Enhanced ferroelectric and piezoelectric properties in SnO₂ modified Ba₀.₈₅Ca₀.₁₅Zr₀.₁Ti₀.₉O₃ lead-free ceramics

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1. Introduction

Piezoelectric materials, which respond mechanically to applied electric field and vice versa, are widely used in electromechanical transducers, high-performance actuators and other electric fields.¹,² The Pb(Zr₁₋ₓTiₓ)O₃ based piezoelectric ceramics have been the mainstream in the electronic industry for decades due to their excellent piezoelectric properties.³ However, its application has been restricted by the driving forces of environment sustainable development and human health, hence stimulating the passion of researching high-performance lead-free piezoceramics.

In recent years, several kinds of lead-free piezoelectric ceramics have attracted the researcher’s interest, such as BaTiO₃-based (BT, for short), (K,Na)NbO₃-based (KNN, for short), (Bi,Na)TiO₃-based (BNT, for short), etc.⁴⁻⁶ Among these materials, high-performance BT-based ceramics such as (Ba₁₋ₓCaₓ)(Zr₁₋ₓTiₓ)O₃ and (Ba₁₋ₓCaₓ)-(Sn₁₋ₓTiₓ)O₃ are considered the most promising piezoelectric materials due to their excellent electrical properties and great potential for technological applications in electric field.⁷ The outstanding feature of BCZT ceramic is that the electrical properties could be tailored by the following ways: (1) varied the ion rations of Ba²⁺/Ca²⁺ and Ti⁴⁺/Zr⁴⁺; (2) doped the metal oxide with specific properties; (3) improved the preparation process of the BCZT ceramics. For example, X.B. Ren et al. reported that the (Ba₀.₉₅Ca₀.₁₅)(Zr₀.₁Ti₀.₉)O₃ possess an excellent piezoelectric constant (∼530 pC/N) due to the construction of the morphotropic phase boundary near room temperature by controlling the ion rations of Ba²⁺/Ca²⁺ and Ti⁴⁺/Zr⁴⁺.⁸ Z. H. Chen optimized the piezoelectric properties of the Ba₀.₉Ca₀.₁Ti₀.₉Sn₀.₁O₃ ceramics with the d₃₃ 490 pC/N due to the coexisting phases of tetragonal and orthorhombic phase by La₃O₅ doped.⁹ In addition, M. G. Stachiotti investigated the grinding process on the phase structure and electrical properties of Ba₀.₈Ca₀.₁₅(Zr₀.₁Ti₀.₉)O₃ ceramic, and indicated that the structural and electrical properties had deteriorated owing to a phase decomposition activated by the mechanical grinding process.¹⁰ Previous studies have improved the flaws of (Ba₁₋ₓCaₓ)(Zr₁₋ₓTiₓ)O₃ ceramic in a certain degree. However, there is still a gap between electrical performance and industrial application. Literature reported that Sn⁴⁺ ions could diffuse into BaTiO₃ lattice and alter the phase inversion temperature of orthorhombic-tetragonal phase, and then inﬂuence its electrical properties.¹¹,¹² In addition, it’s worth noting that the Curie temperature of BT-based ceramics are sensitive to Sn⁴⁺ ions concentration, which obeys the correlation between the structure and property.¹³,¹⁴ Considering the impacts of the unique performance of Sn⁴⁺ cation, we speculated that the SnO₂ doping could adjust the...
electric performance and the Curie temperature of BCZT ceramics.

In this work, \((\text{Ba}_{0.85}\text{Ca}_{0.15})_0.004\text{Ti}_{0.90}\)O\(_3\) + xSnO\(_2\) (x = 0, 0.004, 0.008, 0.012 and 0.016) lead-free piezoelectric ceramic was designed, aiming to investigate the influences of Sn\(^{4+}\) doping on the phase inversion temperature and electrical performances in this system. Next the structure, dielectric, ferroelectric, piezoelectric and electric-field-induced strain properties were surveyed. The result revealed that the electrical performances are sensitive to Sn\(^{4+}\) concentration in \((\text{Ba}_{0.85}\text{Ca}_{0.15})_0.004\text{Ti}_{0.90}\)O\(_3\) + xSnO\(_2\) ceramic.

