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Compositional dependence of phase structure and electrical properties in $(K_{0.50}Na_{0.50})_{0.97}Bi_{0.01}(Nb_{1-x}Zr_x)O_3$ lead-free ceramics

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Abstract

$(K_{0.50}Na_{0.50})_{0.97}Bi_{0.01}(Nb_{1-x}Zr_x)O_3$ (KNBNZ) lead-free ceramics were prepared by the conventional solid-state sintering process. Their phase structure is dependent on the Zr content in the investigated range, and the ceramics endure a phase transition from pseudocubic to orthorhombic with increasing Zr content. Improved piezoelectric properties have been observed when the poling temperature is located at ~100 °C because of the coexistence of orthorhombic and tetragonal phases. Their dielectric and piezoelectric properties were enhanced by doping Zr, the ceramic with $x=0.02$ showing optimal electrical properties, i.e., $d_{33}\sim161$ pC/N, $k_p\sim0.41$, $Q_m\sim81$, $T_c\sim370$ °C, and $T_{o-t}\sim130$ °C. These results show that the KNBNZ ceramic is a promising lead-free piezoelectric material.

Keywords: C. Piezoelectric properties; Ion substitution; $(K_{0.50}Na_{0.50})$ NbO_3; Lead-free ceramics

1. Introduction

$Pb(Zr,Ti)O_3$-based ceramics are conventional piezoelectric materials and have been widely used in sensors and actuators [1]. However, these lead-based ceramics result in serious environmental pollution and human health problem during processing and a waste of products. As a result, it is urgent to develop lead-free piezoceramics with excellent electrical properties for replacing these lead-based ceramics [2–10]. Over the past few years, considerable attention has been given to perovskite lead-free piezoceramics because of their good electrical properties, such as (K, Na)NbO_3, $(Bi_{0.5}Na_{0.5})TiO_3$, and $BaTiO_3$ [2–11]. Among these perovskite lead-free ceramics, (K, Na)NbO_3 (KNN) ceramics intrigue the enthusiasm of the researchers because of their good piezoelectric properties, high Curie temperature, and environmental friendliness [2,3,6–11].

As reported in the previous work, piezoelectric properties of pure KNN ceramic could be greatly improved by some methods [2,3,6–18], such as ion substitution, new preparation technique, the introduction of other compositions, and so on. Among these methods, the ion substitution becomes an effective way to enhance the piezoelectric behavior of KNN-based ceramics [6–11,13,17,18]. It has been reported that the densification of KNN-based ceramics could be improved by doping ZrO_2 [17]. Malic et al. has reported that the microstructure of pure KNN ceramic with ZrO_2 becomes fine and uniform, and then their dielectric and piezoelectric properties are also improved [18]. However, the improvement in its piezoelectric constant ($d_{33}\sim100$ pC/N) is limited by the addition of Zr to KNN [18].

In this work, the Bi and Zr were simultaneously used to modify the KNN ceramic for further improving its d_{33}, and $(K_{0.50}Na_{0.50})_{0.97}Bi_{0.01}(Nb_{1-x}Zr_x)O_3$ (KNBNZ) lead-free piezoelectric ceramics were prepared by the ordinary sintering. The compositional dependence of the phase structure and electrical properties of these ceramics have been studied, the effect of the poling temperature on its piezoelectric properties has been also investigated, and the underlying physical mechanism has been described.

2. Experimental procedure

$(K_{0.50}Na_{0.50})_{0.97}Bi_{0.01}(Nb_{1-x}Zr_x)O_3$ ($x=0$, 0.01, 0.02, 0.04, and 0.05) lead-free piezoelectric ceramics were prepared by the

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conventional mixed oxide method. Na_2CO_3 (99.8%), K_2CO_3 (99.0%), Nb_2O_5 (99.5%), ZrO_2 (99.0%), and Bi_2O_3 (99.0%) were used as starting raw materials, and they were ball milled for 24 h with agate ball media and ethanol. After calcination at 850 °C for 6 h, these calcined powders were again milled for 12 h, and then pressed into disks of ~1.5 cm in diameter and ~1.0 mm in thickness at 10 MPa using PVA as a binder. After burning off PVA, the pellets were sintered at 1110–1130 °C for 3 h in air. Silver paste was fired on both sides of the samples at 700 °C for 10 min to form the electrodes for electrical measurements. These samples were polarized in a silicon oil bath under different temperatures by applying a direct current electric field of 3–5 kV/mm for 20 min.

