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Low-temperature Phase Boundary Dispersion Characteristics and Optimization of Electrical Performance in KNLNS$_x$-BAZ Ceramics

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Abstract: The piezoelectric properties of KNN-based ceramics have been significantly enhanced near room temperature through the successful construction of a polymorphic phase boundary (PPB). However, in practical applications such as aerospace, polar exploration, and low-temperature electronic devices, piezoelectric ceramics are often required to maintain stable performance over a wide temperature range. Currently, research on KNN-based ceramics remains largely focused on phase-boundary regulation and performance optimization near room temperature, while systematic studies on the stability and electrical performance evolution mechanisms under low-temperature conditions are still lacking. This gap severely limits the reliable application of these materials in extreme environments. In this work, a $0.96(K0.48Na_{0.52})_{0.96}Li_{0.04}(Nb_{1-x}Sb_x)O_3$-$0.04(Bi_{0.5}Ag_{0.5})$ ZrO_3 (KNLNS$_x$-BAZ) ceramic system was designed and fabricated by introducing Sb^{5+} ions to substitute the B-site. The incorporation of Sb^{5+} is intended to further regulate phase transition behavior and broaden the phase transition temperature range, thereby constructing a low-temperature multiphase coexistence structure characterized by a "diffuse phase boundary." This diffuse phase boundary can effectively suppress abrupt phase structure changes induced by temperature fluctuations, leading to enhanced stability of piezoelectric and dielectric properties at low temperatures. The influence of Sb^{5+} doping on the phase structure and low-temperature electrical properties of KNLNS$_x$-BAZ ceramics was systematically investigated, providing new insights and experimental foundations for the development of KNN-based piezoelectric ceramics with excellent low-temperature stability.

Keywords: Potassium Sodium Niobate; Relaxor Behavior; Electrical Properties; Temperature Stability.

1. Introduction

Materials as the cornerstone of human civilization, have a developmental history intricately tied to the evolution of social structures. From the primitive tools of the Stone Age to the advanced metallurgical technologies of the Bronze and Iron Ages, each major innovation in materials has profoundly influenced the advancement of productive forces and transformations in societal frameworks. With the rapid progress of science and technology, functional materials-particularly smart materials capable of energy conversion—have emerged as key drivers of modern technological innovation. These materials not only detect changes in their external environment but also respond adaptively, showcasing immense potential for applications in cutting-edge fields such as information technology, precision manufacturing, biomedicine, and aerospace.

Piezoelectric materials as a crucial class of functional materials, hold an irreplaceable core position in various fields, including sensors, actuators, and energy harvesters, owing to their unique ability to convert mechanical energy into electrical energy and vice versa[1, 2]. Based on their crystal structures, piezoelectric ceramics can be broadly classified into three main types: tungsten bronze structure, bismuth layer structure, and perovskite structure. Among these, perovskite-type piezoelectric ceramics demonstrate exceptional performance in mechanical-electrical energy conversion, making them widely utilized in applications such as sensors, actuators, and energy storage devices[3].

Thanks to their exceptional electromechanical coupling properties, straightforward fabrication processes, and low cost, piezoelectric ceramics gained widespread adoption during the mid-to-late 20th century. In 1954, American physicists B. Jaffe et al. discovered that Pb(Zr, Ti)O_3 (commonly referred to as PZT) ceramics exhibit remarkable piezoelectric properties, representing a significant milestone in the development of piezoelectric materials. PZT is a continuous solid solution comprising antiferroelectric $PbZrO_3$ and ferroelectric $PbTiO_3$, characterized by a typical ABO_3-type perovskite structure. Leveraging their outstanding piezoelectric properties, excellent temperature stability, and tunable characteristics, PZT ceramics quickly emerged as the leading material in the piezoelectric ceramics market. They found extensive applications in sensors, actuators, and energy harvesters, greatly advancing related technologies[4].

