FULL PAPER

Enhanced relaxation behavior in Bi_2O_3 modified $(\text{Ba}_{0.85}\text{Ca}_{0.15})(\text{Zr}_{0.1}\text{Ti}_{0.9})\text{O}_3$ ceramicsXiaofang WANG^{1,†}, Pengfei LIANG² and Zupei YANG²¹College of Chemistry and Chemical Engineering, Xianyang Normal University, Xianyang 712000, Shaanxi, People's Republic of China²Key Laboratory for Macromolecular Science of Shaanxi Province, School of Materials Science and Engineering, Shaanxi Normal University, Xi'an 710062, Shaanxi, People's Republic of China

Lead-free piezoelectric ceramics $(\text{Ba}_{0.85}\text{Ca}_{0.15-x}\text{Bi}_x)(\text{Zr}_{0.1}\text{Ti}_{0.9})\text{O}_3$ system were synthesized by conventional solid-state reaction. The structure, dielectric, ferroelectric and piezoelectric properties have been investigated in detail. X-ray diffraction analysis revealed that all specimens displayed typical perovskite structure at room temperature. Scanning electron microscope results showed that the introduction of Bi element could effectively reduce the sintering temperature and favor grain refinement of BCZT ceramics. Dielectric measurements displayed that a typical relaxor behavior was appeared and dramatically enhanced with Bi concentration, which is mainly owing to the composition fluctuation and structural fluctuation after Bi introduction. The maximum relaxation degree ($\gamma = 1.9326$) was obtained with the sample of $x = 0.05$. The ferroelectric properties combined with current-electric field illustrated that the P - E loops became slimmer and leaner, meanwhile J - E curves gradually changed to be a broad and flat current platform. The variation of ferroelectric behavior was closely related with the emergence of relaxation behavior in $(\text{Ba}_{0.85}\text{Ca}_{0.15-x}\text{Bi}_x)(\text{Zr}_{0.1}\text{Ti}_{0.9})\text{O}_3$ ceramics.

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Key-words : Lead-free ceramics, Relaxor behavior, Electrical properties

[Received February 5, 2018; Accepted March 17, 2018]

1. Introduction

$\text{PbZr}_x\text{Ti}_{1-x}\text{O}_3$ (PZT-based) piezoelectric ceramics have played a long leading role for the piezoelectric applications because of their excellent piezoelectric properties and good temperature stability.^{1)–3)} However, environment protection and human health concern are the driving force to eliminate the lead from commercial piezoelectric materials, which intrigue the enthusiasm of developing high performance lead-free piezoelectric ceramics.^{4),5)} In recent years, lead-free perovskite structure can be mainly categorized into three mainstream families: (1) $\text{K}_{0.5}\text{Na}_{0.5}\text{NbO}_3$ -based;⁶⁾ (2) $\text{Na}_{0.5}\text{Bi}_{0.5}\text{TiO}_3$ -based;⁷⁾ (3) BaTiO_3 -based.⁸⁾ Each system attracts a group of researchers worldwide due to its unique advantages and features. Among them, Ca and Zr co-doped $(\text{Ba}_{1-x}\text{Ca}_x)(\text{Zr}_{1-y}\text{Ti}_y)\text{O}_3$ (abbreviated as BCT-BZT) lead-free ceramics have drawn great attention because of their excellent electric properties.

$(\text{Ba}_{0.85}\text{Ca}_{0.15})(\text{Zr}_{0.1}\text{Ti}_{0.9})\text{O}_3$ (BCZT) ceramic was initially prepared by Ren. et al, and has been considered to be a promising candidate for lead-free piezoelectric ceramics because of its large piezoelectric constant ($d_{33} = 583$ pC/N).^{9),10)} The enhanced piezoelectric constant in BCZT

ceramics is attributed to the easy domain polarization reorientation between tetragonal and rhombohedral phases by external electric field or stress near Morphotropic Phase Boundary (MPB). However, it is worth noting that the pure BCZT ceramics have some drawbacks, for example, (1) the particular features which are strongly curved by MPB between rhombohedral BZT and tetragonal BCT structures, and sensitive to processing and fabrication method; (2) poor temperature stability of dielectric properties and higher sintering temperature ($>1400^\circ\text{C}$) impede industrial application. In order to solve the above mentioned problems, extensive efforts in studying BCZT-based ceramics (such as doping metal element, adding low temperature eutectic mixture and modifying process, etc) have been employed in the past decades.

