figures 1(b, e)). The secondary phases were widely observed in KNN-based ceramics because of the

complex sintering process [25, 26]. Even though the pure perovskite structure in XRD patterns, the secondary phases were still observed in the microstructure [22]. Then, we enlarged XRD patterns with $2\theta = 45\text{--}46^\circ$ to judge the variations of the phase structure of the main perovskite structure (Figures 1(c, f)). Generally, an O phase has distinct $\{200\}_{pc}$ diffraction peaks, that is, the intensity of (202)_o peak is twice higher than that of (020)_o peak [27]. Therefore, all KNN-Zr ceramics possess an O phase at room temperature, irrespective of the content of Zr (Figure 1(c)), and KNNS-Bi ceramics also have an O phase at $y = 0\text{--}0.005$. However, the splitting (202)_o and (020)_o peaks coalesce into one at $y = 0.01$ (Figure 1(f)). Such coalescence was deemed as the occurrence of a pseudo-cubic (PC) or a cubic (C) phase [28, 29].

Figure 1. XRD patterns of KNN-Zr (a–c) and KNNS-Bi (d–f) ceramics with $2\theta = 20\text{--}70^\circ$ (a, d), $2\theta = 26\text{--}30^\circ$ (b, e), and $2\theta = 45\text{--}46^\circ$ (c, f). The inverted triangles indicate the secondary phase.

To further reveal the alone effects of Zr^{4+} and Bi^{3+} on the phase structure, we fitted the XRD patterns in Figures 1(c, f) by using the Lorentz fitting and quantified their variations (Figures 2(a-h)) [30]. With increasing Zr^{4+} and Bi^{3+} , 2θ of $(202)_o$ (abbreviated as $2\theta_{202}$) slightly increases, and 2θ of $(020)_o$ (abbreviated as $2\theta_{020}$) rapidly decreases, indicating the accelerated shifting between $(202)_o$ and $(020)_o$ peaks towards each other. The accelerated shifting is well revealed by their difference in 2θ (i.e., $2\theta_{020}-2\theta_{202}$), that is, $2\theta_{020}-2\theta_{202}$ rapidly decreases with increasing Zr^{4+} and Bi^{3+} (Figures 2(b, f)). The reduced $2\theta_{020}-2\theta_{202}$ was believed to originate from the increase in the macro symmetry of the phase structure [31]. Therefore, increasing Zr^{4+} and Bi^{3+} increases the content of the PC phase. Additionally, the full-width-at-half-maximum (FWHM) of $(202)_o$ and $(020)_o$ peaks first rapidly increases and then slightly reduces with increasing Zr^{4+} (Figure 2(c)). However, the FWHM of $(202)_o$ and $(020)_o$ peaks monotonously increases with Bi^{3+} . The increased FWHM was reported to hinge on the reduction in grain size [31-33]. Aliovalent substitutions on Nb^{5+} ($\text{K}^{+}/\text{Na}^{+}$) with Zr^{4+} (Bi^{3+}) generate defect dipoles and then induce the local random electric fields that prevent LRO and form polar nanoregions (PNRs) [21, 34]. Thus, the phase structure shows an increase in the macro symmetry because of the increased content of the PC phase. The difference in valence state and ion radius between $\text{K}^{+}/\text{Na}^{+}$ with Bi^{3+} is much larger than that between Nb^{5+} with Zr^{4+} , which is responsible for the faster occurrence of the macro PC phase in KNNS-Bi ceramics [3, 35]. Then, aliovalent substitutions also greatly hinder the grain growth and cause a reduction in grain size [36, 37], which is responsible for the increased FWHM. Next, we presented detailed evidence for the aforementioned analysis, studied the variations of electrical properties caused by these influences, and revealed their synergetic effects on reducing T_{O-T} .

Figure 2. (a, d) Variations of 2θ of (202)_O and (020)_O peaks; (b, e) the difference in 2θ between (202)_O and (020)_O peaks; (c, f) FWHM of (202)_O and (020)_O peaks.

