Enhanced Electrical Properties of Lead-Free Piezoelectric KNLN-BZ-BNT Ceramics With the Modification of Sm$^{3+}$ Ions

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Environment-friendly lead-free piezoelectric ceramics with great properties and high thermal stability are desired in the industry. In this work, the Sm$^{3+}$-modified lead-free 0.915(K$_{0.45}$Na$_{0.5}$Li$_{0.05}$)NbO$_3$–0.075BaZrO$_3$–0.01(Bi$_{0.5}$Na$_{0.5}$)TiO$_3$ (KNLN-BZ-BNT) ceramics are prepared. The piezoelectric properties are improved with the introduction of Sm$^{3+}$, and the optimal properties ($d_{33}$ = 325 pC/N and $d_{33}^*$ = 384 pm/V) are achieved in the ceramic modified with 0.3 mol% Sm$^{3+}$ ions. Meanwhile, this sample shows good thermal stability such that the values of $d_{33}^*$ decreased less than 20% when the temperature raised from 30 to 180°C. These results show the Sm$^{3+}$-modified KNLN-BZ-BNT ceramics are good for further applications even under high temperature.

Keywords: lead-free piezoelectric, KNN-based ceramics, rare earth, piezoelectric properties, thermal stability

INTRODUCTION

In recent years, environmental problems are a major concern in the whole world (Zhang et al., 2017; Zeng et al., 2020; Zheng et al., 2021). Lead is widely used in various industrial products such as glasses, gasoline, and batteries (Uchino, 1996; Shung, 2015; Wu et al., 2015). Ceramics based on lead zirconate titanate [Pb(Zr, Ti)O$_3$ (PZT)], the most widely used piezoelectric material, also contain PbO more than 60% (Saito et al., 2004; Jiang et al., 2016). The Restriction of Hazardous Substances Directive (RoHS) has been implemented to minimize the use of toxic materials in the end products (Saito et al., 2004; Zhang et al., 2007). Consequently, researches on lead-free piezoelectric materials are highly needed now (Saito et al., 2004; Zhao et al., 2017; Zhao et al., 2019). Among several lead-free piezoelectric materials, such as BaTiO$_3$-, (Bi, Na)TiO$_3$-, and BiFeO$_3$-based piezoelectric materials, the (K, Na)NbO$_3$ (KNN)-based piezoelectric materials, with high Curie temperature and high piezoelectric properties, are considered a potential candidate for PZT-based materials in the industry (Shrout and Zhang, 2007; Zhang et al., 2007).

The morphototropic phase boundary (MPB) between the rhombohedral phase and the tetragonal phase contributes to the excellent performance of PZT-based materials (Shrout and Zhang, 2007; Zhang et al., 2007). Furthermore, as to the vertical MPB, the PZT and PZT-based ceramics show excellent thermal stability. For the lead-free piezoelectric KNN ceramics, a phase boundary between the orthorhombic phase and the tetragonal phase called the polymorphic phase transition appeared at about 200°C (Egerton and Dillon, 1959; Karaki et al., 2013; Wang et al., 2013). By decreasing the
temperature to near room temperature, the electrical properties, especially the piezoelectric property, were dramatically enhanced. Unfortunately, the high piezoelectric coefficients only remain stable in a narrow temperature range (Karaki et al., 2013).

To solve this problem, Karaki et al. constructed an MPB of rhomboheiral and tetragonal phases by the introduction of BaZrO₃ (Karaki et al., 2013). The piezoelectric properties were expectedly improved. Meanwhile, by introducing Bi₀.₅Na₀.₅TiO₃ in an appropriate amount, a vertical MPB has appeared in 0.915(Ko.₄₅Na₀.₅Li₀.₀₅)NbO₃–0.075BaZrO₃–0.₀₁(Bi₀.₅Na₀.₅)TiO₃ (KNLN-BZ-BNT) ceramics, and excellent thermal stability was manifested. In this work, to further improve the properties of KNLN-BZ-BNT ceramics, the doped ceramics with 0.1, 0.3, and 0.5 mol% Sm³⁺ ions are prepared. The crystalline phase, micro-morphologies, electrical properties, and thermal stability are investigated. For comparison, the KNLN-BZ-BNT ceramics in our previous work are discussed together (Quan et al., 2018; Quan et al., 2019; Quan et al., 2020).