However, one of the main components of PZT ceramics is lead oxide, which can comprise up to approximately 70%. This substance is volatile and toxic, posing serious threats to the environment and human health throughout its entire lifecycle, including preparation, usage, and disposal. As environmental protection has become a focal point, various countries have introduced laws and regulations to restrict the use of lead. For instance, in 2006, the European Union adopted and implemented the Waste Electrical and Electronic Equipment (WEEE) Directive and the Restriction of Hazardous Substances (RoHS) Directive, which strictly limit the use of lead in electronic and electrical equipment. Subsequently, North America, Japan, and South Korea have enacted similar laws and regulations. In China, the "Administrative Measure on the Control of Pollution Caused by Electronic Information Products" was issued in 2006, followed by the "Management Methods for the Restriction of the Use of Hazardous Substances in Electrical and Electronic Products" in 2016. The enactment of these regulations has

directly accelerated the transition to lead-free piezoelectric materials, making the development of environmentally friendly lead-free piezoelectric materials a prominent research direction internationally in the field of functional materials[5].

Current research on lead-free piezoelectric ceramics primarily focuses on those with perovskite structures, including $BaTiO_3$ (BT)-based, $Bi_{0.5}Na_{0.5}TiO_3$ (BNT)-based, $BiFeO_3$ (BFO)-based, and $K_{0.5}Na_{0.5}NbO_3$ (KNN)-based systems. Among these, potassium sodium niobate (KNN)-based ceramics have emerged as a promising lead-free alternative to PZT-based ceramics due to their excellent piezoelectric properties and relatively high Curie temperature[6-8].

In the high-altitude and frigid regions of China, including Tibet, Xinjiang, and Heilongjiang, the extreme low-temperature environment imposes rigorous demands on the electrical performance stability of piezoelectric ceramics. This stability is crucial to ensuring the reliability and safety of equipment operating under such conditions, which holds significant importance across various industries. However, the multiphase boundaries of KNN-based lead-free ceramics exhibit a strong temperature dependence. As temperatures decrease, the electrical properties of these ceramics deteriorate, resulting in performance degradation in cold regions and severely limiting their applicability in such environments. Consequently, enhancing the low-temperature stability of lead-free piezoelectric ceramic materials while maintaining high performance has become an urgent challenge. In this study, partial substitution of Nb^{5+} with Sb^{5+} at the B-site was employed to modify the phase structure, leading to improved temperature stability at low temperatures.

2. Experimental Procedure

$0.96(K0_{.48}Na_{0.52})_{0.96}Li_{0.04}(Nb_{1-x}Sb_x)$ O_3-0.04 $(Bi_{0.5}Ag_{0.5})ZrO_3$ is fabricated by a conventional solid-state reaction method with raw material of K_2CO_3 (99%), Na_2CO_3 (99.8%), Li_2CO_3 (99%), Nb_2O_5 (99.95%), Bi_2O_3 (99%), Ag_2O (99.7%), ZrO_2 (99%), Sb_2O_3 (99.99%). All raw materials were weighed according to the KNLNS$_x$-BAZ formula and mixed by ball milled with ZrO_2 balls and alcohol for 24 hours. Next, the mixed raw materials were dried and calcined at 850 ºC for 6h in air. The powders were pressed into pellets with a diameter of 10 mm and thickness of 1mm under 10 MPa with a binder of 8wt% polyvinyl alcohol (PVA). Then, the PVA binder was burned out at 850 ºC for 2h. Finally, the pellets were sintered at 1070-1100 ºC for 3h in air. The sintering temperature for each composition was carefully optimized, as detailed in Table S1. The silver paste was covered on both sides of the ceramics by heating at 600 ºC for 10 min. The samples were poled in silicone oil bath at 30 kV cm^{-1} for 10 min at room temperature.

