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Full Length Article

Coexistence of three ferroelectric phases and enhanced piezoelectric properties in $BaTiO_3$–$CaHfO_3$ lead-free ceramics

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ABSTRACT

Perovskite ferroelectrics possess the fascinating piezoelectric properties near a morphotropic phase boundary, attributing to a low energy barrier that the results in structural instability and easy polarization rotation. In this work, a new lead-free system of (1-x)$BaTiO_3$-$x$$CaHfO_3$ was designed, and characterized by a coexistence of ferroelectric rhombohedral-orthorhombic-tetragonal (*R-O-T*) phases. With the increase amount of $CaHfO_3$ (x), a stable coexistence region of three ferroelectric phases (*R-O-T*) exists at $0.06 \leq x \leq 0.08$. Both large piezoelectric coefficient (d_{33} ~ 400 pC/N), inverse piezoelectric coefficient (d_{33}^* ~ 547 pm/V) and planar electromechanical coupling factor (k_p ~ 58.2%) can be achieved for the composition with $x = 0.08$ near the coexistence of three ferroelectric phases. Our results show that the materials with the composition located at a region where the three ferroelectric *R-O-T* phases coexist would have the lowest energy barrier and thus greatly promote the polarization rotation, resulting in a strong piezoelectric response.

1. Introduction

Lead-based piezoelectric materials (such as $Pb(Zr,Ti)O_3$ (PZT)) have been widely used because of their amazing piezoelectric properties near the morphotropic phase boundary (MPB) [1,2]. Originally, the term 'morphotropic' refers to phase transitions induced by the changes in composition, but it has been mainly used for the common 'morphotropic phase boundaries' (MPB) that separate regions of tetragonal symmetry from those of rhombohedral symmetry by varying the composition in ferroelectrics [3]. Many researchers [4,5] attempted to investigate and explain the mechanism for ultra-high piezoelectric performance of the materials near the MPB. Isupov [6] emphasized the importance of the two phase coexistence: since the rhombohedral and tetragonal structures have eight and six possible polarization orientations, respectively, the ferroelectrics near the MPB have 14 possible polarization orientations, leading to a great piezoelectric coefficient and planar electromechanical coupling factor. In 1999, Noheda et al. [4] found that the monoclinic phase, as the transitional state of rhombohedral and the tetragonal phases, is the reason for the improvement of piezoelectric performance [7,8]. In 2000, Fu and Cohen [9] proposed a widely accepted polarization deflection theory to explain high piezoelectric properties of perovskite-type ferroelectrics. Meanwhile, some researchers suggested that the structural origin of enhanced piezoelectric performance is that the materials possess the multi-level domain structure near the MPB [10–14]. In addition, it is also believed that the physical origin of large piezoelectric response should be assigned to the low energy barrier in the region of phase boundaries [15–18], which can greatly facilitate the process of polarization rotation and extension. Especially, when the direction of polarization increases, the lowest energy barrier could be easily achieved [15]. Based on the aforementioned studies, it can be reasonably anticipated that the perovskite ferroelectrics located at a zone with the coexistence of the ferroelectric rhombohedral-orthorhombic-tetragonal (*R-O-T*) phases would provide more polarization directions than those with the coexistence of two ferroelectric phases or the existence of a single phase, because the orthorhombic structure (i.e., third phase) has 12 possible polarization orientations. Therefore, constructing the coexistence of three ferroelectric phases is pivotal for developing the high-performance piezoelectric ceramics.

Recently, lead-free piezoelectric ceramics have attracted extensive concern [16,19–22]. Similar to the MPB behavior in the PZT system, good piezoelectric properties of lead-free ceramics are also contributed to MPB-like behavior where two phases (or multi-phases) coexist. Ren et al. obtained the rhombohedral-tetragonal-cubic (*R-T-C*) phases coexistence in $Ba(Ti_{0.8}Hf_{0.2})O_3$-$(Ba_{0.7}Ca_{0.3})TiO_3$ ceramic that achieved a high d_{33} of ~ 550 pC/N [16]; however, the cubic phase (third phase) generally leads to the low Curie temperature. In addition, Wu et al. attained the *R-O-T* three ferroelectric phases coexistence in the (1-x-y)

