

Article

Effect of Different Ca^{2+} and Zr^{4+} Contents on Microstructure and Electrical Properties of $(\text{Ba,Ca})(\text{Zr,Ti})\text{O}_3$ Lead-Free Piezoelectric Ceramics

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Abstract: In the preparation of $(\text{Ba,Ca})(\text{Zr,Ti})\text{O}_3$ lead-free piezoelectric ceramics, different Ca^{2+} and Zr^{4+} contents will greatly affect the phase structure, microstructure, and electrical properties of the ceramics. XRD shows that all samples have pure perovskite phase structure, and the $(\text{Ba}_{0.85}\text{Ca}_{0.15})(\text{Zr}_y\text{Ti}_{1-y})\text{O}_3$ ceramics morphotropic phase boundary region from tetragonal phase to rhombohedral phase near $0.08 \leq y \leq 0.1$. From the dielectric temperature curve, the phase transition temperature ($T_{\text{O-T}}$) was found near room temperature at $0.12 \leq x \leq 0.18$ for the $(\text{Ba}_{1-x}\text{Ca}_x)(\text{Zr}_{0.1}\text{Ti}_{0.9})\text{O}_3$ ceramics. Both Ca^{2+} and Zr^{4+} increase have a significant decrease on the Curie temperature T_c . All samples were revealed as relaxers with diffusivities in the range $1.29 \leq \gamma \leq 1.82$. Different from the undoped ceramics, ceramics doped with Ca and Zr ions exhibit saturated P - E hysteresis loops, and their ferroelectric properties are significantly optimized. In particular, the $(\text{Ba}_{0.85}\text{Ca}_{0.15})(\text{Zr}_{0.1}\text{Ti}_{0.9})\text{O}_3$ ceramic demonstrated optimal properties, namely $d_{33} = 330 \text{ pC/N}$, $k_p = 0.41$, $\epsilon_r = 4069$, $P_r = 4.8 \text{ } \mu\text{C/cm}^2$, and $E_c = 3.1 \text{ kV/cm}$, indicating that it is a viable lead-free piezoelectric contender. Variations in Ca and Zr content have a significant effect on the crystal grain sizes and densities of ceramics, which is strongly associated with their piezoelectricity.

Keywords: BCTZ; phase transition; piezoelectric properties; dielectric properties



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1. Introduction

Lead-based piezoceramics are extensively utilized in various electronic devices, including actuators and sensors, owing to their high electrical activity, and their demand in the electronics sector has been steadily increasing in recent years [1,2]. However, as people are becoming increasingly aware of environmental challenges, many countries have issued restrictions on the use of substances involving lead, which limits the development of lead-based piezoelectric ceramics [3,4]. The development of environmentally friendly lead-free piezoelectric ceramics, such as $(\text{K}_x\text{Na}_{1-x})\text{NbO}_3$ -based ceramics [5,6], $(\text{Bi}_x\text{Na}_{1-x})\text{TiO}_3$ -based ceramics [7,8], BiFeO_3 -based ceramics [9,10], and BaTiO_3 (BT)-based ceramics [11,12], is undoubtedly an important research topic for future piezoelectric applications.

Among the abovementioned ceramics, BT-based piezoelectric ceramics have been most extensively investigated. In 2009, Ren et al. [13] reported $\text{Ba}(\text{Zr}_{0.2}\text{Ti}_{0.8})\text{O}_{3-x}(\text{Ba}_{0.7}\text{Ca}_{0.3})\text{TiO}_3$ (BCZT) piezoelectric ceramics with a d_{33} value up to 620 pC/N at optimal composition, which attracted considerable interest from the research community. Several efforts were devoted to further enhancing the d_{33} of BCZT ceramics, including the use of different synthesis methods [14], ion substitutions [15], and compositions [16]. Chen et al. [17] used the molten-salt synthesis method (MSS) to synthesize lead-free BCZT ceramics, indicating

that MSS is a promising design for achieving improvements in the electrical properties of BCZT ceramics, as well as lowering the reaction temperature. Ji et al. [18] tailored the microstructure and properties of BCZT ceramics using the hydrothermal process, obtaining excellent dielectric properties with $\epsilon_m = 14,548$. Bai et al. [19] studied a broad range of processing factors including composition, sintering conditions, particle size of the calcined ceramic powder, structure, and microstructure, with the objective of achieving optimum properties in BCZT ceramics. In addition to the fabrication and processing, the construction of phase boundaries also plays an essential role in enhanced electrical properties for lead-free ceramics. Regarding the origin of the large piezoelectricity of the system, Ren et al. [13] attributed the enhanced piezoelectricity of the BCZT pseudo-binary system to the approach of the morphotropic phase boundary (MPB) from the tricritical point of the rhombohedral (R), tetragonal (T), and cubic (C) phases. Recent research has discovered that the mixed phase region is an intermediate orthorhombic phase (O), resulting in excellent piezoelectric and electromechanical properties [20–22]. Zhou et al. [20] discovered the coexistence of the O and T phases in BCZT ceramics doped with 0.3 mol% LiTaO₃ and obtained a high d_{33} value of 433 pC/N. Kaddoussi et al. [21] investigated the structural transitions in different x of Ca content for BCZT ceramic, revealing two types of phase-transition sequences: R–O–T–C occurring at $x = 0.05$ and O–T–C occurring at $x = 0.2$. Tian et al. [22] showed that the MPB of (Ba_{0.85}Ca_{0.15})(Zr_{0.1}Ti_{0.9})O₃ ceramics was closely related to the occurrence of an intermediate phase (considered as O phase) at narrow regions between R and T phases. Moreover, the high piezoelectric of BCZT ceramics are the result of the microstructural instability and elastic softening by Guo et al. reported [23]. Cai et al. [24] attribute the enhancement of the piezoelectric properties of BCZT ceramics to the synergistic effect of grain size and phase boundaries. Hence, the underlying mechanisms for the phase diagram and piezoelectric performance enhancement of BCZT ceramic systems remain under-investigated.