X-ray diffraction (XRD) characterization of these sintered samples was performed using Cu k_α radiation in the θ–2θ scan mode (Bruker D8 Advanced XRD, Bruker AXS Inc., Madison, WI, CuKa). Scanning electron microscopy (SEM) (Philips, XL30) was employed to study the surface morphology of these ceramics. The temperature dependence of the dielectric constant and the loss of these sintered samples were examined using a programmable furnace with an *LCR* analyzer (HP 4980, Agilent, USA). The. d_{33}. value was measured using a piezo-d_{33} meter (ZJ-3A, China). The mechanical quality factor Q_m and the planar electromechanical coupling factor k_p were measured by using an impedance analyzer (HP 4294A).

3. Results and discussion

Fig. 1(a) shows the XRD patterns of KNBNZ ceramics as a function of Zr content, measured at room temperature. All the ceramics exhibit a typical perovskite structure, and no secondary phases are detected, indicating that Zr has completely diffused into the KNBN ceramic to form a new solid solution. In order to further analyze the effect of the Zr addition on the phase structure of KNBNZ ceramics, the expanded XRD analysis has been performed in the range of $2\theta=21$–23° and 44–47°. Fig. 1 (b) and (c) shows the corresponding XRD patterns of KNBNZ ceramics in the range of $2\theta=21$–24° and 44–47°, respectively. As shown in Fig. 1(b) and (c), the pure KNBN ceramic has a pseudocubic phase at room temperature, and the orthorhombic structure appears and increases continuously with increasing Zr content. Moreover, the peak position is shifted to a higher angle with increasing Zr content. This phenomenon should be attributed to a larger ionic radius of Zr^{3+}, compared with that of Nb^{5+}.

Fig. 2(a)–(c) shows the SEM patterns of KNBNZ ceramics as a function of Zr content with $x=0$, 0.02, and 0.04, respectively. Their grain size increases dramatically with increasing Zr content, reaching a maximum value at $x=0.02$, and decrease quickly with further increasing Zr content. This result indicates that a low concentration of Zr has entered the lattice of KNBN ceramics, promoting the grain growth. However, their grain size reduces rapidly with further increasing Zr content because the excessive Zr segregates at the grain boundary and prohibits the grain growth. Moreover, a denser microstructure is also observed in the ceramic with $x=0.02$. As a result, the introduction of optimal Zr content promotes the grain growth and the density of KNN ceramics.

The temperature dependence of the dielectric constant for KNBNZ ceramics with $x=0$, 0.02, and 0.04 has been measured at 10 kHz, as shown in Fig. 3(a). The pure KNBN ceramic undergoes two phase transitions, i.e., orthorhombic to tetragonal phase ($T_{o\text{-}t}\sim206$ °C) and tetragonal to cubic phase ($T_c\sim383$ °C) [19,20]. Their T_{o-t} value is gradually shifted to a lower temperature, while the T_c value decreases slightly with increasing Zr content [17]. Fig. 3(b) shows the temperature dependence of the dielectric loss for KNBNZ ceramics with $x=0$, 0.02, and 0.04, measured at 10 kHz. The KNBNZ ceramic with $x=0.02$ has a lower dielectric loss in the temperature range of room temperature~250 °C [18].

Fig. 4 plots the dielectric constant (ε_r) and dielectric loss (tan δ) of KNBNZ ceramics as a function of x, measured at room temperature and 100 kHz. Their ε_r value almost drops gradually with increasing x. Their tan δ value firstly decreases, reaching minimum at $x=0.02$, and increases dramatically with further rising x. As a result, the ceramic with $x=0.02$ has a lower tan δ of ~2.46% because of a dense microstructure.

