



# Enhanced piezoelectricity and high-temperature sensitivity of Zn-modified BF-BT ceramics by *in situ* and *ex situ* measuring



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## ABSTRACT

Effect of Zn addition on microstructure, electrical properties and temperature stability and sensitivity of piezoelectric properties for  $0.7\text{Bi}_{1-x}\text{Zn}_x\text{FeO}_3 - 0.3\text{BaTiO}_3$  (abbreviated as BZxF–BT) ceramics was investigated. The improved piezoelectric properties, high-temperature stability and high-temperature sensitivity by *in situ* and *ex situ* measuring were obtained by moderate Zn addition. It was demonstrated that the enhancement piezoelectric properties can be attributed to poling induced texturization degree of ferroelectric domains and increased rhombohedral structural distortions. It was proposed that the depoling temperature where the induced small signal piezoelectricity disappears stemmed from the detexturization of preferred orientation domains. The improved piezoelectric responses and high-temperature sensitivity could be attributed to the thermally activated preferred orientation domains. The good piezoelectric properties together with high-temperature stability suggest that BZxF–BT system is a promising material for high temperature piezoelectric applications.

## 1. Introduction

Piezoelectric-based sensors are shown to exhibit excellent temperature stability, temperature sensitivity, low cost and low power consumption properties in contrast with the other sensing approaches for measuring charge, voltage and frequency dependent mechanisms [1–3]. Traditionally, high-temperature sensors play a significant role in the aerospace, aircraft, automotive and energy industries for achieving improved fuel efficiency, reduced emissions and decreased maintenance cycles and failures [1,2,4]. As a result, contemporary high-temperature sensors in a variety of applications from deep oil well drilling operations to motor control and monitoring in deep space probes rely on the outstanding high-temperature piezoelectric properties exhibited by piezoelectric materials [1–4].

Nevertheless, for as-sintered ferroelectric ceramics, electrical poling to align the polarization direction of the individual domains as near to the electric field direction is indispensable for endowing isotropic ferroelectric polycrystals with a net macroscopic polarization and hence piezoelectricity [5]. Once they are aligned, domain configuration remains unchanged even after electric field is removed. As the operating temperature increasing, the preferred orientation domains have a tendency to randomize, thus degrade the small signal piezo-

electric properties until lose its piezoelectric activity. Degradation of piezoelectric properties at high temperature means that these applications are currently limited to operating temperatures typically at a critical temperature [6]. As a consequence, the depoling temperature ( $T_d$ ) is the most important parameter for the practical use of piezoelectric ceramics. Generally, depoling temperature ( $T_d$ ) is characterized by a loss of long-range ferroelectric order [6–8]. It is worthy of note that the depoling temperature for small signal piezoelectric properties is the thermal re-randomization of preferred orientation domains (piezoelectric depoling) other than the loss of long-range ferroelectric order (ferroelectric depolarization).

On the other hand, a piezoelectric sensor needs a high thermal stability to guarantee a linear response in a wide operating temperature range. However, the *ex situ* technique is cumbersome and cannot follow the actual temperature dependence of the piezoelectric properties due to *ex situ* technique cannot reflects the real performance of materials at temperatures in practice [6–11]. Therefore, the high-temperature sensitivity of piezoelectric properties by *in situ* measuring is more important than the Curie temperature and depoling temperature of piezoelectric devices in high temperature application. Thus, how to optimize high-temperature sensitivity and depoling behavior of piezoelectric properties would be a more urgent and fundamental issue.

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Recently, bismuth perovskites  $\text{BiFeO}_3\text{--BaTiO}_3$  (BF–BT) has been given considerable attention due to its high Curie temperature ( $T_C \sim 400^\circ\text{C}$ ), high depolarization temperature ( $T_d$ ) and relatively good piezoelectric properties [12–14]. It was reported that  $(1-x)\text{BF--}x\text{BT}$  form continuous solid solution with rhombohedral phase ( $x=0\text{--}0.33$ ), pseudocubic phase ( $x=0.33\text{--}0.92$ ), and tetragonal phase ( $x=0.92\text{--}1$ ) [12,14,15]. However, poor control of the bismuth volatility and multiple valences of iron for  $\text{BiFeO}_3$  (led to high conductivity) make poling difficult and the high leakage currents limit the performance of BF–based ceramics at the high temperature environment [16–18].