The objective of this work is thus to understand the reasons for the effect of the Ca and Zr content variation in the (Ba,Ca)(Zr,Ti)O₃ ceramics on their piezoelectric properties. The contribution of the phase structure, microstructure, dielectric, and ferroelectric properties to the piezoelectric properties of the (Ba,Ca)(Zr,Ti)O₃ ceramics are explored.

2. Experimental

2.1. Sample Preparation

The (Ba_{1-x}Ca_x)(Zr_{0.1}Ti_{0.9})O₃ ceramics with $x = 0, 0.06, 0.12$, and 0.18 , as well as (Ba_{0.85}Ca_{0.15})(Zr_yTi_{1-y})O₃ ceramics with $y = 0, 0.08, 0.1$, and 0.12 , were designed for this study. The specimens were prepared via the traditional solid-state reaction method. The reagent-grade powders were used as the starting materials: BaCO₃ (99%), CaCO₃ (99%), ZrO₂ (99%), TiO₂ (99.9%). The powders were mixed, and agate balls were used to ball mill them in alcohol for 12 h. After desiccating the slurry, it was calcined for 4 h at 1180 °C in a closed crucible. Post-calcination, the powders were reground for 10 h. Polyvinyl alcohol (PVA) was used as a binder to compress the powders into disks at 200 MPa. To evaporate the PVA, all samples were sintered at 800 °C for 4 h, followed by 3 h in a covered crucible at 1400 °C. Silver electrodes were applied to the two surfaces of the polished ceramic disks before firing at 550 °C for 10 min. Polarization of the samples in silicone oil by imposition of a DC field of 2 kV/mm for 30 min at 50 °C.

2.2. Characterization

The samples were examined for the evolution of their crystalline structure via X-ray diffraction (XRD, D/Max-2500, Rigaku, Tokyo, Japan). The Archimedes method was used to identify the bulk density (ρ) of the samples (electronic density detector, ZMD-2, Shanghai Fangrui Instrument Limited Company, Shanghai, China). The microstructural characteristics of all the samples were observed using scanning electron microscopy (SEM, JMS-5610LV, Tokyo, Japan) after ultrasonic cleaning and vacuum drying of the sample surface, as well as spraying with gold. Piezoelectric constant (d_{33}) was measured by a

quasistatic piezoelectric d_{33} m (ZJ-3A, Institute of Acoustics, Chinese Academy of Sciences, China). The electromechanical coupling factor (k_p) was determined through the resonance and antiresonance method using an LCR analyzer (HP4294A, Agilent, CA, USA) based on the IEEE standards [25]. The dielectric behavior and curie temperature (T_c) of the samples from room temperature to 160 °C were analyzed using the HP4294A impedance analyzer with an automatic temperature controller system. Measurement of polarization hysteresis loops (P – E) at 10 Hz with a ferroelectric analysis tester (TF2000, aixACCT Systems GmbH, Aachen, Germany).

3. Results and Discussion

3.1. Crystal Phase and Structure

Figure 1a,b illustrates the XRD patterns of the $(\text{Ba}_{1-x}\text{Ca}_x)(\text{Zr}_{0.1}\text{Ti}_{0.9})\text{O}_3$ and $(\text{Ba}_{0.85}\text{Ca}_{0.15})(\text{Zr}_y\text{Ti}_{1-y})\text{O}_3$ ceramics with different Ca and Zr contents. All samples exhibit a single perovskite structure, suggesting that Ca and Zr ions have spread into the BT lattice and formed a new solid solution. Figure 1c–f provides a magnified view of the XRD patterns around $2\theta = 45^\circ$, and 56° for both samples, so that the peak positions and shapes can be easily compared. From Figure 1c, the 200 diffraction peak shifts toward a higher 2θ value with increasing Ca concentration for $(\text{Ba}_{1-x}\text{Ca}_x)(\text{Zr}_{0.1}\text{Ti}_{0.9})\text{O}_3$ ceramics. The same phenomenon is also observed for the 211 diffraction peaks. Conversely, increasing the Zr content causes the peak to shift toward a lower 2θ value for $(\text{Ba}_{0.85}\text{Ca}_{0.15})(\text{Zr}_y\text{Ti}_{1-y})\text{O}_3$ ceramics. According to the Bragg equation $2d\sin\theta = n\lambda$, this is caused by the fact that Ca^{2+} has a smaller ionic radius (99 pm) than Ba^{2+} (135 pm), which results in a reduction in the lattice parameters. Equivalently, Zr^{4+} has a larger ionic radius (72 pm) than Ti^{4+} (60.5 pm), which leads to an increase in the lattice parameters. Figure 1e,f shows that the $(\text{Ba}_{0.85}\text{Ca}_{0.15})(\text{Zr}_y\text{Ti}_{1-y})\text{O}_3$ ceramics present peaks splitting phenomenon, which corresponds to the tetragonal (T) phase structure at $y = 0$. With the increase in the Zr content ($y \leq 0.1$), the distance between the (002) and (200) peaks and also between the (112) and (211) peaks become gradually smaller, indicating the co-existence of the tetragonal and rhombohedral (R-T) phases [22,26]. The estimated increase in the Zr content shows that the (200) and (211) peaks merge into a single peak, which corresponds to the rhombohedral (R) phase structure. Therefore, it can be assumed that a phase transformation from the T to the R with increasing Zr content at room temperature, where MPB between the R and T phases occurs in the region of $0.08 \leq y \leq 0.1$.

