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Phase-transition behavior and piezoelectric properties of lead-free $(Ba_{0.95}Ca_{0.05})(Ti_{1-x}Zr_x)O_3$ ceramics

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ABSTRACT

We report the enhancement of piezoelectric properties of $(Ba_{0.95}Ca_{0.05})(Ti_{1-x}Zr_x)O_3$ (BCTZx) ceramics by optimizing Zr content in the range of $0 \le x \le 15$ at.%. The BCTZx were synthesized by the solid-state reaction method and sintered at 1350 °C in a reducing atmosphere of $pO_2 = 5 \times 10^2$ Pa, for potential co-firing with base metal electrodes (BMEs). The BCTZx ceramics were characterized by an orthorhombic to pseudocubic polymorphic phase transition (PPT) at $5 \le x \le 7$ at.%, based on X-ray diffraction patterns. The orthorhombic to pseudocubic phase-transition temperature T_1 was shifted to 36 °C near room temperature for Zr content of $x = 4$ at.%. The piezoelectric constant d_{33}, electromechanical coupling coefficient k_p, and dielectric constant ε_r were optimized to 338 pC/N, 36%, and 2070, respectively. The results indicate that optimizing Zr content is an effective way to enhance the piezoelectric properties of $(Ba,Ca)(Ti,Zr)O_3$ ceramics, which are promising as a lead-free piezoelectric candidate.

1. Introduction

Environmental concern is calling for lead-free materials to substitute for widely used $Pb(Zr,Ti)O_3$ (PZT) ceramics. Niobate ceramics have become popular since Saito et al. [1] obtain a high d_{33} of 416 pC/N in textured $(K,Na)NbO_3$ (KNN)-based ceramics. Krauss et al. [2] also report good piezoelectric properties in $(Bi_{0.5}Na_{0.5})TiO_3$ by forming a solid solution with $SrTiO_3$. $BaTiO_3$ is a famous material that has been historically used in the field of piezoceramics [3] before the discovery of PZT. Nowadays $BaTiO_3$ is mainly used as a dielectric but not a piezoelectric material, largely owing to the relatively lower piezoelectric properties compared with PZT. For the past several decades $BaTiO_3$ ceramics have been showing a d_{33} level of only 190 pC/N [4]. Recently, surprisingly high d_{33} values of 350 pC/N [5], 419 pC/N [3], and 460 pC/N [6] are reported for $BaTiO_3$ ceramics prepared by microwave sintering, ordinary sintering, and two-step sintering, respectively. Liu and Ren [7] even report a d_{33} as high as 620 pC/N in $BaTiO_3$-based ceramics by optimizing the composition to a tricritical triple point. The findings demonstrate that $BaTiO_3$-based ceramics possess a high possibility of replacing lead-containing PZT materials.

The (Ca,Zr)co-doped $(Ba,Ca)(Ti,Zr)O_3$ ceramics are usually applied to produce the high-permittivity dielectrics of Y5V serials [8]. The $(Ba,Ca)(Ti,Zr)O_3$ have been co-fired with Ni electrodes in reducing atmospheres to produce multilayer ceramic capacitors (MLCCs) with base metal electrodes (BMEs) for a long time [9,10]. The (Ca,Zr) co-doping plays a critical role in maintaining the electrical properties of $BaTiO_3$ ceramics when sintered in a reducing atmosphere [8]. Our previous work [11] shows that a protective atmosphere of $pO_2 = 5 \times 10^2$ Pa has a negligible effect on the phase structure, microstructure, and piezoelectric properties of $(Ba_{0.95}Ca_{0.05})(Ti_{0.88}Zr_{0.12})O_3$ ceramics. A d_{33} of 200 pC/N is obtained for the composition of $(Ba_{0.95}Ca_{0.05})(Ti_{0.88}Zr_{0.12})O_3$ by optimizing sintering temperature at 1350 °C [11]. Thus the $(Ba,Ca)(Ti,Zr)O_3$ ceramics show potential piezoelectric applications for co-firing with BMEs. The piezoelectric properties of $(Ba_{0.95}Ca_{0.05})(Ti_{0.88}Zr_{0.12})O_3$ ceramics could be further enhanced by optimizing the content of dopants provided that there is a morphotropic phase boundary (MPB) or a polymorphic phase transition (PPT) associated with dopant content. Nanakorn et al. [12] recently address the dielectric and ferroelectric properties of $Ba(Ti_{1-x}Zr_x)O_3$ ceramics by optimizing Zr content, but the piezoelectric properties are not reported.