Relaxation ferroelectrics, characterized by a broad and frequency-dispersive permittivity peak versus temperature, have drawn a lot of attention both in fundamental research and industrial applications. The relaxation behavior, which is usually viewed in complex perovskite by metal oxide doping, could effectually modify the dielectric properties in piezoceramics.^{11)–13)} For example, Bahri. et al. reported that the substitution of A-site with Bi element can trigger the relaxor behavior in BaTiO_3 ceramics.¹⁴⁾ Chen. et al. presented Bi element doped $(\text{Sr}_{1-x}\text{Bi}_x)\text{TiO}_3$, showing a crossover from normal ferroelectric to relaxation ferro-

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electric.¹⁵⁾ A widely accepted viewpoint is that a random field induced domain state is suggested to be responsible for the relaxation behavior when Bi element incorporates into the ABO_3 structure.¹⁶⁾ Considering Bi cation owns $6s^2$ lone pair, which is favourable for the relaxation behavior without lead pollution, we decided to employ Bi element to trigger relaxor behavior of BCZT ceramics.

In this work, Bi_2O_3 was adopted in BCZT ceramics, aiming to give rise to relaxation behavior and reduce the sintering temperature. $(Ba_{0.85}Ca_{0.15-x}Bi_x)(Zr_{0.1}Ti_{0.9})O_3$ lead-free ceramics were prepared by the convention solid state reaction. The effects of Bi_2O_3 doping content on phase structure, microstructure, dielectric, ferroelectric, and piezoelectric properties were investigated in detail. The mechanism of relaxation behavior was discussed by Curie–Weiss law, P – E and J – E curves.

2. Experimental procedure

2.1 Synthesis

$(Ba_{0.85}Ca_{0.15-x}Bi_x)(Zr_{0.1}Ti_{0.9})O_3$ ($x = 0.00, 0.01, 0.03$, and 0.05) ceramics were synthesized by the solid-state reaction method. Analytical-grade metal oxides or carbonate powders, $BaCO_3$, $CaCO_3$, ZrO_2 , TiO_2 , and Bi_2O_3 were used for the raw materials. The powders were weighed according to stoichiometric ratios, and mixed by ball milling in alcohol for 16 h. The mixtures were calcined at 900 – 1200°C for 6 h depending on the values of x . Then the powder was mixed with 5 wt % polyvinyl alcohol (PVA) solution and uniaxially pressed into disk pellets with a diameter of 15 mm and a thickness of ~ 2 mm under 10 MPa. Firstly, the pellets were heated at 500°C for 1 h in order to burning out PVA, then the disks were pressureless sintered at 1300 – 1450°C for 6 h, the sintering temperature depending on Bi_2O_3 contents.

2.2 Characterization

The phase structure of the prepared ceramics was characterized by X-ray diffraction (XRD, D/max-2200/PC, Rigaku, Japan, $Cu K\alpha$) with scanning step of 0.02° in

2θ range of 20 – 80° . The morphologies characterization of the ceramics were observed with the scanning electron microscope (SEM, Quanta 200, FEI Co., Eindhoven, Netherlands). Silver electrodes were formed on both surfaces of each sintered disk by firing silver at 840°C for 30 min. Temperature-dependence of dielectric properties were obtained by the LCR meter (Agilent E4980A) connected to a computer-controlled temperature chamber. The polarization and strain hysteresis as a function of external electric field were measured at 1 Hz with a 30 kV/cm by a Radiant Precision Workstation (Albuquerque, NM, USA).