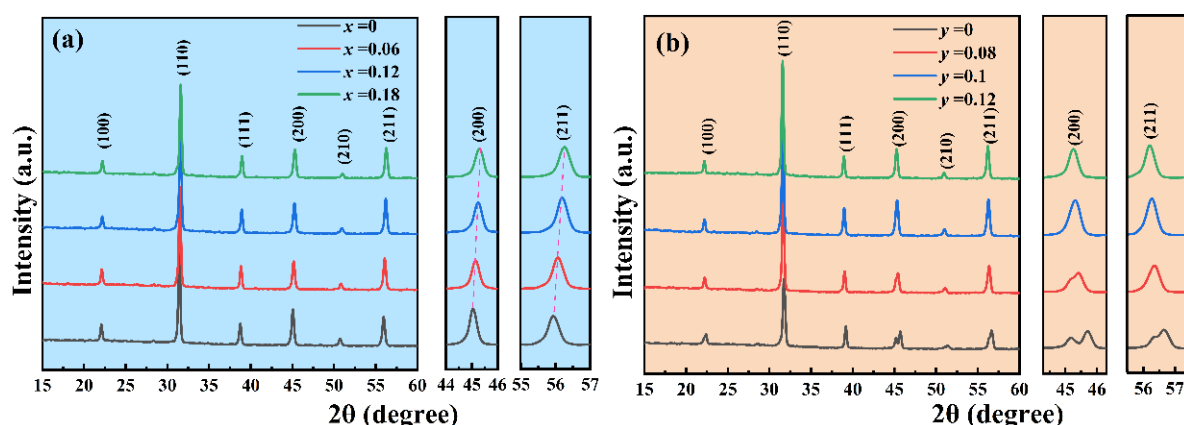


Figure 1. Cont.

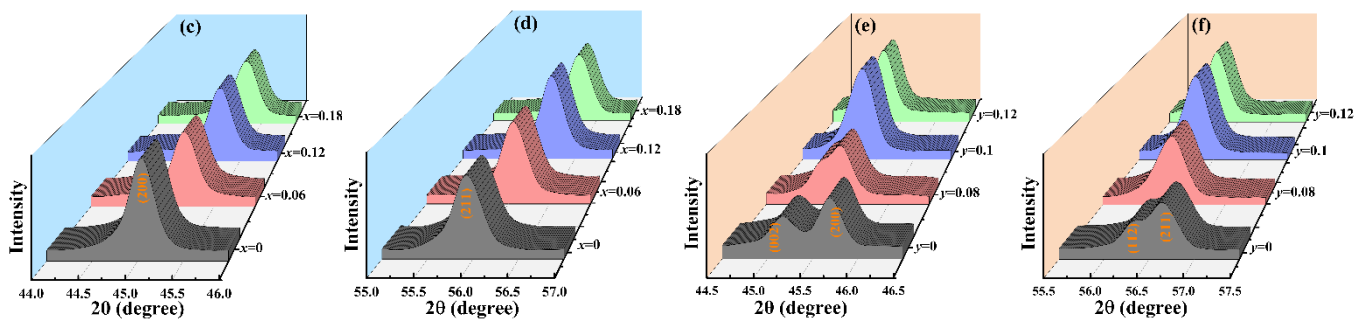


Figure 1. XRD patterns of the (a) $(\text{Ba}_{1-x}\text{Ca}_x)(\text{Zr}_{0.1}\text{Ti}_{0.9})\text{O}_3$ ceramics and (b) $(\text{Ba}_{0.85}\text{Ca}_{0.15})(\text{Zr}_y\text{Ti}_{1-y})\text{O}_3$ ceramics. Magnified view of the XRD patterns of the (c,d) BC_xZT ceramics and (e,f) BCZ_yT ceramics around $2\theta = 45^\circ$, and 56° , respectively.

Figure 2 illustrates the SEM morphology images of the $(\text{Ba}_{1-x}\text{Ca}_x)(\text{Zr}_{0.1}\text{Ti}_{0.9})\text{O}_3$ and $(\text{Ba}_{0.85}\text{Ca}_{0.15})(\text{Zr}_y\text{Ti}_{1-y})\text{O}_3$ ceramics with different Ca and Zr contents. The ceramics show clear grain boundaries, a dense microstructure, and a low porosity. With the introduction of the Ca and Zr ions, the distribution of the grain sizes of the BCZT ceramics becomes more uniform compared with that of the pure BZT ($x = 0$) and BCT ($y = 0$) ceramics. In order to investigate the influences of different Ca and Zr contents on the grain size and density of ceramics, the linear intercept method and the Archimedes method, as illustrated in Figure 3, were used to estimate the average grain size and density, respectively. The addition of Ca to the $(\text{Ba}_{1-x}\text{Ca}_x)(\text{Zr}_{0.1}\text{Ti}_{0.9})\text{O}_3$ ceramics results in the diminution of the grain size and an increase in the density, but a considerable reduction in the density is observed at $x > 0.12$. Furthermore, the addition of Zr increases the grain size and density of the $(\text{Ba}_{0.85}\text{Ca}_{0.15})(\text{Zr}_y\text{Ti}_{1-y})\text{O}_3$ ceramics from 9.9 to 14.9 μm and from 5.61 to 5.69 g/cm^3 , respectively. The substitution of Zr assists in enhancing the grain growth of the materials [26]. Because the rhombohedral phase content progressively rises with increasing Zr content from Figure 1d, the change in microstructure with the introduction of Zr in this study may be explained by the phase transition from the T to the R for BCT ceramics. In addition, the greater radius of Zr^{4+} occupies the B-site of the ABO_3 structure, which contributes to the steady rise in grain size.