We first measured the temperature-dependent relative permittivity (ϵ_r - T) to study the degree of diffuseness (i.e., γ) and further reveal the room-temperature phase structure (Figures 3(a-f)). For KNN-Zr ceramics, Zr_{4+} significantly suppresses the orthorhombic-tetragonal (O-T) phase transition and broadens the tetragonal-cubic (T-C) phase transition (Figure 3(a)). Interestingly, even though the suppressed O-T phase transition, T_{O-T} still slightly increases. Additionally, the tetragonal-cubic phase transition temperature (T_c) shifts to lower temperatures with increasing Zr_{4+} . For KNNS-Bi ceramics, T_{O-T} and T_c reduce at $y = 0-0.005$ (Figure 3(d)). However, T_{O-T} almost disappears and T_c is suppressed at $y = 0.01$ (Figure 3(d)). Therefore, KNN-Zr ceramics with $x = 0-0.04$ have an O phase at room temperature, and KNNS-Bi ceramics possess an O phase at $y = 0-0.005$ but a PC phase at $y = 0.01$, which is consistent with the results from the room-temperature XRD patterns. Thus, Bi_{3+} does decrease T_{O-T} , which coincides with our previous results [13]. Note that even though the secondary phase, the distinct T_{O-T} is still observed in KNN-Zr ($x = 0-0.04$), KNNS-Bi ($y = 0-0.005$), and KNN-Bi ($z = 0-$

0.01) ceramics (Figures 3 and S7), which explains why many studies still discussed the variations of T_{O-T} and phase structure of KNN-based ceramics with secondary phases [38-40]. For example, Rubio-Marcos *et al.* also reported the slightly increased T_{O-T} in $(K_{0.44}Na_{0.52}Li_{0.04})(Nb_{0.86}Ta_{0.10}Sb_{0.04})_{1-x}Zr_{5x/4}O_3$ ($x = 0-0.05$) ceramics that possessed two secondary phases [40], and Zuo *et al.* observed the distinct T_{O-T} in $(Na_{0.52}K_{0.48-x}Li_x)(Nb_{1-x-y}Sb_yTa_x)O_3$ ceramics ($y = 0.09-0.1$) that exhibited a secondary phase $K_2Sb_2O_7$ [38]. Therefore, the secondary phase in this work did not significantly affect the variations of T_{O-T} . By contrast, the disappeared T_{O-T} in KNNS-Bi ($y = 0.01$) and KNN-Bi ($z = 0.015$) ceramics is caused by the significantly destroyed LRO, further proving the importance of Zr^{4+} and A^{+} .

Then, we used the modified Curie-Weiss law to evaluate the degree of diffuseness (γ), as shown in Equation 1:

$$\frac{1}{\varepsilon(T)} - \frac{1}{\varepsilon_m} = \frac{(T-T_m)^\gamma}{C} \quad (1)$$

where ε_m is the maximum value of dielectric permittivity at T_m , C is the Curie-like constant, and γ is the degree of diffuseness [41]. γ is 1 for classical ferroelectrics and 2 for ideal ferroelectric relaxors [41]. Therefore, the slope of the linear fittings between $\ln(T-T_m)$ and $\ln(1/\varepsilon_r - 1/\varepsilon_m)$ is γ (Figures 3(b, e)). For KNN-Zr ceramics, γ increases from 1.14 at $x = 0$ to 1.54 at $x = 0.01$ and then further rises to near 2 at $x = 0.04$ (Figure 3(c)). For KNNS-Bi ceramics, γ slightly increases from 1.4 at $y = 0$ to 1.43 at $y = 0.005$ and then sharply rises to 1.8 at $y = 0.01$ (Figure 3(f)). Therefore, Zr^{4+} and Bi^{3+} indeed enhance the diffuseness degree of KNN-based ceramics, which is attributed to the destroyed LRO and the increased PNRs [21]. Furthermore, Zr^{4+} has a higher solid solubility in KNN-based ceramics compared to Bi^{3+} , which is attributed to their different substitutions. Their substitution reactions can be written as the Equations (2, 3) [22, 42]:

Substituting on K^+/Na^+ with Bi^{3+} causes more defects compared to the substitution on Nb^{5+} with Zr^{4+} when the substitutions are equal in molar percentage. These defects form the local dipoles, such as $\text{Bi}_{\text{Na}}^{\bullet\bullet}-\text{V}_{\text{K/Na}}'$ and $\text{Zr}_{\text{Nb}}'-\text{V}_{\text{O}}^{\bullet\bullet}$, which induce the local random electric fields and then increase the diffuseness degree [21]. Meanwhile, the difference in ion radii between A-site ($\text{K}^+ = 0.164$ nm and $\text{Na}^+ = 0.139$ nm) and $\text{Bi}^{3+} (= 0.145$ nm) is much larger than that between B-site ($\text{Nb}^{5+} = 0.064$ nm) and $\text{Zr}^{4+} (= 0.072$ nm) [35], which also further promotes the increase in diffuseness degree. Therefore, the larger difference in valence state and ion radii between K^+/Na^+ and Bi^{3+} is responsible for the rapid increase in γ in KNNS-Bi ceramics with $y = 0.01$.

Figure 3. (a, b) ϵ_r - T curves measured at $f = 10$ kHz; (b, e) linear fitting between $\ln(T - T_m)$ and $\ln(1/\epsilon_r - 1/\epsilon_m)$; (c, f) variations of T_c and γ with x and y . The arrow in (a, d) indicates the direction where the O-T phase transition shifts.

Then, we studied the alone effects of Zr^{4+} and Bi^{3+} on the grain size (Figures 4 and 5). Similar to other reported KNN ceramics, KNN-Zr ceramics with $x = 0$ show the bimodal distribution containing small

and large grains (Figure 4(a)). However, KNN-Zr ceramics with $x = 0.01$ and 0.03 show only the small grains (Figures 4(b, c)). Similar to KNN-Zr ceramics with $x = 0$, KNNS-Bi ceramics with $y = 0$ and 0.005 also have the bimodal distribution (Figure 4(d)). Furthermore, despite the reduced grain size, the grains of KNNS-Bi ceramics with $y = 0.005$ are more regular compared to those of samples with $y = 0$ and have a cube-like shape, indicating enhanced sinterability (Figure 4(e)) [43]. Finally, KNNS-Bi ceramics with $y = 0.01$ exhibit only the small grains with a cube-like shape (Figure 4(f)). Then, we collected the grain size distributions, as shown in Figures 5(a–f). Samples with $x = 0$ and $y = 0–0.005$ have a wide range in the grain size distribution (GSD), containing the small grains, medium grains, and large grains (Figures 5(a, d, e)), while the GSD of samples with $x = 0.01–0.05$ and $y = 0.01$ has a narrow range within $0–1\ \mu\text{m}$ (Figures 5(b, c, f)). The average grain size (AGS) sharply decreases from $3.25\ \mu\text{m}$ at $x = 0$ to $0.28\ \mu\text{m}$ at $x=0.01$ and then slightly rises to $0.38\ \mu\text{m}$ at $x = 0.03$ (Figure 5(a–c)). The slightly increased AGS at $x = 0.03$ may relate to its higher sintering temperature. Then, the AGS decreases from $2.65\ \mu\text{m}$ at $y = 0$ to $1.44\ \mu\text{m}$ at $y = 0.005$ and then rapidly drops to $0.28\ \mu\text{m}$ at $y = 0.01$ (Figure 5(a–c)). Therefore, Zr^{4+} and Bi^{3+} indeed significantly hinder the grain growth, well demonstrating our aforementioned analysis on the FWHM of XRD patterns (Figures 2(c, f)).

Figure 4. SEM images of the surface of as-sintered samples with $x = 0$ (a), $x = 0.01$ (b), $x = 0.03$ (c), $y = 0$ (d), $y = 0.005$ (e), and $y = 0.01$ (f).

