Phase boundary design and high piezoelectric activity in $(1-x)(\text{Ba}_{0.93}\text{Ca}_{0.07})\text{TiO}_3$ - $x\text{Ba}(\text{Sn}_{1-y}\text{Hf}_y)\text{O}_3$ lead-free ceramics

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Abstract: The $(1-x)(\text{Ba}_{0.93}\text{Ca}_{0.07})\text{TiO}_3$ - $x\text{Ba}(\text{Sn}_{1-y}\text{Hf}_y)\text{O}_3$ (BCTSH- x - y) lead-free ceramics were synthesised by the conventional solid-state reaction method, and the influences of doping elements (Ca, Sn, Hf) content on their phase structure, microstructure, and electrical properties were systematically investigated. The phase boundaries concerning the orthorhombic and tetragonal (O-T) phases were found in the $0.925(\text{Ba}_{0.93}\text{Ca}_{0.07})\text{TiO}_3$ - $0.075\text{Ba}(\text{Sn}_{1-y}\text{Hf}_y)\text{O}_3$ ceramics with $0 \leq y \leq 0.25$, and then the enhanced piezoelectric properties with $d_{33} \sim 550 \text{ pC N}^{-1}$ were obtained. In addition, the addition of Hf can also improve the Curie temperature (T_C) and ferroelectric properties of the ceramics. As a result, the electrical properties of BaTiO_3 can be optimized by the construction of phase boundaries through Ca, Sn, and Hf co-doping.

Keywords: Lead-free piezoelectric; Barium titanate; Co-doping; Phase boundary; Electrical properties

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1. Introduction

Lead-based piezoelectric ceramics represented by $\text{Pb}(\text{Zr}_{1-x}\text{Ti}_x)\text{O}_3$ (PZT) are widely used in the commercial electronic devices due to their superior dielectric and piezoelectric properties [1]. However, the commercial manufacture and application of lead-based piezoceramics will be restricted because of its hazardous effects on the surrounding environment. Therefore, developing lead-free piezoelectric materials to replace PZT is a boost mission to reduce environmental contamination. Recently, a series of typical lead-free piezoelectric systems {i.e., BaTiO_3 (BT), $(\text{Bi,Na})\text{TiO}_3$ (BNT), and $(\text{K,Na})\text{NbO}_3$ (KNN)} have been highlighted to substitute for PZT [1–4]. Among these candidates, BaTiO_3 -based piezoceramics have been extensively investigated due to a high piezoelectricity, which are considered as a promising candidate for the replacement of lead -based ceramics [4–5].

Previously, it was reported that the enhanced piezoelectric properties of $\text{Ba}(\text{Zr}_{0.2}\text{Ti}_{0.8})\text{O}_3$ - $(\text{Ba}_{0.7}\text{Ca}_{0.3})\text{TiO}_3$ ceramics can be attained due to the involvement of morphotropic phase boundary (MPB) [4]. The physical origin for the improved piezoelectric activity should be assigned to a low energy barrier in the MPB region, which can greatly facilitate the process of polarization rotation and extension [4]. In addition, the phase instability located at phase boundaries can induce a low energy barrier, and the multiphase coexistence can increase the phase instability, hence leading to a high piezoelectric behavior [4, 6–7]. Meanwhile, there are three kinds of phase transitions of a BaTiO_3 material as the measurement temperatures increase, i.e., rhombohedral-orthorhombic phase transition temperature ($T_{\text{R-O}}$), orthorhombic-tetragonal phase transition temperature ($T_{\text{O-T}}$), and tetragonal-cubic phase transition temperature (T_{C}) [5]. Therefore, it is highly expected to construct the

phase boundaries of BT by shifting their T_{R-O} and T_{O-T} through doping other isovalent elements, thus resulting in the enhanced piezoelectric properties. In recently years, the addition of Ca and Sn, or Ca and Hf has been used to modify the A- and B-sites of BaTiO₃ materials [5, 8–10], forming the phase boundaries at/near room temperature by shifting their T_{R-O} and T_{O-T} , and then a large piezoelectric activity can be achieved. However, there are few systematical studies on the phase boundary and piezoelectric properties of Ca, Sn, and Hf co-doped BaTiO₃ ceramics.

