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Original Article

Y_2O_3 doped $Ba_{0.9}Ca_{0.1}Ti_{0.9}Sn_{0.1}O_3$ ceramics with improved piezoelecrtric properties

Zhi-hui Chen[a,*], Zhi-wei Li[a], Jian-hua Qiu[a], Tian-xiang Zhao[a], Jian-ning Ding[a], Xu-guang Jia[a], Wei-qin Zhu[b], Jiu-jun Xu[c,*]

[a] School of Materials Science and Engineering, Jiangsu Collaborative Innovation Center of Photovolatic Science and Engineering, Jiangsu Province Cultivation base for State Key Laboratory of Photovoltaic Science and Technology, Changzhou University, Changzhou, 213164, Jiangsu, China
[b] Suzhou Institute of Nano-Tech and Nano-bionics, Chinese Academy of Sciences, Suzhou, 215123, Jiangsu, China
[c] Dalian Maritime University, Dalian, Liaoning 116026, China

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ABSTRACT

Lead-free $Ba_{0.90}Ca_{0.10}Ti_{0.90}Sn_{0.10}O_3$-$xY_2O_3$ (BCTSY, x = 0–0.09) ceramics were prepared by traditional solid-state sintering method. All the BCTSY samples showed pure perovskite structures without detectable impurity. Orthorhombic/tetragonal phase coexisted in the sample of x = 0.03 to 0.07. Remarkable enhancement of the electric properties were achieved at x = 0.03 with d_{33} of 650 pC/N, K_p of 59.6%, and the remnant polarization P_r of 10.2 μC/cm^2. The strengthened temperature stability of piezoelectricity is beneficial to the application of the piezoceramics.

1. Introduction

Lead zirconate titanate (PZT) based materials have dominated almost all the piezoelectric applications due to their superior piezoelectric properties [1]. However, the environment legislastion and human health concern pushed the development of lead-free piezoelectrics with enviromnental friendliness and good piezoeletric properties, such as barium titanate, $BaTiO_3$ (BT) based pseudo-binary ceramcs and (K,Na)NbO_3 based pseudo-ternary ceramics [2–5]. Ca^{2+} and Zr^{4+} co-doped BT system [6,7], typicallly, $Ba(Zr_{0.2}Ti_{0.8})_{0.3}$-x $(Ba_{0.7}Ca_{0.3})TiO_3$ (BCZT) with exceptional high piezoeletric constant (d_{33} = 620pC/N [8]) matches with the conventionally used PZT-5H. Ca^{2+} and Sn^{4+} co-doped BT ceramics with d_{33} up to 578pC/N was developed to a high performance (Ba, Ca)(Ti, Sn)O_3 (BCTS)system [9]. Recent studies further confirmed the high piezoelectric coefficient (> 440 pC/N) of the BCTS system [10,11]. It is generally recognized that the high piezoelectric properties are related to the composition induced MPB with the coexistence of the rhombohedral and tetragonal phases near room temperature. However, in most cases, the piezoelectric properties improvment inevitably combined with the unfavorable decrease of Curie temperature (T_C), which shortens the usage temperature range of the devices. To achieve both excellent piezoelectricity and high Curie temperature in BCTS piezoceramics, the substitution ions that could raise T_C are desired. In this work, a non-Pb pseudobinary Y^{3+} doped BCTS ferroelectric system is designed. $Ba_{0.9}Ca_{0.1}Ti_{0.9}Sn_{0.1}O_3$ is selected as a composition near the MPB based on our prior research on preparing BCTS ceramics [12–14]. The effects of Y^{3+} doping on the phase structure, T_{O-T}, T_C, dielectric property and piezoelectricity are systemically discussed.

2. Experiments

$BaCO_3$ (99.9%), $CaCO_3$ (99.9%), TiO_2 (99.9%), SnO_2 (99.5%) and Y_2O_3 (99.99%) powders were used as starting chemicals. The stoichiometric amounts of the starting materials were mixed for 1 h in ethanol medium according to the compositional formula $Ba_{0.90}Ca_{0.10}Ti_{0.90}Sn_{0.10}O_3$-$xY_2O_3$ (x = 0–0.09). The mixed mixture was calcined at 1200 °C for 4 h in air. The synthesized powders were mixed with 8 wt% polyvinyl alcohol (PVA) binder solution and then dry pressed into pellets. The pellets were sintered at 1460 °C for 2 h after burning out the binder at 550 °C for 2 h.

