

Characteristics of ZnO nanoparticles and their application to improve the physical properties of $0.975(\text{Li}_{0.04}\text{K}_{0.48}\text{Na}_{0.48})(\text{Nb}_{0.95}\text{Sb}_{0.05})\text{O}_3-0.025\text{Bi}_{0.5}\text{Na}_{0.5}\text{HfO}_3$ materials

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Abstract

This study synthesized spherical ZnO nanoparticles, *n*-ZnO, using the co-precipitation method, with spherical *n*-ZnO having sizes ranging from ~10 nm to ~30 nm. The synthesized *n*-ZnO was doped into the $(\text{Li}_{0.04}\text{K}_{0.48}\text{Na}_{0.48})(\text{Nb}_{0.95}\text{Sb}_{0.05})\text{O}_3-\text{Bi}_{0.5}\text{Na}_{0.5}\text{HfO}_3$ (LKNNS–BNH) ceramics. Experimentally, *n*-ZnO was found to be effective as a lubricant during sintering and provided capillary pressure, resulting in microstructures with a high density of 4.47 g cm^{-3} (relative density of 98.1%). Moreover, the incorporation of *n*-ZnO significantly enhanced the electrical performance of the LKNNS–BNH ceramics, with the optimal composition at 0.2 wt.% exhibiting high values of $k_p = 0.40$; $k_t = 0.41$; $d_{33} = 236 \text{ pC N}^{-1}$; $\epsilon_r = 1191$ and $\epsilon_{\text{max}} = 5335$. Notably, this study provides an effective strategy to obtain *n*-ZnO-doped LKNNS–BNH ceramic materials with excellent piezoelectric properties, which opens up more possibilities in device applications.

Supplementary material for this article is available [online](#)

Keywords: lead-free ceramics, *n*-ZnO-doped LKNNS–BNH, ZnO nanoparticles

1. Introduction

Piezoelectric materials are core components of ultrasonic transducers. The selection of piezoelectric materials is critical to achieve high sensitivity and a broad bandwidth in the development of high-frequency ultrasonic transducers [1]. However, commercial ultrasonic transducers primarily use

lead-based $\text{Pb}(\text{Zr}, \text{Ti})\text{O}_3$ (PZT) as the piezoelectric material, since PZT has excellent piezoelectric response and stability [2, 3]. However, lead-based ceramics are not conducive to sustainable development, as they cause lead pollution and harm the human body and environment, particularly in clinical medicine involving direct contact with the human body [4, 5]. Therefore, studying lead-free materials with good performance is highly significant to replace PZT-based ceramics. As is well known, the high Curie temperature and relatively good piezoelectric properties of (K, Na)NbO₃-based ceramics

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make them promising lead-free piezoelectric materials, which are considered suitable candidates to replace toxic PZT-based ceramics [4]. However, achieving an extremely high piezoelectric coefficient d_{33} and good thermal stability remains difficult, since phase transitions and evaporation of alkali elements during sintering form secondary phases, which reduce the piezoelectric properties and hinder further applications of (K,Na)NbO₃-based ceramics [6, 7].

In our earlier work [8], lead-free (Li_{0.04}K_{0.48}Na_{0.48})(Nb_{0.95}Sb_{0.05})O₃ (LKNNS) ceramics demonstrated optimized electrical performance, achieving $k_p = 0.33$, $k_t = 0.35$, and $d_{33} = 195$ pC N⁻¹ under a two-step sintering process with $T_1 = 1150$ °C for $t_1 = 5$ min, and $T_2 = 1050$ °C for $t_2 = 4$ h. Meanwhile, Zhang *et al* [9] found that the 0.955KNNS – 0.045BNH ceramic possessed outstanding piezoelectric behavior with $d_{33} = 540$ pC N⁻¹, which was attributed to the coexistence of rhombohedral, orthorhombic, and tetragonal (*R–O–T*) phases. Similarly, Tao and groups [10] reported that 0.965KNNS–0.035BNH ceramics near the rhombohedral–tetragonal (*R–T*) phase boundary exhibited enhanced piezoelectric performance, reaching $d_{33} \approx 418$ pC N⁻¹ and $k_p \approx 0.45$, mainly due to the beneficial influence of the phase coexistence region.

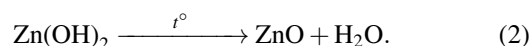
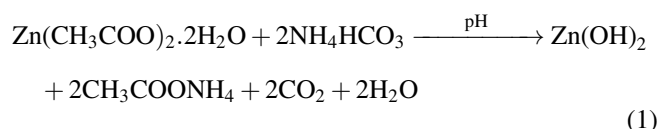
Recent studies have shown that using sintering aids or nanoparticles is an effective solution to address this problem [11]. Using a conventional one-step sintering process, Gio *et al* [12] successfully prepared ZnO-modified 0.96(K_{0.5}Na_{0.5})NbO₃–0.04LiNbO₃ + x wt.% ZnO ($x = 0.0 \rightarrow 0.7$) ceramics. The composition containing 0.5 wt.% ZnO exhibited the best electrical performance, with $k_p = 0.35$, $d_{31} = 52$ pC N⁻¹, and $P_r = 8.0$ μC cm⁻² [12]. In a related investigation, Li *et al* [13] examined ZnO-added Li_{0.06}(Na_{0.535}K_{0.48})_{0.94}NbO₃ ceramics with the aim of enhancing their piezoelectric response, achieving improved properties for $k_p = 0.45$ and $d_{33} = 250$ pC N⁻¹. Liu *et al* reported that ZnO doping in ZnO was highly effective when doped into 0.96K_{0.48}Na_{0.52}Nb_{0.96}Sb_{0.04}O₃–0.04Bi_{0.5}Na_{0.5}HfO₃ ceramics effectively generated defect dipoles, thereby promoting distortion of the BO₆ ceramics effectively generated defect dipoles, thereby promoting distortion of the $k_p \approx 0.46$ and $d_{33} \approx 344$ pC N⁻¹ [11]. Meanwhile, the ZnO dopant formed a liquid phase during air-sintering, which could reduce sintering temperatures and prevent the volatilization of alkali metal elements [14]. However, the use of ZnO nanoparticles to enhance the sintering behavior and electrical properties of KNN ceramics is rarely reported. Therefore, this study synthesized, characterized, and applied ZnO nanoparticles (*n*-ZnO) to improve several physical properties of the (Li, K, Na)NbO₃-based materials, and the promising results demonstrate the good candidacy of these ceramics for ultrasonic applications.

