

Article

Microstructure and Electric Properties of Bi₂O₃-Doped (K_{0.5}Na_{0.5})NbO₃ Lead-Free Ceramics

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Abstract: In this paper, Bi₂O₃-doped (K_{0.5}Na_{0.5})NbO₃ (x = 0.1, 0.2, 0.3, 0.4) lead-free ceramics are prepared by a conventional solid-state reaction and analyzed by studying the structure, ferroelectric, and piezoelectric properties. It is found that the doping of Bi₂O₃ increases the proportion of the trigonal phase in KNN ceramics, thus enabling the construction of KNN ceramics with an orthogonal–trigonal phase boundary at room temperature. At the same time, doping with Bi₂O₃ can reduce the grain size and improve grain size uniformity of the ceramics. The KNN-0.1%Bi₂O₃ ceramic has the best piezoelectric properties in all composition; the results are as follows: $d_{33} = 121\text{pC/N}$, $k_p = 0.474$, $k_t = 0.306$.

Keywords: KNN lead-free ceramics; Bi₂O₃ doping; grain effects; piezoelectric property



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1. Introduction

The ceramic potassium sodium niobate (K_{0.5}Na_{0.5})NbO₃ (KNN) was first discovered in 1959 [1]. In 2004, Saito et al. [2] found that KNN-based ceramics had higher piezoelectric properties ($d_{33} = 416\text{pC/N}$) by the texture method. Since then, research into KNN-based ceramics has become a “hot topic”, with different doping elements and components to improve electric properties being studied [3–6]. As a kind of perovskite structure, the electric properties of KNN-based ceramics are significantly improved by a ferroelectric phase transition [7]. However, the polymorphic phase transition (PPT) is different from the morphotropic phase boundary (MPB); it is not only affected by composition, but also by temperature for KNN-based ceramics [8]. Therefore, KNN-based ceramics can achieve high electrical performance in the phase boundary regulation or by the construction of new phase boundary.

In recent years, it is clear that the doping of Li, Ta, and other elements and solid solutions with other perovskite-structured components methods can improve the electric performance through phase boundary regulation or the construction of new phase boundaries [9–16]. In particular, the electric properties are improved when the phase boundary is close to room temperature. The (0.96-x)(K_{0.48}Na_{0.52})(Nb_{0.96}Sb_{0.04})O₃-0.04(Bi_{0.5}Na_{0.5})ZrO₃-xBaZrO₃ piezoelectric ceramics have a perfect piezoelectric property ($d_{33} = 610\text{pC/N}$) with a three-phase coexistence of trigonal–orthogonal–tetragonal phases at room temperature [3]. In addition, the grain size effect has also been found to have a great influence on the piezoelectric properties [17–22]. For example, La and Mn can solve the problem of uneven grain size and excessive leakage current in KNN-based ceramics [23,24]. Doping with Bi₂O₃ can reduce the grain size and inhibit the leakage current [25,26].

The current research shows that the phase structure and grain size have a significant effect on the electric performance of KNN-based ceramics. However, there is still no clear

explanation for the control mechanism of the phase boundary. Grain size has been found to be closely related to ceramic properties in many studies [27,28]. Therefore, the purpose of this study is to examine KNN-ceramics doped with Bi_2O_3 , and to analyze the effect of Bi element doping on the phase structure and grain size.

2. Materials and Methods

KNN- $x\%\text{Bi}_2\text{O}_3$ ($x = 0.1, 0.2, 0.3, 0.4$) ceramics are prepared by a conventional solid-state reaction. Na_2CO_3 powder (purity higher than 99.50%), K_2CO_3 powder (purity higher than 99%), Nb_2O_5 powder (purity higher than 99.90%), and Bi_2O_3 powder (purity higher than 99.90%) are raw materials obtained from Aladdin (Shanghai, China). First, the raw material powder is weighed in the desired stoichiometric ratio. Then, all powders are ball-milled in alcohol for 12 h. Second, the mixture is dried and calcined at 900°C for 4 h. Afterwards, the slurries are ball-milled in ethanol for 24 h, mixed with polyvinyl alcohol as a binder, and pressed into disks of 13 mm in diameter and 1.0 mm in thickness under pressure of 10 MPa. At $x = 0.1$, the sintering condition of the ceramic sample is 1103°C for 6 h; at $x = 0.2, 0.3, 0.4$, the sintering condition is 1106°C for 6 h. Finally, the ceramics are polished and silver electrodes were printed on both sides of the ceramics and then fired at 550°C for 30 min. The specimens for the measurement of the electric properties are poled in oil for 15 min at room temperature under an electric field of 30 kV/cm.