In this work, the objective is to drive the formation of different phase boundaries by Ca, Sn, and Hf co-doped in the BaTiO₃ ceramics, and then obtain good electrical properties (e.g., dielectric, ferroelectric, and piezoelectric properties) and unveil its physical mechanisms in detail. We systematically studied the composition dependence of phase structure and electrical properties of $(1-x)(\text{Ba}_{0.93}\text{Ca}_{0.07})\text{TiO}_3-x\text{Ba}(\text{Sn}_{1-y}\text{Hf}_y)\text{O}_3$ {abbreviated as BCTSH- x - y , $0 \leq x \leq 0.15$, $0 \leq y \leq 1.0$ } lead-free ceramics prepared by the normal sintering reaction method. It was found that the phase boundary types are profoundly dependent on the Ca Sn, and Hf contents, and we obtained the R-O/O-T multiphases in BCTSH- x ceramics with $x=0.075$ and the O-T phase coexistence at $0 \leq y \leq 0.25$ for BCTSH- y ceramics. Finally, the enhanced piezoelectric activity was reached at these phase boundaries region.

2. Experimental procedure

The $(1-x)(\text{Ba}_{0.93}\text{Ca}_{0.07})\text{TiO}_3-x\text{Ba}(\text{Sn}_{0.50}\text{Hf}_{0.50})\text{O}_3$ {abbreviated as BCTSH- x ($y=0.50$)} and $0.925(\text{Ba}_{0.93}\text{Ca}_{0.07})\text{TiO}_3-0.075\text{Ba}(\text{Sn}_{1-y}\text{Hf}_y)\text{O}_3$ {abbreviated as BCTSH- y ($x=0.075$)} lead-free piezoelectric ceramics were prepared by the conventional solid-state method. Barium carbonate (BaCO₃, 99%), calcium carbonate (CaCO₃,

99%), stannic oxide (SnO_2 , 99.8%), hafnium oxide (HfO_2 , 99%), and titanium dioxide (TiO_2 , 98%) were used as the raw materials. All raw materials of this work were bought from Sinopharm Chemical Reagent Co., Ltd. The weighed powders were ball-mixed for 24h with ZrO_2 balls using ethanol as the medium. After drying the slurry, the dried mixtures were calcined at 1280°C for 3h. The resultant powders were remixed and pressed into disks of 10 mm diameter and 1 mm thickness under 10MPa using 8wt% polyvinyl alcohol (PVA) as the binder, followed by burning the binder at 850°C for 2h and all the samples were sintered at 1450°C for 3h in air. The sintered specimens were coated with silver paint on the upper and bottom surfaces and fired at 600°C for 10min for electrical measurements. The poling process was performed under a direct current electric field of 3kV/mm at suitable temperatures for 30 min in a silicone oil bath.

The phase structure of the samples was analyzed by X-ray diffraction with a $\text{Cu K}\alpha$ radiation ($\lambda=1.5406 \text{ \AA}$) (XRD, Bruker D8 Advanced XRD, Bruker AXS Inc., Madison, WI). Field emission-scanning electron microscopy (FE-SEM) (JSM-7500, Japan) was used to investigate the surface morphologies and element mapping of the sintered samples. The temperature dependence of dielectric properties was examined using an *LCR* meter (TH2816A, China) at 10 kHz under the temperature range of $-150^\circ\text{C}\sim 180^\circ\text{C}$. Ferroelectric properties (Polarization-Electric field loops) were measured using a Radiant Precise Workstation (Radiant Technologies, Medina NY) with a frequency of 10 Hz. Measurement of longitudinal piezoelectric coefficient (d_{33}) was characterized using a piezoelectric coefficient d_{33} testing meter (ZJ-3A, China), and the planar electromechanical coupling coefficient k_p was measured using an impedance analyzer (HP 4299A). The strain-electric field ($S-E$) curves were

measured by a strain analyzer (MT-2000).