Figure 5. Statistics of grain size distribution of as-sintered samples with $x = 0$ (a), $x = 0.01$ (b), $x = 0.03$ (c), $y = 0$ (d), $y = 0.005$ (e), and $y = 0.01$ (f). The letters “S”, “M”, and “L” represent the small grains, medium grains, and large grains, respectively.

Then, we studied the alone effects of Zr^{4+} and Bi^{3+} on ferroelectric domains by using the out-of-plane PFM (OP-PFM) (Figures 6 and 7). For KNN-Zr ceramics, samples with $x = 0$ show abundant ferroelectric domains and the clear phase contrast (Figures 6(a-f)). Furthermore, we observed the typical striped domains with a size of 200–500 nm (Figures 6(b, e)), which were also reported in other works and deemed as 90° domains [22, 44]. Additionally, the ferroelectric domains also exhibit a strong response to the tip voltage, which is demonstrated by the bright contrast in Figures 6(a-c). However, samples with $x = 0.04$ exhibit a serious reduction in the quantity and size of ferroelectric domains compared to samples with $x = 0$ (Figures 6(g-l)). Its domains are highly isolated and much smaller than 100 nm (Figures 6(g-i)). Furthermore, the phase contrast is much weaker compared to the domains of samples with $x = 0$ (Figures 6(j-l)). Considering the significant difference in the domain response of two compositions, we further measured their domains under a lower driven voltage of 2 V. A similar phenomenon is still observed, that is, samples with $x = 0$ show abundant striped domains with the strong phase contrast, whereas samples with $x = 0.04$ exhibit seriously decreased domains with the weak phase contrast (Figures S2 and S4, Supplementary Material).

Figure 6. OP-PFM images of KNN-Zr ceramics with $x = 0$ (a–f) and 0.04 (g–l). (c) is the enlarged view of the black box in (b). The topography is shown in Figure S1 in Supplementary Material.

KNNs-Bi ceramics show a similar tendency in ferroelectric domains to that of KNN-Zr ceramics (Figures 7(a–l)). Samples with $y = 0$ have plentiful ferroelectric domains consisting of striped domains and irregular domains (Figures 7(a–c)). These domains also show a strong response to tip voltage and the distinct phase contrast and have a size of 200–500 nm (Figures 7(a–f)). Similar to KNN-Zr ceramics with $x = 0.04$, samples with $y = 0.01$ also show a severe reduction in the quantity and size of ferroelectric domains (Figures 7(g–i)). The difference is that ferroelectric domains of samples with y

= 0.01 still exhibit the distinct phase contrast (Figures 7(j–l)).

Figure 7. OP-PFM images of KNNS-Bi ceramics with $y = 0$ (a–f) and 0.01 (g–l). (b) is the enlarged view of the black box in (a). The topography is shown in Figure S3 in Supplementary Material.

We measured the switching spectroscopy PFM (SS-PFM) loops of KNNS-Bi ceramics to reveal the variations of the local domain response (Figure 8). Samples with $y = 0$ show two types of SS-PFM loops. One is the highly asymmetric and the other one is symmetric (Figures 8(a1–a2, b1–b2)). The asymmetry is caused by the local random electric fields formed by the local dipoles [45]. Indeed, for type 1, the voltage of 10 V cannot induce sufficient domain switching, resulting in the low amplitude and the negligible phase contrast (Figures 8(a1, a2)). However, the voltage of 15 V overcomes the