Crystal structure of the sintered BCTSY ceramics was investigated by X-ray diffractometer (Rigaku D/max-2500/PC, Japan, Cu $K\alpha_1$, λ = 1.5406 Å). Unit cell volumes of the ceramics were calculated from the diffraction data using the Wincell and Winplote software. The densities of the sintered pellets were determined by Archimedes' method. Scanning electron microscope (SEM, HITACHI S-4300) was used to observe the surfaces of the ceramics after thermally etched at 1150 °C for 2 h. The sintered pellets for electrical property measurements were well polished on both sides to obtain parallel surfaces. Silver paste on the surfaces was fired at 550 °C for 30 min to obtain

* Corresponding authors.
E-mail addresses: czh@cczu.edu.cn (Z.-h. Chen), jjxu@dlmu.edu.cn (J.-j. Xu).

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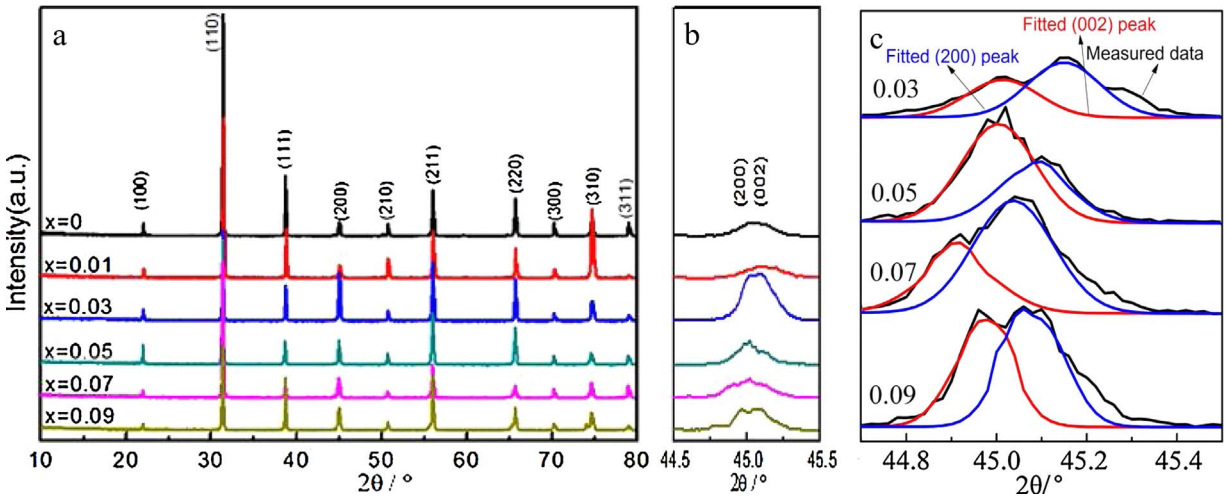

Fig. 1. XRD patterns of the BCTSY ceramics at x = 0 to 0.09°.

electrodes. Dielectric property was measured by a TH2818 Automatic Component Analyzer (Changzhou Tonghui Electronic Co., Ltd., China). Polarization–electric field (P–E) hysteresis loops of the sintered samples were characterized by a Radiant Precision Premier LC ferroelectric material test system (Radiant Technologies Inc., USA). The specimens were polarized under an electric field of 1.5–3.5 kV/mm with an interval of 0.5 kV/mm for 15 min in silicon oil at room temperature, and the poled pellets were insulated for 2 h at every anneal temperature from 30 °C to 90 °C. The corresponding piezoelectric constant was measured by a quasi-static d_{33} meter (ZJ-3AN, China).

