Journal of Alloys and Compounds 637 (2015) 137–142

Contents lists available at ScienceDirect

Journal of Alloys and Compounds

journal homepage: www.elsevier.com/locate/jalcom

# Phase transition and enhanced electrical properties in $0.725BiFeO_3$-$0.275Ba_{0.85}Ca_{0.15}Ti_{0.9}Zr_{0.1-x}Sn_xO_3$ multiferroic ceramics

Donghui Zhang, Yujie Gan, Tingkai Chen, Shenghong Yang, Yueli Zhang *

*State Key Laboratory of Optoelectronic Materials and Technologies, School of Physics & Engineering, Sun Yat-sen University, Guangzhou 510275, PR China*

ARTICLE INFO

*Article history:*
Received 18 December 2014
Received in revised form 14 February 2015
Accepted 16 February 2015
Available online 23 February 2015

*Keywords:*
Phase transition
Relaxor ferroelectrics
Curie temperature
Sn doping

ABSTRACT

Lead-free $0.725BiFeO_3$-$0.275Ba_{0.85}Ca_{0.15}Ti_{0.9}Zr_{0.1-x}Sn_xO_3$ (BF-BCTZS-1000$x$, $x = 0$, 0.025, 0.050, 0.075, 0.100) multiferroic ceramics were fabricated via a conventional solid-state reaction method. Effects of Sn substitution on the structural, electrical and magnetic properties have been studied. The XRD patterns reveal that the pseudocubic structure of the ceramics transforms into rhombohedral after Sn substitution for Zr. The SEM images show that Sn doping effectively facilitates the grain growth and densification of the ceramics. Room-temperature dielectric properties are apparently improved. The temperature-dependent dielectric results show that the Curie temperature of the BF-BCTZS-1000$x$ increases almost linearly from 401.0 °C to 418.8 °C with the increasing Sn content, and the diffusivity $\gamma$ of the system decreases from 1.958 to 1.361. Both remnant polarization and hysteresis loop squareness of BF-BCTZS-1000$x$ ceramics are improved obviously after Sn substitution. Piezoelectric coefficient shows a sharp increase after Sn substitution and decreases slightly with further increase of Sn content. Weak ferromagnetism is revealed in all BF-BCTZS-1000$x$ ceramics, but is weakened for Sn-doped samples.



## 1. Introduction

As a single-phase multiferroic material, bismuth ferrite ($BiFeO_3$, BF) shows linear magnetoelectric effect at room temperature [1]. By the magnetoelectric effect, the magnetization of a material can be manipulated through an applied electric field, and the polarization of the material can be induced with an applied magnetic field [2]. The multiferroic materials have wide potential applications in multifunctional instruments [2–5]. For instance, they can be utilized to produce multistate memories that can be electrically written and magnetically read, combining the advantages of high-speed writing and nondestructive reading operations [6–9].

Being the only room-temperature-stable single-phase multiferroic material, BF is antiferromagnetic below 370 °C and ferroelectric below 830 °C [10]. BF faces several obstacles on its way of application: instability during high-temperature processing, high conductivity and weak magnetoelectric coupling [2,8,11].

To suppress the conductivity and impurity phases of BF, an incorporation of BF with barium titanate- (BT-) based piezoelectric materials is often used [12–14], and the resultant solid solutions show improved resistivity and ferroelectric properties. The antiferromagnetic canting structure of BF can be deteriorated in the solid solution, turning the materials into ferromagnetic. Moreover, when a ferromagnetic material incorporates with a ferroelectric material, a multiferroic composite will be formed, whose magnetoelectric coefficient is larger than that of a single-phase multiferroic material [2,15].

In the recent years, a new and highlighted member of BT-based piezoelectrics, $(Ba_{0.85}Ca_{0.15})(Ti_{0.9}Zr_{0.1})O_3$ (BCTZ), has attracted much attention for its extraordinary piezoelectric properties ($d_{33}$ = 630 pC/N) [16–19]. The strong piezoelectric properties make the BCTZ a perfect candidate as the ferroelectric component of a multiferroic composite. In 2012, Wu et al. [20] fabricated $(1-x)$BCTZ-$x$BF ceramics at $0 \leqslant x \leqslant 1.0$ mol% with a solid-state reaction method, and obtained a high $d_{33}$ of 405 pC/N at $x = 0.2$ mol%. In 2014, Lin et al. [21] prepared $(1-x)$BF-$x$BCTZ ceramics at $0.15 \leqslant x \leqslant 0.35$, and observed weak ferromagnetism and enhanced ferroelectricity close to a rhombohedral–pseudocubic morphotropic phase boundary (MPB) formed at $0.275 \leqslant x \leqslant 0.30$.

