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## Original Article

Enhanced piezoelectric response and high-temperature sensitivity by site-selected doping of BiFeO<sub>3</sub>-BaTiO<sub>3</sub> ceramicsKai Tong<sup>a,b</sup>, Changrong Zhou<sup>a,b,\*</sup>, Qingning Li<sup>a</sup>, Jun Wang<sup>a,b</sup>, Ling Yang<sup>a</sup>, Jiwen Xu<sup>a,b</sup>, Guohua Chen<sup>a,b</sup>, Changlai Yuan<sup>a,b</sup>, Guanghui Rao<sup>a,b</sup><sup>a</sup> Guangxi Key Laboratory of Information Materials, Guilin University of Electronic Technology, Guilin, Guangxi, 541004, PR China<sup>b</sup> School of Material Science and Engineering, Guilin University of Electronic Technology, Guilin, Guangxi, 541004, PR China

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## ABSTRACT

Effect of Zn site-selected doping on electrical properties, high-temperature stability and sensitivity of piezoelectric response for BiFeO<sub>3</sub>-BaTiO<sub>3</sub> ceramics was investigated. The results revealed that the addition of Zn led to an evident modification of the microstructure. The B-site selected doping was a more effective approach in improving piezoelectric properties as well as their thermal stability than those of A-site selected doping. Moreover, the enhanced piezoelectric properties accompanying by excellent high-temperature stability and sensitivity in B-site selected doping ceramics were obtained. The microstructure, domain switching behavior and temperature-dependent piezoelectric response in Zn site-selected doping ceramics were investigated, and their relationships with improving piezoelectric properties and high-temperature stability were explored. These results showed that the B-site selected doping ceramics had excellent piezoelectric properties ( $d_{33} = 192\text{pC/N}$ ) along with a high-temperature stability ( $T_d = 450\text{ }^\circ\text{C}$ ).

## 1. Introduction

High-temperature piezoelectric materials have been widely used for piezoelectric actuators, sensors and other electromechanical devices ascribing to their high performance, high-temperature stability and high-temperature sensitivity [1–4]. Among the studied high-temperature piezoelectric materials, three piezoelectric material systems have become the focus of research in recent years. The first one is Pb(Zr<sub>1-x</sub>Ti<sub>x</sub>)O<sub>3</sub>-based (PZT) piezoceramics. However, the Curie temperatures ( $T_C$ ) of commercial PZT piezoceramics are mostly lower than 300 °C, whose safe operating temperatures are generally limited to 200 °C due to the instability of piezoelectric properties [4–6]. The second system is bismuth layer-structured, for example, CaBi<sub>4</sub>Ti<sub>3.95</sub>Nb<sub>0.05</sub>O<sub>15</sub> ( $T_C = 790\text{ }^\circ\text{C}$ ,  $T_d = 700\text{ }^\circ\text{C}$ ) and Bi<sub>3</sub>TiNbO<sub>9</sub> ( $T_C = 940\text{ }^\circ\text{C}$ ). But their piezoelectric coefficients are relatively low ( $d_{33}$ , mostly < 30pC/N) in practical application [7,8].

The third important piezoelectric material system is lead-free BiFeO<sub>3</sub>-BaTiO<sub>3</sub> (BF-BT), which has been considered as one of the most promising high-temperature piezoelectric systems due to its excellent piezoelectric properties together with good thermal stability [9–11]. It was reported that ions substitution for the Bi<sup>3+</sup> or/and Fe<sup>3+</sup> sites in BF-BT was an effective way to promote its piezoelectric response and/or high-temperature stability [9,12–17]. At the same time, a series of