3. Results and Discussion

To investigate the effect of Sb^{5+} doping on the phase structure of the KNLNS$_x$-BAZ ceramic system, the crystal structures of the ceramic samples were characterized at room temperature using X-ray diffraction (XRD). The XRD patterns for samples with varying levels of Sb^{5+} doping are presented in Figure 1(a). All diffraction peaks were distinct and well-aligned with the standard pattern of a perovskite structure. No significant diffraction peaks from secondary or impurity phases were detected within the measurement range, indicating that all compositions of the ceramics possessed a pure perovskite structure. This confirms the successful incorporation of the doped Sb^{5+} ions into the ceramic lattice, establishing a crystallographic foundation for the subsequent optimization of electrical properties. A locally magnified XRD pattern in the 2θ range of 44.5-46.5º is illustrated in Figure 1(b). The characteristics and relative intensities of the diffraction peaks in this region are crucial for determining the phase structure of perovskite ferroelectric ceramics. As clearly observed, the $(002)_{pc}$ and $(200)_{pc}$ diffraction peaks for all doped compositions exhibit a distinct doublet structure, with their intensities showing pronounced asymmetry characterized by a higher right peak and a lower left peak. This indicates that the Sb^{5+}-doped KNLNS$_x$-BAZ ceramics possess a pure tetragonal (T) phase structure at room temperature.

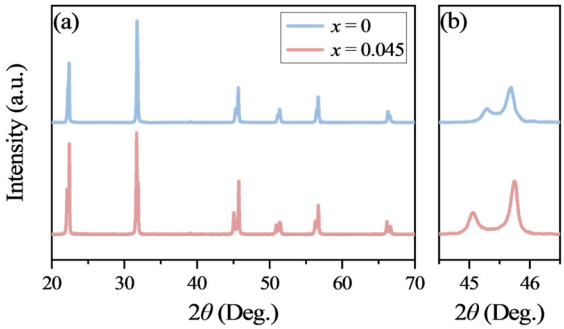


Figure 1. XRD pattern of the KNLNS$_x$-BAZ ceramics with different composition: (a) 2θ = 20-70º, (b) 2θ = 44.5-47.5º

To investigate the influence of Sb^{5+} doping on the phase transition behavior and the diffuseness of the phase boundary in KNLNS$_x$-BAZ ceramics, the diffuse characteristics of the samples were analyzed. For a typical relaxor ferroelectric, the dielectric constant (ε_r) follows the Curie-Weiss law above the phase transition temperature ($T > T_m$). According to the modified Curie-Weiss law:

$$\frac{1}{\varepsilon} - \frac{1}{\varepsilon_m} = \frac{(T - T_m)^\gamma}{C} \quad (1 \le \gamma \le 2) \qquad (1)$$

where ε_r, ε_m and C represent the dielectric constant, the maximum dielectric constant, and the Curie-Weiss constant, respectively. The logarithmic relationship between $1/\varepsilon_r - 1/\varepsilon_m$ and $T-T_m$ was analyzed based on this formula, as shown in Figure 2. The parameter γ is the relaxation factor. Typically, γ = 1 corresponds to a normal ferroelectric, γ = 2 to an ideal relaxor, and $1 < \gamma < 2$ indicates a relaxor ferroelectric. A larger γ value signifies stronger relaxor behavior and a higher degree of phase transition diffuseness. The analysis results indicate that γ increases with the Sb^{5+} doping level, demonstrating that the introduction of Sb^{5+} effectively enhances the relaxor characteristics of the ceramics. The physical origin of this enhancement lies in the substitution of the smaller Sb^{5+} ion (0.6 Å) for the Nb^{5+} ion (0.64 Å). This substitution introduces nanoscale chemical inhomogeneity into the lattice, enhancing compositional and structural heterogeneity and disrupting the long-range order. Consequently, the system is promoted to form polar nanoregions (PNRs) with diverse orientations and non-uniform distribution at the nanoscale. These PNRs do not vanish simultaneously at a single temperature during heating; instead, they gradually lose their polarity over a broad temperature range. Macroscopically, this manifests as a diffuse phase transition and enhanced relaxor properties (an

increased γ value). Therefore, increasing the Sb^{5+} doping level essentially intensifies the chemical disorder of B-site ions, thereby promoting the diffuseness of the phase boundary.

