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Effect of Zr^{4+} substitution on thermal stability and electrical properties of high temperature $BiFe_{0.99}Al_{0.01}O_3$–$BaTi_{1-x}Zr_xO_3$ ceramics

Zhenyong Cen [a], Changrong Zhou [a,*], Jun Cheng [a], Xiujuan Zhou [a], Weizhou Li [b], Chunle Yan [a], Songlin Feng [a], Yueqiang Liu [a], Daosong Lao [a]

[a] School of Material Science and Engineering, Guilin University of Electronic Technology, Guilin, Guangxi 541004, PR China
[b] School of Materials Science and Engineering, Guangxi University, Nanning, Guangxi 530004, PR China

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ABSTRACT

High-temperature Pb-free ceramics of $0.72BiFe_{0.99}Al_{0.01}O_3$–$0.28BaTi_{1-x}Zr_xO_3$ (BFA–BZ_xT) have been prepared through solid state reaction route. The influence of the Zr^{4+} substitution for Ti^{4+} on microstructure, thermal stability and electrical properties of the BFA–BZ_xT ceramics was investigated. The results showed single-phase solid solutions occurred for compositions $x = 0$–0.12 and a morphotropic phase boundary (MPB) separating rhombohedral and pseudocubic phases existed near $x = 0.03$. The substitution of Zr^{4+} for Ti^{4+} caused significant change of grain size for BFA–BZ_xT ceramics. The optimum piezoelectric properties of $d_{33} = 157$ pC/N, $k_p = 0.33$, combined with improved depoling temperature $T_d = 425$ °C, are obtained around the MPB composition of $x = 0.03$. The results indicate that BFA–BZ_xT ceramics have a great potential to apply in high temperature field.

1. Introduction

High temperature piezoelectric materials are used widely in space exploration, electric aircraft, oil and geothermal well-drilling tools, and automotive smart brakes. With the development of science and technology, the higher operation temperature (>300 °C) of piezoelectric materials were required [1,2]. The poled piezoelectric ceramics often begin to lose their piezoelectric properties at a temperature due to the thermal instability of polarization [3,4]. Strong piezoelectric temperature dependence is often very undesirable for practical applications. It's worth noting that the instability of piezoelectric properties with increasing operation temperature will lead to the damage of device. Meanwhile, considering environmental problems, lead has recently been expelled from many commercial applications and materials (for example, from solder, glass, pottery glaze, gasoline and ceramics) due to its toxicity [5].Therefore, The Pb-free ceramics with excellent piezoelectric properties and high depolarization temperature ($T_d \geqslant 300$ °C) are the only feasible solution.

Till now, $BiFeO_3$–$BaTiO_3$(BF–BT) solid solution has been fully investigated, because it is lead-free and has high Curie temperature $T_c = \sim 450$ °C and high depolarization temperature $T_d = \sim 400$ °C and favorable piezoelectric constant $d_{33} = \sim 130$ pC/N at MPB [6–9]. Recently, Yang et al. reported that $(1-x)BiFeO_3$–$xBaTiO_3$ ceramics exhibited optimum electrical properties of $d_{33} = 136$ pC/N, $k_p = 0.312$ and good temperature stability of $T_c = 485$ °C, $T_d = 420$ °C at the MPB composition $x = 0.275$ [10]. Therefore, $(1-x)BiFeO_3$–$xBaTiO_3$ lead-free piezoelectric ceramic is potential to be applied at an operation temperature higher than 300 °C. However, the coexistence of Fe^{2+} and Fe^{3+} in $BiFeO_3$–$BaTiO_3$ ceramics results in high electrical conductivity at high temperatures and valence state of Ti^{4+} is also unstable in $BaTiO_3$ at high temperatures due to $Ti^{4+} + e^- \rightarrow Ti^{3+}$, which is against the domains reorientation along the direction of electric field [11–13]. Our previous studies have found that Al^{3+} substitution for Fe^{3+} induced higher thermal stability of piezoelectric properties for $x = 0.01$ $0.72Bi(Fe_{1-x}Al_x)O_3$–$0.28BaTiO_3$ ceramics [14].

On the other hand, among many solid solutions, Zr^{4+} is chemically more stable than Ti^{4+} [15,16]. For Ba(Zr, Ti)O_3 (BZT) solid solution, Zr^{4+} substituted for Ti^{4+} in B site of ABO_3 structure, which resulted in the low leakage current remains at level [12]. Meanwhile, a high d_{33} (236 pC/N) and a large remanent polarization ($P_r = 13.3$ μC/cm^2) were obtained for the $Ba(Zr_{0.05}Ti_{0.95})O_3$ ceramics [17]. Therefore, we expect that the Zr^{4+} ions substitute for Ti^{4+} ions in $0.72Bi(Fe_{0.99}Al_{0.01})O_3$–$0.28BaTiO_3$ ceramics can lead to improved piezoelectric properties and thermal stability.