2. Experimental and characterization

2.1. Preparation of nanosized ZnO particles

Zinc acetate dihydrate, (Zn(CH₃COO)₂·2H₂O), was used to synthesize *n*-ZnO via the precipitation method. An 10 g of Zn(CH₃COO)₂·2H₂O was added to 250 ml of deionized water

to obtain an aqueous solution. Subsequently, the NH₄HCO₃ solution was slowly added until the pH value reached 8, and a milky solution was obtained. Small suspended particles appeared in the solution after about an hour of reaction, which separated the solution into a clear upper layer and a lower layer of cloudy precipitate. The clear layer was decanted to recover the precipitate. The resulting precipitate was repeatedly rinsed with distilled water and then dried at 100 °C, yielding a fine Zn(OH)₂ powder (figure S1, equation (1)). The following equations describe the formation and development process of *n*-ZnO:



Finally, the obtained *n*-ZnO was calcined at 500 °C for 1 h (equation (2)). Figure S1 presents a graphical representation of the synthesis procedure. The synthesized ZnO nanoparticles exhibited a spherical morphology, with an average particle size range of 10–30 nm, as shown in figure 1. This is discussed in the next section.

2.2. Synthesis of *n*-ZnO-doped LKNNS–BNH ceramics

A two-step sintering process was used to synthesize ceramics 0.975(Li_{0.04}K_{0.48}Na_{0.48})(Nb_{0.95}Sb_{0.05})O₃–0.025Bi_{0.5}Na_{0.5}HfO₃ (LKNNS–BNH) doped with x wt.% of *n*-ZnO ($x = 0.0; 0.1; 0.2; 0.3$, and 0.4), which are denoted as LKNNS–BNH + x wt.% *n*-ZnO. The Na₂CO₃, K₂CO₃, and Li₂CO₃ carbonates and the Nb₂O₅, Bi₂O₃, Sb₂O₃, and HfO₂ oxides (purity ≥ 99%) were used as starting materials. The effect of moisture was minimized by drying the K₂CO₃, Na₂CO₃, and Li₂CO₃ powders for 2 h in an oven at 150 °C before weighing. The mixed powders were weighed and subsequently ball-milled in ethanol using a planetary mill for 20 h. Homogeneity of the composition was achieved by calcining twice at 850 °C for 2 h. Afterward, x wt.% of *n*-ZnO ($x = 0.0; 0.1; 0.2; 0.3$ and 0.4) was introduced into the LKNNS–BNH powders, followed by additional mixing in ethanol using a planetary ball mill for 2 h. The resulting powders were then compacted into disk-shaped green bodies with a diameter of 12 mm and a thickness of 1.5 mm under an applied pressure of the 1.5 T cm⁻².

All samples were subjected to two-step sintering to analyze the influence of adding *n*-ZnO on LKNNS–BNH ceramics, similar to our previous work [8]. The green compacts were first heated at a rate of 5 °C min⁻¹ up to the first-step sintering temperature ($T_1 = 1150$ °C) and maintained for a short dwell time ($t_1 = 5$ min) to induce the formation of localized liquid phases [8]. Subsequently, the temperature was rapidly reduced at 10 °C min⁻¹ to the second-step sintering temperature ($T_2 = 1050$ °C), where the samples were held for an extended period ($t_2 = 4$ h). This two-step thermal schedule promoted grain growth while simultaneously refining the microstructure of the ceramics.

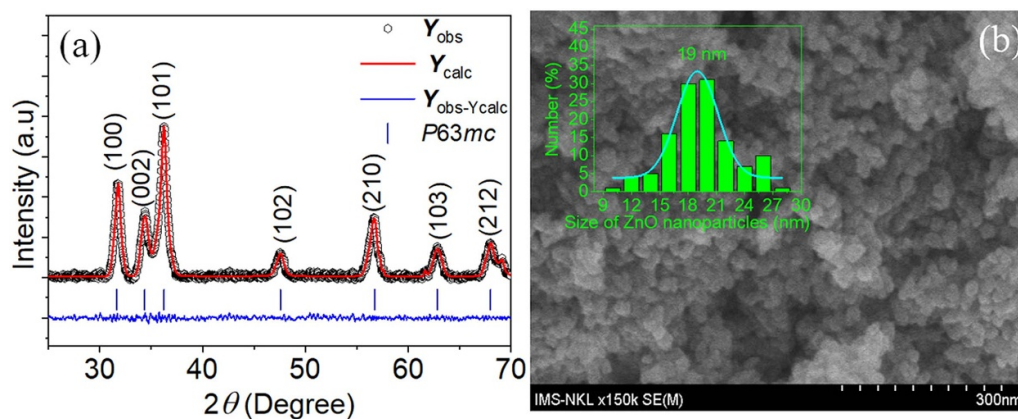


Figure 1. The structure (a) and microstructure (b) of *n*-ZnO calcined at 500 °C.

To investigate the structural characteristics, microstructural features, and surface morphology of the *n*-ZnO and LKNNS–BNH samples, x-ray diffraction (XRD), scanning electron microscopy (SEM), energy-dispersive x-ray spectroscopy (EDS), and elemental mapping techniques were utilized. To measure the electrical properties, both surfaces of the ceramic samples were first coated with silver at 500 °C for 15 min and then poled in a silicone oil bath at 60 °C, with an electric field of 30 kV cm^{−1} applied for 30 min. d_{33} was measured using a d_{33} meter (YE2730A). In addition, the other piezoelectric parameters (k_p , k_t) were calculated from the resonance and anti-resonance frequencies, using an impedance analyzer (RLC HIOKI 3532).

3. Results, analysis, and discussion

3.1. Investigation of the structure and microstructure of ZnO nanoparticles

After being calcined at 500 °C for 1 h, the ZnO powder was subjected to XRD and SEM to examine the structural and microstructural characteristics of the *n*-ZnO sample, as presented in figure 1. Figure 1(a) shows that several distinct diffraction peaks appear from $2\theta = 31.63^\circ$, 34.37° , 36.23° , 47.55° , 56.74° , 62.84° to 67.98° . These peaks are indexed to the (100), (002), (101), (102), (210), (103), and (212) crystallographic planes, respectively. They confirm the hexagonal wurtzite structure of ZnO with the *P63mc* space group, in good agreement with the JCPDS card No. 75-0576 [15]. The obtained structural features are consistent with those reported by Zhou *et al* [16]. The calculated lattice constants of the *n*-ZnO unit cell are $a = b = 3.2522$ Å and $c = 5.2064$ Å.