3. Results and discussion

Figures 1(a) and (c) respectively show the XRD patterns of BCTSH- x and BCTSH- y ceramics, measured in $2\theta=20\text{--}70^\circ$ and $T=20\text{ }^\circ\text{C}$. In order to further judge their phase evolution, their amplified XRD patterns with $2\theta=44\text{--}46^\circ$ also display in Figs. 1(b) and (d). The standard diffraction peaks cited from BaTiO_3 with R, O, and T-symmetries (PDF#85-1797, PDF#81-2200 and PDF#05-0626) are indicated by vertical lines for comparison. As shown in Fig. 1, all samples have a pure phase of perovskite structure referring to the standard diffraction peaks, implying that Ca^{2+} , Sn^{4+} , and Hf^{4+} have been merged into the lattice of BCTSH- x - y to form a stable solid solution. More importantly, the phase structure of BCTSH- x - y ceramics is strongly dependent on the doping element concentrations. We can know from Fig. 1(b) that the diffraction peaks tend to shift to a lower angle with increasing x , indicating a shrinkage or expansion of unit cell in the ceramics [11]. The shifts of XRD peak positions should be attributed to the different radii of B-site ions in this system [12]. It is well known that the ionic radius of Ti^{4+} ($0.605\text{\AA}$) is smaller than those of Sn^{4+} ($0.69\text{\AA}$) and Hf^{4+} ($0.71\text{\AA}$), resulting in the increased lattice parameters with rising x when y (the content of Ca^{2+}) is fixed [12–14]. Meanwhile the diffraction peak positions for BCTSH- y ceramics are almost unchanged with increasing y due to similar radius between Sn and Hf [14], as shown in Fig. 1(d). In addition, the phase structure of the ceramics will be further identified using the correspondingly temperature-dependent dielectric constant (ϵ_r - T) curves (See Fig. 2). For the BCTSH- x ceramics, one can see from Fig. 1(b) that the T phase was observed in the ceramics with $x=0$ at room temperature, which matches the characteristics of reported BaTiO_3 , where left diffraction peaks approximate half of

right diffraction ones [15]. The O-T phase coexistence is shown in the ceramics with $x=0.05$, the R-O/O-T coexistence is found in the ones with $x=0.075$, the R-O phase coexistence is revealed with $x=0.10$, and the R phase is discovered for $0.125 \leq x \leq 0.15$. For the BCTSH- y ceramics, it also can be seen from Fig. 1(d) that the O-T phase coexistence was observed for $0 \leq y \leq 0.25$, and the R-O/O-T multiphase coexistence is shown at $y=0.5 \sim 1$.

Subsequently, we confirmed the composition dependence of the phase structure of BCTSH- x - y ceramics by characterizing ε_r - T curves. Figures 2(a) and (b) show the ε_r - T curves of BCTSH- x and BCTSH- y ceramics, measured at $-145 \sim 180^\circ\text{C}$ and 10 kHz. The insets are the corresponding expanded ε_r - T curves. It can be seen from Fig. 2 that three kinds of dielectric peaks (e.g., $T_{\text{R-O}}$, $T_{\text{O-T}}$, and T_{C}) can be clearly observed. As previously reported, their $T_{\text{R-O}}$ and $T_{\text{O-T}}$ can be shifted to a higher temperature and T_{C} decreases to lower temperature by replacing B-site (Ti^{4+}) using other equivalent elements [16–17]. We can see from Fig. 2(a) that $T_{\text{R-O}}$ and $T_{\text{O-T}}$ of BCTSH- x ceramics gradually shift to a higher temperature and T_{C} gradually lowers as the Sn and Hf contents increase. Consequently, both $T_{\text{R-O}}$ and $T_{\text{O-T}}$ linearly rise and gradually close, and finally merge into the T_{C} line with increasing x [18]. And for BCTSH- y ceramics, $T_{\text{R-O}}$, $T_{\text{O-T}}$, and T_{C} gradually shift to a higher temperature with increasing y (that is, increasing Hf content), which suggests that the addition of Hf can increase T_{C} value for the ceramics. The phenomenon of BCTSH- x - y ceramics more clearly display in their phase diagram, and finally the shifting of $T_{\text{R-O}}$ and $T_{\text{O-T}}$ results in different multiphase coexistence, as shown in Figs. 3(a)-(b).