2. Experimental procedure

\((\text{Ba}_{0.85}\text{Ca}_{0.15})_0.004\text{Ti}_{0.90}\)O\(_3\) + xSnO\(_2\) (x = 0, 0.004, 0.008, 0.012 and 0.016) ceramics were prepared using the solid-state method. Analytical reagents, CaCO\(_3\), BaCO\(_3\), TiO\(_2\), ZrO\(_2\), and SnO\(_2\) were acted as the initial raw materials. The reagents were weighed based on the stoichiometric ratio. Then the compounds were mingled in alcoholic with zirconia grinding media for 12 h. The mixture powder was dried in oven, and calcinated at 1200 °C for 6 h after grinding. The compounds were mingled with 5 wt% PVA, and compressed into disk shape with a thickness of ~2 mm and a diameter of 10 mm at ~10 MPa. The discs were heated at 540 °C for draining away PVA. Then the discs were sintered at 1400–1450 °C for 6 h. The surfaces were ground and polished for brushing silver paste. The discs coated with silver paste was sintered at 820 °C for 90 min to form electrodes.

The XRD data of the sintered pellets was collected by X-ray fractometer (D/MAX-2200/VPC, Rigaku, Japan) in the 2θ configuration with a scanning step of 0.02°. The surface structure of the sintered pellets was observed with the electron microscope (Quanta 200, FEI, USA). The dielectric properties were measured as by the 4980A-LCR meter (Agilent, USA). The Hysteresis and strain measurements were tested with a high voltage amplifier (AixACCT-FT2000, Trek, USA) at a frequency of 1 Hz. The piezoelectric constant was obtained by a piezoelectric d\(_{33}\) apparatus (ZJ-3, Institute of Acoustics, China).

3. Results and discussion

3.1 Structural characteristics

Figure 1 displays the XRD patterns of various compositions of \((\text{Ba}_{0.85}\text{Ca}_{0.15})_0.004\text{Ti}_{0.90}\)O\(_3\) + xSnO\(_2\) (x = 0, 0.004, 0.008, 0.012 and 0.016) ceramics recorded at room temperature. All the peaks could be indexed using perovskite structure (PDF#79-1482) as shown for the compositions with x = 0.016 on top pattern in Fig. 1. It can be seen that all the specimens had a complete perovskite structure without any detectable traces or other impurities. This indicates that the Ca\(^{2+}\), Zr\(^{4+}\), Sn\(^{4+}\) ions had thoroughly diffused into the host lattice of BaTiO\(_3\) to form a solid solution.

Figures 2(a)–2(e) exhibits SEM microscope photographs obtained from the surface of \((\text{Ba}_{0.85}\text{Ca}_{0.15})_0.004\text{Ti}_{0.90}\)O\(_3\) + xSnO\(_2\) (x = 0, 0.004, 0.008, 0.012 and 0.016) ceramics with different SnO\(_2\) content (x). All specimens presented a compact and quite dense micro-structure. A heterogeneous grain size was shown at x = 0 in Fig. 2(a). With the introduction of SnO\(_2\), the grain sizes changed distinctly by the influence of SnO\(_2\) concentration. The grain size increased with increasing x, and the largest grain size was obtained at x = 0.016 in Figs. 2(a)–2(e), suggesting that the addition of Sn can facilitate the grain growth of the BCZT ceramics. The formation of large grains may be attributed to the enhanced mass transport induced by O vacancies which derived from the addition of SnO\(_2\) in BaTiO\(_3\).13

3.2 Dielectric properties

The temperature dependence of the relative dielectric constant of \((\text{Ba}_{0.85}\text{Ca}_{0.15})_0.004\text{Ti}_{0.90}\)O\(_3\) + xSnO\(_2\) (x = 0.00, 0.004, 0.008, 0.012 and 0.016) ceramics was measured at 10 kHz with a heating rate 3 °C/min as shown in Fig. 3(a). For each composition, two dielectric peaks which corresponded to the phase transition from orthorhombic (O)-tetragonal (T) and tetragonal (T) to cubic (C) phase, respectively, are clearly observed around ambient temperature and 70–100 °C, resulting from the ferroelectric transition. Moreover, it can be seen that the maximum dielectric constant reached over 10000 for the sample of x = 0.00. While for the sample of SnO\(_2\) doping, the maximum dielectric constant had obtained more than 13000 in Fig. 3(a). The variation of maximum dielectric constant indicated that the doping SnO\(_2\) could significant improve the dielectric properties of BCZT ceramics. The results are in accordance with (Ba,Ca)(Sn,Ti)O\(_3\) ceramics, and the reason could be attributed to the the exceptional performance of Sn\(^{4+}\) cation in \((\text{Ba}_{0.85}\text{Ca}_{0.15})_0.004\text{Ti}_{0.90}\)O\(_3\) + xSnO\(_2\) ceramics.