In order to characterize the structure of ceramics, XRD was performed with D/max-r-B12kW X-ray diffractometer (Rigaku Corporation, Tokyo, Japan), and the grain morphology of ceramics was observed with FEI-Quanta200-FEG scanning electron microscope (FEI Corporation, Hillsboro, OR, USA). The experimental test temperature range of the dielectric properties is $50\text{--}450^\circ\text{C}$; the test frequencies are 500 Hz, 1 kHz, 5 kHz, 10 kHz, 100 kHz, 200 kHz. Ferroelectric performance was tested using Radiant Technologies Precision Premier II Ferroelectric Measurement Integrated System. The ZJ-4AN quasi-static d_{33} measuring instrument (Institute of Acoustics, Chinese Academy of Sciences, Beijing, China) was used to measure the piezoelectric constant.

3. Results and Discussions

Figure 1 shows the XRD patterns of KNN- $x\text{Bi}_2\text{O}_3$ ceramics, and the test range is from 20° to 60° at room temperature. It can be seen from the XRD pattern that the sample is a perovskite structure with no impurity phase. Table 1 contains the unit cell parameters for KNN- $x\%\text{Bi}_2\text{O}_3$ ($x = 0.0, 0.1, 0.2, 0.3$) ceramics. When the doping concentration x is 0.1, the ratio of the peak intensities of the diffraction peaks (220) and (002) is approximately 2:1 at 45° , indicating that the sample is in the orthorhombic phase at room temperature. With the increase in doping concentration, the difference in the peaks (220) and (002) is narrowed, and the ratio of the peak intensities approaches 1.5:1, indicating that the proportion of the trigonal phase in the sample increased and that the orthogonal–trigonal phase was formed at room temperature. The reason for this is that the atomic radius of Bi^{3+} is larger than that of Na^+ and K^+ , and the oxygen octahedral structure is distorted after the substitution of the A site, which increases the proportion of the trigonal phase in the ceramic at room temperature, and creates an orthogonal–trigonal phase boundary at room temperature.

Figure 2 shows the microscopic topography of KNN- $x\text{Bi}_2\text{O}_3$ piezoelectric ceramics, and tetragonal grains can be clearly observed in all samples. Moreover, with the increase in Bi^{3+} content, the grain size of ceramics gradually decreases. The reason for this phenomenon may be that the atomic radius of Bi^{3+} is smaller than that of Na^+ and K^+ ; the doped Bi is located at grain boundaries and excessive voids inhibit grain growth [29,30]. Therefore, the reduction in grain size occurs because the added Bi^{3+} replaces the position of the A ion in the ABO_3 perovskite structure. From Figure 2a–c, it can be seen that the pores increase with an increase in doped Bi^{3+} concentration in the ceramics. The melting point of Bi_2O_3 is lower than the sintering temperature of KNN ceramics, and the liquid phase appears during the sintering process, resulting in an increase in the contact area of the grain boundaries. With

an increase in grain boundary mobility, the pore discharge rate becomes lower than the grain growth rate and defects appear in the ceramics.