In order to illuminate the relationships between grain sizes and compositions of

BCTSH- x - y ceramics, their FE-SEM images were carried out, as shown in Fig. 4. All samples featured a relatively dense microstructure. Meanwhile, we can find from Fig. 4 that their grain sizes are strongly dependent on the doping element contents. It can be seen from Fig. 4(g) that the grain sizes of BCTSH- x ceramics firstly increase and then decrease with increasing x . As shown in Fig. 4(h), the grain sizes of BCTSH- y ceramics firstly decrease and then almost keep unchanged with increasing y . Furthermore, we can know from Fig. 8 that d_{33} of BCTSH- x - y ceramics displays a similar changed trend comparing with their grain sizes, which implies that relatively large grain sizes can help obtain a high piezoelectric property [19]. In addition, Figures 5(a) and (b) show the composition dependence of element mapping of BCTSH- x - y ceramics in order to clearly display the elements distribution. One can see that all elements are homogenously distributed into the ceramics matrix

The different phase boundaries were successfully constructed in the BCTSH- x - y ceramics by tailoring the content of Ca, Sn, and Hf, and then the relationships among compositions, phase boundary types, and electrical properties were illustrated systematically. Figures 6(a) and (b) respectively show the composition dependence of polarization-electric field (P - E) loops of BCTSH- x and BCTSH- y ceramics, measured at 10 Hz and room temperature. The insets in Fig. 6 show the variations of remnant polarization P_r and coercive field E_c against the compositions. We can know that all ceramics exhibit typical and saturated P - E loops. For BCTSH- x , P_r firstly increases from $x=0$ to 0.075, and then dramatically decreases for $0.075 < x \leq 0.15$. However, E_c keeps a decreased trend with increasing x . Consequently, both higher P_r and lower E_c can be obtained for $x=0.075$ with the R-O/O-T phase boundaries, indicating that phase boundaries play an important role in the improved ferroelectric properties. Meanwhile,

one can know from Fig. 6(b) that the BCTSH- y ceramics exhibit similar P - E loops, confirming the similar ferroelectric characteristics of all ceramics. Their P_r values slightly change and then increase with further rising Hf content. In addition, their E_c values slightly fluctuate with varied y . As a result, the addition of Hf can optimize the ferroelectric properties of BCTSH- x - y ceramics.

Figures 7(a) and (b) respectively plot the composition dependence of dielectric constant ϵ_r and dielectric loss $\tan \delta$ of BCTSH- x and BCTSH- y ceramics, measured at 1 kHz and room temperature. As shown in Fig. 7(a), ϵ_r slightly increases at $0 \leq x \leq 0.10$ and dramatically increases at $x=0.10 \sim 0.15$ for BCTSH- x ceramics. The $\tan \delta$ presents a similar various trend, possessing a relatively low $\tan \delta$ (<0.03) for all the ceramics. For BCTSH- y ceramics, ϵ_r firstly decreases at $0 \leq y \leq 0.50$ and then basically keeps unchanged from $y=0.50$ to 1.0. And their $\tan \delta$ keeps changed with increasing y and also keeps a low $\tan \delta$ (<0.03).

Figures 8(a) and (b) respectively show the composition dependence of piezoelectric properties (d_{33} and k_p) of BCTSH- x and BCTSH- y ceramics. There is a similarly changed tendency of both d_{33} and k_p for BCTSH- x ceramics. d_{33} and k_p firstly increase and then decrease with increasing x , reaching the peak value of ~ 435 pC N⁻¹ and $k_p=0.51$ for the ones with $x=0.075$ due to the involvement of R-O/O-T phase boundary. Although the O-T phases coexist at $x=0.05$, the O-T phase boundary locates in a broad temperature region [See Fig. 3(a)], hence resulting in a weakly enhanced effect on piezoelectric properties [17, 20]. For BCTSH- y ceramics, they all possess high piezoelectric properties ($d_{33} > 435$ pC N⁻¹) due to the formation of the convergent O-T and R-O/O-T phase boundaries. The improved piezoelectric activity should be due to

the low energy barriers in the weak polarization anisotropy region, which can greatly facilitate the process of polarization rotation and extension [4, 6–7]. In addition, the phase instability at phase boundaries can also induce a low energy barrier, and the multiphase coexistence in a narrow temperature or composition region can increase the phase instability, hence resulting in a high piezoelectricity [6, 16, 22–26]. Here, the highest piezoelectric property of $d_{33}=550 \text{ pC N}^{-1}$ reached at $x=0$, and then basically remain unchanged ($d_{33}>525 \text{ pC N}^{-1}$) for BCTSH- y ceramics with $y=0$ to 0.25. As x further increases, d_{33} begins to slightly drop at $0.25<y\leq 0.50$, finally fluctuates slightly from $y=0.50$ to 1.0. However, k_p exhibits a different trend, and it slightly increases when d_{33} decreases. Consequently, the different phase boundary types (O-T at $0\leq y\leq 0.25$ and R-O/O-T at $0.50\leq y\leq 1.0$) should be responsible for the fluctuant piezoelectric properties of BCTSH- y ceramics.