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$K_{0.5}Na_{0.5}Nb_{0.96}Sb_{0.04}O_3$-$x$$BaSnO_3$-$y$$Bi_{0.5}Na_{0.5}ZrO_3$ ceramics using the variations of x and y, and the material exhibited a large d_{33} of ~480 pC/N [21]. Obviously, designing the materials with two phases or multi phases coexistence near room temperature can contribute to the enhancement of the piezoelectric properties. It should be noted that barium titanate ($BaTiO_3$)-based ferroelectrics have become the hotspots in recent years because basic rules of perovskite $BaTiO_3$ are applicable to complex perovskite material systems [9,23]. As is known to all, the $BaTiO_3$ undergoes three phase transitions as the temperature increases, i.e., rhombohedral-orthorhombic phase transition (T_{R-O}) at −90 °C, orthorhombic-tetragonal phase transition (T_{O-T}) at 5 °C, and tetragonal-cubic phase transition (T_C) at ~120 °C. It has been reported that T_{R-O} and/or T_{O-T} may be tuned by the partial substitutions of isovalent elements for Ba^{2+} in the A sites and/or Ti^{4+} in the B sites [15,24]. For example, the phase transformation temperatures from tetragonal to orthorhombic (T_{O-T}) and orthorhombic to rhombohedral phase (T_{R-O}) can be shifted to room temperature by doping Sn^{4+} [25], Zr^{4+} [26], Hf^{4+} [16] at the B-site in the $BaTiO_3$-based system, while the A-site replacement of Ba^{2+} by Ca^{2+} [27] and Sr^{2+} [28] can shift the T_{O-T} and T_{R-O} to low temperatures in the $BaTiO_3$-based system. Therefore, in this work, a lead-free system of (1-x)$BaTiO_3$-$x$$CaHfO_3$ (abbreviated as (1-x)BT-xCH) with the coexistence of three ferroelectric phases (rhombohedral, orthorhombic and tetragonal phases) was designed and obtained by co-substituting Ca^{2+} and Hf^{4+} for Ba^{2+} and Ti^{4+}. The phase structure and physical origin of strong piezoelectricity in the ceramics were investigated.

2. Experimental

The lead-free ceramics of (1-x)$BaTiO_3$-$x$$CaHfO_3$ were synthesized using a conventional solid-state reaction. Raw materials of $BaCO_3$ (99.9%), $CaCO_3$ (99.9%), TiO_2 (99.9%) and HfO_2 (99.9%) in the stoichiometric ratio of (1-x)$BaTiO_3$-$x$$CaHfO_3$ were mixed thoroughly in ethanol using zirconia balls for 10 h. After calcined at 1100 °C for 4 h, the mixture was ball-milled for 8 h again. The resultant powders were remixed utterly with a polyvinyl alcohol (PVA) binder solution, and then pressed into disks of 10 mm diameter and 1 mm thickness. Followed by burning the binder at 650 °C for 2 h, the samples were sintered at 1350 °C for 2 h. Silver pastes were fired on the top and bottom surfaces of the sintered ceramics at 650 °C for 30 min for electrical measurements. The ceramics were poled under a dc field of 3 kV/mm at room temperature for 30 min in a silicone oil bath.

The crystal structure of the ceramics was studied by XRD with CuKα radiation (SmartLab, Rigaku, Japan). A continuous scanning was carried out at a scan step of 0.01° in the 2θ range of 20°–70°. The microstructure of the ceramics was observed using scanning electron microscopy (FEI-Quanta250, FEI, Netherlands). The bulk densities of ceramics were measured by the Archimedes' method. The average grain sizes were obtained by multiplying the average linear intercept length of grains by 1.56 [29–31]. The relative permittivity ε_r of the sintered samples was measured by an LCR meter (Agilent E4980A, Agilent Technologies Inc, Malaysia) from −120 to 180 °C controlled by the temperature controlled probe stage (LinkamTS1500E, Linkam Scientific Instruments Ltd, Britain). The planar electromechanical coupling factor k_p was measured by the resonance method according to the IEEE Standards 176 using an impedance analyzer (Agilent 4294A, Agilent Inc, Malaysia). The polarization versus electric field (P–E) hysteresis loops were measured at room temperature using a precision materials measuring system (Premier II, Radiant Technologies Inc, USA). The strain electric field (S-E) curves were measured by a strain analyzer (Precision multiferroelectric, Radiant Technologies Inc., Albuquerque, NM) connected with an accessory laser interferometer vibrometer (AE SP-S 120E, SIOS Meβtechnils, GmbH, llmenau, Germany). The piezoelectric constant d_{33} was measured using a quasistatic piezoelectric meter (ZJ-6A, Chinese Academic Society, China) for the poled samples. The DSC curves were measured by a differential scanning calorimetry (Discovery DSC, America). The room-temperature Raman spectra of the ceramics were measured using a LabRAM HR Evolution (Horiba JobinYvon Company, French) spectrometer. And the variable temperature Raman spectra of the $1.12BaTiO_3$-$0.08CaHfO_3$ ceramic were recorded by a THMS600 spectrometer (Horiba JobinYvon Company, French).