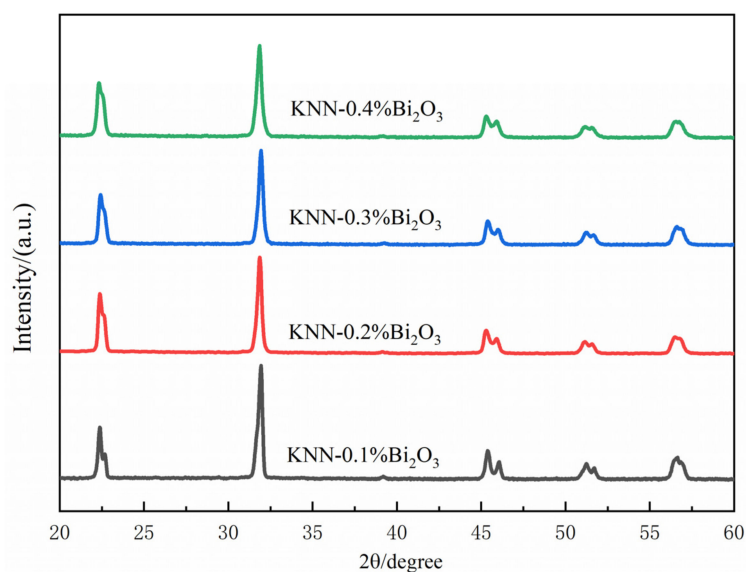


Figure 1. XRD pattern of KNN- x Bi₂O₃ piezoelectric ceramics.

Table 1. Cell parameters of KNN- x %Bi₂O₃ ($x = 0.0, 0.1, 0.2, 0.3$) ceramics.

x (wt%)	0.1	0.2	0.3
$a(\text{\AA})$	3.9655	3.9801	3.9700
$b(\text{\AA})$	5.7482	5.6841	5.6846
$c(\text{\AA})$	5.6344	5.7130	5.7064

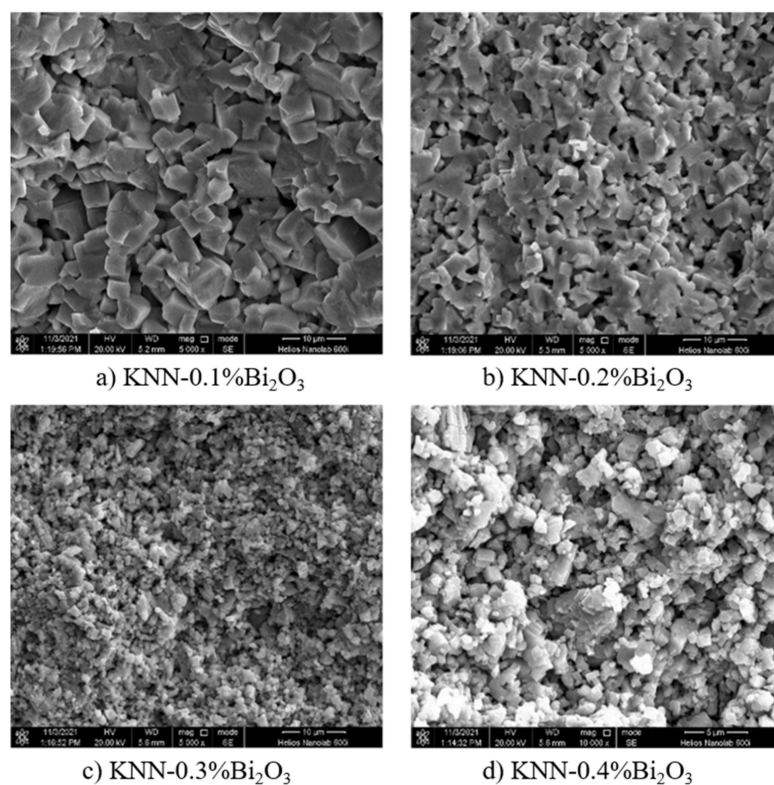


Figure 2. SEM of KNN- x Bi₂O₃ piezoelectric ceramics.

Figure 3 shows the particle size distribution of the KNN- $x\text{Bi}_2\text{O}_3$ piezoelectric ceramics. When the doping concentration x is 0.1, the distribution of grain size is not uniform; the grain size ranges from 0.5 μm to 4.5 μm . With an increase in doping concentration, the grain size decreases and the uniformity of grain size increases. When the doping concentration x is 0.4, the grain size fluctuates around 1 μm and the average grain size reaches the minimum value of 0.49 μm . The SEM data show that Bi_2O_3 doping can effectively reduce the grain size of the ceramics and improve the uniformity of grains. However, when the doping concentration x is greater than or equal to 0.2, the pores will increase, so the doping concentration of Bi_2O_3 should be adjusted reasonably.