In order to establish the relationships among dielectric, ferroelectric, and piezoelectric properties, the equation of $d_{33}\sim a\varepsilon_r P_r$ can be used to illuminate their relationships. Figures 9(a) and (b) respectively plot both $\varepsilon_r P_r$ and d_{33} of BCTSH- x ceramics and BCTSH- y , where ε_r , P_r , and d_{33} come from the data of Figs. 6–8. One can see that both $\varepsilon_r P_r$ and d_{33} firstly increase and then decrease, and the same peak value of $\varepsilon_r P_r$ and d_{33} can be attained in the region of phase boundaries for BCTSH- x ceramics. In addition, $\varepsilon_r P_r$ and d_{33} decrease slightly at $0\leq y\leq 0.25$ and then dramatically decrease from $y=0.25$ to 0.50, finally keeping unchanged from $y=0.50$ to 1.0. Consequently, we can see that both $\varepsilon_r P_r$ and d_{33} present a similarly changing tendency, that is, d_{33} reaches a maximum value when $\varepsilon_r P_r$ gets a peak value. This phenomenon indicates that high $\varepsilon_r P_r$ also plays an important role on getting high piezoelectric properties. It was proved that phase boundaries can lead to the enhanced ferroelectric property and

high dielectric constant, and hence a high d_{33} would be attained in BCTSH ceramics due to the formation of phase boundaries.

4. Conclusions

In this work, a large d_{33} of ~ 550 pC N⁻¹ has been attained in the $(1-x)(\text{Ba}_{0.93}\text{Ca}_{0.07})\text{TiO}_3-x\text{Ba}(\text{Sn}_{1-y}\text{Hf}_y)\text{O}_3$ ceramics prepared by the conventional solid-state method. We found that the phase boundary types strongly depend on the composition, which plays an important role on the enhanced piezoelectric activity and the optimized dielectric and ferroelectric properties. In addition, the addition of Hf can influence the electrical properties of the ceramics, and doping Hf can rise T_C and optimize the ferroelectric properties. As a result, the optimization of phase boundaries types as well as enhanced dielectric and ferroelectric properties are totally responsible for the high piezoelectric properties.

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Figure captions

Fig. 1 XRD patterns of BCTSH- x - y ceramics as a function of (a) x ($y=0.5$) and (c) y ($x=0.075$) in the 2θ range of $20\text{--}70^\circ$. (b) and (d) are their corresponding XRD patterns at $2\theta=44\text{--}46^\circ$.

Fig. 2 Temperature dependence of dielectric constant at 10 kHz of the ceramics as a function of (a) x ($y=0.5$) and (b) y ($x=0.075$). The insets are the corresponding expanded ε_r - T curves.

Fig. 3 Phase diagram of BCTSH- x - y ceramics with (a) x ($y=0.5$) and (b) y ($x=0.075$).

Fig. 4 FE-SEM images of BCTSH- x ceramics with (a) $x=0$, (b) $x=0.075$, and (c) $x=0.15$, BCTSH- y ceramics with (d) $y=0$, (e) $y=0.25$, and (f) $y=1.0$.

Fig. 5 Element mappings of the ceramics with (a) $x=0.075$ and $y=0.5$, (b) $x=0.075$ and $y=0.25$.

Fig. 6 Ferroelectric hysteresis loops of BCTSH- x - y ceramics with (a) x ($y=0.5$) and (b) y ($x=0.075$), where the insets in (a) and (b) are their corresponding P_r and E_c values.

Fig. 7 Composition dependence of ε_r and $\tan \delta$ for the BCTSH- x - y ceramics with (c) x and (d) y .

Fig. 8 Composition dependence of d_{33} and k_p for the BCTSH- x - y ceramics with (a) x and (b) y .

Fig. 9 Composition dependence of $\varepsilon_r P_r$ and d_{33} of (a) BCTSH- x and (b) BCTSH- y ceramics

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