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Phase boundary design and high piezoelectric activity in $(1-x)(Ba_{0.93}Ca_{0.07})TiO_3$-$xBa(Sn_{1-y}Hf_y)O_3$ lead-free ceramics

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ABSTRACT

The $(1-x)(Ba_{0.93}Ca_{0.07})TiO_3$-$xBa(Sn_{1-y}Hf_y)O_3$ (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 $0.925(Ba_{0.93}Ca_{0.07})TiO_3$-$0.075Ba(Sn_{1-y}Hf_y)O_3$ ceramics with $0 \le y \le 0.25$, and then the enhanced piezoelectric properties with $d_{33} \sim 550$ 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.

1. Introduction

Lead-based piezoelectric ceramics represented by $Pb(Zr_{1-x}Ti_x)O_3$ (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), $(Bi,Na)TiO_3$ (BNT), and $(K,Na)NbO_3$ (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 $Ba(Zr_{0.2}Ti_{0.8})O_3$-$(Ba_{0.7}Ca_{0.3})TiO_3$ 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 ($T_{R\text{-}O}$), orthorhombic-tetragonal phase transition temperature ($T_{O\text{-}T}$), and tetragonal-cubic phase transition temperature (T_C) [5]. Therefore, it is highly expected to construct the phase boundaries of BT by shifting their $T_{R\text{-}O}$ and $T_{O\text{-}T}$ 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 $BaTiO_3$ materials [5,8–10], forming the phase boundaries at/near room temperature by shifting their $T_{R\text{-}O}$ and $T_{O\text{-}T}$, 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 $BaTiO_3$ ceramics.

In this work, the objective is to drive the formation of different phase boundaries by Ca, Sn, and Hf co-doped in the $BaTiO_3$ 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

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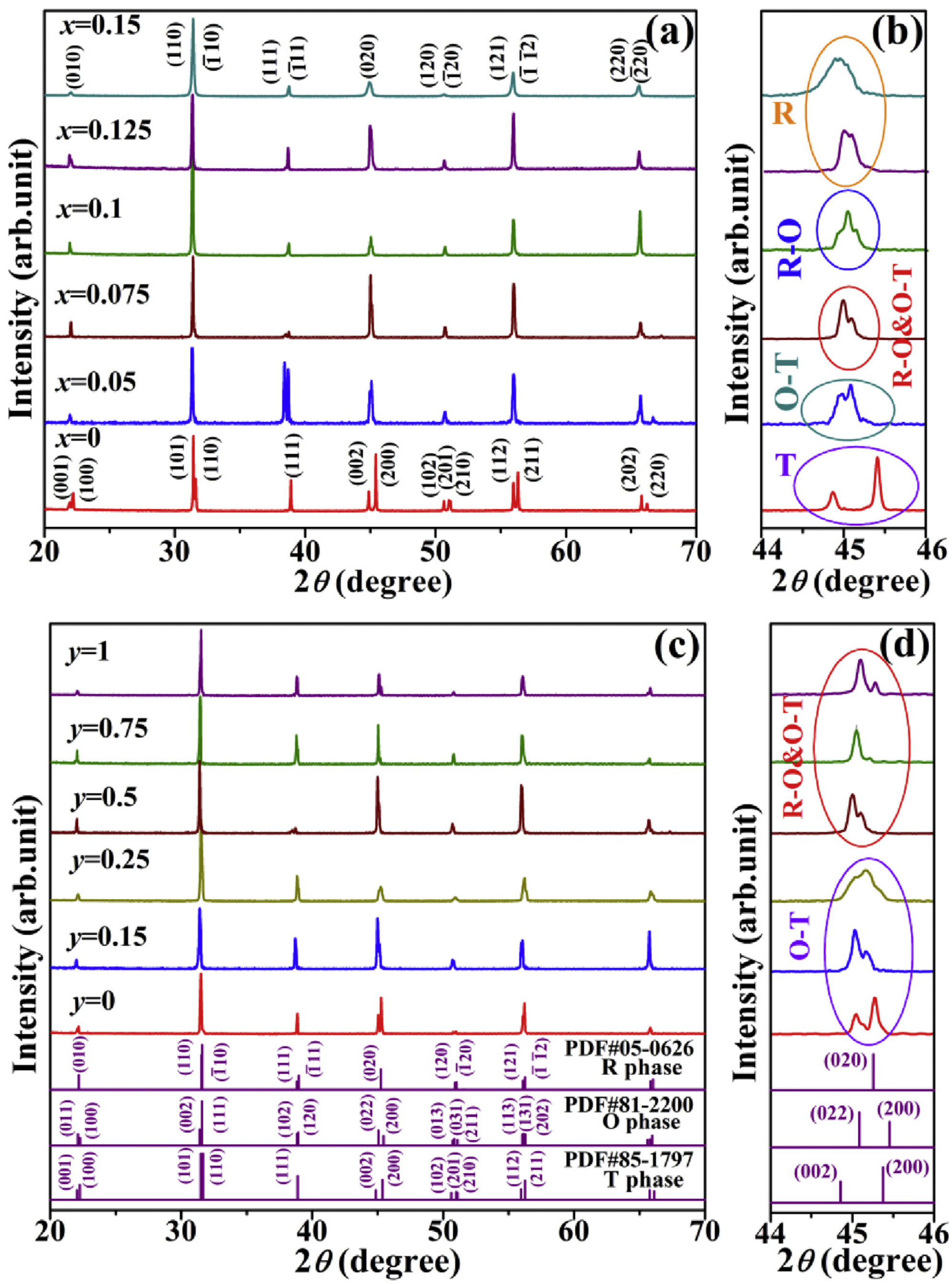

Fig. 1. XRD patterns of BCTSH-x-y ceramics as a function of (a) x (y = 0.5) and (c) y (x = 0.075) in the 2θ range of 20–70°. (b) and (d) are their corresponding XRD patterns at 2θ = 44–46°.

$(1-x)(Ba_{0.93}Ca_{0.07})TiO_3$-$x$$Ba(Sn_{1-y}Hf_y)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 $(1-x)(Ba_{0.93}Ca_{0.07})TiO_3$-$x$$Ba(Sn_{0.50}Hf_{0.50})O_3$ {abbreviated as BCTSH-x ($y = 0.50$)} and $0.925(Ba_{0.93}Ca_{0.07})TiO_3$-$0.075Ba(Sn_{1-y}Hf_y)O_3$ {abbreviated as BCTSH-y ($x = 0.075$)} lead-free piezoelectric ceramics were prepared by the conventional solid-state method. Barium carbonate ($BaCO_3$, 99%), calcium carbonate ($CaCO_3$, 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 24 h with ZrO_2 balls using ethanol as the medium. After drying the slurry, the dried mixtures were calcined at 1280 °C for 3 h. The resultant powders were remixed and pressed into disks of 10 mm diameter and 1 mm thickness under 10 MPa using 8 wt% polyvinyl