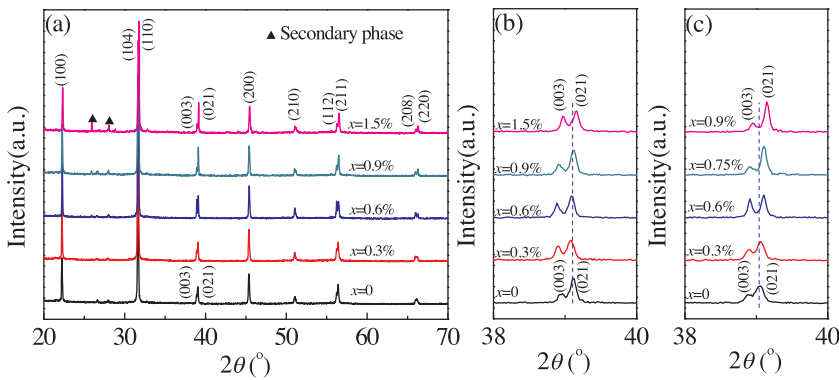
previous research on the moderate addition of ZnO into the Pb-based and lead-free ceramics was carried out and resulted in the enhancement of grain size, and improvement in the dielectric, ferroelectric and piezoelectric properties of those ceramics [18–21]. Additionally, it was reported that the depolarization temperature could be increased obviously by introducing semiconducting ZnO particles into the relaxor ferroelectric 0.94Bi<sub>0.5</sub>Na<sub>0.5</sub>TiO<sub>3</sub>-0.06BaTiO<sub>3</sub> matrix [22]. On the other hand, the ionic radius of Zn<sup>2+</sup> (6CN, 0.074 nm) is very close to that of Li<sup>+</sup> (6CN, 0.076 nm) and Mg<sup>2+</sup> (6CN, 0.072 nm). A number of previous research on the Bi<sub>0.5</sub>Na<sub>0.5</sub>TiO<sub>3</sub>-based systems supports that the introduced Li<sup>+</sup> and Mg<sup>2+</sup> cations would incorporate into both A and B-sites of perovskite lattice for their relatively small radii [23–26]. It is well-known that ions in the middle of rare earth series usually show the amphoteric behavior, which can occupy both A and B lattice sites. Therefore, it is reasonably deduced that Zn<sup>2+</sup> ions can be used to replace the Bi site or/and Fe site in BF-BT system. As a consequence, two site-selected doping strategies of BF-BT ceramics with A-site or B-site substitution 0.7(Bi<sub>1-x</sub>Zn<sub>x</sub>)FeO<sub>3</sub>-0.3BaTiO<sub>3</sub> (abbreviated as BZxF-BT) and 0.7Bi(Fe<sub>1-x</sub>Zn<sub>x</sub>)O<sub>3</sub>-0.3BaTiO<sub>3</sub> (abbreviated as BFZx-BT), respectively, were constructed by the Zn-doping in this work.

On the other hand, the studies on high-temperature piezoelectric properties in the literatures enabling one to estimate the real performance at the operation temperatures are limited. The thermal stability

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**Fig. 1.** The room temperature XRD patterns of (a) BFZx-BT compositions measured at 20–80°, (b) BFZx-BT compositions measured at 38–40° and (c) BZxF-BT compositions measured at 38–40°.

and depolarization behaviors are typically given only in terms of dielectric permittivity measurement or in terms of  $d_{33}$  measured *ex situ* on thermally annealed and cooled samples by Berlincourt meter, neither of which reflects the real performance of materials at temperatures for practical implementation [27–29]. Given this situation, we reported on the electromechanical coupling coefficient of BFZx-BT and BZxF-BT ceramics measured *in situ* as a function of the temperature. The effect of A-site or B-site substitution on structure, piezoelectric properties and their temperature response was compared with each other and discussed, respectively. Our study indicated that the site-selected doping at  $\text{Bi}^{3+}$  and  $\text{Fe}^{3+}$  ions showed different effects on piezoelectric responses and their high-temperature sensitivity. Conclusive direct experimental evidence could be given that B-site selected doping of Zn is more effective in improving piezoelectric properties and their thermal stability, comparing with those of the A-site selected doping. The result suggested that the A-site or B-site selected doping of  $\text{Zn}^{2+}$  for  $\text{Bi}^{3+}$  or  $\text{Fe}^{3+}$  was an effective strategy to achieve an appropriate balance between enhancing piezoelectric activity and improving thermal stability simultaneously for practical applications. Particularly, the excellent thermal stability with depolarization temperature close to Curie temperature is presented in the B-site selected doping BFZx-BT ceramics, which represents one of the highest known thermal stability for the BF-BT system.

## 2. Experimental procedure

The  $0.7(\text{Bi}_{1-x}\text{Zn}_x)\text{FeO}_3 \cdot 0.3\text{BaTiO}_3 + 0.3\text{wt}\%\text{MnO}_2 \cdot 0.3\text{wt}\%\text{MnO}_2$  (BZxF-BT,  $x = 0\text{--}0.9\%$ ) ceramics and  $0.7\text{Bi}(\text{Fe}_{1-x}\text{Zn}_x)\text{O}_3 \cdot 0.3\text{BaTiO}_3 + 0.3\text{wt}\%\text{MnO}_2 \cdot 0.3\text{wt}\%\text{MnO}_2$  (BFZx-BT,  $x = 0\text{--}1.5\%$ ) ceramics were fabricated by the conventional solid-state reaction method. The excess 5 mol%  $\text{Bi}_2\text{O}_3$  was added to compensate for its volatility during the heat treatments. Raw materials (Xilong Scientific) of  $\text{Bi}_2\text{O}_3$  (99.0%),  $\text{Fe}_2\text{O}_3$  (99.0%),  $\text{BaCO}_3$  (99.9%),  $\text{TiO}_2$  (99.9%),  $\text{MnO}_2$  (99.0%), and  $\text{ZnO}$  (99.0%) were first mixed thoroughly in ethanol by zirconia balls for 24 h, and then dried and calcined in alumina crucible at 800 °C for 3 h. Finally, the calcined powders were mixed in polyvinyl alcohol and pressed into pellets with a diameter of 12 mm and a thickness of 1.0 mm at 100 MPa. After burning out polyvinyl alcohol at 600 °C for 3 h, the pellets were sintered at 980 °C for 3 h in air. Silver electrodes were fired on the surfaces of the sintered samples at 600 °C for 30 min, and then the samples were poled at 120 °C for 10 min in a silicone oil bath under a DC field of 50 kV/cm.