Based on Scherer's formula [17], the crystallite size determined for *n*-ZnO was in the range of 9.74–17.13 nm, with an average crystallite size of 12.8 nm (table S1) in accordance with recent [18, 19]. Additionally, this was consistent with the SEM imaging results shown in figure 1(b). As shown in the surface morphology of *n*-ZnO calcined at 500 °C in the inset of figure 1(b), spherical nanoparticles with an average particle size of 10–30 nm were formed, similar to recent reports by Mustapha *et al* [17] and Nepal *et al* [18]. Zaidia *et al* reported

that co-precipitation is a low-cost and simple method to synthesize *n*-ZnO, yielding spherical nanoparticles with an average particle size of 27–37 nm on a large scale [15]. Several recent studies have shown that ZnO is a useful sintering aid for reducing sintering temperature while simultaneously increasing the electrical properties of materials [13, 14]. The ZnO sintering aid forms a liquid phase during air-sintering, which can reduce sintering temperatures to prevent volatilization of alkali metals and is beneficial for KNN-based ceramics [14]. Using the conventional mixed-oxide synthesis method, Li *et al* obtained ZnO-doped Li_{0.06}(Na_{0.535}K_{0.48})_{0.94}NbO₃ ceramics prepared by the conventional mixed-oxide method possess a dense microstructure, along with a high mechanical quality factor ($Q_m = 235$), and favorable piezoelectric properties ($d_{33} = 250$ pC N^{−1}; $k_p = 0.45$) [13]. Hayati *et al* reported that a low *n*-ZnO content could improve the densification and electrical properties of KNN-based ceramics [20]. Thus, doping *n*-ZnO into LKNNS–BNH ceramics is expected to effectively improve their density and electrical properties, which is discussed in the next section.

3.2. The influence of *n*-ZnO nanoparticles on the physical properties of LKNNS–BNH ceramics

The bulk and relative densities of LKNNS–BNH + *x* wt.% *n*-ZnO ($x = 0.0$; 0.1; 0.2; 0.3; and 0.4) ceramics were synthesized using two-step sintering technique are shown in figure 2. The bulk and relative densities initially increased with increasing *x*, attaining maximum values of 4.47 g cm^{−3} and 98.1% at $x = 0.2$, respectively, before decreasing at higher *x* values. In other words, the bulk and relative densities of LKNNS–BNH reached peak values with increasing ZnO content. It had been reported in the [21] that the density of (Li_{0.04}K_{0.44}Na_{0.52})(Nb_{0.86}Ta_{0.1}Sb_{0.04})O₃ ceramics sintered at 1125 °C tended to decrease as the ZnO content increased, with the bulk density decreasing from 4.69 to 4.57 g cm^{−3} as the ZnO content increased from 0 to 1 wt.%. Cheng *et al* [22] suggested that *x* wt.% ZnO doped (Li_{0.058}K_{0.480}Na_{0.535})_{0.966}(Nb_{0.9}Ta_{0.1})O₃ ceramics exhibited increased bulk and relative densities as *x* increased, reaching the highest values of 4.56 g cm^{−3} and 98% at value

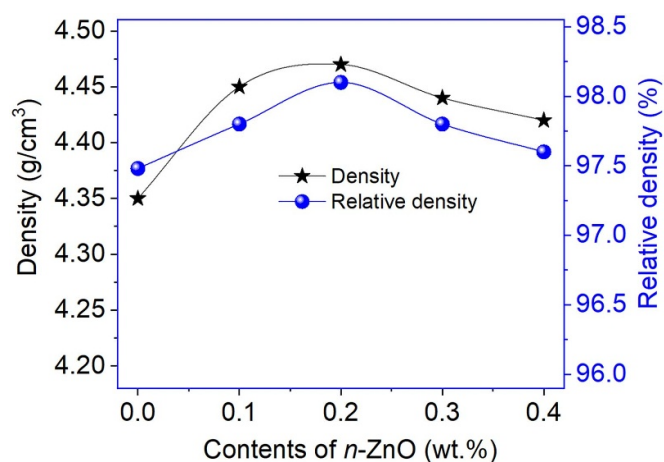


Figure 2. Change of measured density and relative density of LKNNS-BNH + *x* wt.% *n*-ZnO.

x = 0.6, respectively, followed by a subsequent decrease with further increase in *x*, similar to that reported by Li *et al* [13].

First of all, the incorporation of ZnO can lower the sintering temperature, thereby minimizing the volatilization of alkali metal components [14]. Second, the low melting point of the Bi-Zn system is beneficial for generating a eutectic liquid phase at 730 °C [23], which can serve as a sintering aid by acting as a lubricant, improving wetting of solid particles, and generating capillary forces between them. These effects enhance atomic diffusion, thereby promoting better microstructural development and higher densification of the samples, in agreement with the results reported by Truong-tho and Le Vuong [24].

Figure 3(a) presents the XRD patterns of LKNNS-BNH + *x* wt.% *n*-ZnO (*x* = 0.0; 0.1; 0.2; 0.3; and 0.4) ceramics recorded at room temperature in the 2θ range of 20–70°. The seven distinct peaks at about 22.12°, 31.52°, 38.81°, 45.17°, 50.80°, 56.10°, and 65.76° correspond to the (100), (110), (022), (200), (102), (201), and (211) planes. All samples exhibit a perovskite structure with predominant orthorhombic symmetry and an ideal I_{022}/I_{200} ratio of 2:1. Furthermore, the XRD patterns were refined using the Fullprof program, constraining the refinement to point groups $P4mm$ and $Amm2$, to clarify the influence of *n*-ZnO on the structure of *n*-ZnO-doped LKNNS-BNH ceramics (figure 3(c) and figures S2(a)–(e)). The lattice parameters of the ceramics are listed in table S2.

From the fitting analysis of peak profiles, peak positions, structural parameters, and background evaluated using the profile R_{wp} factors, it was confirmed that all samples possess perovskite structures (figure S2). The orthorhombic $Amm2$ phase dominates with a high fraction of 75%–98%, while the tetragonal $P4mm$ phase appears as a minor component ranging from 2% to 25% (see figure 3(d) and table S2). The increase in the $P4mm$ phase content was attributed to *n*-ZnO doping into the LKNNS-BNH matrix, since Zn^{2+} ions replaced the *B*-site ionic species as observed in figure 3(b). From a crystallographic perspective, Zn^{2+} substitution at the *B*-site distorted the lattice and modified the ceramics due to the small differences in ionic radii among Zn^{2+} (0.74 Å); Nb^{5+} (0.64 Å);

Sb^{3+} (0.76 Å); Sb^{5+} (0.60 Å); and Hf^{4+} (0.76 Å), which was consistent with the reports in [3, 25]. In other words, the combined effect of cation disorder and the applied electric field leads to the emergence of a broad region where multiple phases coexist, in agreement with the interpretation proposed by Chen *et al* [7].