Previous studies have found that utilizing Ga, La, Cu and Mn modification of BF–BT, exhibited excellent electrical properties along with good thermal stability with  $d_{33}=136\text{pC/N--}170\text{pC/N}$ ,  $T_C=434\text{--}494^\circ\text{C}$ ,  $T_d=320\text{--}480^\circ\text{C}$  in the morphotropic phase boundary (MPB) [19–22]. Up to date, there is still lack of study on the temperature dependence of piezoelectric properties measured *in situ* and *ex situ* for BF–BT system material. On the other hand, it was reported that the depolarization temperature increased by introducing semiconducting ZnO particles into the relaxor ferroelectric  $0.94\text{Bi}_{0.5}\text{Na}_{0.5}\text{TiO}_3\text{--}0.06\text{BaTiO}_3$  matrix, due to the semiconducting nature of ZnO providing charges to partially compensate the ferroelectric depolarization field [23]. It is well known that ions from middle of rare earth series show amphoteric behavior, *i.e.* they can occupy both A and B lattice sites. Similarly, a series of researches on the  $\text{Bi}_{0.5}\text{Na}_{0.5}\text{TiO}_3$  based solid solutions support that the introduced  $\text{Li}^+$ ,  $\text{Al}^{3+}$  and  $\text{Mg}^{2+}$  cations would incorporate into both A and/or B sites of perovskite lattice for its relatively small radius [24–27]. The ionic radius of  $\text{Zn}^{2+}$  (6CN) is 0.074 nm, which is very close to that of  $\text{Li}^+$ ,  $\text{Al}^{3+}$  and  $\text{Mg}^{2+}$ . Therefore, it is supposed that  $\text{Zn}^{2+}$  ion could be used to replace its Bi site or/and Fe site in BF–BT system.

In this work, a specially-designed new composition system of  $0.7\text{Bi}_{1-x}\text{Zn}_x\text{FeO}_3\text{--}0.3\text{BaTiO}_3$  (abbreviated as  $\text{BZxF--BT}$ ) was constructed by Zn-doping. The microstructure, electrical properties and their high-temperature sensitivity and depoling temperature of piezoelectric properties for the  $\text{BZxF--BT}$  ceramics were systematically investigated. It was found that the piezoelectric response had been enhanced with Zn addition and increasing operating temperature. The temperature invariant properties from room temperature to  $400^\circ\text{C}$  operating temperature have been obtained due to the compensation of enhanced piezoelectric response for the part thermal loss of piezoelectric properties with increasing temperature. Moreover, the deferred thermal depolarization and temperature independent properties along with excellent piezoelectric properties suggest that the  $\text{BZxF--BT}$  ceramics are an excellent candidate for high-temperature applications in sensors.

## 2. Experimental procedure

The  $\text{BZxF--BT}$  with  $x=0\text{--}0.75\%$  ceramics were prepared using the conventional oxide-mixed method. The excess 5 mol%  $\text{Bi}_2\text{O}_3$  was added to compensate for its volatility during the heat treatments. Addition  $\text{MnO}_2$  (0.6 wt%) was used as a donor to reduce oxygen vacancies formed during calcination and sintering. The starting raw materials of  $\text{Bi}_2\text{O}_3$ ,  $\text{Fe}_2\text{O}_3$ ,  $\text{BaCO}_3$ ,  $\text{TiO}_2$ ,  $\text{MnO}_2$ , and  $\text{ZnO}$  (with the purity of over 99%) were mixed thoroughly in ethanol using zirconia balls for 24 h, and then dried at  $80^\circ\text{C}$  and calcined at  $800^\circ\text{C}$  for 3 h. The calcined powers were mixed with 7 wt% polyvinyl alcohol and pressed into discs with 13 mm in diameter and 0.7 mm in thickness under 100 MPa uniaxial pressure. After the binder was burned out at  $600^\circ\text{C}$  for 2 h, the pellets were sintered at  $980^\circ\text{C}$  for 3 h in the covered alumina crucible. Silver electrodes were formed on the surfaces of the discs and fired at  $600^\circ\text{C}$  for 30 min. The sintered samples were poled in a silicone oil bath under a DC field of 50 kV/cm for 10 min.