3. Results and discussion

3.1 Phase structure

Figure 1 illustrates the room temperature XRD patterns of $(Ba_{0.85}Ca_{0.15-x}Bi_x)(Zr_{0.1}Ti_{0.9})O_3$ ceramic as a function of Bi_2O_3 content ($0 \leq x \leq 0.05$). A complete perovskite structure is formed and no traces of secondary phase can be observed in Bi_2O_3 doping range between 0.00 and 0.05 mol % in Fig. 1(a), suggesting that Bi diffuses into the $BaTiO_3$ lattice to form a solid solution. In order to further clarify the impact of Bi_2O_3 addition on BCZT ceramic, the XRD patterns around 45° were magnified and displayed in Fig. 1(b). It can be observed that the diffraction peaks at 2θ from 44 to 46.5° shifted toward higher degree with the introduction of Bi_2O_3 , indicating a shrinkage of the unit cell. Considering the smaller ionic radii of Bi^{3+} ($1.17 \text{ \AA}$) compared with Ba^{2+} ($1.61 \text{ \AA}$) and Ca^{2+} ($1.34 \text{ \AA}$), the result may be attributed to the lattice deformation caused by Bi^{3+} occupying the position of Ba^{2+} and Ca^{2+} partly. A similar phenomenon induced by the partial substitution of a smaller-ionic-radius element for larger-ionic-radius element is also observed in Bi_2O_3 modified BT ceramics.¹⁶⁾

3.2 SEM micrographs

The SEM images of samples surface for BCZT sintered at 1450°C , and $(Ba_{0.85}Ca_{0.15-x}Bi_x)(Zr_{0.1}Ti_{0.9})O_3$ ceramics

Fig. 1. XRD pattern of $(Ba_{0.85}Ca_{0.15-x}Bi_x)(Zr_{0.1}Ti_{0.9})O_3$ ceramics between the 2θ range of 20 – 80° (a); expanded XRD pattern in the 2θ range of 44 – 47° (b).

Fig. 2. SEM micrograph of $(\text{Ba}_{0.85}\text{Ca}_{0.15-x}\text{Bi}_x)(\text{Zr}_{0.1}\text{Ti}_{0.9})\text{O}_3$ ceramics: (a) $x = 0.00$ (sintered at 1450°C); (b) $x = 0.01$ (sintered at 1400°C); (c) $x = 0.03$ (sintered at 1350°C); and (d) $x = 0.05$ (sintered at 1300°C).

sintered at $1300\text{--}1400^\circ\text{C}$ are displayed in **Fig. 2**. All specimens displayed dense structure and clear boundary in Figs. 2(a)–2(d). The result means that the introduction of Bi could act as sintering aid, and effectively reduce the sintering temperature from 1450 to 1300°C of BCZT ceramics. The sample of $x = 0.00$ possesses an inhomogeneous grain distribution in Fig. 2(a). With the introduction of Bi, the grain sizes of the specimen are gradually developed to be more uniform. Additionally, it can be observed that the grain size obviously decreases to $2\text{ }\mu\text{m}$ at $x = 0.05$. The result indicates that the Bi addition has effect on refining grain and reducing sintering temperature in BCZT ceramics, which may be attributed to the low melting point of Bi_2O_3 (860°C), and then improve the sintering behavior of BCZT-based ceramics.

3.3 Dielectric properties

Figures 3(a)–3(d) presents temperature dependence of dielectric properties at different frequencies for $(\text{Ba}_{0.85}\text{Ca}_{0.15-x}\text{Bi}_x)(\text{Zr}_{0.1}\text{Ti}_{0.9})\text{O}_3$ ceramics. For the sample of $x = 0.00$, three dielectric peaks can be observed, implying that three different phase transition were appeared: rhombohedral-orthorhombic at -20°C (R-O), orthorhombic-tetragonal near 25°C (O-T) and tetragonal-cubic at 90°C (T-C), respectively.¹⁷⁾ With the introduction of Bi_2O_3 , the rhombohedral phase becomes weak, and the orthorhombic phase is rapidly vanished. For the sample of $x = 0.01$, only two phase transitions corresponded with R-T and T-C can be observed due to the disappearing of the orthorhombic phase. Moreover, it is worth noting that

the phase transition temperature of T-C demonstrates a small rise in Fig. 3(b). For the samples of $x = 0.03$ and 0.05 , single dielectric peak corresponded with the phase transition of T-C is detected. Both the traces of rhombohedral phase and orthorhombic phase are difficult to be observed. The result reveals that the addition of Bi_2O_3 with appropriate amount could stabilize the tetragonal phase in BCZT ceramics. A similar variation trend in dielectric performance is also observed in Y modified BCZT ceramics.¹⁸⁾