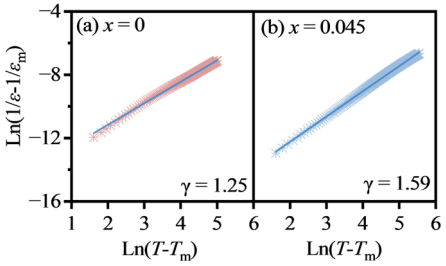


Figure 2. $\mathrm{Ln}(1/\varepsilon\text{-}1/\varepsilon_m)$ as a function of $\mathrm{Ln}(T-T_m)$ for the $KNLNS_x$-BAZ ceramics the solid lines are linear fitting results): (a) x = 0, (b) x = 0.045

The temperature-dependent dielectric constant (ε_r) curves of KNLNSx-BAZ ceramics with varying compositions, measured over the range of -150 °C to 500 °C at a frequency of 100 kHz, are shown in Figure 3. With increasing doping levels (x), a gradual shift of the Curie temperature (T_c) toward lower temperatures is observed, while the $T_{R\text{-}O}$ and $T_{O\text{-}T}$ transition temperatures exhibit a slight shift toward higher temperatures. This diffuse, multi-phase coexistence structure demonstrates low sensitivity to temperature fluctuations, offering an optimal structural basis for achieving excellent temperature stability in the material's properties.

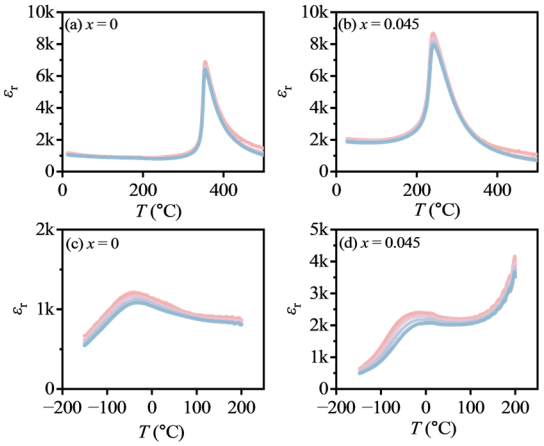


Figure 3. Variation of the relative dielectric constant of $KNLNS_x$-BAZ ceramics with temperature: (a)-(b) T = 20-500 ºC, (c)-(d) T = -150-200 ºC

To gain a deeper understanding of the impact of the constructed low-temperature diffuse multi-phase coexistence structure on the temperature stability of dielectric response, the field-induced dielectric responses of $KNLNS_x$-BAZ ceramics with varying compositions were measured under a bias electric field of 40 kV cm^{-1} across the temperature range of -40 ºC to 30 ºC, as depicted in Figure 4. The dielectric response under zero bias field (ε_0) is theoretically approximately equivalent to the relative dielectric constant (ε_r) measured at the corresponding temperature. Notably, the Sb^{5+}-doped composition with x = 0.045 exhibits exceptional temperature stability in its dielectric properties across the tested range. The variation in ε_r with temperature remains minimal, maintaining an almost constant value throughout the entire interval without significant abrupt changes. This observation indicates that Sb^{5+} doping effectively promotes the formation of a diffuse multi-phase coexistence structure, which successfully mitigates the sharp fluctuations in dielectric constant typically associated with abrupt structural transitions near phase transition points in conventional ferroelectrics. Furthermore, this advantageous effect persists even at low temperatures.