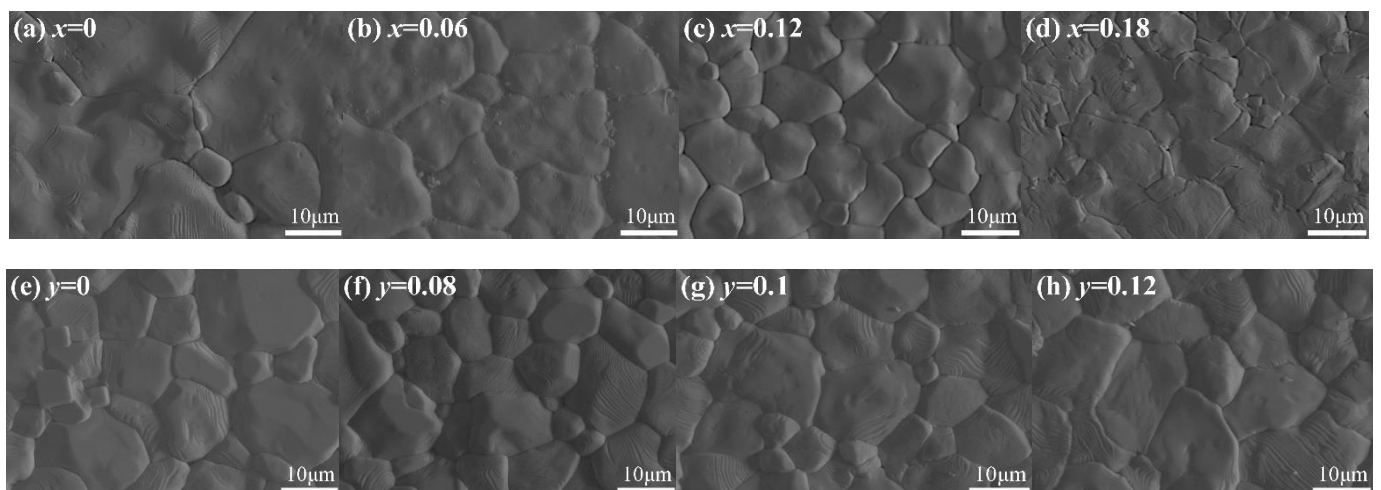


Figure 2. SEM images of the $(\text{Ba}_{1-x}\text{Ca}_x)(\text{Zr}_{0.1}\text{Ti}_{0.9})\text{O}_3$ ceramics for Ca content at (a) $x = 0$, (b) $x = 0.06$, (c) $x = 0.12$, and (d) $x = 0.18$, and $(\text{Ba}_{0.85}\text{Ca}_{0.15})(\text{Zr}_y\text{Ti}_{1-y})\text{O}_3$ ceramics for Zr content at (e) $y = 0$, (f) $y = 0.08$, (g) $y = 0.1$, and (h) $y = 0.12$.

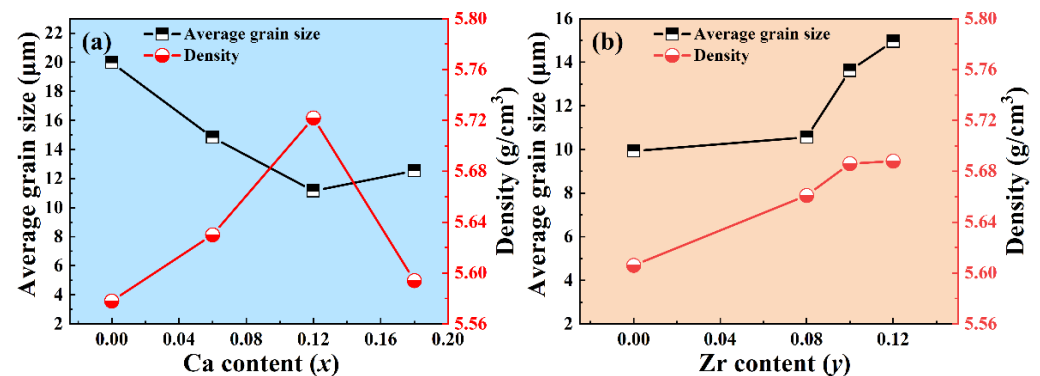


Figure 3. Average grain size and density of (a) $(\text{Ba}_{1-x}\text{Ca}_x)(\text{Zr}_{0.1}\text{Ti}_{0.9})\text{O}_3$ ceramics and (b) $(\text{Ba}_{0.85}\text{Ca}_{0.15})(\text{Zr}_y\text{Ti}_{1-y})\text{O}_3$ ceramics.

3.2. Dielectric Properties

Figure 4 displays the dielectric behavior of $(\text{Ba}_{1-x}\text{Ca}_x)(\text{Zr}_{0.1}\text{Ti}_{0.9})\text{O}_3$ and $(\text{Ba}_{0.85}\text{Ca}_{0.15})(\text{Zr}_y\text{Ti}_{1-y})\text{O}_3$ ceramics for various temperatures at 0.1, 1, 10, 100, and 1000 kHz. All of the samples show a distinct dielectric anomaly, which is attributed to the shift from the ferroelectric-to-paraelectric phase. This dielectric anomaly occurs at a temperature that corresponds to the Curie temperature (T_c) and reduces along with increasing Ca and Zr content. As presented in Table 1, the addition of the Ca and Zr ions reduces the T_c of the $(\text{Ba}_{1-x}\text{Ca}_x)(\text{Zr}_{0.1}\text{Ti}_{0.9})\text{O}_3$ and $(\text{Ba}_{0.85}\text{Ca}_{0.15})(\text{Zr}_y\text{Ti}_{1-y})\text{O}_3$ ceramics from 87 °C to 73 °C and from 120 °C to 66 °C, respectively. The dielectric peaks shift toward a lower temperature, which may be due to the reduced internal stress in the structure [27]. The results demonstrate that the addition of Zr ions has a more pronounced impact on the T_c than that of Ca ions, which can be attributed to the reduction in the tetragonality shown in Figure 1d. As the relatively active Ti ions are replaced by the relatively passive Zr ions, the cell parameter ratio decreases, the polarization becomes extremely irregular, and the overall domain structure is disrupted, causing the T_c to shift toward a lower temperature [28].