local random electric field and then induces sufficient domain switching, resulting in the high amplitude and the phase contrast near 180° (Figures 8(a1, a2)). The further increasing voltage gradually increases the amplitude and maintains the phase contrast to be 180° (Figures 8(a1, a2)). For type 2, the voltage of 10 V can induce sufficient domain switching, resulting in the high amplitude and the phase contrast near 180° (Figures 8(b1, b2)). The further increasing voltage gradually increases the amplitude and maintains the phase contrast near 180° (Figures 8(b1, b2)). Conversely, KNNS-Bi ceramics with $y = 0.01$ show a severe reduction in amplitude and phase contrast despite the voltage is as high as 60 V. The local random electric fields were believed to widely exist in piezoceramics even without doping because of the complex sintering process, particularly for the ones containing volatile elements, such as KNN ceramics [22]. Therefore, two types of SS-PFM in samples with $y = 0$ occur reasonably. In connection with the aforementioned variations of ferroelectric domains, we demonstrated that Zr^{4+} and Bi^{3+} indeed break long-range ordered ferroelectric domains, form local random electric fields, and severely deteriorate the local domain response.

Figure 8. SS-PFM loops of KNNS-Bi ceramics with $y = 0$ (a1, a2, b1, b2) and 0.01 (c1, c2).

Because Zr^{4+} and Bi^{3+} significantly break LRO, the piezoelectric properties are expected to decrease. Indeed, d_{33} and k_p rapidly reduce at $x = 0\text{--}0.01$ and then slightly increase at $x = 0.01\text{--}0.04$ (Figure 9(a)). Meanwhile, the increased PNRs also greatly affect the room-temperature dielectric properties [46]. Therefore, the increased ϵ_r at $x \geq 0.01$ and the increased $\tan \delta$ at $x = 0\text{--}0.02$ are attributed to the increased PNRs, and the decreased $\tan \delta$ at $x = 0\text{--}0.02$ is ascribed to the higher sintering temperature (Figure 9(b)). Conversely, d_{33} and k_p first slightly increase at $y = 0\text{--}0.005$ and then sharply decrease at $y = 0.005\text{--}0.01$ (Figure 9(c)). The increased d_{33} at $y = 0.005$ is ascribed to the well-maintained O phase and the promoted sinterability (Figure 4), which is further demonstrated by the reduced $\tan \delta$ at $y = 0.005$ (Figure 9(d)). As y further rises to 0.01, d_{33} and k_p dramatically decrease, and ϵ_r and $\tan \delta$ sharply increase because of the completely disappeared LRO and the increased PNRs. Additionally, the broken LRO and the increased PNRs make it more and more difficult to achieve the sufficient domain switching and the saturated poling, which is demonstrated by the reduction in the phase angle (θ) of the poled samples (Figure S5, Supplementary Material).

Figure 9. d_{33} , k_p , ϵ_r , and $\tan \delta$ of (a, b) KNN-Zr and (c, d) KNNS-Bi ceramics.

Then, we further studied the alone effects of Zr^{4+} and Bi^{3+} on ferroelectric and strain properties (Figures 10 and 11). For KNN-Zr ceramics, the P - E loop is significantly suppressed when rising x from 0 to 0.01 and then almost remains unchanged at $x = 0.01$ –0.04 (Figure 10(a)). Therefore, the maximum polarization ($P_{\max}$) and the remanent polarization (P_r) first significantly reduce at $x = 0$ –0.01 and then slightly increase at $x = 0.01$ –0.04 (Figure 10(d)). Conversely, the coercive field (E_c) first increases at $x = 0$ –0.01 and then slightly reduces at $x = 0.01$ –0.04 (Figure 10(d)). Adding Zr^{4+} into KNN ceramics breaks LRO and reduces the grain size, which is responsible for the significant decrease in $P_{\max}$ and P_r and the increase in E_c at $x = 0$ –0.01. The slight increase in $P_{\max}$ and P_r and the decrease in E_c at $x = 0.01$ –0.04 may relate to the increase in grain size caused by the higher sintering temperature. Then, bipolar strain curves and d_{33} curves are gradually suppressed with increasing x because of the reduction in ferroelectric domains (Figures 10(b, c)) [47]. Therefore, the positive strain (S_{pos}), the negative strain (S_{neg}), and the poling strain ($S_{\text{pol}} = S_{\text{pos}} + S_{\text{neg}}$) decrease with increasing x because they hinge on both ferroelectric domains and the phase structure (Figures 10(e, f)) [31].