Meanwhile, it is remarkable that the dielectric peak of T-C becomes wider and smoother with the increase of Bi_2O_3 concentration in Figs. 3(a)–3(d). It can be seen that the temperature in accord with the dielectric maximum (T_m) shifts toward to high temperature by increasing of the measurement frequency, suggesting that the dielectric relaxation behavior could arise by Bi_2O_3 doping in BCZT ceramics. In order to inquiry the degree of dielectric relaxation behavior, the modified Curie–Weiss law has been adopted for the quantitative parameters:¹⁹⁾

$$\frac{1}{\varepsilon_r} - \frac{1}{\varepsilon_{\max}} = \frac{(T - T_{\max})^\gamma}{C}$$

where $\varepsilon_{\max}$ expresses the maximum relative permittivity, ε_r represents the relative permittivity at temperature T , $T_{\max}$ corresponds to as the appeared maximum constant, C is the Curie–Weiss constant, and γ describes the degree of relaxation, taking the values between 1 and 2. The values of 1 and 2 mean the normal ferroelectric and the ideal relaxor ferroelectric. **Figure 4** illustrates the plots of

Fig. 3. Temperature dependence of dielectric constant and dielectric loss tangent at 1, 10, 100 kHz of $(\text{Ba}_{0.85}\text{Ca}_{0.15-x}\text{Bi}_x)(\text{Zr}_{0.10}\text{Ti}_{0.90})\text{O}_3$ ceramics: (a) $x = 0.00$; (b) $x = 0.01$; (c) $x = 0.03$; and (d) $x = 0.05$.

Fig. 4. Plots of $\ln(1/\varepsilon_r - 1/\varepsilon_{\max})$ as a function of $\ln(T-T_m)$ at 10 kHz of $(\text{Ba}_{0.85}\text{Ca}_{0.15-x}\text{Bi}_x)(\text{Zr}_{0.10}\text{Ti}_{0.90})\text{O}_3$ ceramics: (a) $x = 0.00$; (b) $x = 0.01$; (c) $x = 0.03$; and (d) $x = 0.05$.

$\ln(1/\varepsilon_r - 1/\varepsilon_{\max})$ as a function of $\ln(T-T_m)$ at 10 kHz for all specimens. A linear relationship is observed in Figs. 4(a)–4(d). As increasing of Bi_2O_3 content, the value of γ rises gradually from 1.6592 at $x = 0.00$ to 1.926 at $x = 0.05$, suggesting that the relaxation behavior is obviously strengthened by Bi_2O_3 doping. The result may be partly ascribed to composition fluctuation and structural fluctuation caused by different radius and valence of Bi^{3+} compared to Ba^{2+} , Ca^{2+} , Zr^{4+} , and Ti^{4+} . Generally, the variation of ionic radius and valence state at one or more equivalent crystallographic sites will lead to disordered distribution, leading in the formation of random local fields and then enhancing the relaxation behavior.

Figures 5(a) and 5(b) displays the temperature-dependent dielectric constant (ε_r) and dielectric loss ($\tan \delta$) of $(\text{Ba}_{0.85}\text{Ca}_{0.15-x}\text{Bi}_x)(\text{Zr}_{0.1}\text{Ti}_{0.9})\text{O}_3$ ceramics from -100 to 200°C at 1 kHz. It is observed that the Curie temperature (T_c) gradually shifts to lower temperature with increasing of x , demonstrating that the doping Bi_2O_3 could depress the T_c of BCZT ceramics. But the T_c of all samples is still above room temperature in Fig. 5. In addition, it can be seen that the value of ε_r keeps a relative large more than 2000, and $\tan \delta$ remains very small less than 0.07 over the temperature range from 0 to 200°C . The fine values of ε_r , $\tan \delta$ and T_c mean the prospect of potential industrial application for $(\text{Ba}_{0.85}\text{Ca}_{0.15-x}\text{Bi}_x)(\text{Zr}_{0.1}\text{Ti}_{0.9})\text{O}_3$ lead-free ceramics.