Table 1. Room-temperature physical properties of the $(\text{Ba}_{1-x}\text{Ca}_x)(\text{Zr}_{0.1}\text{Ti}_{0.9})\text{O}_3$ ceramics and $(\text{Ba}_{0.85}\text{Ca}_{0.15})(\text{Zr}_y\text{Ti}_{1-y})\text{O}_3$ ceramics.

Composition	$x = 0$	$x = 0.06$	$x = 0.12$	$x = 0.18$	$y = 0$	$y = 0.08$	$y = 0.1$	$y = 0.12$
d_{33} (pC/N)	70	102	300	231	122	302	330	211
k_p	0.16	0.20	0.44	0.31	0.24	0.43	0.41	0.27
ϵ_r	2398	1744	2632	3928	928	2942	4069	3832
$\tan\delta$	9.8%	3.9%	1.1%	1.2%	9.7%	1.1%	1.5%	1.6%
T_c (°C)	87.1	86.6	78.5	73.1	119.3	91	80.5	66.05
P_r ($\mu\text{C}/\text{cm}^2$)	-	4.5	6.3	3.6	3.5	5.7	4.8	5.1
E_c (kV/cm)	-	0.9	2.3	3.1	3.3	4.6	3.1	1.1

In particular, an extra dielectric anomaly is observed in Figure 4b,c corresponding to the temperature of the O-T phase transition (T_{O-T}) of $(\text{Ba}_{1-x}\text{Ca}_x)(\text{Zr}_{0.1}\text{Ti}_{0.9})\text{O}_3$ ceramics. The dielectric peak of T_{O-T} is not observed in Figure 4a,d because T_{O-T} is close to T_c and covered by ϵ_m due to the diffuse phase transition behavior at $x = 0$ [22], and T_{O-T} shifts to below room temperature at $x = 0.18$. The frequency dispersion is negligible for all samples, demonstrating their excellent frequency stability.