It was reported that in $BaTiO_3$–$BaSnO_3$ [22] and $BaTiO_3$–$x(0.4CaTiO_3$–$0.6BaSnO_3)$ [23], the Sn-containing ends stabilize the rhombohedral phase from orthorhombic and tetragonal phases. In Ba(Sn, Ti)$O_3$-$x$(Ba, Ca)$O_3$ (BST-BCT), the rhombohedral phase transforms into tetragonal after BCT is introduced [24]. In these cases, piezoelectric and ferroelectric properties are improved due

* Corresponding author. Tel.: +86 20 84113398; fax: +86 20 84113397.
*E-mail address:* stszyl@mail.sysu.edu.cn (Y. Zhang).

http://dx.doi.org/10.1016/j.jallcom.2015.02.127
0925-8388/

to phase transitions between the rhombohedral and other ferroelectric phases. Accordingly, the addition of Sn into pseudocubic 0.725BF-0.275BCTZ may also induce a rhombohedral phase, and the ferroelectric and piezoelectric properties may be enhanced.

In this work, $0.725BiFeO_3$-$0.275Ba_{0.85}Ca_{0.15}Ti_{0.9}Zr_{0.1-x}Sn_xO_3$ ceramics were fabricated with a conventional solid-state reaction method. Before sintering, 1 mol% $MnO_2$ was added as a sintering aid to facilitate densification, maintain charge neutrality, and suppress impurity phases [11,25–27]. The structure of BF-BCTZS-1000*x* ceramics was examined with XRD, and its dielectric, ferroelectric, piezoelectric and magnetic properties were obtained.

## 2. Experimental procedure

Lead-free $0.725BiFeO_3$-$0.275Ba_{0.85}Ca_{0.15}Ti_{0.9}Zr_{0.1-x}Sn_xO_3$ (BF-BCTZS-1000*x*, $x = 0$, 0.025, 0.050, 0.075, 0.100) ceramics were prepared by a conventional solid-state reaction method. AR-grade $BaCO_3$, $CaCO_3$, $TiO_2$, $ZrO_2$, $SnO_2$, $Bi_2O_3$, $Fe_2O_3$ reagents were used as starting materials, and were grinded with ethanol in stainless-steel jars for 10 h. The powders were dried and calcined at 800 °C for 4 h. The calcined powders were mixed with 1 mol% $MnO_2$ via ball milling, and then the resultant mixtures were dried and pressed into tablets with diameters of 10 mm under 10 MPa. The tablets were sintered at 930 °C for 4 h in air. Mn is added as a sintering aid before the sintering procedure. In our experiments, the same amount of Mn is added in all samples, so the effect of Mn addition is the same to all samples.

The structure of BF-BCTZS-1000*x* was examined by X-ray diffraction (XRD) (D-MAX 2200VPC, RIGAKU, Japan) via Cu-α radiation (1.541 Å). Surface morphology of the BF-BCTZS-1000*x* ceramics was obtained with scanning electron microscopy (SEM) (Quanta 400F, FEI/OXFORD/HKL, the Netherlands). Sintered tablets were grinded into powders in an agate mortar for magnetic measurements. Magnetic field dependence of magnetization was recorded at room temperature with a physical property measurement system (PPMS, Quantum Design, America). Silver electrodes were fired on both sides of the tablets for electrical measurements. The frequency and temperature dependent dielectric response of the BF-BCTZS-1000*x* ceramics was obtained with a precision LCR meter (E4980A, Agilent Inc., America). Ferroelectric properties were examined via a ferroelectric test system (Precision Premier II, Radiant Technologies Inc., America). Before $d_{33}$ measurements, the electrode tablets were polarized under 7.0 kV/mm at 90 °C for 40 min in silicon oil bath. The piezoelectric coefficient ($d_{33}$) of the tablets was obtained with a $d_{33}$ meter (ZJ-4AN, Institute of Acoustics, Academic Sinica, China).

## 3. Results and discussion

The XRD patterns of the BF-BCTZS-1000*x* ceramics are shown in Fig. 1. A pure perovskite structure is revealed in all BF-BCTZS-1000*x* samples, suggesting that the Sn ions have diffused into the lattice of BF-BCTZ. Peaks of impurity phases were found existing in calcined powders of BF-BCTZS-1000*x* but absent in sintered tablets, indicating that the addition of $MnO_2$ into the solid solutions has suppressed the impurity phases. The XRD patterns of undoped BF-BCTZ ceramics reveal a pseudocubic (referred to as PC) structure, while the splitting of $(111)_{PC}$ into $(006)_R$ and $(202)_R$ in the vicinity of 39° clearly shows that the Sn-doped samples are rhombohedral (R).