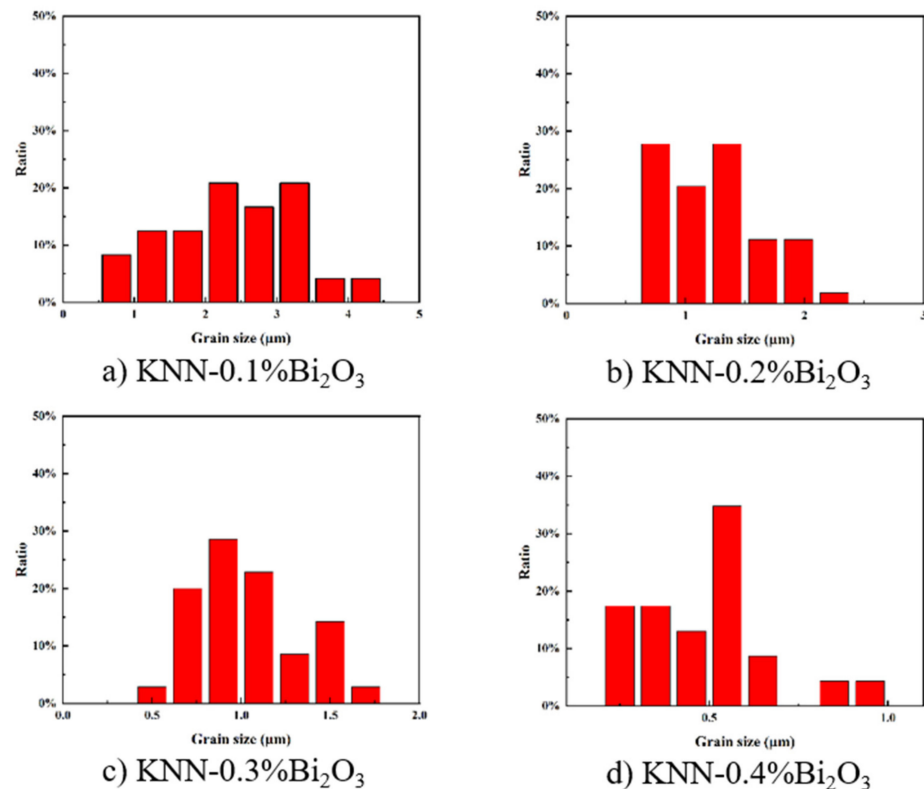


Figure 3. Particle size distribution of KNN- $x\text{Bi}_2\text{O}_3$ piezoelectric ceramics.

Figure 4 shows the dielectric temperature spectrum of KNN- $x\text{Bi}_2\text{O}_3$ ceramics. The mesothermal spectrum of KNN ceramics is shown in Figure 4a. KNN ceramics have an orthorhombic phase structure at room temperature and undergo trigonal–tetragonal and tetragonal–cubic phase transitions at 209 $^{\circ}\text{C}$ and 304 $^{\circ}\text{C}$, respectively. Figure 4b–e present the dielectric spectra of KNN- $x\text{Bi}_2\text{O}_3$ ceramics, corresponding to samples with doping concentrations of 0.1%, 0.2%, 0.3%, and 0.4%. From Figure 4b, it can be observed that there are three distinct peaks in the dielectric temperature map. The peak at 281 $^{\circ}\text{C}$ corresponds to the depolarized dielectric peak. After this peak, the remaining two peaks correspond to the quadrature at 194 $^{\circ}\text{C}$. The tetragonal phase transition at the dielectric peak and the tetragonal–cubic phase transition dielectric peak at 429 $^{\circ}\text{C}$. There are also three peaks in Figure 4c–e, which correspond to the orthogonal–trigonal phase transition dielectric peak, the orthorhombic–tetragonal phase transition dielectric peak, and the tetragonal–cubic phase transition dielectric peak, respectively; the corresponding temperatures are 57 $^{\circ}\text{C}$, 215 $^{\circ}\text{C}$, and 433 $^{\circ}\text{C}$, respectively. It can be seen Bi^{3+} doping can increase the orthogonal–trigonal phase transition temperature of KNN-based ceramics around 50 $^{\circ}\text{C}$. Figure 4f presents the orthorhombic–tetragonal phase transition temperature and dielectric constant under different concentrations of bismuth oxide doping. Except for individual singular points, the overall trend of the two is an improvement with the increase of bismuth oxide doping concentration. Among them, the overall improvement in $T_{\text{O-T}}$ is relatively low, but

the dielectric constant is significantly improved. When the doping concentration x was 0.4, the dielectric constant is increased by nearly 30% compared with KNN ceramics. This is because Bi^{3+} doping increases the proportion of the trigonal phase at room temperature, making the orthogonal–trigonal mixed phase structure at room temperature. Therefore, the dielectric properties of KNN ceramics can be improved by doping Bi^{3+} .