Figure 10. (a) P - E loops, (b) bipolar strain curves, and (c) d_{33} curves of KNN-Zr ceramics; variations of (d) $P_{\max}$, P_r , E_c , (e) S_{pos} , S_{neg} , S_{pol} , and (f) d_{33} values.

Similar to the tendency of d_{33} , the ferroelectric and strain properties of KNNS-Bi ceramics are slightly enhanced at $y = 0.005$ because of the well-maintained O phase and promoted sinterability (Figures 11(a-c)), which is responsible for the increased $P_{\max}$, P_r , S_{pos} , S_{neg} , S_{pol} , and d_{33} values at $y = 0.005$ (Figures 11(d-f)). However, the rapid reduction in these parameters is still observed at $y = 0.01$ because of the destroyed LRO and the increased PNRs (Figures 11(d-f)).

Figure 11. (a) P - E loops, (b) bipolar strain curves, and (c) d_{33} curves of KNNS-Bi ceramics; variations of (d) $P_{\max}$, P_r , E_c , (e) S_{pos} , S_{neg} , S_{pol} , and (f) d_{33} values.

We presented clear evidence above for our initial analysis of how Zr^{4+} and Bi^{3+} alone affect the phase structure, ferroelectric domains, and electrical properties. Doping Zr^{4+} or Bi^{3+} alone breaks LRO of KNN-based ceramics and then worsens the macro piezo/ferroelectric properties. Furthermore, we also observed the similar variations in terms of the phase structure, ε_r - T curves, grain size, domain structure, and electrical properties in KNN-Bi and KNNS-Bi ceramics (see Figures S6-S10, Supplementary Material). In particular, although replacing K^+/Na^+ with Bi^{3+} indeed reduces $T_{\text{O-T}}$ of KNN-Bi and KNNS-Bi ceramics, it already significantly destroyed LRO before shifting $T_{\text{O-T}}$ to room temperature, indicating the importance of Zr^{4+} and A^+ . Even though the slightly increased $T_{\text{O-T}}$, replacing Nb^{5+} with

Zr⁴⁺ within $x = 0-0.04$ remains a macro O phase. Thus, Zr⁴⁺ can replace Nb⁵⁺ at a high content, and Bi³⁺ can but replace K⁺/Na⁺ at very low content. Note that the high content and the low content mainly refer to the minimum content that significantly destroys macro LRO (i.e., losing the macro O phase and ferro/piezoelectric properties).

Therefore, how did Bi_{0.5}A_{0.5}ZrO₃ gradually decrease T_{O-T} at a relatively wide doping content without significantly destroying LRO? The answer is the synergetic contributions from Zr⁴⁺, Bi³⁺, and A⁺. As discussed above, Zr⁴⁺ slightly increases T_{O-T} , and ZrO₂ induces $2Zr'_{Nb} + V_{\ddot{O}}$ defects (Figure 12(a)). In particular, KNN ceramics have high tolerability with Zr⁴⁺, which endows KNN-Zr ceramics with an O phase, even at high contents ($x = 0.04$). Conversely, although Bi³⁺ indeed decreases T_{O-T} , it also induces $2Bi_{\ddot{K}/Na} + 4V'_{K/Na}$ defects that dramatically destroy LRO and degenerate the macro phase structure (Figure 12(b)). Therefore, KNN ceramics have low tolerability with Bi³⁺. Interestingly, when simultaneously adding Zr⁴⁺ and Bi³⁺ into KNN ceramics in the form of Bi_{0.5}A_{0.5}ZrO₃, such as Bi_{0.5}Na_{0.5}ZrO₃, the substitutions can be understood by Equation (4):