The SEM images of the LKNNS-BNH + *x* wt.% *n*-ZnO (*x* = 0.0; 0.1; 0.2; 0.3; and 0.4) ceramics were analyzed to clarify the influence of *n*-ZnO on the microstructure, and the results are shown in figure 4. The results showed microstructural variations as a function of *n*-ZnO content. An increase in *x* slightly increased the grain size and decreased the pore volume. The grains grew to form larger grains, and the pores were removed from the grain boundaries, resulting in a highly dense ceramic (figure 4(c)). The grain size distribution of the LKNNS-BNH + *x* wt.% *n*-ZnO (*x* = 0.0; 0.1; 0.2; 0.3 and 0.4) ceramics was calculated using Lince software on SEM images and is illustrated in the inset of figure 4. For *x* = 0.0, the grain size distribution was from 0.6 to 3.2 (μm) with an average grain size of about 1.54 μm being observed (figure 4(a)). As *x* increased from 0.1 to 0.2, the grains grew slightly larger, the grain size distribution extended to 0.5–4.0 μm, and the pores gradually decreased (figures 4(b) and (c)). In the samples with *x* = 0.3 and 0.4, the grains became larger, accompanied by a few abnormally large grains that could slightly reduce the bulk density, as discussed earlier (from figures 4(d)–(f)). Thus, the average grain size of the ceramics slightly increased as *n*-ZnO content, which contributed to increase in density and electrical properties of the samples and was similar to that reported earlier [13].

According to Li *et al*, the improved densification, featuring reduced porosity and enlarged grains, is likely associated with liquid-phase sintering induced by ZnO in LKNNS-BNH ceramics [13]. However, in this study, the liquid phase may not be pure ZnO due to its high melting point of about 1500 °C. Thus, *n*-ZnO could combine with certain elements in the LKNNS-BNH matrix to form a liquid phase with a lower melting point. This prediction is further supported by Gong *et al*, who demonstrated that the low melting point of the Bi-Zn system facilitates the formation of a eutectic liquid phase at 730 °C [23], which can function as a sintering lubricant, enhancing elemental diffusion and promoting the formation of highly dense, pore-free microstructures [25], as illustrated in figure 4.

To provide clear evidence of the elemental homogeneity in the *n*-ZnO-doped LKNNS-BNH ceramics, EDS along with elemental mapping was carried out on the polished tablet surface, as presented in figure 5. The obtained results confirm that all constituent elements are evenly distributed throughout the sample, in good agreement with the designed composition. These elements include K, Na, Nb, Sb, Bi, Hf, Zn, and O in the LKNNS-BNH + 0.2 wt.% *n*-ZnO ceramic (figures 5(b)–(i)). From insert of figure 5(a), it can be further observed that Bi and Zn species tend to accumulate at the grain boundaries. This observation supports the possibility of Bi-Zn formation at the grain boundaries in the *n*-ZnO-doped LKNNS-BNH system.

Figure 6(a) displays the dielectric constant (ϵ_r) and dielectric loss ($\tan\delta$) of the LKNNS-BNH + *x* wt.% *n*-ZnO (*x* = 0.0;

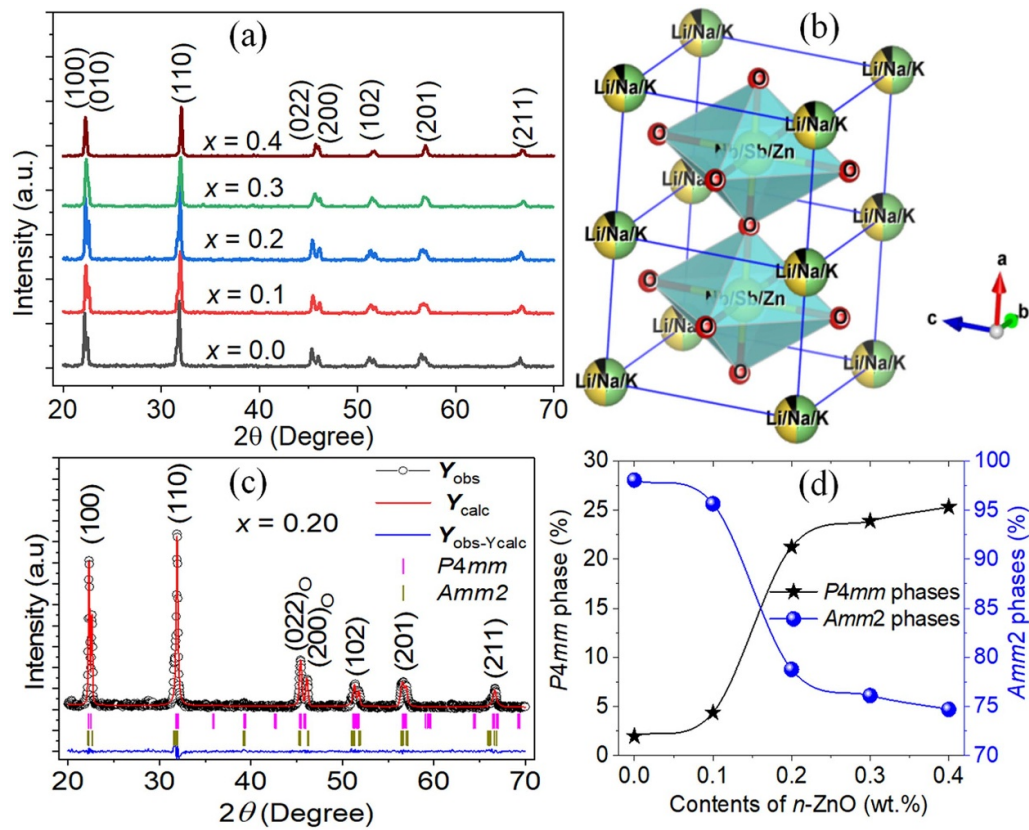


Figure 3. (a) The XRD patterns of LKNNS–BNH + x wt.% n -ZnO ceramics under conditions of varying x ; (b) ABO_3 structural model; (c) Rietveld refinement of XRD patterns of materials; (d) Phase fraction ratios.

