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Microstructure and electrical properties in Zn-doped $Ba_{0.85}Ca_{0.15}Ti_{0.90}Zr_{0.10}O_3$ piezoelectric ceramics

Zhihao Zhao, Xiaolei Li *, Huiming Ji, Yejing Dai, Ting Li

Key Laboratory for Advanced Ceramics and Machining Technology of Ministry of Education, School of Material Science and Engineering, Tianjin University, Tianjin 300072, China

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ABSTRACT

Piezoelectric ceramics doped with small amounts of elements usually cause significant improvement in piezoelectric properties. In this study, we prepared $Ba_{0.85}Ca_{0.15}Ti_{0.90}Zr_{0.10}O_3$–$x$ wt% ZnO ($0 \leqslant x \leqslant 0.16$) ceramics via a conventional solid-state reaction method. The evolution of domain structure, relaxor behavior, ferroelectric and piezoelectric properties with Zn doping was systematically investigated. The ceramics with $x = 0.08$ possess slender domain patterns and high domain wall density. The $Ba_{0.85}Ca_{0.15}Ti_{0.90}Zr_{0.10}O_3$–8 wt% ZnO ceramics show maximum remnant polarization and spontaneous polarization ($P_r = 10.14\ \mu C/cm^2$, $P_s = 19.68\ \mu C/cm^2$). A giant piezoelectric coefficient of $d_{33} = 603$ pC/N and high planar electromechanical coupling factor of $k_p = 0.56$ were obtained for the sample of $x = 0.08$, showing the potential possibilities for lead-free piezoelectric application.

1. Introduction

Lead-free piezoelectric ceramics with excellent electrical properties have been actively investigated in recent years as a replacement for the current lead-based ceramics [1,2]. The most commonly used piezoelectric ceramics are represented by Pb(Zr, Ti)O_3 (PZT) and are used in sensors, actuators and transducers due to their excellent piezoelectric properties close to the morphotropic phase boundary (MPB) between rhombohedral and tetragonal [3–5]. However, lead-free piezoelectric ceramics such as (Bi, Na)TiO_3- and (K, Na)NbO_3-based systems show inferior piezoelectric coefficients ($d_{33} < 490$ pC/N) [6–8] compared with that of the lead-based piezoelectric ceramics ($d_{33} = 300$–650 pC/N) [9].

Barium titanate ($BaTiO_3$), which is the earliest known perovskite-type ferroelectric ceramics and has been widely studied, has five kinds of phase structures at different temperatures. In order to improve the piezoelectric and dielectric properties, $BaTiO_3$ is used to form solid solution to create the morphotropic phase boundary (MPB) by doping other elements [10,11]. In 2009, pseudo binary $Ba(Zr_{0.2}Ti_{0.8})O_3$–$x(Ba_{0.7}Ca_{0.3})TiO_3$ (BZT–BCT) ferroelectric system was reported [12]. This system has a morphotropic phase boundary that is similar to $PbTiO_3$–$PbZrO_3$ system near $Ba_{0.85}Ca_{0.15}Ti_{0.90}Zr_{0.10}O_3$ (BCZT) composition at room temperature, which has attracted great attention because of excellent piezoelectric properties ($d_{33} = 560$–620 pC/N). This composition has been modified by optimizing sintering process [13,14] or adding dopants in A/B site to improve the piezoelectric property [15–18] or temperature stability [19,20]. The addition of dopants optimizes the electric properties due to the transformation of microstructure. However, few systematical studies of the domain structure effects on the electrical properties of doped BCZT ceramics have been carried out to date.

In this paper, the effects of Zn substitution on phase structure, domain structure, dielectric, relaxor behavior, ferroelectric and piezoelectric properties of $Ba_{0.85}Ca_{0.15}Ti_{0.90}Zr_{0.10}O_3$ (BCZT) have been investigated systematically. It has been found that domain structure, relaxor behavior, dielectric, ferroelectric, piezoelectric properties show a strong association with doping ZnO. A possible origin of strong electrical properties in Zn-doped $Ba_{0.85}Ca_{0.15}Ti_{0.90}Zr_{0.10}O_3$ piezoelectric ceramics is proposed.

2. Experimental procedure

$Ba_{0.85}Ca_{0.15}Ti_{0.90}Zr_{0.10}O_3$–$x$ wt% ZnO (BCZT–xZn) piezoelectric ceramics with $x = 0$, 0.04, 0.08, 0.10, 0.12, 0.16 were synthesized by the conventional solid-state reaction process, starting from the raw materials of analytical grade $BaCO_3$ (99.0%), TiO_2 (98.0%), ZrO_2 (99.0%), $CaCO_3$ (99.0%), ZnO (99.0%). The raw materials apart from ZnO powder were ball-milled with the addition of alcohol for 4 h. The dried mixtures were calcined at 1300 °C for 2 h. Thereafter, the calcined mixtures were remixed with ZnO powder with adding alcohol for 4 h. The mixed powder is pressed into 12 mm diameter discs and consolidated by isostatic pressing at 200 MPa. All samples were sintered at 1450 °C for 4 h in a sealed alumina crucible after burning out polyvinyl alcohol (PVA) binder at 650 °C for 30 min.

Density of the sintered samples was measured by the Archimedes method and theoretical density of each composition was calculated from the XRD data. To characterize the phase structure, the sintered samples were mirror-polished. Thereafter,

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* Corresponding author. Tel.: +86 22 27406114.
E-mail address: lxlei@tju.edu.cn (X. Li).