Fig. 5 shows the piezoelectric constant (d_{33}), the planar electromechanical coupling factor (k_p), and the mechanical quality factor (Q_m) of KNBNZ ceramics as a function of x. As shown

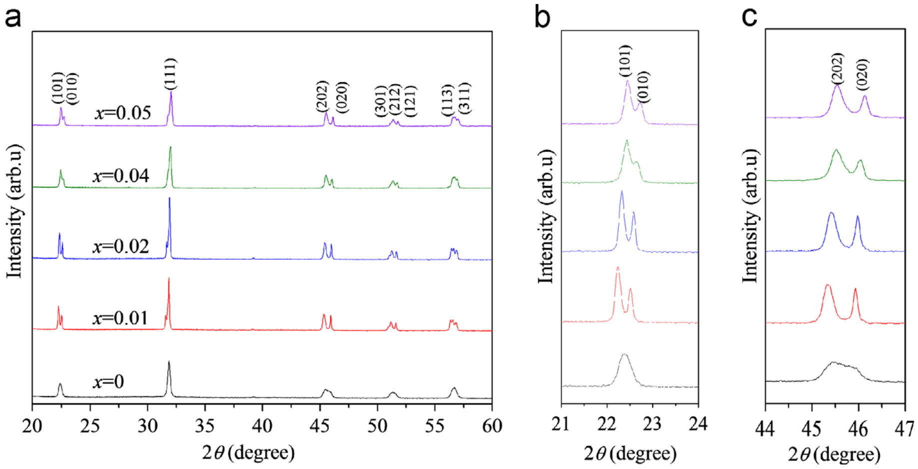

Fig. 1. (a) XRD patterns as well as (b) and (c) expanded XRD patterns of KNBNZ ceramics.

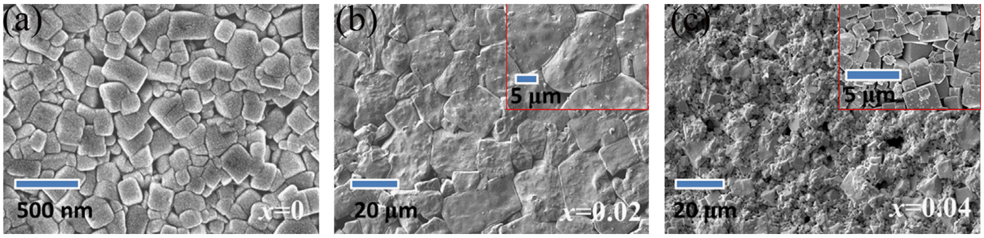

Fig. 2. SEM patterns of KNBNZ ceramics as a function of Zr content: (a) $x=0$, (b) $x=0.02$, and (c) $x=0.04$.

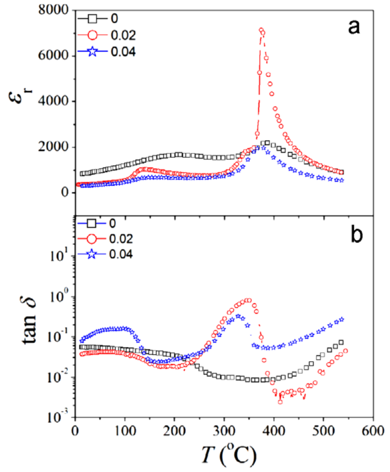

Fig. 3. Temperature dependence of (a) dielectric constant and (b) dielectric loss of KNBNZ ceramics.

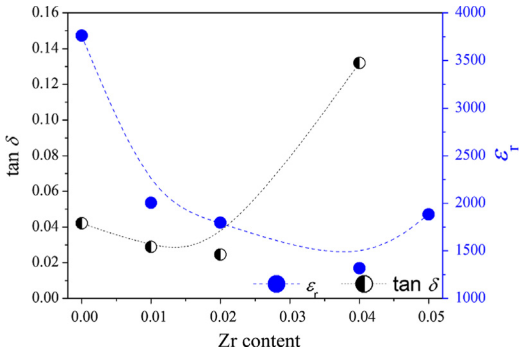

Fig. 4. Dielectric constant and dielectric loss of KNBNZ ceramics as a function of Zr content.