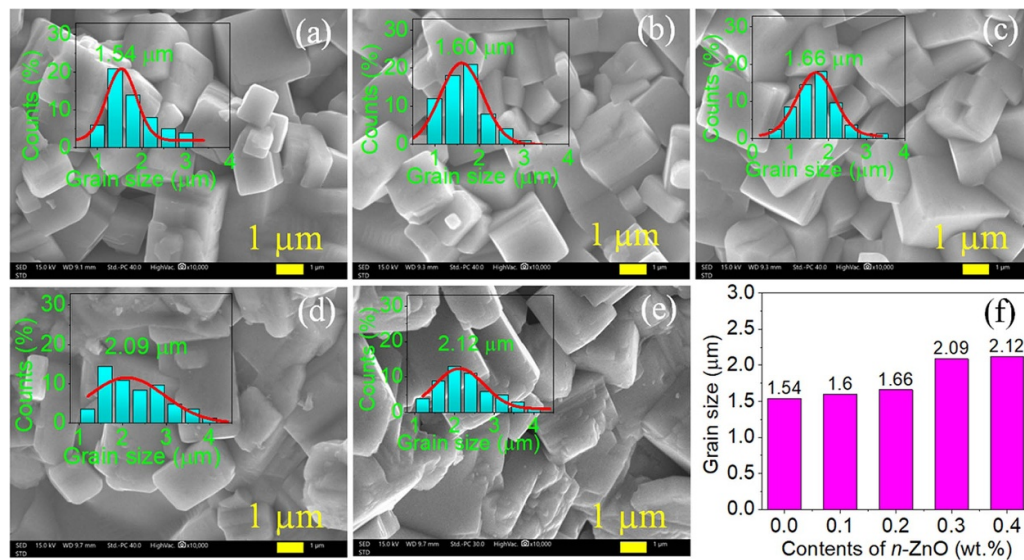


Figure 4. The microstructure and grain size distribution of LKNNS–BNH + x wt.% n -ZnO materials: (a) $x = 0.0$, (b) $x = 0.1$, (c) $x = 0.2$, (d) $x = 0.3$, (e) $x = 0.4$ and (f) the grain size.

0.1; 0.2; 0.3; and 0.4) ceramics measured using an impedance analyzer (RLC HIOKI 3532). As x content increased from 0.0 to 0.4, the ε_r value initially increased to reach a maximum value of 1191 at $x = 0.2$, then tended to decrease. This change could be related to the increase in grain size and ceramic density. Meanwhile, the $\tan\delta$ value tended to decline as x increased

from 0.0 to 0.4, as the microstructure improved with reduced porosity and fewer grain boundaries, consistent with previous studies. This suggests that the presence of n -ZnO improved the sinterability and perfected the microstructure, which reduced grain boundaries and porosity, facilitating polarization processes by promoting easier domain switching. As a result, the

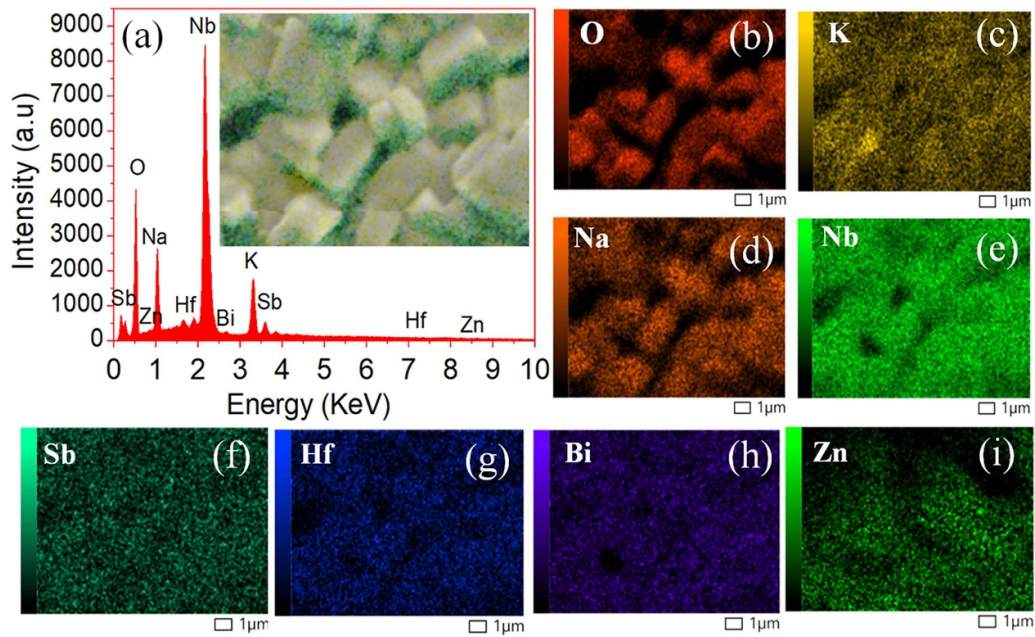


Figure 5. EDS analysis and elemental mapping analysis of LKNNS–BNH ceramics doped with 0.2 wt.% *n*-ZnO.