In this study, $(Ba_{0.95}Ca_{0.05})(Ti_{1-x}Zr_x)O_3$ $(0 \le x \le 15$ at.%) are selected as lead-free compositions to investigate the compositional dependence of structure and electrical properties on Zr content. The enhancement of piezoelectric properties by optimizing Zr content in the $(Ba_{0.95}Ca_{0.05})(Ti_{1-x}Zr_x)O_3$ ceramics is demonstrated.

2. Experimental details

Analytical-grade $BaCO_3$, $CaCO_3$, TiO_2, and ZrO_2 powders (99.9%, Xilong Chemical Reagent, China) were used as raw materials. The powders were weighed according

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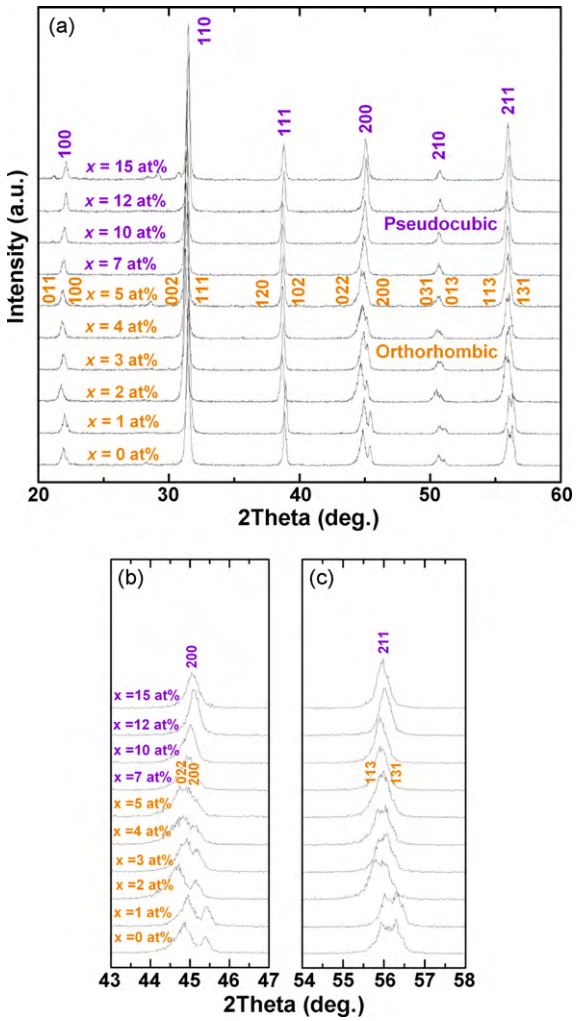

Fig. 1. X-ray diffraction patterns of the BCTZ*x* ($0 \le x \le 15$ at.%) ceramics sintered at 1350 °C for 2 h in industrial N_2 gas.

to the chemical formula $(Ba_{0.95}Ca_{0.05})(Ti_{1-x}Zr_x)O_3$ ($0 \le x \le 15$ at.%), abbreviated as BCTZ*x*, and then ball mixed with ZrO_2 balls for 4 h using ethanol as the medium. The slurry was dried and then calcined at 1200 °C for 6 h in air. The calcined powders were mixed with a polyvinyl alcohol (PVA) binder solution and compacted into disk samples under 200 MPa. After burning out the binder at 700 °C for 30 min, the samples were sintered at 1350 °C for 2 h in an industrial N_2 gas (oxygen content: 0.5 vol.%) [11]. The chamber pressure was maintained at the atmospheric pressure of 1.01×10^5 Pa, thus giving an oxygen partial pressure of 5×10^2 Pa. Silver pastes were fired at 520 °C for 30 min on both sides of the sintered disk samples as electrodes for electrical measurements. The samples were poled at room temperature in a silicone oil bath under a dc field of ~3.0 kV/mm for 20 min.