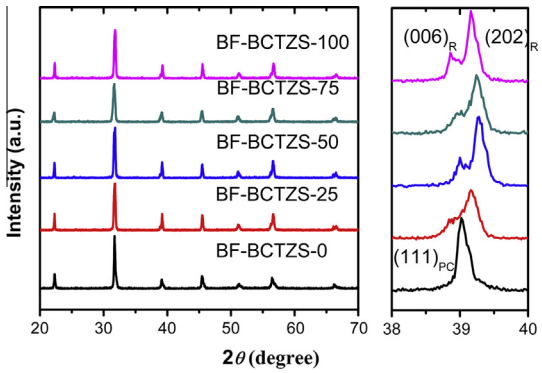


**Fig. 1.** XRD patterns of BF-BCTZS-1000*x* ceramics.

The SEM images of BF-BCTZS-1000*x* ceramics are shown in Fig. 2(a)–(e), and the variation of average grain size with their error bars is depicted in Fig. 2(f). The error bars indicate the 95% confidence interval for all compositions. The error bar for BF-BCTZS-0 could not be seen since it is smaller than the size of the symbol. It can be seen that Sn doping has significant influence on the morphology: compared with the observed pores and relatively small grain size in the undoped sample, dense micrographs are observed in Sn-modified samples; moreover, an obvious grain growth is manifested. According to the Ref. [28], some Sn ions serve as acceptors at the B sites of $BaTiO_3$ in the form of $Sn^{2+}$ and/or $Sn^{3+}$. Therefore, when Sn ions substitute for Zr ions in BF-BCTZS-1000*x*, oxygen vacancies would be created. Oxygen vacancies can promote grain growth due to an accelerated oxygen ion motion [29,30], and this effect may explain the sharp increase of grain size and the elimination of pores after Sn doping. These observed results indicate that the addition of Sn is beneficial to the grain growth and densification of the samples.

As shown in Fig. 3(a) and (b), obvious low-frequency dispersion is revealed in BF-BCTZS-1000*x* ceramics. For all samples, dielectric constant ($\varepsilon_r$) decreases with increasing frequency, while dielectric loss ($\tan\delta$) increases with increasing frequency. Both the dielectric constant and loss of BF-BCTZS-1000*x* ceramics are obviously improved after Sn doping. The BF-BCTZS-75 shows the optimized room-temperature dielectric performance (10 kHz): $\varepsilon_r = 407$, $\tan\delta = 0.030$. The improvement of room-temperature dielectric properties may be due to both intrinsic and extrinsic factors. The pseudocubic–rhombohedral structural phase transition can induce a striking change in dielectric properties, while the enlarged grain size and decreased porosity may also be related.

The dielectric constant at 10 kHz of BF-BCTZS-1000*x* ceramics is shown as a function of temperature in Fig. 3(c). The dielectric anomaly revealed in the vicinity of 410 °C corresponds to the Curie temperature, at which the ferroelectric–paraelectric phase transition occurs, and the present observation is consistent with previous report [21]. The dielectric anomaly is rather broad in the case of the undoped BF-BCTZ samples, indicating the diffuse nature of such phase transition [31]. This anomaly becomes much more pronounced after the substitution of Sn. The diffuseness of the phase transition can be quantitatively depicted with the diffusivity $\gamma$, which is defined in the modified Curie–Weiss law [32]:

$$1/\varepsilon_r - 1/\varepsilon_{max} = (T - T_C)^{\gamma}/C \quad (T > T_C), \tag{1}$$

where $\gamma = 1$ represents a normal ferroelectric material, and $\gamma = 2$ represents a complete relaxor ferroelectric material. The $\gamma$ decreases monotonically from 1.958 to 1.361 with $x = 0$ to 0.100, revealing that the BF-BCTZS-1000*x* system undergoes a compositional relaxor-to-ferroelectric phase transition with the increasing Sn content. In BF-based ceramics, the $T_C$ usually increases with the increase of the tolerance factor [33]. Accordingly, in the case of BF-BCTZ whose tolerance factor is $0.988 < 1$, the increase of the tolerance factor resulting from the substitution of a smaller B-site dopant will lead to an increase of the $T_C$. As a B-site dopant, $Sn^{4+}$ ion has a radius of 0.69 Å, smaller than 0.73 Å for $Zr^{4+}$ [34], thus the $T_C$ of BF-BCTZS-1000*x* increases as the Sn content increases. The $T_C$ as a function of composition ($x$) is shown in the inset of Fig. 3(c), and an almost linear increase from 401.0 °C to 418.8 °C is revealed with the increasing Sn content, which is consistent with the above analysis.

The dielectric loss vs. temperature curves at 10 kHz are shown in Fig. 3(d). Concave segments can be recognized at temperatures slightly lower than the Curie temperatures. The concave segment of the undoped BF-BCTZ ceramic is much broader than those of