In this work, we investigated that electrical properties and thermal stability of Zr^{4+} substitution for Ti^{4+} in $0.72BiFe_{0.99}Al_{0.01}O_3$–$0.28BaTi_{1-x}Zr_xO_3$ ceramics ($x = 0$, 0.03, 0.06, 0.09, 0.12).

2. Experiment procedure

Specimens with the compositions of $0.72BiFe_{0.99}Al_{0.01}O_3$–$0.28BaTi_{1-x}Zr_xO_3$ (BFA–BZ_xT, $x = 0$, 0.03, 0.06, 0.09, 0.12) were prepared by conventional solid-state synthesis route. The starting raw materials were Bi_2O_3, Fe_2O_3, $BaCO_3$, TiO_2, Al_2O_3, ZrO_2 (>99%, Analytically pure). They were weighed and ball-milled with zirconia

* Corresponding author. Tel.: +86 773 2291434; fax: +86 773 2290129.
E-mail address: zcr750320@yahoo.com.cn (C. Zhou).

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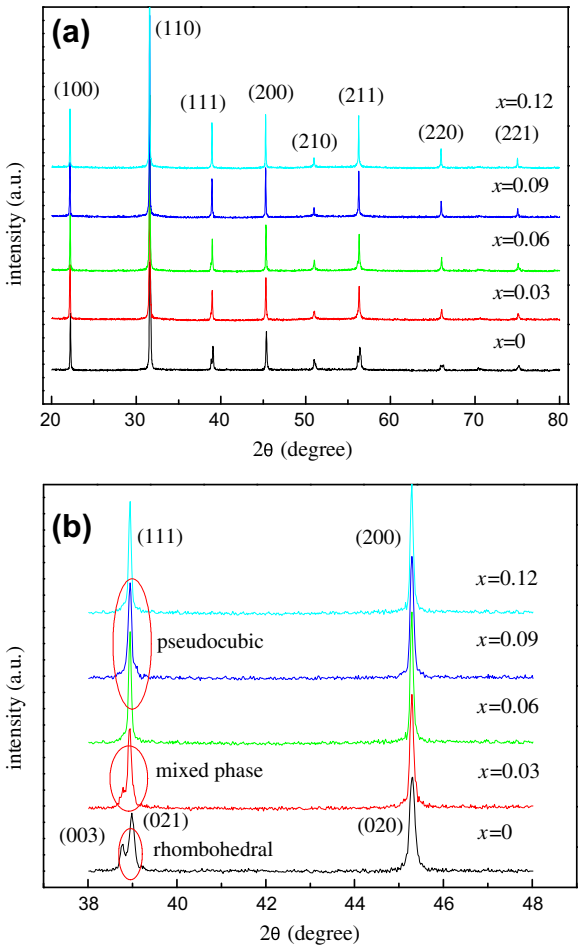

Fig. 1. Room-temperature XRD patterns of BFA–BZ_xT ceramics, (a) 2θ = 20–80° and (b) 2θ = 38–48°.

balls and ethanol for 24 h. After drying at 100 °C, the powders were ground and calcined at 800 °C for 4 h in a closed crucible. The calcined powders were again ground. To improve the green strength of the powder compact, 7 wt.% polyvinyl alcohol (PVA) solution (5%) was added to the powder before pressing pellets of 12 mm diameter and 1 mm thickness under 100 MPa uniaxial pressure. Following removal of binder at 600 °C for 2 h, pellets were sintered at 980 °C in air atmosphere for 3 h.

X-ray diffraction (XRD) characterization of the ceramics was performed by Cu Kα radiation (λ = 1.54178 Å) in the mode of θ–2θ scan (D8 Advance, Bruker Inc, Germany). Surface microstructures of the ceramics were observed using a scanning electron microscopy (SEM, JSM-5610LV, Japan). Sintered ceramics were coarsely polished and silver paste electrodes were formed on both surfaces of the disk-shaped specimens after firing at 600 °C for 30 min. The samples were poled at 100 °C in a silicone oil bath under a dc field of 50 kV/cm for 20 min. The direct piezoelectric coefficient (d_{33}) was measured approximately 24 h after poling using a Berlincourt d_{33} meter (ZJ–3 A, China). Piezoelectric and dielectric properties were measured using an impedance analyzer (Agilent 4294 A). The temperature dependence of the dielectric constant of the samples was examined using a programmable furnace with an impedance analyzer (Agilent 4294 A). The polarization–electric field (P–E) loops were observed at room temperature and 1 Hz using a ferroelectric tester (Premier II, Radiant Technologies). The depoling temperature was measured by the temperature dependence of d_{33}, which was measured *ex situ* in the temperature range from 23 °C to 500 °C.