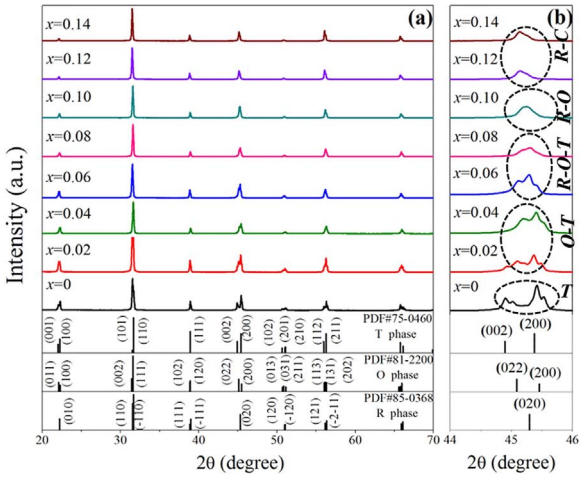

Fig. 1. XRD patterns of BTCH ceramics in the 2θ of (a) 20 °–70 °, and (b) 44 °–46 °.

3. Results and discussion

Fig. 1 displays the room temperature XRD patterns of (1-x)BT-xCH ceramics with x. From Fig. 1(a), all ceramics present a pure perovskite structure without any secondary phases, suggesting that $CaHfO_3$ has completely diffused into the lattice of $BaTiO_3$ to form a homogeneous solid solution. One can see that a typical tetragonal phase could be identified at $x = 0$, which is similar to the previous report [24]. With x increasing from 0.02 to 0.04, the phase structure of the ceramics shifts from the tetragonal to the orthorhombic phase, and the rhombohedral (R), orthorhombic(O), and tetragonal (T) phases coexist in the composition of $0.06 \le x \le 0.08$. As x further increases to 0.10, the ceramics show the mixed phase of R and O, while the R and C phases coexist at $0.12 \le x \le 0.14$.

In order to characterize the phase transition, the Rietveld refinement for the ceramics with $x = 0.02$, 0.06, 0.08, 0.12 were conducted using General Structure Analysis System (GSAS) software package, and the results and corresponding structural parameters are shown in Fig. 2 and Table 1, respectively. One can clearly notice from Fig. 2 and Table 1, for all refinements, the final factors of χ^2, R_{wp}(%) and R_p(%) are not lager than 1.882, 4.02% and 3.13%, respectively, suggesting a good agreement between the observed and calculated patterns. For $x = 0.02$, the contents of P4 mm (tetragonal) and Amm2 (orthorhombic) phases are 66.8% and 33.2%, respectively. For $x = 0.06$ and $x = 0.08$, the contents of P4 mm (tetragonal), Amm2 (orthorhombic) and R3 m (rhombohedral) phases are 34.8%, 32.1% and 33.1% ($x = 0.06$) and 29.6%, 35.8% and 34.6% ($x = 0.08$), respectively, indicating that the R-O-T three ferroelectric phases coexist. And for $x = 0.12$, the R3 m (rhombohedral) and Pm–3 m (cubic) phases are found with the contents of 57% and 43%, respectively. Wu [32] reported that regardless of the presence of MPB or polymorphic phase transition (PPT) characteristics, the polarization of a piezomaterial can be more easily rotated among different symmetries when the composition is located at the phase boundaries. The easy rotations of polarization axes can be induced in the compositions near such a phase boundary, resulting in an enhancement of dielectric and piezoelectric properties. Therefore, it can be inferred that the optimal piezoelectric response may be obtained in the ceramics at $x = 0.06$ or 0.08.

Fig. 3(a–h) shows the temperature dependences of ε_r of all samples at 1 kHz, while the insets are the corresponding expanded ε_r-T curves. It