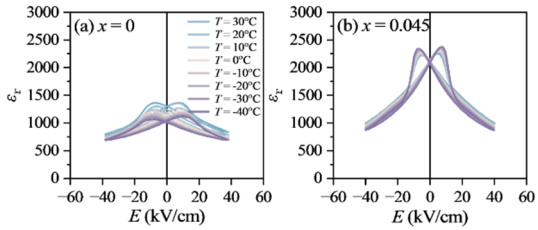


Figure 4. ε_r-E loops changes of $KNLNS_x$-BAZ ceramics with different temperature: (a) x = 0, (b) x = 0.045

The polarization-electric field (P-E) hysteresis loops of $KNLNS_x$-BAZ ceramics with varying compositions, measured over the temperature range of -40 ºC to 30 ºC under a bias electric field of 40 kV/cm, are shown in Figure 5. The analysis reveals that the remnant polarization (P_r) for the composition with x = 0.045 exhibits excellent temperature stability within this range, displaying minimal fluctuation with temperature variation. This behavior aligns with the highly stable dielectric constant (ε_r) observed in temperature-dependent dielectric measurements, collectively highlighting the stabilizing effect of the low-temperature diffuse multi-phase coexistence structure, induced by Sb^{5+} doping, on the polarization ordering of the material. Unlike conventional potassium sodium niobate-based piezoelectric ceramics, where P_r often changes near phase transition temperatures and degrades at low temperatures, the P_r of the $KNLNS_x$-BAZ ceramics remains stable at low temperatures. This indicates that the phase transition behavior has been effectively broadened and diffused, mitigating abrupt changes associated with temperature variations and achieving temperature-insensitive ferroelectric polarization. Additionally, the coercive field (E_c) for all compositions decreases with increasing temperature. This phenomenon is attributed to the thermal activation effect, which facilitates domain wall motion; as the temperature rises, the activation energy barrier for polarization switching is reduced, resulting in a lower E_c.

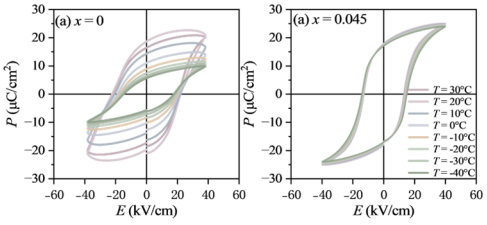


Figure 5. P-E loops changes of $KNLNS_x$-BAZ ceramics with different temperature: (a) x = 0, (b) x = 0.045

4. Conclusion

This study investigates the comprehensive effects of Sb^{5+} doping on the phase structure and low-temperature electrical properties of $0.96(K0_{.48}Na_{0.52})_{0.96}Li_{0.04}(Nb_{1\text{-}x}Sb_x)$ O_3-0.04 $(Bi_{0.5}Ag_{0.5})$ ZrO_3 ($KNLNS_x$-BAZ) ceramics. The dielectric and ferroelectric properties, along with their temperature dependence for different doping compositions (x = 0, 0.045), were comparatively analyzed using temperature-dependent

electrical measurements and characterization techniques such as X-ray diffraction (XRD). The experimental results indicate that the introduction of Sb^{5+} broadens the phase structure into a continuous diffuse phase transition region, successfully inducing a low-temperature diffuse multi-phase coexistence structure. This diffuse phase structure has a relatively low energy barrier, facilitating easier polarization under an applied electric field, which is advantageous for achieving high piezoelectric performance and good temperature stability. Electrical property measurements demonstrate that, compared to the undoped composition, the composition with x = 0.045 exhibits the best overall performance at low temperatures. While maintaining high performance, the fluctuations of key electrical parameters within the -40 ºC to 30 ºC temperature range are less than 5%. This confirms that the construction of a low-temperature diffuse multi-phase coexistence structure through Sb^{5+} doping in $KNLNS_x$-BAZ ceramics is an effective approach for simultaneously achieving high piezoelectricity and excellent low-temperature stability. This work provides a key material candidate system and theoretical foundation for developing piezoelectric devices suitable for applications that require a broad operational temperature range and high stability.

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