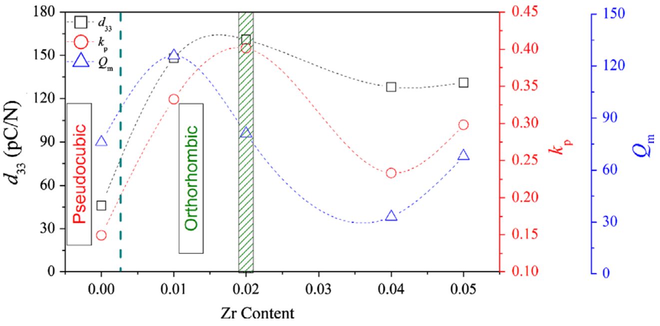

Fig. 5. Piezoelectric properties and mechanical quality factor of KNBNZ ceramics as a function of Zr content.

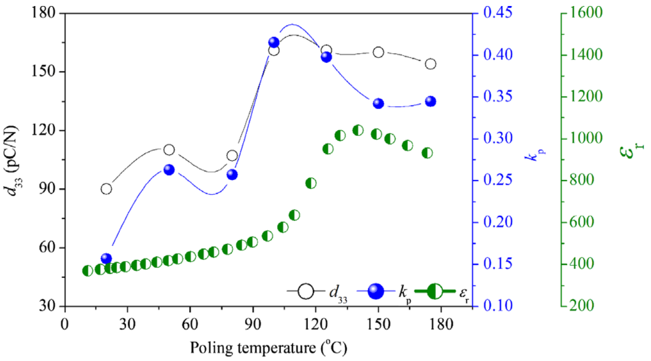

Fig. 6. Effect of the poling temperature on the piezoelectric properties of KNBNZ ceramics with $x=0.02$.

in Fig. 5, the d_{33} value increases with increasing x, reaches maximum (~161 pC/N) at $x=0.02$, and then decreases with further increasing x. Similarly to the change of d_{33} values, the k_p value also reaches maximum (~0.40) at $x=0.02$. A low Q_m value is demonstrated in the range of 22–126. These results indicate that the KNBNZ ceramic ($x=0.02$) possesses better piezoelectric properties at room temperature, which is twice that of pure KNN ceramic [19,20]. As a result, the phase transition from pseudocubic to orthorhombic plays an important role in improving the piezoelectric properties of KNBNZ ceramics, together with a dense microstructure induced by the introduction of optimal Zr content [18]. Moreover, the larger grain results in the reduction of the grain boundary of KNBNZ ceramic with $x=0.02$, which makes the domain easily switch and results in a high piezoelectricity [21].

Fig. 6 plots the effect of the poling temperature on the d_{33} and k_p values of KNBNZ ceramics with $x=0.02$. Both d_{33} and k_p almost increase with increasing poling temperature, and reach maximum (d_{33}~161 pC/N and k_p~0.41) when polarized at 100 °C In order to illuminate its underlying physical mechanism, the temperature of the ε_r of KNBNZ ceramics with $x=0.02$ was also shown in Fig. 6. Similarity to the change of d_{33} and k_p values, a similar phenomenon has also been observed in the curve of ε_r vs. T, and the poling temperature is close to the $T_{o\text{–}t}$ of KNBNZ ceramics. As a result, improved piezoelectric properties were obtained when the poling temperature is ~100 °C because of the coexistence of orthorhombic and tetragonal phases.

4. Conclusions

$(K_{0.50}Na_{0.50})_{0.97}Bi_{0.01}(Nb_{1-x}Zr_x)O_3$ (KNBNZ) lead-free piezoelectric ceramics with improved electrical properties were synthesized by the conventional solid-state reaction. Their compositional dependence of phase structure and electrical properties has been studied, and the poling temperature significantly affects the piezoelectric properties of KNBNZ ceramics. Enhanced electrical properties have been observed in the ceramic with $x=0.02$, showing that the introduction of Zr is an effective way to improve the piezoelectric properties of KNN-based ceramics.

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