To better understand the influence of SnO\(_2\) doping on the phase inversion temperature of BCZT ceramics, Fig. 3(b) displays the temperature of O–T and T–C phase inversion varied with the amount of SnO\(_2\) concentration. As can be seen that the temperature of O–T phase inversion moved towards to higher temperature, while the temperature of T–C phase transition moved towards to lower
temperatures with increasing $x$. For the sample of $x = 0$, the temperature of O–T and T–C phase transition was observed about 30 and 96 °C. With the introduction of SnO$_2$, the temperature of O–T phase transition was increased with the content of SnO$_2$ doping, and the maximum temperature appeared at 45 °C. However, the temperature of T–C phase transition was reduced with the content of SnO$_2$ doping, and the minimum temperature was obtained at 72 °C. As is well know, there is an increase in the O–T transition temperatures, whereas a decrease in the T–C transition temperature in Sn, Hf, Zr doped BaTiO$_3$-based ceramics. Similar trends are presented in (Ba$_{0.85}$Ca$_{0.15}$)(Zr$_{0.1}$Ti$_{0.9}$)O$_3$ + $x$SnO$_2$ ceramics. The result may be attributed to the formation of defects in the form of nonferroelectric SnO$_6$ octahedra which would disturb the cooperative linking between the ferroelectric active TiO$_6$ octahedra, like Zr$^{4+}$ doping. 

### 3.3 Ferroelectric properties

Figure 4 displays the $P$–$E$ loops of the (Ba$_{0.85}$Ca$_{0.15}$)-(Zr$_{0.1}$Ti$_{0.9}$)O$_3$ + $x$SnO$_2$ ($x = 0$, 0.004, 0.008, 0.012 and 0.016) ceramics. The measurement of polarization hysteresis curves was conducted under an electric field of 30 kV/cm with 1 Hz frequency at room temperature. All compositions show typical well-saturated and slim ferroelectric hysteresis $P$–$E$ loops, as shown in Fig. 4(a). Moreover, more rectangular $P$–$E$ loops were observed in the SnO$_2$ modified samples. In order to further investigate the ferroelectric properties as a function of composition on the (Ba$_{0.85}$Ca$_{0.15}$)(Zr$_{0.1}$Ti$_{0.9}$)O$_3$ + $x$SnO$_2$ ceramics, the $P_r$ and $E_c$ dependence on SnO$_2$ concentration are summarized in Fig. 4(b). It could be seen that the $P_r$ gradually increases with the increasing of SnO$_2$ concentration, whereas as the $E_c$ is lowered with the SnO$_2$ concentration, indicating the ferroelectric properties are significantly improved in

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**Fig. 2.** SEM micrographs on surface for (Ba$_{0.85}$Ca$_{0.15}$)(Zr$_{0.1}$Ti$_{0.9}$)O$_3$ + $x$SnO$_2$ ceramics: (a) $x = 0$; (b) $x = 0.004$; (c) $x = 0.008$; (d) $x = 0.012$; (e) $x = 0.016$.