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the ceramic samples were annealed at 800 °C for 2 h and cooled to room temperature at a very slow rate to release the stress caused by polishing [21]. The phase structure of samples were analyzed by X-ray diffractometer (XRD, Rigaku D/Max 2500, Tokyo, Japan) using Cu Kα_1 radiation as the radiation source (λ = 1.5418 Å) with slow scanning at 0.01 °/s. The poled samples etched for 30 s in mixtures of HCl and HF aqueous solution. The HCl is a 5% aqueous solution. The ratio of the HF and HCl aqueous solution is 3 drops of HF: 20 ml HCl solution. Scanning electron microscopy (SEM, S4800, Hitachi, Japan) was used to observe the microstructure of the ceramics and domain structure. The average grain sizes were obtained from over 300 grains.

Silver electrodes were painted on the upper and bottom surfaces of the polished samples and fired at 600 °C for 15 min for dielectric and piezoelectric characterization. Sintered samples were poled in silicone oil at room temperature under 3.0 kV/mm for 20 min. Dielectric property, impedance |Z| and phase angle θ were measured by an LCR meter (Agilent E4980A, Santa Clara, CA). Planar electromechanical coupling factor k_p were calculated following IEEE standards. The temperature dependence of the dielectric constant and the dissipation factor of the samples were measured between −30 °C and 150 °C at a step of 1 °C/min. The piezoelectric constant d_{33} was measured by quasistatic d_{33} meter (ZJ-3AN, Institute of Acoustics Academic Sinica, Beijing, China) based on Berlincourt method. The ferroelectric hysteresis P–E loops were determined with a standard ferroelectric tester (WS-2000, Tsinghua University, Beijing, China) at a frequency of 1 kHz.

3. Results and discussion

Fig. 1a shows the room temperature (T = 20 °C) XRD patterns of the BCZT–xZn ceramics. All samples have a pure phase of

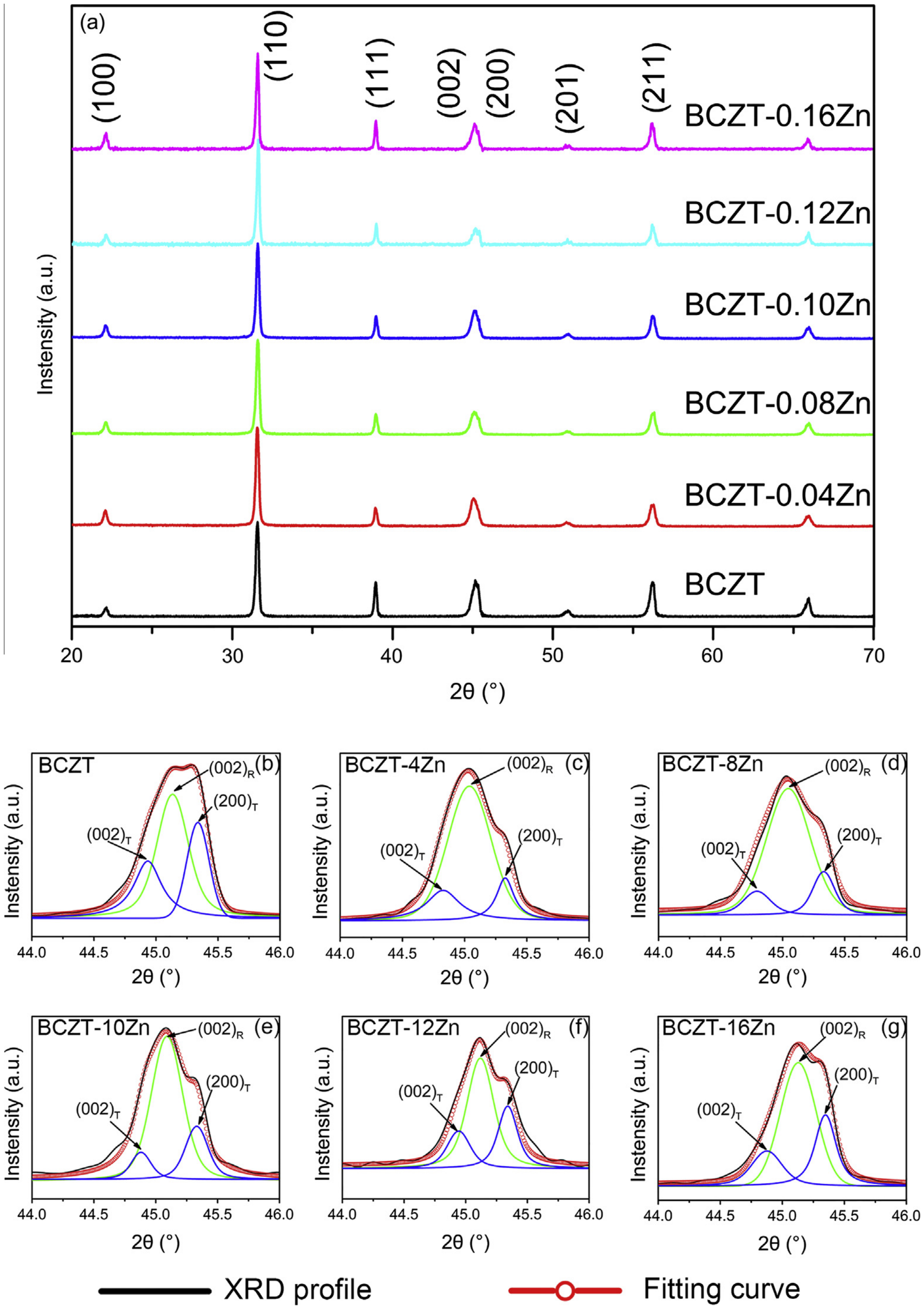

Fig. 1. (a) X-ray diffraction patterns of the BCZT–xZn ceramics sintered at 1450 °C for 4 h. (b)–(g) X-ray diffraction patterns and fitting curves in the 2θ range of 44.0–46.0°. The Cu Kα_2 was stripped and the background was removed.