The phase structural of the sintered samples were measured using X-ray diffraction (XRD) (D8-2-Advance, Bruker Inc., Karlsruhe, Germany) with  $\text{Cu K}_\alpha$  radiation, and the surface microstructure was

characterized using the scanning electron microscope (SEM) (JSM-5610LV, JEOL, Tokyo, Japan). The piezoelectric coefficient ( $d_{33}$ ) was measured 1 d after poling using a  $d_{33}$  meter (ZJ-3A, CAS, Shanghai, China). Piezoelectric properties and dielectric properties were measured with a precision impedance analyzer (Agilent 4294A, Agilent Inc., Bayan, Malaysia). The temperature dependence of dielectric properties was measured in a controlled furnace with temperature range of  $26\text{--}550^\circ\text{C}$ . Polarization–electric field ( $P\text{--}E$ ) and current–electric field ( $J\text{--}E$ ) were measured using a ferroelectric test system (TF Analyzer 2000HS, aixACCT Systems GmbH, Aachen, Germany) at 1 Hz and room temperature. The temperature dependence of the planar electromechanical coupling factor  $k_p$  was measured *in situ* and *ex situ* using an impedance analyzer (Agilent 4294A, Agilent Inc., Bayan, Malaysia) in the temperature range from  $25^\circ\text{C}$  to  $500^\circ\text{C}$ . *Ex situ* measurements were performed in which the samples were annealed at a set temperature for 30 min in a furnace, after which they were removed and the  $k_p$  was measured when the sample cooled down to room temperature. *In situ* measurements were carried out in which the samples were heated into a set temperature for 10 min.

## 3. Results and discussion

Fig. 1(a) shows the XRD patterns of  $\text{BZxF--BT}$  ceramics in the  $2\theta$  range of  $20\text{--}80^\circ$ . The diffraction peaks can be closely matched well with a single perovskite structure for  $x \leq 0.60\%$   $\text{BZxF--BT}$  ceramics. Whereas, a small additional peak indexed with a triangle in the XRD patterns is observed for  $x=0.75\%$   $\text{BZxF--BT}$  ceramic, indicating the formation of secondary phase. For clear observation, the enlarged XRD patterns of two typical peaks at  $2\theta=39^\circ$  and  $45.5^\circ$  were given in Fig. 1(b). It can be seen that a typical rhombohedral symmetry could be identified, as evidenced by the peak splitting of (003) and (021) diffraction lines and a sharp and narrow (200) peak. Another feature shared by the Fig. 1(b) is the increasing relative intensity of the (003) lines with  $x$ , indicating that the rhombohedral distorted symmetry is more obvious with increasing Zn-doped content from  $x=0$  to 0.60%. It could be, however, supposed that higher Zn content would give a second phase, thus producing the little reduction of relative intensity of the (003) line with  $x=0.75\%$ .

The surface microstructure of  $\text{BZxF--BT}$  ceramics sintered at  $980^\circ\text{C}$  for 3 h are demonstrated in Fig. 2. Clearly, all the samples exhibit dense microstructures and the introduction of Zn has an obvious influence on the evolution of the microstructure. With the doping of Zn, the average grain size, as estimated with a linear interception method, is significantly increased from  $\sim 1.5\ \mu\text{m}$  for the  $x=0$  sample to  $\sim 6\text{--}7\ \mu\text{m}$  for  $x=0.60\%$  and  $0.75\%$  samples. It should be explained that  $\text{Zn}^{2+}$  substitutes for higher valence ions ( $\text{Bi}^{3+}$ ), which will result in the formation of oxygen vacancies to retain the charge neutrality. The increase of oxygen vacancies promotes lattice diffusion, thereby assisting in the process of grain growth.

Fig. 3 depicts the polarization–electric field ( $P\text{--}E$ ) hysteresis loops and the corresponding current–electric field ( $J\text{--}E$ ) loops measured under an electric field of 6 kV/mm. Clearly, a nearly saturated and square  $P\text{--}E$  loop together with a single diffusion polarization current peak ( $J_1$ ) was observed, which are characteristic of normal ferroelectrics. A summary of the measured coercive field  $E_C$  and remnant polarization  $P_r$  and  $J_1$  is given in Table I. It is reported that the current peaks in  $J\text{--}E$  loops correspond to domain switching in ferroelectrics [28]. It can be seen from Fig. 3(b) and Table I, that the  $x=0.60\%$  composition exhibits the highest peak current value. This is generally associated with the high switching rate of domains during loading electric field, which correspond to a peak value of remnant polarization ( $P_r$ ) at the composition  $x=0.60\%$ , as shown in Fig. 3(a). The maximum  $J_1$  and  $P_r$  display the high domains reorientation degree at  $x=0.60\%$ .

The piezoelectric constant  $d_{33}$  and electromechanical coupling factor  $k_p$  for poled ceramics are shown in Fig. 4. It can be observed that the  $k_p$  increases from 0.23 to 0.28 and the  $d_{33}$  increases from 128

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