The crystalline structure was analyzed by X-ray diffraction (XRD) using a Cu Kα radiation (λ = 1.5416 Å) filtered through a Ni foil (Rigaku, RAD-B system, Japan). The sintered samples were polished and thermally etched at 1210–1260 °C for 30 min to inspect the microstructure using a scanning electron microscope (SEM, JSM-6460, Japan). The piezoelectric constant was measured 24 h after poling using a quasi-static piezoelectric d_{33} testing meter (ZJ-3A, Institute of Acoustics, China). The dielectric properties were measured from −20 to 180 °C using an Agilent precision impedance analyzer (4294A, Hewlett-Packard, USA). The room-temperature dielectric constant was measured using an automatic component analyzer (TH2828S, Tonghui Electronics, China). Ferroelectric hysteresis loops were measured at room temperature using a ferroelectric tester (RT6000HVA, Radiant Technologies Inc., USA).

3. Results and discussion

Fig. 1(a) shows the XRD patterns of the BCTZ*x* ceramics sintered at 1350 °C for 2 h in the industrial N_2 gas. All the compositions exhibited a pure perovskite structure and no trace of impurity phase was observed, indicating that Ca^{2+} and Zr^{4+} have completely diffused into $BaTiO_3$ lattices to form solid solutions in the studied composition range. The BCTZ*x* ceramics were identified by two diffraction patterns of an orthorhombic symmetry (PDF card #81-2200) for $0 \le x \le 5$ at.% and a pseudocubic symmetry (PDF card #31-0174) for $7 \le x \le 15$ at.%. The orthorhombic to pseudocubic phase transition occurred at a phase boundary of $5 \le x \le 7$ at.% at room temperature. The phase transition is caused by the distortion of crystal lattices induced by Ca^{2+} ($r = 0.99$ Å) occupying Ba^{2+} sites (1.34 Å) and Zr^{4+} (0.79 Å) occupying Ti^{4+} (0.68 Å) sites. Fig. 1(b) shows the enlarged reflection lines in the 2θ range of 43–47°. With increasing Zr content from 0 to 5 at.% the diffraction peaks shifted to lower diffraction angles, since the substitution of Ti^{4+} by larger Zr^{4+} would expand the crystals of BCTZ*x*. This is the same case for the reflection lines in the 2θ range of 54–58° in Fig. 1(c).

Fig. 2 shows the SEM observations of the BCTZ*x* ceramics sintered at 1350 °C for 2 h in the industrial N_2 gas. With increasing Zr content the average grain size increased from ~9 μm ($x = 0$) to the maximum value of ~14 μm ($x = 5$ at.%), before gradually decreasing to ~6.5 μm ($x = 15$ at.%, not shown). This result shows the effect of Zr content on the microstructure evolution of the BCTZ*x* ceramics. Ramam and Lopez [13] have suggested that Ba doping increases the grain size of PZT-based ceramics, while excess Ba addition restrains the grain growth.

Fig. 3 shows the variations of dielectric constant and dielectric loss with temperature from −20 to 180 °C for the poled BCTZ*x* samples, measured at 1 kHz. In the investigated temperature range, the BCTZ*x* ceramics ($x \le 12$ at.%) exhibited two phase-transition temperatures of Curie temperature $T_c > 50$ °C and T_1 near room temperature. The T_1 was determined from the peaks in the ε_r–T curves shown in the inset to Fig. 3(a). Furthermore, Fig. 3(b) clearly describes the abrupt changes in dielectric loss $\tan\delta$ at T_1 and T_c, respectively, which are in accordance with the observations in Fig. 3(a). For pure $BaTiO_3$ ceramics the T_c and T_1 are 120 and 5 °C, respectively [14]. The T_c of the BCTZ*x* ceramics was found to monotonously decrease towards lower temperatures with increasing *x*, which is consistent with the results reported for $Ba(Ti_{1-x}Zr_x)O_3$ ceramics [12] and $Ba(Ti_{1-x}Zr_x)O_3$ single crystals [15]. The BCTZ*x* ceramics at higher Zr contents showed broader dielectric constant-temperature (ε_r–T) peaks at the vicinity of T_c, presenting some characteristics of diffuse ferroelectric phase transition [16].