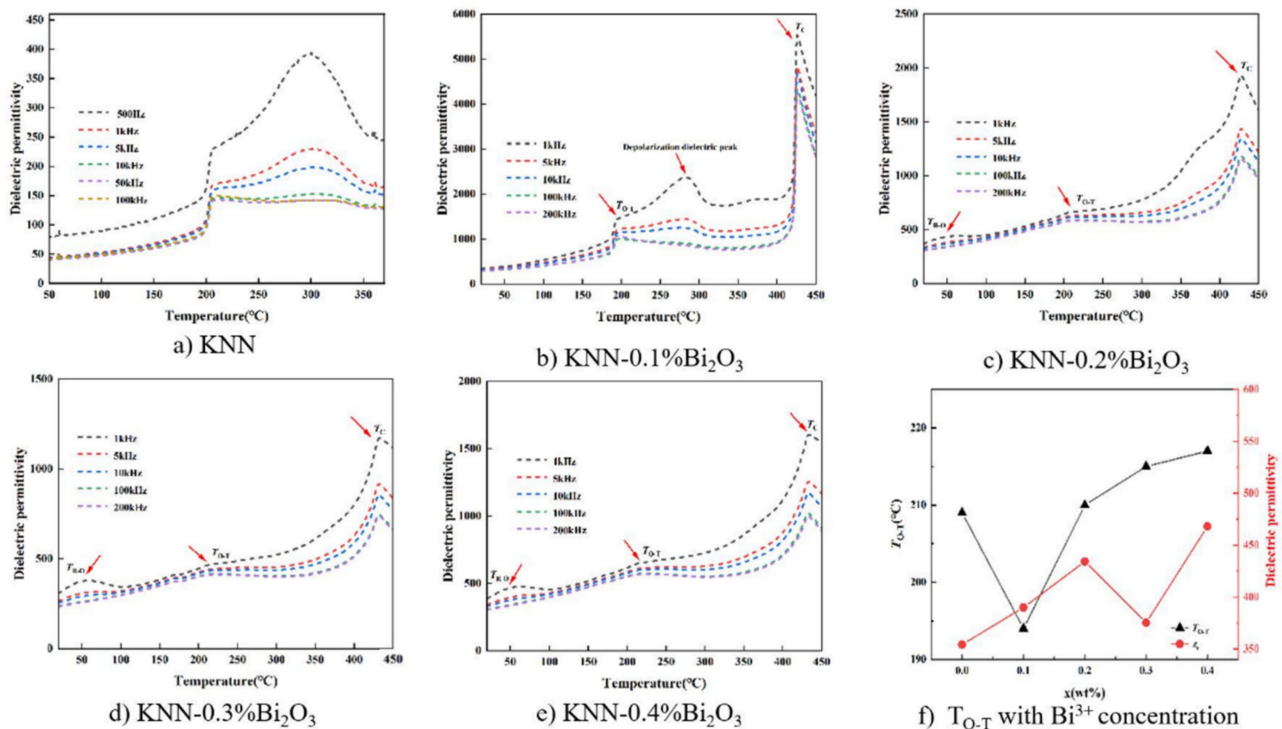


Figure 4. Temperature dependence of dielectric permittivity and T_{O-T} , and dielectric constant ϵ_r dependence for KNN- $x\%\text{Bi}_2\text{O}_3$ ($x = 0.0, 0.1, 0.2, 0.3, 0.4$) ceramics.

Figure 5 shows the change in dielectric loss during the heating process of KNN- $x\text{Bi}_2\text{O}_3$ piezoelectric ceramics. It can be seen that the dielectric loss of the sample changes drastically at the phase transition, which is due to the lattice distortion caused by the phase transition as the temperature increases, resulting in a dramatic increase in dielectric loss. Figure 5f shows the variation in the dielectric loss of the ceramics with Bi^{3+} content at 50 °C and 1 kHz. It can be observed from the figure that the dielectric loss of the sample increases with the increase in doping concentration; moreover, at the Bi^{3+} content of 0.3, the dielectric loss of the sample reaches its peak value, because the pores increase, causing more defects in the sample, and the dielectric loss increases.