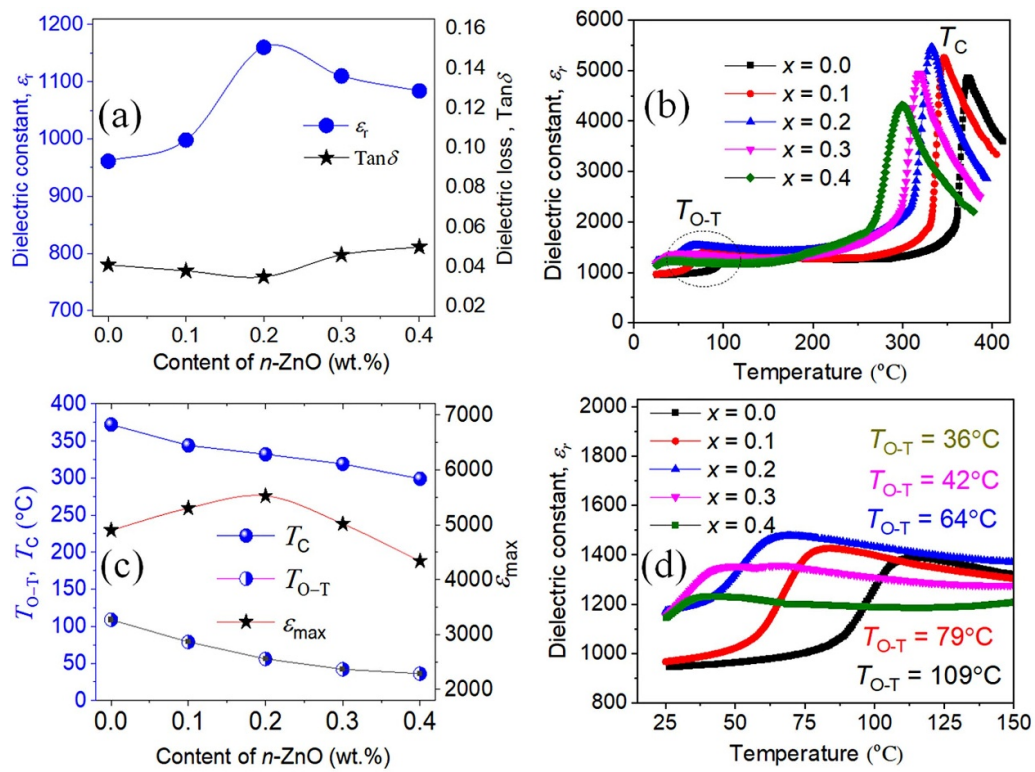


Figure 6. Dielectric behavior of LKNNS–BNH ceramics doped with *x* wt.% *n*-ZnO for different *x* values.

dielectric performance of the samples is enhanced, consistent with earlier studies [25].

The temperature dependence of ϵ_r for the LKNNS–BNH + *x* wt.% *n*-ZnO (*x* = 0.0; 0.1; 0.2; 0.3; and 0.4) ceramics is shown in figure 6(b). As observed, the dielectric response shows two distinct transition points, corresponding to the T_{O-T} and T_C temperatures. This behavior is in good

agreement with recent reports [4, 25]. The T_C and T_{O-T} values tended to decrease as *x* increased. In other words, for samples with *x* = 0.0; 0.1; 0.2; 0.3 and 0.4, the T_C values were 373, 346, 332, 319 °C and 305 °C, and the corresponding T_{O-T} values were 109, 79, 64, 42, and 36 °C, respectively (figures 6(c) and (d)). This phenomenon could be related to the increase in lattice cell size and the transformation of the crystal phase

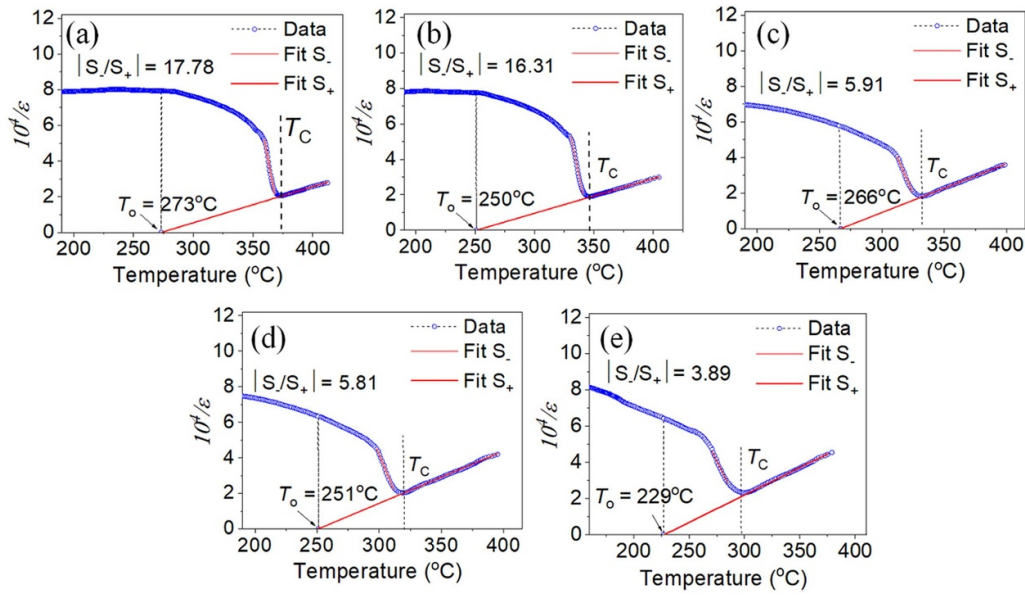


Figure 7. Inverse dielectric constant as a function of temperature for LKNNS–BNH + x wt.% n -ZnO materials: (a) $x = 0.0$; (b) $x = 0.1$; (c) $x = 0.2$; (d) $x = 0.3$ and (e) $x = 0.4$.

structure as Zn^{2+} ions replaced the B-site ions. Due to the small differences in ionic radii among Zn^{2+} (0.74 Å); Sb^{5+} (0.60 Å); Sb^{3+} (0.76 Å); and Nb^{5+} (0.64 Å), Zn^{2+} substitution at the B-site resulted in a higher degree of disorder, leading to local compositional fluctuations and decreased phase transition temperatures, similar to other reports [4, 25]. As presented in figure 6(c), the ε_{max} value of the ceramics increased as x increased to reach the greatest value of 5335 at $x = 0.2$ and then tended to decrease as x continued to increase. These samples exhibited enhanced dielectric properties with n -ZnO addition, likely due to improved densification. In other words, the increase in ε_{max} could be attributed to the role of ZnO in improving the sintering ability of LKNNS–BNH ceramics, and perfected the microstructure, which reduced grain boundaries and porosity, which improved polarization efficiency due to easier domain switching.

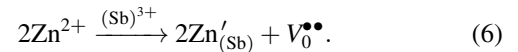
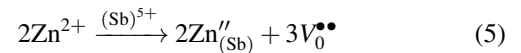
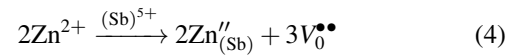
The results in figure 6(b) indicated that the LKNNS–BNH + x wt.% n -ZnO ($x = 0.0$; 0.1; 0.2; 0.3; and 0.4) ceramics exhibited normal ferroelectric behavior, which implies that the dielectric constant inversion was a function of temperature and followed the Curie–Weiss law [26]. As depicted in figure 7, the slope of the dielectric constant inversion ($10^4/\varepsilon$) below and above T_C for the LKNNS–BNH + x wt.% n -ZnO materials followed the Curie–Weiss law (equation (3)) [26]:

$$\varepsilon = \frac{C}{T - T_0} \quad (3)$$

where C is the Curie–Weiss constant; and T_0 is the Curie–Weiss temperature, respectively [26]. The red and green lines represent the linear fitting results around T_C . Additionally, S_- and S_+ are slopes of $10^4/\varepsilon$ below and above T_C , respectively.