Furthermore, the Na⁺ in Bi_{0.5}Na_{0.5}ZrO₃ compensates for the stability of the perovskite phase to some degree, as shown in the Equation (5):

$$t = \frac{(R_A + R_O)}{\sqrt{2}(R_B + R_O)} \quad (5)$$

where t is the tolerance factor, and R_A , R_B , and R_O are the ion radii of A-site cations, B-site cations, and oxygen anion, respectively [5, 48]. Bi³⁺ (Zr⁴⁺) has a smaller (larger) ion radius than K⁺/Na⁺ (Nb⁵⁺), leading to the rapidly decreased t when simultaneously adding Bi³⁺ and Zr⁴⁺ into KNN ceramics, which degenerates the stability of the perovskite phase [5, 49]. Therefore, combining Bi³⁺ with Na⁺ in the

form of $(\text{Bi}_{0.5}\text{Na}_{0.5})_{2+}$ reduces not only the Bi_{3+} content but also the degree of ion radius difference between Bi_{3+} and K^+/Na^+ , which compensates for the stability of the perovskite phase (Figure 12(c)). Besides, K^+ , Ag^+ , and $(\text{Na}_{0.82}\text{K}_{0.18})^+$ also work as Na^+ does, which explains the highly approximate R-T phase transition temperature ($T_{\text{R-T}}$) in $0.96(\text{K}_{0.48}\text{Na}_{0.52})(\text{Nb}_{0.95}\text{Sb}_{0.05})\text{O}_3$ - $0.04(\text{Bi}_{0.5}\text{A}_{0.5})\text{ZrO}_3$ ceramics ($\text{A} = \text{Na}, \text{K}, \text{Ag}, \text{and } (\text{Na}_{0.82}\text{K}_{0.18})$) [50].

Therefore, Zr_{4+} acts as a buffer, Bi_{3+} is an accelerator, and A^+ (e.g., Na^+) is a stabilizer. Substituting on A-site with $(\text{Bi}_{0.5}\text{Na}_{0.5})_{2+}$ enhances the covalency of A-O bonds because of the high hybridization between the Bi 6s and O 2p orbitals, which stabilizes the T phase and thus decreases $T_{\text{O-T}}$ [16-18]. Therefore, Bi_{3+} is the decisive factor for reducing $T_{\text{O-T}}$ and deemed as an accelerator. The buffer (Zr_{4+}) can exist in KNN ceramics at high contents and neutralize the charges caused by introducing $(\text{Bi}_{0.5}\text{Na}_{0.5})_{2+}$, and the stabilizer (Na^+) compensates for the stability of the perovskite phase by forming $(\text{Bi}_{0.5}\text{Na}_{0.5})_{2+}$ (Figure 12(c)). Therefore, their synergetic effects continuously reduce $T_{\text{O-T}}$ of KNN ceramics without significantly destroying LRO (Figure 12(c)) [24, 51]. Therefore, as we previously demonstrated, the phase structure did return to an O phase from a PC phase after substituting on Nb_{5+} with Zr_{4+} in $(\text{K}_{0.50}\text{Na}_{0.50})_{0.97}\text{Bi}_{0.01}(\text{Nb}_{1-x}\text{Zr}_x)\text{O}_3$ ceramics [52]. When adding the appropriate Sb_{5+} into KNN ceramics in advance, $\text{Bi}_{0.5}\text{Na}_{0.5}\text{ZrO}_3$ rapidly reduces $T_{\text{O-T}}$ of KNNS ceramics to room temperature and then significantly enhances the piezoelectric properties (Figure 12(c)), which is one of the most widely used strategies for achieving high d_{33} values [3, 24, 53, 54]. However, their synergetic effects are valid within a certain content because of the gradually destroyed LRO induced by the aliovalent substitutions [21, 34]. Therefore, the ferroelectric-relaxor phase transition has been observed when the content of $\text{Bi}_{0.5}\text{A}_{0.5}\text{ZrO}_3$ exceeded 5~6 molar percentage, and the relaxors have a

PC phase and a single $\{200\}_{pc}$ diffraction peak [28-30, 51]. Similarly, the ferroelectric-relaxor phase transition has also been reported in $MZrO_3$ -doped $(K_{0.5}Na_{0.5})NbO_3$ ceramics ($M = Ba, Sr, \text{ and } Ca$) because of the aliovalent substitutions on both A- and B-sites [48, 55].