One of the most desirable properties for dielectric material is the temperature stability of dielectric performances. Figure 6(a) shows the temperature coefficient of capacitance (TCC) curves for the BCZT-based ceramics as a function of Bi_2O_3 content over the temperature range from -50 to 150°C . The pure BCZT ceramic displays a poor TCC curve. The values of TCC fluctuates between -0.75 to 2.68 in Fig. 6(a), in which the value is much larger than the standard of X-7R.[20] With the doping of Bi_2O_3 , the variations of TCC become rapidly relaxation and stable. For the sample of $x = 0.05$, the TCC curve is flat in which the value fluctuated between -0.46 to 0.02 . Though the capacitance displays a significant improvement in temperature stability with the addition of Bi_2O_3 , the numerical value still cannot meet the X7R specification.²⁰⁾ According to the previous relevant studies,^{21),22)} the enhanced temperature stability of BaTiO_3 -based ceramic are attributed to the formation of core-shell microstructure. The core-shell structure is generated by binary-system or the rare-earth doping, such as $\text{BaTiO}_3-(\text{NaBi})(\text{MgTi})\text{O}_3$,

Fig. 5. Temperature dependence of dielectric constant of (Ba_{0.85}Ca_{0.15-x}Bi_x)(Zr_{0.10}Ti_{0.90})O₃ ceramics at 10 kHz (a); temperature dependence of dielectric loss at 10 kHz.

Fig. 6. Capacitance changes with temperature for specimen (a); the figure of merit as functions of Bi₂O₃ content and temperature (b).

Y₂O₃-BaTiO₃ ceramics. The improvement temperature stability should be ascribed to the change in internal stress grain shell and grain core caused by the variation of Curie temperature. Therefore, improving the temperature stability of dielectric properties in BCZT-based ceramic should adopt the method by optimizing the preparation and forming core-shell structure in a follow-up study.

Figure 6(b) depicts the variation of the quality factor (Q_m) as a function of Bi₂O₃ content. It is observed that the value of Q_m increases from 138 to 416 with the addition of Bi₂O₃. The enhancement of Q_m should be partly attributed to the acceptor doping effect of Bi₂O₃. It is well known that the acceptor-doping could restrain the domain movement and promote the formation of defection complexes with dipole characteristic, then stabilize the polarization behavior. In addition, it can be observed that the Q_m maintain a stable value with the variation of temperature, and reached a larger value near the Curie temperature. The result indicates that the doping of Bi₂O₃ in BCZT ceramics could improve the quality factor.

3.4 Ferroelectric properties

Room-temperature P - E hysteresis loops and the displacement current density-electric field J - E curves measured with an applied electric field at 30 kV/cm and 1 Hz frequency for (Ba_{0.85}Ca_{0.15-x}Bi_x)(Zr_{0.1}Ti_{0.9})O₃ ceramics are shown in Figs. 7(a)–7(d). Typical ferroelectric hysteresis loops are observed for all samples. Moreover, it can be seen that the P - E loop becomes slimmer and leaner with

increasing of Bi₂O₃ content. The remnant polarization (P_r) and coercive field (E_c) dependence on Bi₂O₃ content are summarized in Fig. 7(e). Compared to the ferroelectric performance of pure BCZT, the value of P_r gradually drops with increasing x , implying that the reduction of ferroelectric property in (Ba_{0.85}Ca_{0.15-x}Bi_x)(Zr_{0.1}Ti_{0.9})O₃ ceramics. In order to further illustrate the impacts on ferroelectric performance of Bi₂O₃ addition, J - E curves are showed in Figs. 7(a)–7(d). Generally, the presence of J - E peak corresponds to the E_c value, that is, a field responsible for domain switching for a saturated loop.^{23),24)} A single sharp polarization current peak appeared at $x = 0.00$ in Fig. 7(a), which could be attributed to domain switch. The phenomenon means a ferroelectric materials with a long-range ferroelectric ordering.²⁵⁾ As increasing of x , gradual changes with a broad and flat current platform are obtained in current peaks. The feature is typical for ergodic relaxor.²⁶⁾ The different ferroelectric behavior may be associated with the emergence of ferroelectric relaxation in (Ba_{0.85}Ca_{0.15-x}Bi_x)(Zr_{0.1}Ti_{0.9})O₃ ceramics. With increasing Bi₂O₃ addition, the ferroelectric domains of sample are frozen, which will prevent to destroy the long-range polar, so the ferroelectric properties becomes weak in (Ba_{0.85}Ca_{0.15-x}Bi_x)(Zr_{0.1}Ti_{0.9})O₃ ceramics.^{23),27)}