**Fig. 3.** Temperature-dependence of dielectric properties for (Ba$_{0.85}$Ca$_{0.15}$)(Zr$_{0.1}$Ti$_{0.9}$)O$_3$ + $x$SnO$_2$ ceramics (a); the temperature of O–T and T–C phase transition varied with SnO$_2$ concentration (b).
$(\text{Ba}_{0.85}\text{Ca}_{0.15})(\text{Zr}_{0.1}\text{Ti}_{0.9})\text{O}_3 + x\text{SnO}_2$ ceramics. Both the highest $P_r$ and lowest $E_c$ was detected for the sample of $x = 0.012$. The excellent ferroelectric properties may be ascribed to the homogeneous and dense micro-structure in Fig. 2(d). The higher $E_c$ would be interpreted as the enhancement in polarization reverse and more conducive to the orientation of charges, and then improved the ferroelectric properties. The lower $E_c$ means that there were lower energy barriers in electric field polarization, which can contribute to the polarization rotation and extension of dipole, as well as effectively improve the ferroelectric properties.\(^{18-20}\) The changes of $P_r$ and $E_c$ indicated that the moderate doping of SnO$_2$ could significantly improved the ferroelectric properties in $(\text{Ba}_{0.85}\text{Ca}_{0.15})(\text{Zr}_{0.1}\text{Ti}_{0.9})\text{O}_3 + x\text{SnO}_2$ ceramics.

3.4 Piezoelectric properties

Figure 5 displays the piezoelectric constant ($d_{33}$) and the electro-mechanical coupling factor ($k_p$) of the $(\text{Ba}_{0.85}\text{Ca}_{0.15})(\text{Zr}_{0.1}\text{Ti}_{0.9})\text{O}_3 + x\text{SnO}_2$ ($x = 0, 0.004, 0.008, 0.012$ and $0.016$) ceramics. All samples display excellent piezoelectric properties, and the values of $d_{33}$ have exceeded 450 pC/N in Fig. 5. The values of $d_{33}$ and $k_p$ elevated first and then decreased with increasing $x$. The maximum $d_{33} = 656$ pC/N was appeared at the sample of $x = 0.012$, which was associated with the low energy barrier in polarization rotation and extension of dipole orientation.\(^{21,22}\)

The enhancement piezoelectric properties are considered to derive from the more homogeneous micro-structure and the easily rotated polarization direction. In addition, the approaching temperature of O–T and T–C phase transition may be also attributed to the excellent piezoelectric properties in $(\text{Ba}_{0.85}\text{Ca}_{0.15})(\text{Zr}_{0.1}\text{Ti}_{0.9})\text{O}_3 + x\text{SnO}_2$ ceramics.

3.5 Strain properties

Figure 6 shows the bipolar strain curves tested at 30 kV/cm for $(\text{Ba}_{0.85}\text{Ca}_{0.15})(\text{Zr}_{0.1}\text{Ti}_{0.9})\text{O}_3 + x\text{SnO}_2$ ceramics. All ceramics exhibited a typical butterfly-like strain curves, which is the feature of piezoelectric materials for bi-axial field. It could be seen that the strain value gradually increased with $x$ increasing, and reached a maximum value ($S = 0.090\%$) at $x = 0.012$ in Fig. 6. The fluctuation in strain loops is similar to the variation of ferroelectric and piezoelectric performances. The higher value of strain may be ascribed to the easier rotated polarization direction and the closer temperature of O–T and T–C phase transition. Moreover, the homogeneous micro-structure are also contribute to the improvement of S–E loops in $(\text{Ba}_{0.85}\text{Ca}_{0.15})(\text{Zr}_{0.1}\text{Ti}_{0.9})\text{O}_3 + x\text{SnO}_2$ ceramics.

4. Conclusions

The $(\text{Ba}_{0.85}\text{Ca}_{0.15})(\text{Zr}_{0.1}\text{Ti}_{0.9})\text{O}_3 + x\text{SnO}_2$ ($x = 0, 0.004, 0.008, 0.012$ and $0.016$) ceramic was synthesized by the conventional solid state reaction. The XRD reveals that the perovskite structure was formed in all compositions. Dielectric measurement revealed that the temperature of
O–T and T–C phase transition varied with the Sn$^{4+}$ concentration. The maximum dielectric constant reached over 13000 in the specimens of SnO$_2$ doped BCZT ceramics. The ferroelectric properties, piezoelectric performances and the bipolar electric-field-induced strain are significantly enhanced in (Ba$_{0.85}$Ca$_{0.15}$)(Zr$_{0.1}$Ti$_{0.9}$)O$_3$ + xSnO$_2$ ceramics. The enhanced electrical properties of samples indicated that the (Ba$_{0.85}$Ca$_{0.15}$)(Zr$_{0.1}$Ti$_{0.9}$)O$_3$ + xSnO$_2$ ceramics are promising for lead-free practical applications.

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