As is well known, the phase transition is first-order when the S_- and S_+ values are around 8 or $T_0 < T_C$ [26]. In this study, the slope ratio (S_-/S_+) decreased from 17.78 ($x = 0.0$, ranging from figure 7(a) to 3.89 at $x = 0.4$ (figure 7(e)) and

T_0 for all samples was lower than T_C (figure 7), indicating that the ferro-paraelectric phase transition of the ceramics is first-order, similar to that reported by Tan *et al* [26]. The narrowing of the temperature gap, $\Delta T = T_C - T_0$, accompanied by the decrease in S_-/S_+ , reflects a weakening of the first-order phase transition with ZnO doping into the LKNNS–BNH matrix due to the similarity in ionic radii but difference in valence. In other words, due to the small differences in ionic radii among Zn^{2+} (0.74 Å); Sb^{5+} (0.60 Å); Sb^{3+} (0.76 Å); and Nb^{5+} (0.64 Å); Zn^{2+} substitution at the B-site increased disorder, which reduced the values of ΔT and S_-/S_+ , consistent with the report of Li *et al* [13]. Besides, the changes in first-order phase transition characteristics could be attributed to defect chemistry and the formation of oxygen vacancies, as predicted from equations (4)–(6) as [27],



The formation of oxygen vacancies from equations (4)–(6) shifted the B-site ion away from the center of the oxygen octahedron, increasing the electric dipole moment and promoting the transition from normal ferroelectric to relaxor behavior, while reducing first-order phase transition characteristics. When the concentration of oxygen vacancies becomes sufficiently high, the material no longer exhibits a sharp transition typical of a normal ferroelectric phase. Instead, it evolves into an ergodic relaxor state, which is characterized by the presence of polar nanoregions. Although these defects can promote relaxor behavior, they also tend to increase leakage current and

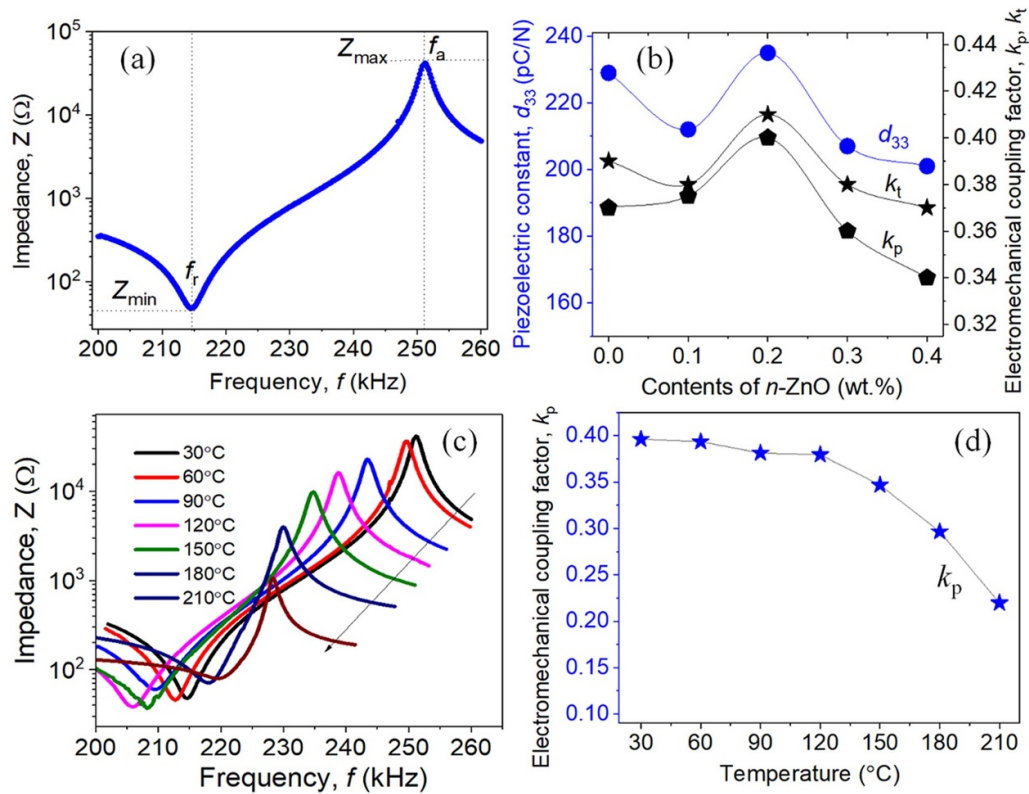


Figure 8. (a) and (b) The piezoelectric property of LKNNS–BNH + x wt.% n -ZnO materials ($x = 0.0$ – 0.4); (c) and (d) The piezoelectric resonance spectrum and the k_p values are functions of temperature for samples $x = 0.2$.

dielectric loss, thereby degrading the overall electrical performance of the material. A similar trend has been reported by Li *et al* [27], and further discussion is provided in the following section.

The piezoelectric resonance spectrum was measured at room temperature (figure 8(a)) to calculate the piezoelectric parameters of the LKNNS–BNH + x wt.% n -ZnO ($x = 0.0$; 0.1 ; 0.2 ; 0.3 ; and 0.4) ceramics, as illustrated in figure 8(b). The piezoelectric parameters (k_p , k_t , and d_{33}) initially decreased slightly at $x = 0.1$ and then increased as x increased, reaching maximum values of $k_p = 0.40$, $k_t = 0.41$, and $d_{33} = 236$ pC N^{−1} at $x = 0.2$, then decreased with further increase in x . The authors suggest that the role of ZnO is not fully realized at low n -ZnO contents. As discussed above, the LKNNS–BNH + 0.1 wt.% n -ZnO ceramic is predominantly composed of the orthorhombic phase, while the tetragonal phase accounts for only about 4.36%. Such a low fraction of the tetragonal phase is insufficient to fully exploit the phase boundary contribution. In addition, the microstructure is not uniform, consisting of a mixture of small and large grains. This irregular grain distribution limits the effective utilization of grain size effects. Consequently, this sample exhibits relatively poor piezoelectric performance. However, as the n -ZnO content increased for n -ZnO contents exceeding 0.1 wt.% could combine with Bi in the LKNNS–BNH matrix to generate a eutectic liquid phase at 730 °C, promoting sintering and resulting in highly dense microstructures without pores, thereby enhancing the piezoelectric properties.