The crystal structure of the ceramic samples was analyzed by X-ray diffraction (XRD, D8-2-Advance, Bruker Inc., Karlsruhe, Germany, 35 kV, 30 mA) at room temperature. The grain morphology of the sintered samples was examined on a scanning electron microscopy (SEM, JSM-5610LV, JEOL, Tokyo, Japan). The backscattered electron (BSE) imaging of the sintered samples was observed using a field-emission scanning electron microscope (FE-SEM, Quanta FEG 450, FEI, Hillsboro, USA) coupled with energy-dispersive spectrometry (EDS, X-

Max20, Oxford Instruments Inc., Oxford, UK). The samples were prepared by grinding and polishing, followed by thermal etching at 850 °C for 1 h. The piezoelectric coefficient ( $d_{33}$ ) was measured approximately 1 day after poling using a quasi-static piezo- $d_{33}$  meter (ZJ-3A, CAS, Shanghai, China). The planar electromechanical coupling factor ( $k_p$ ) and the maximum phase angle ( $\theta_{\text{max}}$ ) of poled samples were measured *via* a piezoelectric resonance-antiresonance method using an impedance analyzer (Agilent 4294A, Agilent Inc., Bayan, Malaysia). Temperature dependence (25 °C to 550 °C) of relative dielectric constant ( $\epsilon_r$ ), dielectric loss ( $\tan\delta$ ), and  $k_p$  (measured *in situ*) for poled samples were measured by an impedance analyzer (Agilent 4294A, Agilent Inc., Bayan, Malaysia). Here, *in situ* measurements were conducted using samples that were heated at the set temperature for 10 min in a furnace, and then the electromechanical coupling coefficient was measured at the set temperature. The strain-electric field (*S-E*), polarization-electric field (*P-E*), and current-electric field (*I-E*) hysteresis loops were determined using a ferroelectric test system (TF Analyzer 2000HS, aixACCT Systems GmbH, Aachen, Germany) coupled with fiber-optic sensor (MTI-2100, MTI Instruments Inc., USA) at  $f = 1$  Hz and room temperature.

## 3. Results and discussion

Fig. 1(a) shows the room temperature XRD patterns for B-site selected doping BFZx-BT compositions. Local XRD patterns of (003) and (021) diffraction lines in the  $2\theta$  range of 38°–40° for BFZx-BT ceramics and BZxF-BT ceramics are shown in Fig. 1(b) and (c), respectively. All compositions could be indexed according to perovskite structure with trace impurity phase. The intensity of small diffraction peaks of impurity phases (marked with a triangle in the XRD patterns) in the  $2\theta$  range of 25°–30° is increased with high doping level, reflecting the increasing content of impurity phase. As shown in Fig. 1(b), the BFZx-BT ceramic with  $x = 0$  exhibit rhombohedral structure as evidenced by splitting (003)/(021) diffraction peaks at  $2\theta \sim 39^\circ$ . The intensity of (003) peak is increased with  $x$ , which can be assigned to the change of the content of the unit cell. The crystallographic structure evolution for A-site selected doping BZxF-BT compositions is similar to that of the B-site selected doping BFZx-BT compositions, as displayed in Fig. 1(c).

On the other hand, the XRD peaks of A-site doping BZxF-BT ceramics shift to a high angle with an increase in Zn content (Fig. 1 (c)). It is well known that the ionic radius of  $\text{Zn}^{2+}$  (0.74 Å, CN6) is much smaller than that of A-site ions ( $\text{Bi}^{3+}$ : 1.45 Å, CN12). The substitution of  $\text{Zn}^{2+}$  ions for A-site of BZxF-BT would lead to the decrease of lattice parameter. However, the B-site selected doping BFZx-BT compositions display distinct effects on XRD peaks. The XRD peaks of BFZx-BT ceramics shift slightly to a low angle with an increase in Zn content when  $x < 0.6\%$ , then it shifts obviously to a high angle when  $x$  further increases to 1.5%. Undoubtedly, the introduction of Zn is the reason for the shifts of diffractions peaks. As it is known, the ionic radius of  $\text{Zn}^{2+}$  (0.74 Å, CN6) is larger than that of B-site ions ( $\text{Fe}^{3+}$ : 0.645 Å, CN6). Therefore, the substitution of Zn ions for B-site of BFZx-BT would lead

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