EXPERIMENTAL DETAILS

0.915(Ko.₄₅Na₀.₅Li₀.₀₅)NbO₃–0.075BaZrO₃–0.₀₁(Bi₀.₅Na₀.₅)TiO₃, where x = 0.1, 0.3, 0.5, ceramics were synthesized by a solid oxide reaction process. Reagent-grade oxide/carbonate powders, K₂CO₃ (99%), Na₂CO₃ (99.8%), Li₂CO₃ (98%), Nb₂O₅ (99.5%), BaCO₃ (99%), ZrO₂ (99%), Bi₂O₃ (99%), TiO₂ (98%), and Sm₂O₃ (99%), were selected as starting raw materials. The powders were weighed according to stoichiometry and mixed through ball milling, with partially stabilized ZrO₂ balls as media, in alcohol for 15 h at 300 rpm. After drying at 80°C, the powder mixtures were calcined at 800°C for 2 h. The calcined powders were re-milled for 15 h and then pressed into disks of 8 mm diameter and 1 mm thickness at 200 MPa. The green disks were heated at 600°C for 2 h to remove the organics and then sintered at 1,200 °C for 4 h in a sealed alumina curable. To minimize the volatilization of volatile elements, the green compacts were embedded in the calcined powders during sintering. The final pellets were polished and coated with silver paste on both sides, to characterize the electrical properties.

The crystalline phase structure was evaluated using an X-ray diffractometer (D/MAX-2400, Rigaku, Cu Kα radiation, Japan). The temperature dependence of the dielectric constant and dielectric loss was measured using an LCR meter (4980A, Agilent Technologies, Inc.). A ferroelectric testing system (TF Analyzer 2000E, aixACCT) was used to characterize the piezoelectric strain and the P–E and S–E hysteresis loops. The piezoelectric coefficients were measured by a piezoelectric testing system (ZJ-1, CAS), after poling in a silicon oil bath at 30 kV/cm for 10 min.

RESULTS AND DISCUSSION

The X-ray diffraction (XRD) patterns of un-doped and doped KNLN-BZ-BNT ceramics with different amounts of Sm³⁺ ions are shown in Figure 1A. It can be seen that all the samples show a pure perovskite structure. The introduction of Sm³⁺ ions (less than 0.5 mol%) hardly changes the crystalline phase of ceramics. The details of (200) and (002) peaks for all samples are shown in Figure 1B, showing an invisible difference, attributed to fewer Sm³⁺ ions. Besides, the splits of (002) and (200) become a little bit wider with the addition of Sm³⁺, suggesting a phase close to the tetragonal one after Sm³⁺ addition.

Figure 2A shows the room-temperature polarization–electrical field (P–E) hysteresis loops of the un-doped and doped samples with different amounts of Sm³⁺ ions. All the samples show a well-saturated P–E loop. The un-doped KNLN-BZ-BNT ceramic shows the lowest remanent polarization, Pₑ, of 9.70 μC/cm². The 0.1 mol% Sm³⁺-doped ceramic shows the highest Pₑ of 12.3 μC/cm². The decreased Pₑ values for 0.3 and 0.5 mol% Sm³⁺-doped KNLN-BZ-BNT ceramics could be attributed to the more tetragonal phase. The variation of maximum polarization (Pₑ max) with the amount of Sm³⁺ ions shows the same trend as the Pₑ. The lowest and highest Pₑ max appeared in the un-doped and 0.1 mol % Sm³⁺-ion-doped KNLN-BZ-BNT ceramics, respectively. The bipolar electric field–strain (S–E) loops are shown in Figure 2B. Those S–E loops show typical butterfly shapes with high strain, suggesting a typical ferroelectric property. It can be seen that the KNLN-BZ-BNT ceramics show improved piezoelectric strains after doping with Sm³⁺ ions. The highest strain appeared in the 0.3 mol% and 0.5 mol% Sm³⁺-doped ceramics, which is around 0.12%.

The temperature dependence of dielectric constants and dielectric losses at the frequency of 1 kHz for all samples is shown in Figure 3. At room temperature, the dielectric constant of the un-doped KNLN-BZ-BNT ceramic is 1,441. Doping with the Sm³⁺ ions, all the ceramics show a high dielectric constant of 1800 and a low dielectric loss of ~3%, suitable for further applications. It can be noticed that introducing Sm³⁺ ions did not affect the Curie temperatures (T_C) of KNLN-BZ-BNT ceramics, and all the samples show a T_C of 240°C. On further inspection, all the samples did not show dielectric anomaly before the temperature was up to T_C, indicating a good ferroelectric-stable characteristic. The temperature of 240°C is enough for some high-temperature applications, such as actuators in car engines (Turner et al., 1994).