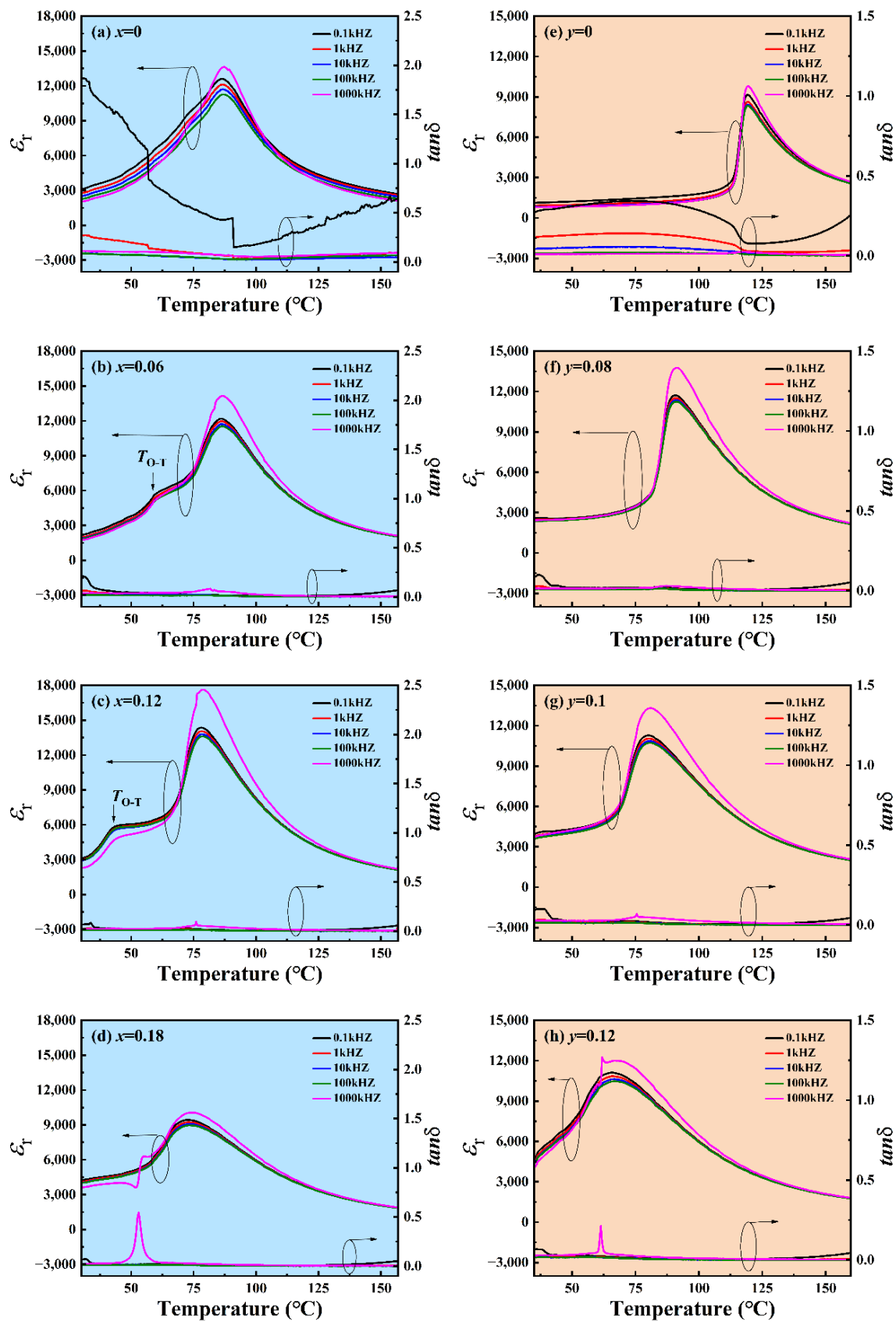


Figure 4. The temperature and frequency dependence of ϵ_r and $\tan\delta$ of the $(\text{Ba}_{1-x}\text{Ca}_x)(\text{Zr}_{0.1}\text{Ti}_{0.9})\text{O}_3$ ceramics with (a) $x = 0$, (b) $x = 0.08$, (c) $x = 0.1$, (d) $x = 0.12$ and $(\text{Ba}_{0.85}\text{Ca}_{0.15})(\text{Zr}_y\text{Ti}_{1-y})\text{O}_3$ ceramics with (e) $y = 0$, (f) $y = 0.08$, (g) $y = 0.1$, (h) $y = 0.12$.

Furthermore, Figure 4 shows that the morphologies of the curves at the Curie peak exhibit a broad trend with adding Ca and Zr ions. The Curie–Weiss law is suitable for describing the dielectric behavior of relaxer ferroelectrics, and the parameter γ can be used to estimate the degree of diffuseness by plotting $\ln(1/\epsilon_r - 1/\epsilon_m)$ as a function of $\ln(T - T_m)$ at a frequency of 1 kHz. The dielectric characteristics can be expressed by the following modified Curie-Weiss relationship:

$$\frac{1}{\epsilon_r} - \frac{1}{\epsilon_m} = \frac{(T - T_m)^\gamma}{C} \quad (1 \leq \gamma \leq 2) \quad (1)$$

where ϵ_r is the dielectric constant at temperature T , ϵ_m is the maximum dielectric constant at the transition temperature (T_m), C is the Curie constant, and γ is the indicator of the degree of diffuseness, which takes a value between 1 (for a normal ferroelectric) and 2 (for a completely diffuse phase transition). As shown in Figure 5, the addition of the Ca and Zr ions increases the γ values of the samples from 1.39 to 1.80 and from 1.29 to 1.82, respectively, thus suggesting that the as-prepared $(\text{Ba}_{1-x}\text{Ca}_x)(\text{Zr}_{0.1}\text{Ti}_{0.9})\text{O}_3$ and $(\text{Ba}_{0.85}\text{Ca}_{0.15})(\text{Zr}_y\text{Ti}_{1-y})\text{O}_3$ ceramics are typical relaxer ferroelectrics. The addition of the Ca and Zr ions drastically affects the degree of the dielectric relaxation of the BCZT piezoelectric ceramics.

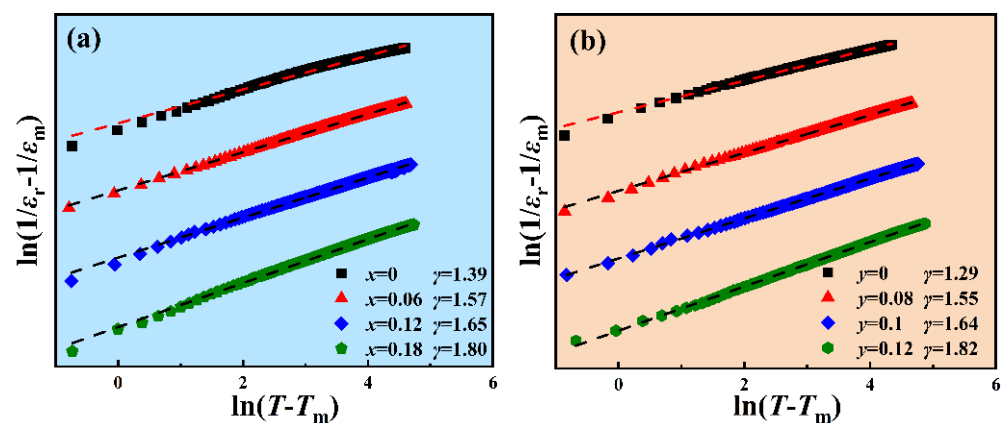


Figure 5. Diffusivity of dielectric behavior about $\ln(1/\epsilon_r - 1/\epsilon_m)$ function versus $\ln(T - T_m)$ for (a) $(\text{Ba}_{1-x}\text{Ca}_x)(\text{Zr}_{0.1}\text{Ti}_{0.9})\text{O}_3$ ceramics and (b) $(\text{Ba}_{0.85}\text{Ca}_{0.15})(\text{Zr}_y\text{Ti}_{1-y})\text{O}_3$ ceramics at 1 kHz.