As shown in Fig. 3, the sample with $x = 0$ had a T_1 of −5 °C. The T_1 gradually shifted to higher temperatures above room temperature with increasing *x* from 4 to 7 at.%. Further increasing *x* from 7 to 12 at.% caused T_1 to shift to below room temperature again. When $x = 15$ at.% the two phase transitions of T_1 and T_c merged together and only one broad peak was observed at T_m, as shown in Fig. 3(a). At the same time, the dielectric loss showed no $\tan\delta$–T peaks in the investigated temperature range due to the merging of T_1 and T_c, as shown in Fig. 3(b). The result is in accordance with the $Ba(Ti_{1-x}Zr_x)O_3$ ($0 \le x \le 30$ at.%) system [17]. This is the well-known pinching effect for the three phase transitions of pure $BaTiO_3$ when Ti^{4+} is substituted with Zr^{4+} [18]. The findings clearly demonstrate that the orthorhombic to pseudocubic phase transition observed in Fig. 1 is associated with a PPT behavior [19,20], but not a MPB behavior that is featuring a temperature stability of phase-transition composition. The MPB can be typically observed in $Pb(Zr_{1-x}Ti_x)O_3$ near the composition of Zr/Ti = 52/48 [18].

Special attention is paid to the $(Ba_{0.95}Ca_{0.05})(Ti_{1-x}Zr_x)O_3$ compositions having a phase-transition temperature close to room temperature because the dielectric and piezoelectric properties were evaluated under ambient conditions in the present study. Released literature [20–22] reveals that shifting polymorphic phase-transition temperature downward to near room temper-