To measure the d_{33} of the samples, the unipolar strains are measured and shown in Figure 4A. The d_{33} was calculated by (Zhu et al., 2015; Li et al., 2018)

\[ d_{33} = \frac{S}{E} \]

(1)

where S is the strain under E (electric field). The un-doped KNLN-BZ-BNT ceramic shows the lowest strain of 0.087%. The Sm³⁺-doped ceramics show the enhanced unipolar strains. The strain of the 0.1% Sm³⁺-doped ceramic is 0.105%. A similar strain of 0.114% was obtained in the doped ceramics with 0.3 mol% and 0.5 mol% Sm³⁺. Figure 4B plots the variation of d_{33} and d_{33} of all the ceramics with the amount of Sm³⁺. It can be seen that the lowest value
appeared in the un-doped KNLN-BZ-BNT ceramic. With the increasing amount of Sm$^{3+}$ ions, the $d_{33}$ and $d_{33}^*$ increased and the highest values were obtained in the ceramic doped with 0.3 mol% Sm$^{3+}$ ions. The highest $d_{33}$ and $d_{33}^*$ are 325 pC/N and 384 pm/V, respectively. These results indicate that the 0.3 mol% Sm$^{3+}$ addition is the most effective way to improve the piezoelectric response of KNLN-BZ-BNT ceramics.

The doping of Sm$^{3+}$ improved the piezoelectric and ferroelectric properties of KNLN-BZ-BNT ceramics. And the optimal performances were achieved in the sample with 0.3 mol% Sm$^{3+}$ addition. To investigate the thermal stability of the Sm$^{3+}$-doped KNLN-BZ-BNT ceramics, the temperature dependence of unipolar strain and $P$–$E$ loops is shown in Figures 5A,B, respectively. The strain under 30 kV/cm at room temperature is 0.114%; then, it decreased slightly with the increasing temperature. When the temperature went up to 180°C, the unipolar strain remained 0.094%, which shows good thermal stability. The samples show good ferroelectric

![Figure 1](image1.png)  
**FIGURE 1** | XRD patterns of un-doped (Quan et al., 2018) and Sm$^{3+}$-modified KNLN-BZ-BNT ceramics. (A) $2\theta$ is between 10 and 60°, and (B) $2\theta$ is between 44.5 and 46°.

![Figure 2](image2.png)  
**FIGURE 2** | (A) Room-temperature polarization–electrical field hysteresis loops; (B) bipolar electric field–strain curves of un-doped (Quan et al., 2018) and Sm$^{3+}$-modified KNLN-BZ-BNT ceramics.

![Figure 3](image3.png)  
**FIGURE 3** | Temperature-dependent dielectric constant and dielectric loss of un-doped (Quan et al., 2018) and Sm$^{3+}$-modified KNLN-BZ-BNT ceramics.
The properties of KNLN-BZ-BNT with 0.3 mol% Sm³⁺ ions were characterized. The remanent polarization, \( P_r \), decreased from 11.19 \( \mu \)C/cm² at room temperature (30°C) to 7.91 \( \mu \)C/cm² at 180°C, and the \( P_{\text{max}} \) decreased from 19.29 \( \mu \)C/cm² to 16.15 \( \mu \)C/cm². To manifest the temperature dependence of ferroelectric and piezoelectric properties of KNLN-BZ-BNT with 0.3 mol% Sm³⁺ ions, the variation of \( P_r \) and normalized \( d_{33}^* \) with temperature is plotted in Figure 5C. It can be found that the normalized \( d_{33}^* \) of the sample decreased less than 20% when the temperature raised from 30 to 180°C, which is better than that in the PZT-5H ceramics (Fang et al., 2019).

**CONCLUSION**

The un-doped and doped KNLN-BZ-BNT ceramics with 0.1, 0.3, and 0.5 mol% Sm³⁺ ions were prepared. The remanent polarization, \( P_r \), and piezoelectric coefficients, \( d_{33} \) and \( d_{33}^* \), were improved with the introduction of Sm³⁺ ions. The best performances appeared in the sample with 0.3 mol% Sm³⁺ ions, showing a \( d_{33} \) of 325 pC/N, a \( d_{33}^* \) of 384 pm/V, a \( P_r \) of 11.19 \( \mu \)C/cm², and a high strain of 0.114% at 30 kV/cm. Furthermore, the 0.3 mol% Sm³⁺-doped KNLN-BZ-BNT ceramic shows good thermal stability. The \( d_{33}^* \) values decreased less than 20% when the temperature raised from 30 to 180°C. These excellent results show the Sm³⁺-modified KNLN-BZ-BNT ceramics are good for further applications even under high temperature.
DATA AVAILABILITY STATEMENT

The original contributions presented in the study are included in the article/Supplementary Material, and further inquiries can be directed to the corresponding authors.

AUTHOR CONTRIBUTIONS

YQ did the experiments and wrote this article. LW (second author), WR, JZ (fourth author), and TK designed this work and helped in writing. KZ and ZW helped in performing the experiments. ZJ and LW (10th author) helped in performing the data test.

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The remaining authors declare that the research was conducted in the absence of any commercial or financial relationships that could be construed as a potential conflict of interest.

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