3. Results and discussion

Fig. 1 shows the room temperature XRD patterns of BFA–BZ_xT ceramics. All ceramics have a pure perovskite phase, and no secondary phases can be observed. As shown in Fig. 1b, for the pure BFA–BZ_xT ceramics (x = 0), the splitting of diffraction peaks of (003)/(021) is observed near 38–40° obvious and the existence of a single (200) peak near 45–46°, suggesting that the ceramics possess a perovskite structure with rhombohedral symmetry. However, it is noted that as x increases from 0.03 to 0.12, the BFA–BZ_xT ceramics gradually transforms to a pseudocubic symmetry. This is evidenced by the splitting of the (003) and (021) diffraction peaks merge into a single (111) diffraction peak as observed in the BFA–BZ_xT ceramics. Therefore, a morphotropic phase transition (MPB) of BFA–BZ_xT ceramics is identified in the composition range of x = ~0.03. The phase structural transformation of BFA–BZ_xT ceramics is indicated in Table 1.

Fig. 2 shows the surface micrographs of BFA–BZ_xT ceramics with x = 0, 0.03, 0.06, 0.09 and 0.12. The substitution of Ti^{4+} by Zr^{4+} caused obviously change of the microstructure for BFA–BZ_xT ceramics with x = 0–0.12. For the pure BFA–BZ_xT ceramic (i.e., x = 0), the grains have a diameter in the range of 6–8 μm, and a small amount of pores are observed (Fig. 2a). With the increase of x to 0.03, the grains become slightly larger and more uniform (Fig. 2b). At x = 0.06, there are distinct grains of diameter about 10–12 μm uniformly distributed among the grains. The grains become relatively smaller in size again for the ceramics with x > 0.06. The decrease in grain size could be attributed to the inhibition of the grain growth as the introduction of further Zr^{4+} content (x > 0.06) gather into crystal boundary of the BFA–BZ_xT ceramics.

Fig. 3 shows the hysteresis loops for BFA–BZ_xT ceramics at room temperature. With an increasing Zr^{4+} substituted level, the leakage current for BFA–BZ_xT ceramics improves weakly. On the other hand, remnant polarization P_r for BFA–BZ_xT ceramics increases with x (0–0.03), and then decreases with further increase of x (0.06–0.12).The coercive field E_c reduce slowly at x = 0–0.03, then decrease fleetly at x = 0.06–0.12. The values of P_r and E_c with Zr^{4+} substitution for BFA–BZ_xT ceramics are listed in Table 1. It implies that the proper introduction of Zr^{4+} can reduce the leakage current properly and improve remnant polarization P_r, making the poling easier [18]. Therefore, the piezoelectric properties of BFA–BZ_xT ceramics would be improved at x = 0.03.

Fig. 4 shows the piezoelectric constant d_{33} and electromechanical coupling factor k_p of BFA–BZ_xT ceramics as a function of Zr^{4+} concentration. As Zr^{4+} content increases from 0 to 0.03, d_{33} increases from 134 pC/N to 157 pC/N. Further increase in Zr^{4+} concentration results in a significant reduction in d_{33}. Similarly, k_p increases from 0.27 to 0.33, when Zr^{4+} content increases from 0 to 0.03. The observed trends in d_{33} and k_p are in good agreement with polarization hysteresis loops (Fig. 3). It well-known that mor-

Table 1
Room-temperature phase structure, piezoelectric coefficients d_{33}, coercive field E_c, remnant polarization P_r, Curie temperatures T_c, depolarization temperatures T_d and breaking point of temperature (T_{BP}) for BFA_x–BT ceramics.

Composition	Phase structure	d_{33} (pC/N)	E_c (μC/cm^2)	P_r (kV/cm)	T_c (°C)	T_d (°C)	T_{BP} (°C)
x = 0	R	134	27.0	11.4	450	404	290
x = 0.03	MPB	157	26.5	13.6	435	425	312
x = 0.06	P	150	25.6	11.6	415	320	330
x = 0.09	P	121	23.5	9.1	385	278	355
x = 0.12	P	104	20.3	7.1	376	236	350

R – refers to rhombohedral and P – refers to pseudocubic.