Figure 6a displays the hysteresis loops of KNN- $x\%\text{Bi}_2\text{O}_3$ ceramics under the electric field of 25 kV/cm. With the addition of Bi^{3+} , the squareness of the hysteresis loops of the samples increased with the increase in Bi^{3+} concentration, indicating that the ferroelectric properties of the ceramics also improved with the increase in Bi^{3+} concentration. The hysteresis loop of the sample with doping concentration $x = 0.3$ is poor. Combined with SEM data analysis, it was observed that there were many pores in the sample, which result in excessive internal leakage current. Figure 6b shows the relationship between remanent polarization, coercive field, and saturation polarization with doping concentration. Bi^{3+} doping can soften KNN ceramics, making it easier for domains to flip. The influence of polarization intensity is greater, and they all follow an increasing trend. When the doping concentration x is 0.1, the increase reaches 70%. However, with an increase in the Bi^{3+} doping concentration, the magnitude will decrease. In addition, the coordination number around the pores may also be increased due to grain size reduction. When the coordination number is greater than or equal to 6, the grain growth will slow down the

shrinkage of the pores [29]. The remanent polarization and the maximum polarization of the ceramic decrease.

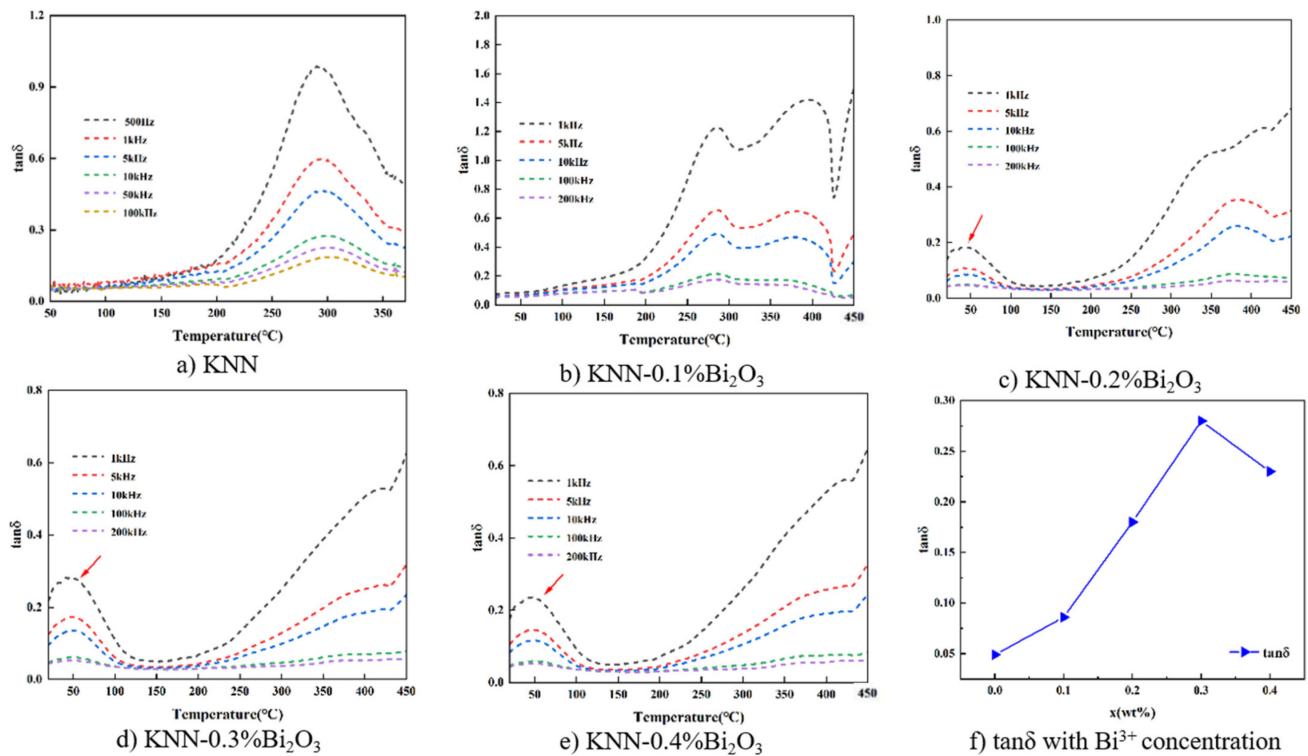


Figure 5. Temperature dependence of dielectric loss $\tan\delta$ for KNN- $x\%$ Bi₂O₃ ($x = 0.0, 0.1, 0.2, 0.3, 0.4$) ceramics.