3.3. Piezoelectric Properties

Figure 6 plots the piezoelectric coefficient d_{33} and electromechanical coupling coefficient k_p for the $(\text{Ba}_{1-x}\text{Ca}_x)(\text{Zr}_{0.1}\text{Ti}_{0.9})\text{O}_3$ and $(\text{Ba}_{0.85}\text{Ca}_{0.15})(\text{Zr}_y\text{Ti}_{1-y})\text{O}_3$ ceramics. Figure 6a shows that the d_{33} value incrementally increases with Ca content until a peak value of 300 pC/N at $x = 0.12$, and declines subsequently with further increase in x . The k_p value's fluctuating pattern with x is comparable to the d_{33} value, and the highest value of k_p at $x = 0.12$ being 0.44. The enhanced piezoelectric properties are closely related to the gradual approach to room temperature of the T_{O-T} dielectric peak observed in Figure 4a–d. The polarization state becomes unstable due to the composition-induced O–T phase transition, permitting the polarization direction to simply be turned by an external stress or electric field, leading to the strong piezoelectricity.

Regarding the $(\text{Ba}_{0.85}\text{Ca}_{0.15})(\text{Zr}_y\text{Ti}_{1-y})\text{O}_3$ ceramics, the change in the piezoelectric properties shown in Figure 6b is consistent with that of the $(\text{Ba}_{1-x}\text{Ca}_x)(\text{Zr}_{0.1}\text{Ti}_{0.9})\text{O}_3$ ceramics, with maximum d_{33} and k_p values of 330 pC/N and 0.41 obtained at $y = 0.1$, respectively. The improvement of the piezoelectric properties can be attributed to the coexistence of the T and R phases at $y = 0.1$, as revealed by the XRD patterns shown in Figure 1d. Figure 6c,d presents the contour plots of the d_{33} and k_p values for the $(\text{Ba}_{1-x}\text{Ca}_x)(\text{Zr}_y\text{Ti}_{1-y})\text{O}_3$ ceramics with $0 \leq x \leq 0.18$ and $0 \leq y \leq 0.12$. In particular, the $(\text{Ba}_{0.85}\text{Ca}_{0.15})(\text{Zr}_{0.1}\text{Ti}_{0.9})\text{O}_3$ ceramic has optimal piezoelectric properties. Tian et al. [22] also reported the best properties at

this composition, although both ceramics were prepared by the conventional solid-phase method, but differences in the pre-firing, sintering, and polarization processes can cause the piezoelectric properties to be affected [19]. In our work, the $(\text{Ba}_{0.85}\text{Ca}_{0.15})(\text{Zr}_{0.1}\text{Ti}_{0.9})\text{O}_3$ ceramic exhibits high d_{33} and k_p values, which can be attributed to the existence of the O-T and R-T MPBs at room temperature and well-formulated microstructure.

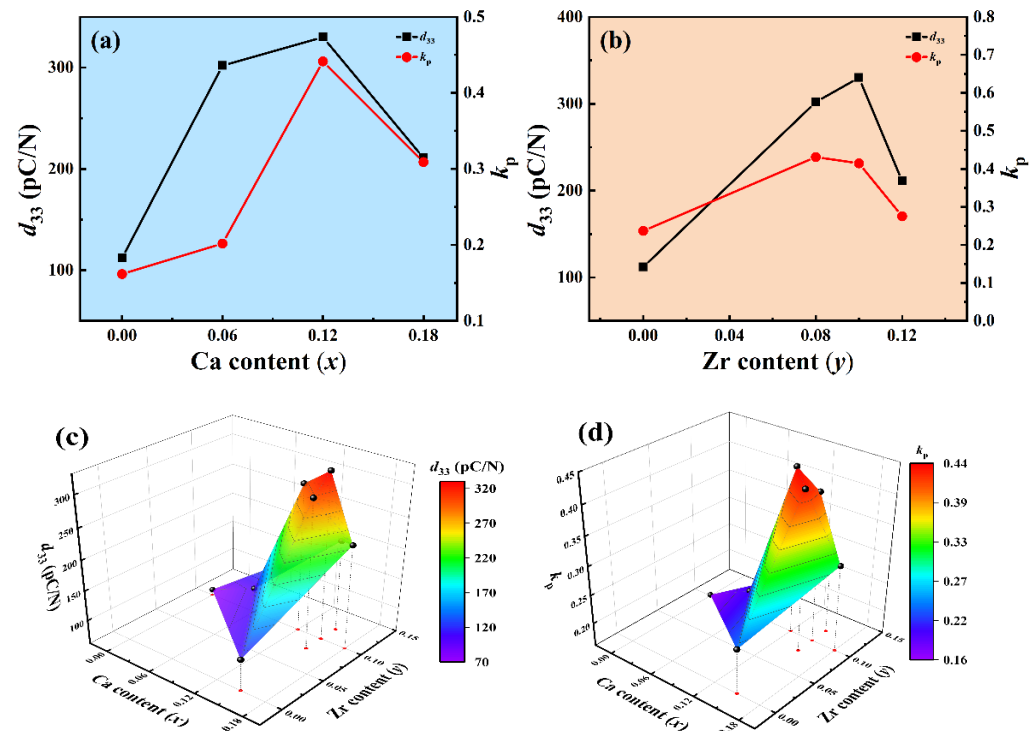


Figure 6. The d_{33} and k_p of (a) $(\text{Ba}_{1-x}\text{Ca}_x)(\text{Zr}_{0.1}\text{Ti}_{0.9})\text{O}_3$ ceramics and (b) $(\text{Ba}_{0.85}\text{Ca}_{0.15})(\text{Zr}_y\text{Ti}_{1-y})\text{O}_3$ ceramics at room temperature. Contour maps of (c) d_{33} and (d) k_p of the $(\text{Ba}_{1-x}\text{Ca}_x)(\text{Zr}_y\text{Ti}_{1-y})\text{O}_3$ ceramics with $0 \leq x \leq 0.18$ and $0 \leq y \leq 0.12$.