3. Results and discussion

Fig. 1a shows normalized XRD patterns of the BCTSY ceramics with different Y content. All the sintered samples present pure perovskite structure without detectable impurity within the detection limitation of the XRD measurement, indicating that Y^{3+}, Ca^{2+} and Sn^{4+} ions may diffuse into the $BaTiO_3$ lattice to form complete solid solution in the discussed composition. The samples of x = 0 and x = 0.01 exist single peak of (200) at θ near 45°, which exhibits splitting trend into two mixed diffraction peaks in the samples of x = 0.03 to 0.07, suggesting an orthorhombic/tetragonal coexistence phase shown in Fig. 1b [10,15,16]. To further identify the phase evolution, diffraction peaks of the samples of x = 0.03–0.09 were fitted using the full diffraction profile fitting of the MDI Jade 5.0 software and were shown in Fig. 1c [17]. The intensity of the (200) peak grows stronger in the samples of x = 0.03–0.07, showing a phase transition trend from orthorhombic to tetragonal phase. The intensities of (002) and (200) peaks become almost the same at x = 0.09, suggesting the formation of tetragonal phase. For the samples of x = 0.01 to 0.05, the diffraction peaks shift to higher angle with increasing x, indicating that Y^{3+} (0.123 nm, CN = 12) substitute in Ba^{2+} (0.135 nm) site and the unit cell of the structure shrinks as shown in Fig. 3. For the samples of x > 0.05, the diffraction peaks shift to lower angle, corresponding to the increase of the unit cell volume. This may be mostly attributed to the Y^{3+} ions (0.090 nm, CN = 6) [18] substitution in the Ti^{4+} (0.068 nm) or Sn^{4+} (0.071 nm) site of the structure. As reported by Tsur [19], the ions might occupy both A-site and B-site with different ratios of the perovskite ABO_3 structure, if the ionic radius is between 0.087 nm and 0.094 nm [20,21]. The peak shifting extent depends on the different compensation mechanisms at specific content [22,23].

Fig. 2 shows SEM micrographs of the BCTSY ceramics with x = 0–0.09. Few pores exit in the grain boundary of the un-doped BCTS ceramics (x = 0). The microstructures become uniformly distributed with the addition of Y_2O_3. The corresponding relative density of the samples is 94.8%, 96.7%, 96.8%, 96.3%, 93.3%, and 93.1% at x = 0, 0.01, 0.03, 0.05, 0.07 and 0.09, respectively as shown in Fig. 3. It is notable that excess amount of Y_2O_3 leads to the decrease of the densities, which suggests that the addition of appropriate amount of Y_2O_3 is beneficial to motivate the formation of homogeneous microstructures during sintering. The inset of each micrograph in Fig. 2 shows that the average grain size decreases gradually from 53 μm at x = 0 to 33 μm at x = 0.09 with increasing Y content. The effect in restraining grain growth of Y_2O_3 is consistent with the literature [24,25].

The poling electric field influence on the piezoelectric constant d_{33} and electromechanical coupling factor K_p is given in Figs. 4 and 5, respectively. Both d_{33} and K_p of the BCTSY ceramics increase with the poling electric field from 1.5–3.5 kV/mm, and exhibit maximum values under 3.0–3.5 kV/mm due to the non−180° domains switching under higher poling electric field. Additionally, the d_{33} value increases from 496 pC/N (x = 0) to 558 pC/N (x = 0.01), and reaches a maximum value to 650 pC/N at x = 0.03, then decreases to 579 pC/N (x = 0.05), and keeps decreasing to values lower than the pure BCTS. Similar changing tendency is observed in K_p, which increases to the maximum value of 59.6% at x = 0.03. The improvement of the piezoelectric properties at x = 0.03–0.07 is related to the MPB effect [26–28] and the microstructure. The free energy around the MPB composition is isotropic and is in dependent of the poling direction, which leads to a low energy barrier for the polarization rotation, thus giving rise to high piezoelectric properties [4,8]. In the case of the ionic radii, the A-site substitution as donor at x = 0.01 to 0.05 can be formulated according to Jeong [23].

$$Y_2O_3 + 2TiO_2 \rightarrow 2Y^{\circ}_{Ba} + 2Ti_{Ti} + 6O_o + \frac{1}{2}O_2 + 2e' \quad (1)$$

$$3Y_2O_3 + 6TiO_2 \rightarrow 6Y^{\circ}_{Ba} + 6Ti_{Ti} + V''_{Ba} + V'''_{Ti} + 21O_o \quad (2)$$

The generated vacancies can provide larger space, making strain energy decreases during the domain rotation process. The reducing of the energy consumption facilitates the movement of the domains, thus contributes to the improvement of the piezoelectric properties. The grain size of the ceramics becomes smaller with the increase of Y