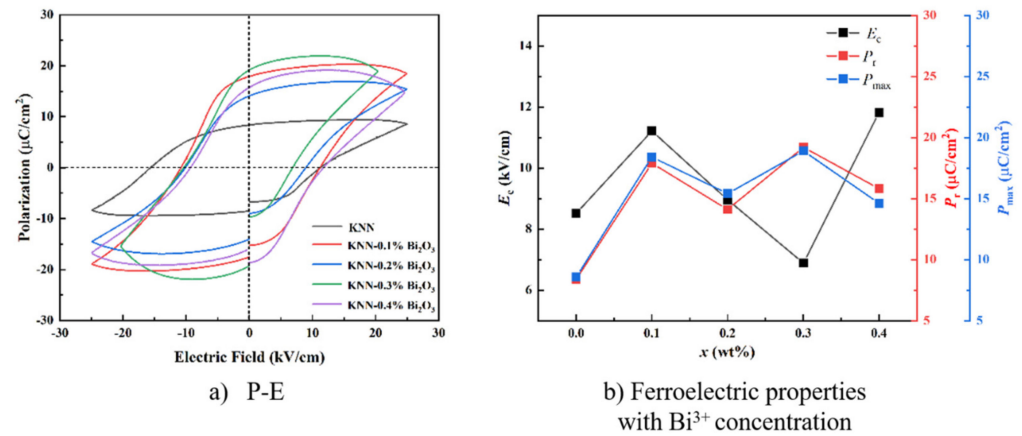


Figure 6. Ferroelectric properties of KNN- x Bi₂O₃ piezoelectric ceramics.

Table 2 presents the characterization of the piezoelectric properties of KNN- x Bi₂O₃ ceramics, including electromechanical coupling coefficients k_p , k_t , and piezoelectric constants. A small amount of Bi³⁺ doping can significantly improve the piezoelectric properties of ceramics. When the doping concentration x is 0.1, d_{33} reached 121 pC/N. The reason for this is that a small amount of doped Bi³⁺ entered the lattice, significantly improving the electromechanical coupling coefficient. The thickness of the electromechanical coupling coefficient k_t reached 0.306 and the plane electromechanical coupling coefficient k_p reached 0.474. When the doping concentration increases, excess Bi³⁺ will not enter the interior of the lattice, but hinder the growth of grains at the grain boundaries. Although the grain size tends to shrink, there are more pore defects and poorer ceramic performance. The planar

electromechanical coupling coefficient of the sample ceramic with a doping concentration of $x = 0.3$ is the highest among the experimental samples, but its thickness electromechanical coupling coefficient drops to 0.138, the electromechanical coupling coefficients k_p and k_t cannot be improved, and the piezoelectric performance of the ceramic decreases at the same time.

Table 2. Electromechanical coupling coefficient of KNN- $x\text{Bi}_2\text{O}_3$ ceramics.

x (wt%)	0.1	0.2	0.3	0.4
k_p	0.474	0.276	0.478	0.270
k_t	0.306	0.166	0.140	0.145
d_{33} (pC/N)	121	81	80	82

4. Conclusions

In this paper, KNN- $x\text{Bi}_2\text{O}_3$ ceramics are prepared by a solid-state reaction method. The doping of Bi element can increase the proportion of the tripartite phase in the ceramic. When the doping concentration x is higher than 0.2%, the orthogonal-tripartite phase boundary is created, which can improve the electrical properties of ceramics. When the doping concentration x is 0.1, the piezoelectric constant reached 121 pC/N. When the doping concentration x is 0.4, the dielectric constant reached a maximum value of 468.03. Therefore, high-performance lead-free potassium niobate nano-ceramics can be prepared by adjusting the phase boundary and grain size by doping with a small amount of Bi_2O_3 .

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