Furthermore, the enhanced piezoelectric performance of the n -ZnO-doped LKNNS–BNH ceramics can be explained by the combined effects of grain growth and the presence of the orthorhombic–tetragonal (O – T) phase boundary. These factors promote higher polarization efficiency by facilitating easier domain switching. As discussed previously, the increase in the $P4mm$ phase fraction is induced by n -ZnO incorporation into the LKNNS–BNH matrix (figure 3(d)), leading to an extended coexistence region of O – T phases. This phase coexistence improves domain-wall mobility, thereby enhancing the overall electrical properties of the ceramics. However, a further increase in ZnO content reduced the piezoelectric properties, which was attributed to the solubility limit of Zn²⁺ in the LKNNS–BNH matrix.

The piezoelectric resonance spectrum was measured at different temperatures in the 30 °C– 210 °C range to evaluate the thermal stability of the piezoelectric property for LKNNS–BNH + 0.2 wt.% n -ZnO ceramics, as shown in figure 8(c). As the measured temperature increased, the oscillation spectrum changed, with f_r increasing and f_a decreasing, which implied that $\Delta f = f_a - f_r$ decreased and the piezoelectric properties decreased with temperature. As seen in figure 8(d), the samples exhibited good thermal stability, and k_p for the ceramics slightly decreased with temperature from 30 °C to 210 °C values. Notably, a relatively high k_p value is retained up to 210 °C, corresponding to about 50% of its room-temperature value, which demonstrates good thermal stability for practical applications [28]. As shown in figures 9(b) and (d), the

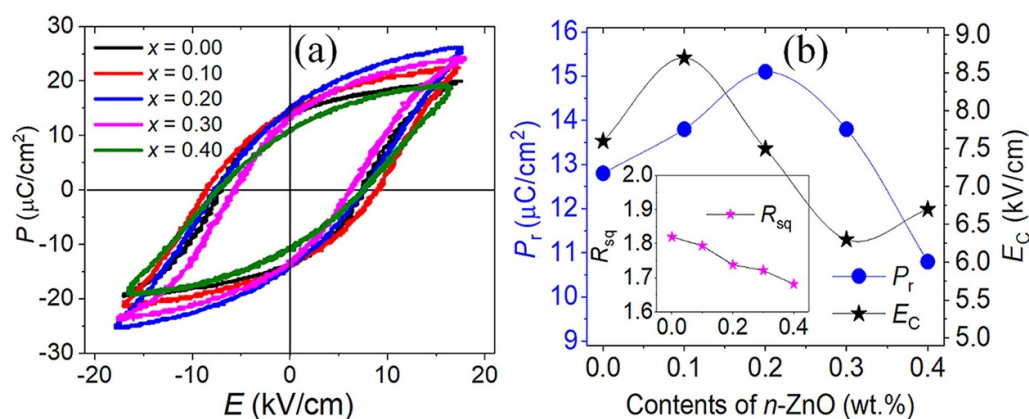


Figure 9. Ferroelectric properties of LKNNS–BNH + x wt.% n -ZnO materials at different x .

coexistence of orthorhombic and tetragonal phases persists over the temperature range from 30 °C to 210 °C. This phase coexistence enhances domain-wall mobility and helps preserve the piezoelectric response. When the temperature rises above 210 °C, thermal fluctuations of dipoles become more pronounced. As a result, their alignment under an external electric field becomes less effective, leading to a gradual deterioration of the piezoelectric properties, in agreement with previous reports [28]. It is generally accepted that the working temperature of piezoelectric transducers is rarely higher than approximately one-half of the Curie temperature of the ceramic materials [29]. The retention of high piezoelectric properties was attributed to the high phase transition temperature T_C of the ceramics ($T_C = 332$ °C, figure 6(c)). Therefore, these ceramics exhibited good thermal stability, making them suitable for practical applications.

The ferroelectric hysteresis loop of the LKNNS–BNH + x wt.% n -ZnO ($x = 0.0; 0.1; 0.2; 0.3$; and 0.4) ceramics was measured and presented (figure 9(a)). Additionally, the ferroelectric parameters, such as the remanent polarization (P_r), and the coercive field (E_c) were determined using the Sawyer–Tower method as shown in figure 9(b). The ferroelectric parameters of the ceramics were dependent on x . As x increased from 0.0 to 0.40, the P_r values increased to reach a maximum of $15.1 \mu\text{C cm}^{-2}$ at $x = 0.2$, after which a decreasing trend was observed as x continued to increase, which was consistent with the dielectric and piezoelectric properties discussed earlier. Meanwhile, the increase in E_c at $x = 0.1$ was attributed to the increase in oxygen vacancies, as shown in equations (4)–(6). The oxygen vacancies pinned domain-wall motion, which increased E_c and was similar to the report by Li et al [13]. However, with increasing n -ZnO content, the grain size of the ceramics tends to grow, which facilitates domain-wall motion owing to the reduction in the coercive field E_c . In general, the ferroelectric behavior of n -ZnO-doped LKNNS–BNH ceramics is governed by several factors, including grain size, crystal structure, and lattice defects such as oxygen vacancies.

4. Conclusion

This study employed the co-precipitation method to synthesize the crystalline phase of n -ZnO. The average size of the spherical n -ZnO was between 10 and 30 nm, and the lattice parameters of the unit cell were $a = b = 3.2522$ Å, $c = 5.2064$ Å. The effectiveness of n -ZnO in sintering resulted in a dense microstructure with clear grain boundaries and 98.1% relative density, which improved the dielectric, ferroelectric, and piezoelectric properties of the LKNNS–BNH ceramics. For a n -ZnO content of 0.2 wt.%, the LKNNS–BNH ceramic exhibited enhanced properties, including: $k_p = 0.40$; $k_t = 0.41$; $d_{33} = 236 \text{ pC N}^{-1}$; $\epsilon_r = 1191$ and $\epsilon_{\text{max}} = 5335$. Notably, the high k_p value was maintained at 210 °C, with about 50% relative k_p . The LKNNS–BNH ceramic exhibited good thermal stability, which is beneficial for practical applications.

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