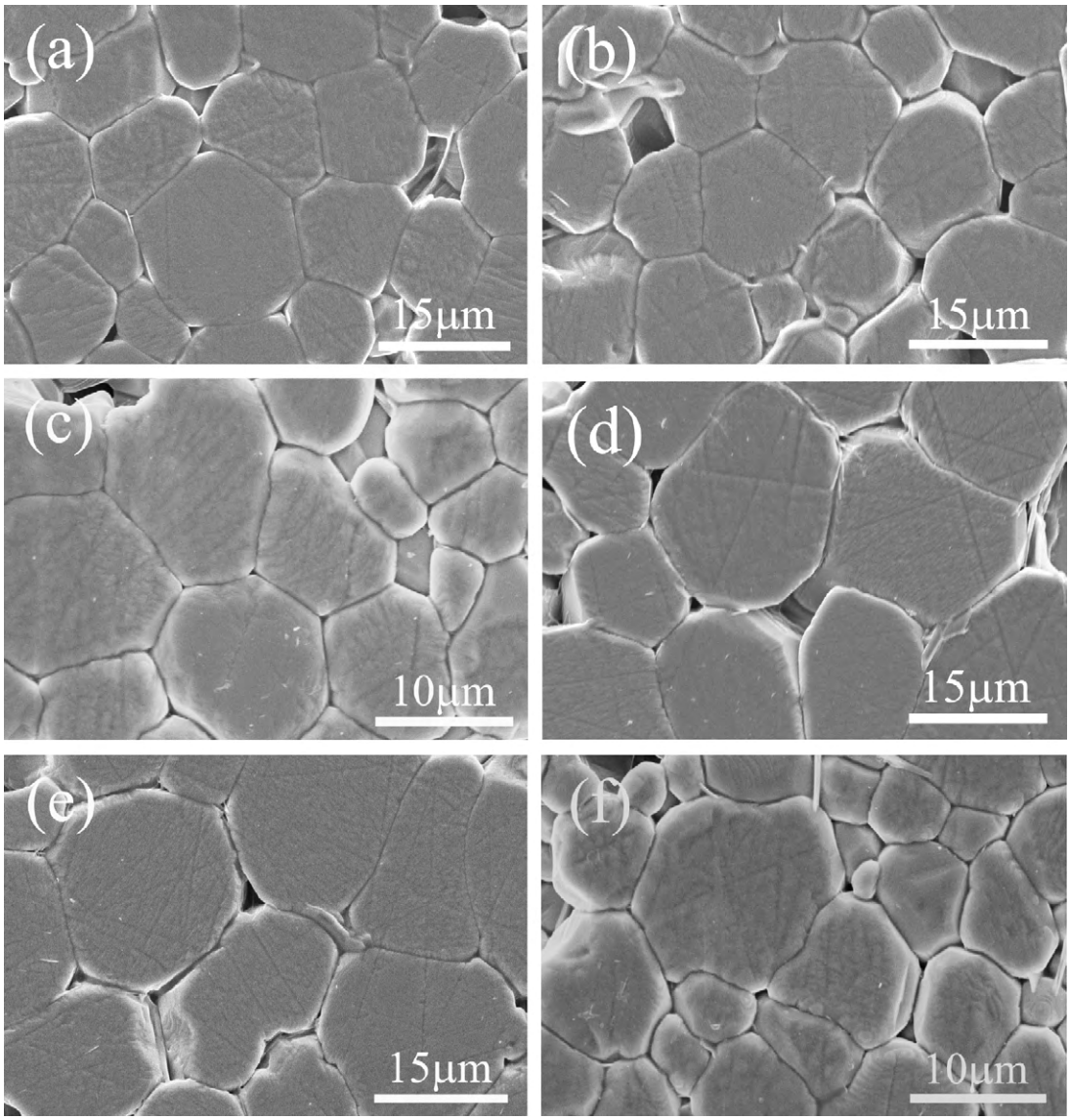

Fig. 2. SEM images of the BCTZ*x* ceramics sintered at 1350 °C for 2 h in industrial N_2 gas with various Zr contents: (a) 0 at.%, (b) 3 at.%, (c) 4 at.%, (d) 5 at.%, (e) 7 at.%, and (f) 10 at.%.

ature greatly enhances piezoelectric properties of KNN-based ceramics. For the investigated BCTZ*x* ceramics two compositions had a T_1 close to room temperature, i.e., ~36 °C for $x = 4$ at.% and ~13 °C for $x = 12$ at.%. It is noted that the PPT composition $x = 7$ at.% had a T_1 of ~50 °C, which is farther away from room temperature compared with $x = 4$ at.%. Although the T_1 for another PPT composition of $x = 5$ at.% was not given this value should be in between 36 and 50 °C deduced reasonably from the variation tendency in Fig. 3, and is also farther away from room temperature compared with $x = 4$ at.%. It is generally accepted that a PPT composition determined at room temperature should also have a T_1 near room temperature [20]. One could ascribe the above inconsistence to the reducing atmosphere of N_2 used in this study. Nevertheless, previous investigations have shown that the sintering atmosphere of N_2 has no substantial effect on the transition temperatures T_1 or T_c of $(Ba_{0.95}Ca_{0.05})(Ti_{0.88}Zr_{0.12})O_3$ ceramics [11]. The interpretation to this inconsistence still remains open.

Fig. 4 shows the dielectric constant ε_r and dielectric loss tan δ as functions of Zr content for the BCTZ*x* ceramics. With increasing Zr content the ε_r values first increased to a peaked value of 2070 at $x = 4$ at.% and then decreased slightly to 1478 at $x = 7$ at.%, before increasing sharply to the maximum value of 2838 at $x = 15$ at.%. In the range of $0 \le x \le 15$ at.%, the ε_r values totally increased with increasing Zr content. Generally speaking, the pseudocubic-structured BCTZ*x* ceramics exhibited higher dielectric constants than the orthorhombic-structured ones.

It is well known that dielectric constant abruptly increases at a phase-transition point. When the phase-transition point is close to room temperature, the dielectric constant measured at room temperature will be greatly increased. In this study, the peaked ε_r at $x = 4$ at.% is in agreement with the fact that the T_1 of 36 °C was close to room temperature. The T_1 of 13 °C close to room temperature also increased greatly the ε_r value at $x = 12$ at.%. Since the T_c was shifted close to room temperature the sample of $x = 15$ at.% had the highest ε_r value, as shown in Fig. 4. The tan δ of the BCTZ*x* ceramics also tended to increase with increasing x in the studied range and the maximum value was <0.036.