Figure 12. Schematic diagrams showing how (a) ZrO₂, (b) Bi₂O₃, and (c) their combination Bi_{0.5}Na_{0.5}ZrO₃ affect the T_{O-T} of KNN-based ceramics. ϵ_r - T curves of KNN-BNZ and KNNS-BNZ ceramics are obtained from Refs. 51 and 24, with permission from the Wiley-VCH (2017) and the Royal Society of Chemistry (2014).

4. Conclusions

In the present work, to reveal how $\text{Bi}_{0.5}\text{A}_{0.5}\text{ZrO}_3$ ($\text{A} = \text{K}, \text{Na}, \text{Ag}, \text{ and } (\text{Na}_{0.82}\text{K}_{0.18})$) reduces $T_{\text{O-T}}$ of KNN ceramics, we first studied the alone effects of Zr^{4+} and Bi^{3+} on $T_{\text{O-T}}$ by exampling $\text{K}_{0.48}\text{Na}_{0.52}\text{Nb}_{(1-4x)/5}\text{Zr}_x\text{O}_3$, $(\text{K}_{0.48}\text{Na}_{0.52})_{1-3y}\text{Bi}_y\text{Nb}_{0.955}\text{Sb}_{0.045}\text{O}_3$, and $(\text{K}_{0.48}\text{Na}_{0.52})_{1-3z}\text{Bi}_z\text{NbO}_3$ ceramics. We found that the aliovalent substitutions on K^+/Na^+ (Nb^{5+}) with Bi^{3+} (Zr^{4+}) inevitably destroy LRO and worsen piezo/ferroelectric properties. Specifically, Zr^{4+} can substitute on Nb^{5+} within a high content ($\sim 4\%$ molar ratio), remain a macro O phase, and slightly increase $T_{\text{O-T}}$. Substituting on K^+/Na^+ with Bi^{3+} reduces $T_{\text{O-T}}$ of KNN and KNNS ceramics, but the effective content is limited within a $1\sim 1.5\%$ molar ratio because of the rapidly destroyed LRO, resulting in the disappeared macro ferro/piezoelectric properties before reducing $T_{\text{O-T}}$ to room temperature. Therefore, the alone effects revealed that Bi^{3+} is responsible for reducing $T_{\text{O-T}}$, and Zr^{4+} and A^+ affect $T_{\text{O-T}}$ in other ways.

Then, we revealed their synergetic effects and found that Zr^{4+} acts as a buffer, Bi^{3+} is an accelerator, and A^+ is a stabilizer. Substituting on A-site with $(\text{Bi}_{0.5}\text{Na}_{0.5})^{2+}$ enhances the covalency of A-O bonds and thus stabilizes the T phase, resulting in the decreased $T_{\text{O-T}}$. Therefore, Bi^{3+} is the decisive factor for reducing $T_{\text{O-T}}$ and deemed as an accelerator. The buffer (Zr^{4+}) can replace Nb^{5+} at high contents and neutralize the charges caused by introducing $(\text{Bi}_{0.5}\text{Na}_{0.5})^{2+}$. The stabilizer (e.g., Na^+) combines with Bi^{3+} in the form of $(\text{Bi}_{0.5}\text{Na}_{0.5})^{2+}$ and reduces not only the Bi^{3+} content but also the degree of ion radius difference between Bi^{3+} and K^+/Na^+ , compensating for the stability of the perovskite phase. Therefore, their synergetic effects explain why $\text{Bi}_{0.5}\text{A}_{0.5}\text{ZrO}_3$ can continuously reduce the $T_{\text{O-T}}$ of KNN ceramics without significantly destroying LRO. Therefore, our work helps understand how $\text{Bi}_{0.5}\text{A}_{0.5}\text{ZrO}_3$ decreases $T_{\text{O-T}}$ and further design the phase boundary of KNN ceramics.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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