3.4. Ferroelectric Properties

Figure 7 displays polarization–electrical field (P – E) hysteresis loops of the $(\text{Ba}_{1-x}\text{Ca}_x)(\text{Zr}_{0.1}\text{Ti}_{0.9})\text{O}_3$ and $(\text{Ba}_{0.85}\text{Ca}_{0.15})(\text{Zr}_y\text{Ti}_{1-y})\text{O}_3$ ceramics with different Ca and Zr contents. Figure 7a displays that the BZT ($x = 0$) ceramic exhibits no ferroelectric hysteresis loop. However, ferroelectric properties appear after the addition of the Ca ions, and the best performance is achieved at $x = 0.12$, namely $P_r = 6.3 \mu\text{C}/\text{cm}^2$ and $E_c = 2.3 \text{ kV}/\text{cm}$. The room-temperature P_r and E_c values are summarized in Table 1. The enhancement of the ferroelectric properties may be explained by the fact that the Ca substitution diffuses the phase transition of BZT and causes the dielectric peak of T_{O-T} to shift toward room temperature as the Ca content increases. As shown in Figure 7b, the P – E loops of the $(\text{Ba}_{0.85}\text{Ca}_{0.15})(\text{Zr}_y\text{Ti}_{1-y})\text{O}_3$ ceramics show a small ferroelectric contribution with a remnant polarization $2P_r < 10 \mu\text{C}/\text{cm}^2$ at $y = 0$. However, as the Zr content increases, the loops become well-saturated and P_r increases, approaching $5 \mu\text{C}/\text{cm}^2$ for all ceramics at $0.08 \leq y \leq 0.12$. Additionally, E_c decreases gradually, reaching values of 4.6, 3.1, and $1.1 \text{ kV}/\text{cm}$ at $y = 0.08, 0.1$, and 0.12 , respectively, indicating an easy polarization mechanism of the material. In summary, both Ca and Zr elements have a significant effect on the ferroelectric properties of the BCZT ceramics.

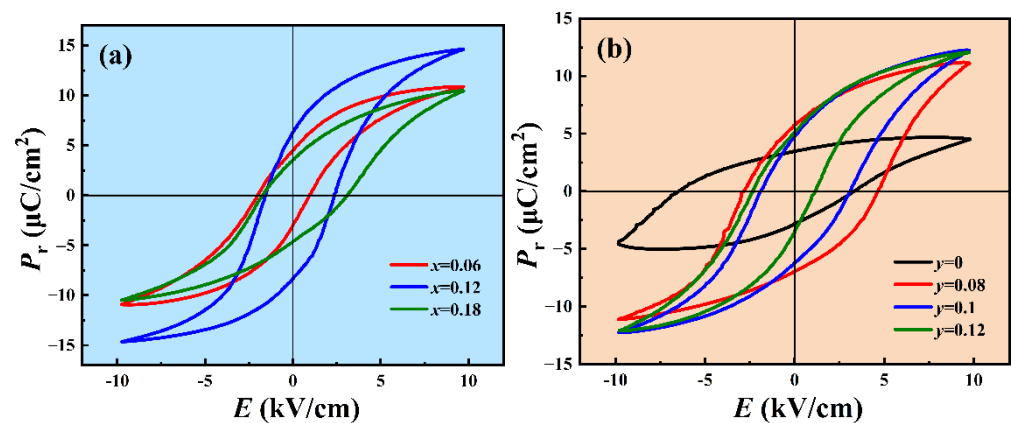


Figure 7. P - E loops of (a) the $(\text{Ba}_{1-x}\text{Ca}_x)(\text{Zr}_{0.1}\text{Ti}_{0.9})\text{O}_3$ ceramics and (b) $(\text{Ba}_{0.85}\text{Ca}_{0.15})(\text{Zr}_y\text{Ti}_{1-y})\text{O}_3$ ceramics.

4. Conclusions

In summary, the influences of Ca and Zr contents on the phase transition and electrical performances of $(\text{Ba}_{1-x}\text{Ca}_x)(\text{Zr}_{0.1}\text{Ti}_{0.9})\text{O}_3$ ($x = 0, 0.06, 0.12$, and 0.18) ceramics and $(\text{Ba}_{0.85}\text{Ca}_{0.15})(\text{Zr}_y\text{Ti}_{1-y})\text{O}_3$ ($y = 0, 0.08, 0.1$, and 0.12) ceramics have been systematically researched. The phase of $(\text{Ba}_{1-x}\text{Ca}_x)(\text{Zr}_{0.1}\text{Ti}_{0.9})\text{O}_3$ transforms from orthogonal to tetragonal near room temperature at $0.12 \leq x \leq 0.18$ via dielectric temperature curve. For $(\text{Ba}_{0.85}\text{Ca}_{0.15})(\text{Zr}_y\text{Ti}_{1-y})\text{O}_3$ ceramics, MPB region from tetragonal phase to rhombohedral phase at composition $0.08 \leq y \leq 0.1$ via XRD patterns. Moreover, the doped ceramics exhibited saturated P - E hysteresis loops and significantly optimized ferroelectric properties compared with the undoped ceramics. Results indicate that optimal electrical properties of $d_{33} = 330$ pC/N, $k_p = 0.41$, $\epsilon_r = 4069$, $P_r = 4.8$ $\mu\text{C}/\text{cm}^2$, and $E_c = 3.1$ kV/cm are achieved for the $(\text{Ba}_{0.85}\text{Ca}_{0.15})(\text{Zr}_{0.1}\text{Ti}_{0.9})\text{O}_3$ ceramic. Our study demonstrates the contribution of the Ca and Zr additions to the piezoelectric properties of BCZT ceramics in terms of the phase transition, microstructure, dielectric properties, and ferroelectricity, demonstrating a potential value of these lead-free ceramics.

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