Fig. 5 shows the piezoelectric constant d_{33} and planar electromechanical coupling coefficient k_p as functions of Zr content for the BCTZ*x* ceramics. There was a strong composition dependence of the piezoelectric properties. The highest piezoelectric properties were obtained at $x = 4$ at.%, yielding a d_{33} of 338 pC/N and

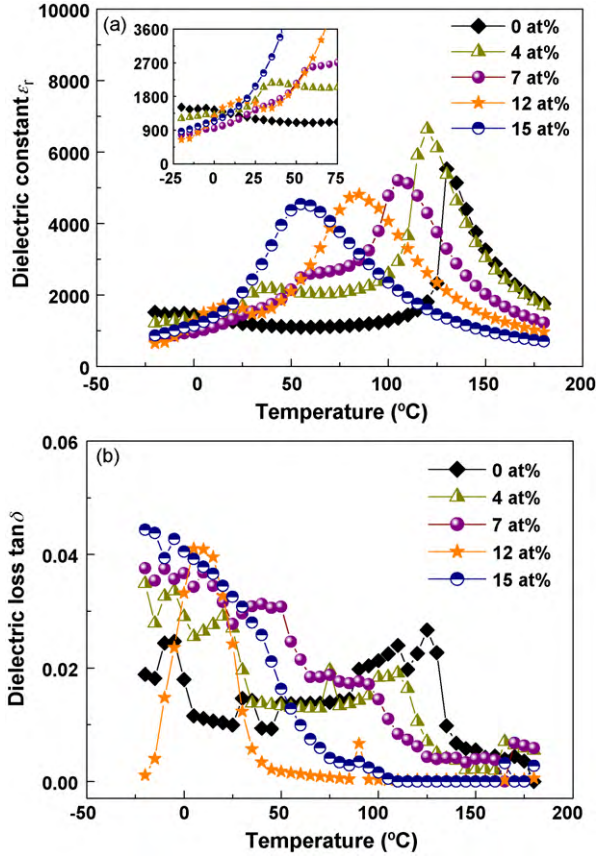

Fig. 3. Temperature dependences of (a) dielectric constant and (b) dielectric loss for the BCTZx ($0 \le x \le 15$ at.%) ceramics sintered at 1350 °C for 2 h in industrial N_2 gas. Inset in (a) shows the enlarged ε_r–T curves in the temperature range of −25 to 75 °C.

a k_p of 36%. The d_{33} and k_p values were significantly enhanced by optimizing Zr content compared with previously reported $(Ba_{0.95}Ca_{0.05})(Ti_{0.88}Zr_{0.12})O_3$ ceramics [11]. The BCTZx ceramics also exhibited piezoelectric properties comparable to some lead-based ceramics.

As shown in Fig. 5, the d_{33} value was peaked at $x = 4$ at.% for the BCTZx samples. This result is supported by the finding that the phase-transition temperature T_1 for $x = 4$ at.% was 36 °C, close to room temperature. The $x = 12$ at.% with $T_1 = 13$ °C close to room temperature also had a peaked d_{33} value. It is revealed that shifting

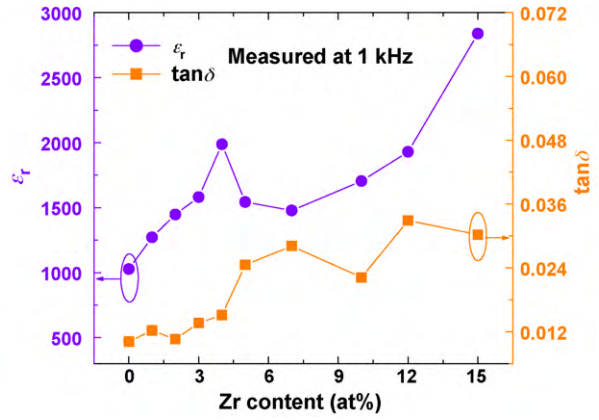

Fig. 4. Zr content dependences of dielectric constant and dielectric loss for the BCTZx ($0 \le x \le 15$ at.%) ceramics sintered at 1350 °C for 2 h in industrial N_2 gas.