3.5 Piezoelectric properties

Figure 8 depicts the variation in piezoelectric constant (d_{33}) as a function of Bi₂O₃ addition. The d_{33} value drops gradually with increasing of x . The minimum value

Fig. 7. P - E hysteresis and J - E loops of $(\text{Ba}_{0.85}\text{Ca}_{0.15-x}\text{Bi}_x)(\text{Zr}_{0.10}\text{Ti}_{0.90})\text{O}_3$ ceramics at room temperature: (a) $x = 0.00$; (b) $x = 0.01$; (c) $x = 0.03$; (d) $x = 0.05$; and (e) composition of the remnant polarization P_r and coercive field E_c .

Fig. 8. Piezoelectric constant d_{33} of $(\text{Ba}_{0.85}\text{Ca}_{0.15-x}\text{Bi}_x)(\text{Zr}_{0.10}\text{Ti}_{0.90})\text{O}_3$ ceramics.

appears 102 pC/N with the sample of $x = 0.05$. The weakened piezoelectric may be partly attributed to the distorted crystal structure, many defect electron complexes, or enhanced relaxation behavior in $(\text{Ba}_{0.85}\text{Ca}_{0.15-x}\text{Bi}_x)(\text{Zr}_{0.10}\text{Ti}_{0.90})\text{O}_3$ ceramics. In addition, a strong dependence of piezoelectric property on the grain size was observed in BCZT ceramic, in which the high performance was obtained by grain sizes larger than $\sim 15 \mu\text{m}$.¹⁰⁾ Therefore, the deteriorated piezoelectric properties in $(\text{Ba}_{0.85}\text{Ca}_{0.15-x}\text{Bi}_x)(\text{Zr}_{0.10}\text{Ti}_{0.90})\text{O}_3$ ceramics may be correlate with the grain size distribution induced by Bi_2O_3 addition.

4. Conclusions

$(\text{Ba}_{0.85}\text{Ca}_{0.15-x}\text{Bi}_x)(\text{Zr}_{0.10}\text{Ti}_{0.90})\text{O}_3$ lead-free piezoelectric ceramics with an enhanced relaxation behavior were

obtained by solid-state reaction. Phase structure, microstructure, and electrical properties were investigated for varying Bi content. The $(\text{Ba}_{0.85}\text{Ca}_{0.15-x}\text{Bi}_x)(\text{Zr}_{0.10}\text{Ti}_{0.90})\text{O}_3$ ceramics owns a single perovskite phase structure and a dense microstructure. The Bi element doping was able to drop significantly the sintering temperature of BCZT ceramics. An enhanced relaxation behavior was observed in $(\text{Ba}_{0.85}\text{Ca}_{0.15-x}\text{Bi}_x)(\text{Zr}_{0.10}\text{Ti}_{0.90})\text{O}_3$ ceramics due to the composition fluctuation and structural fluctuation which induced by Bi ions. A typical ferroelectric hysteresis loops were observed, and the addition of Bi_2O_3 could continuously decrease the ferroelectric and piezoelectric properties of $(\text{Ba}_{0.85}\text{Ca}_{0.15-x}\text{Bi}_x)(\text{Zr}_{0.10}\text{Ti}_{0.90})\text{O}_3$ ceramics.

Acknowledgment This work was supported by National Science Foundation of China (NSFC) (Grant No. 51172136, 21401123 and 51107077), the Science and Technology Program of education department in Shaanxi Province (Grant Nos. 17JK0830).

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