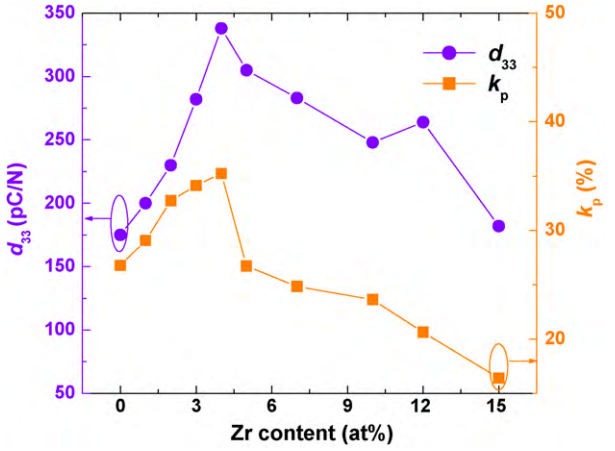

Fig. 5. Piezoelectric constant and electromechanical coupling coefficient as functions of Zr content for the BCTZx ($0 \le x \le 15$ at.%) ceramics sintered at 1350 °C for 2 h in industrial N_2 gas.

transition temperature downward to near room temperature can greatly enhance the piezoelectric properties of KNN-based piezoceramics [22]. For example, Zhang et al. [21] significantly enhance the piezoelectric constant d_{33} from 127 pC/N for KNN ceramics to 265 pC/N for 0.948KNN–0.052$LiSbO_3$ ceramics by shifting the orthorhombic to tetragonal phase-transition temperature from 195 °C for KNN to 35 °C for 0.948KNN–0.052$LiSbO_3$ with doping $LiSbO_3$. However, it is noted that the two compositions of $x = 4$ and 12 at.% were not in the range of $5 \le x \le 7$ at.% that was identified for PPT in the present study. This implies that the proximity of phase-transition temperature to room temperature plays more important roles in enhancing piezoelectric properties of the BCTZx ceramics.

Fig. 6 shows the hysteresis loops (P versus E) of the BCTZx ceramics with various Zr contents. The Zr content was found to have an obvious effect on the ferroelectric properties of the $(Ba_{0.95}Ca_{0.05})(Ti_{1-x}Zr_x)O_3$ ceramics. As shown in the inset to Fig. 6, the remnant polarization P_r decreased gradually from 15.12 to 5.27 μC/cm^2 with increasing x from 0 to 15 at.%. The result suggests that the orthorhombic-structured BCTZx ceramics possess higher P_r values than the pseudocubic-structured ones, which is consistent with reported $Ba(Ti_{1-x}Zr_x)O_3$ single crystals [15]. Further explanation is the summation of spontaneous polarization directions for an orthorhombic phase is more than that for a pseudocubic phase [21].

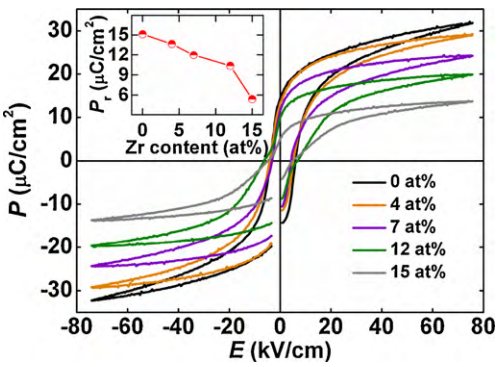

Fig. 6. P–E hysteresis loops measured for the BCTZx ($0 \le x \le 15$ at.%) ceramics sintered at 1350 °C for 2 h in industrial N_2 gas. Inset represents the variation of remnant polarization P_r as a function of Zr content.

4. Conclusions

The $(Ba_{0.95}Ca_{0.05})(Ti_{1-x}Zr_x)O_3$ $(0 \le x \le 15$ at.%) piezoceramics were synthesized by the solid-state reaction method and sintered at 1350 °C for 2 h in the industrial N_2 gas. The PPT of orthorhombic to pseudocubic for the BCTZ*x* ceramics was identified at $5 \le x \le 7$ at.% through XRD patterns. Excellent electrical properties of $d_{33} = 338$ pC/N, $k_p = 36\%$, and $\varepsilon_r = 2070$ were obtained at $x = 4$ at.% near the PPT compositions. The results indicate that appropriate Zr addition $(4 \le x \le 7$ at.%) can significantly improve the piezoelectric properties of $(Ba_{0.95}Ca_{0.05})(Ti_{1-x}Zr_x)O_3$ ceramics. The present study demonstrates that (Ba,Ca)(Ti,Zr)O_3 ceramics are a promising candidate for lead-free piezoceramics.

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