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Phase transition behavior and enhanced electromechanical properties in $(Ba_{0.85}Ca_{0.15})(Zr_xTi_{1-x})O_3$ lead-free piezoceramics

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Abstract

Lead-free $(Ba_{0.85}Ca_{0.15})(Zr_xTi_{1-x})O_3$ (BCZT,$0.03 \leq x \leq 0.25$) ceramics were synthesized in a wide compositional range to investigate the relationship between its phase diagram and electromechanical properties. The effects of Zr content on microstructure, phase transition behavior, ferroelectric, dielectric, piezoelectric and strain properties of BCZT ceramics were systemically studied. The morphotropic phase boundary (MPB) of BCZT ceramics was closely connected with the presence of orthorhombic phase between rhombohedral and tetragonal phases at a narrow region, which could meet in a region that is termed the diffuse ferroelectric phase transition region (DPTR) in this work. As a result, the composition $x=0.08$ located at near MPB region close to tetragonal phase side exhibited the outstanding electrical behavior at room temperature: $d_{33}=349$ pC/N, $k_p=43\%$, $S=0.185\%$ and $S_{max}/E_{max}=463$ pm/V. Furthermore, pure electrostrictive effect with large electrostrictive coefficient Q_{11} of 0.036 $m^4\,C^{-2}$ had also been observed in the composition $x=0.20$, and large Q_{11} of MPB composition showed superior temperature stability in the investigated temperature range.

Keywords: D. Perovskites; Electrostriction; Lead-free ceramics; Strain response

1. Introduction

Piezoelectric materials have been demonstrated to possess various functional applications, such as sensors, actuators and transducers. In general, lead zirconate titanate $Pb(Zr_{1-x}Ti_x)O_3$ (PZT)-based compositions have been the mainstay for high-performance actuators and transducers for over half a century owing to their superior electromechanical properties [1–3]. However, due to environmental concerns over the toxicity of lead, PZT is facing global restrictions in its usage in electronic equipment. Thus, environment-friendly lead-free piezoelectric materials with high-performance have received tremendous attention worldwide in the past decade [4,5]. Currently, many reports have been focusing on the relationship between phase structure and electrical behavior of $K_{0.5}Na_{0.5}NbO_3$ (KNN) and $Bi_{0.5}Na_{0.5}TiO_3$ (BNT)-based ceramics systems, which show lower piezoelectric properties ($d_{33}=200$–250 pC/N) compared to the lead-based materials of high-end PZT ($d_{33}=500$–600 pC/N) [2,6–8].

Among the most studied lead-free systems, barium calcium zirconate titanate $(BaZr_{0.2}Ti_{0.8}O_3)-x(Ba_{0.7}Ca_{0.3}TiO_3)$(BCZT) solid solutions, which was first reported by Liu and Ren in 2009 [9], stands out for its exceptionally high piezoelectric properties featured by a high piezoelectric coefficient of $d_{33}\sim620$ pC/N at the morphotropic phase boundary (MPB) composition ($x=0.5$). This high value exceeds those for competing lead-free compositions and even for most PZT materials [2,4]. Subsequently, extensive studies have been reported to do research on the Curie temperature [10,11], documenting the elastic, piezoelectric,

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and dielectric properties [12], manufacturing of ceramics *via* a sol–gel process [13,14], investigation of electromechanical coupling [15–17], microstructure studies [18–20], and poling studies to further increase piezoelectric properties [13,21–23]. With respect to the origin of large piezoelectricity for this system, Ren et al. ascribed the enhanced piezoelectricity for a BCZT pseudo-binary system to the proximity of MPB starting from the tricritical point (TCP) of rhombohedral (R), tetragonal (T), and cubic(C) phases [9]. Damjanovic et al. [24] proposed that the polarization rotation and polarization extension should be responsible for the enhancement of their electrical properties. It was proposed from a microstructural perspective that this composition in its virgin state contains nanoscale ferroelectric domains, facilitating polarization rotation during electrical poling and enhancing piezoelectricity [18]. As demonstrated in KNN-based and BNT-based ceramics, the effective polarization alignment and extensive phase transition during poling are cited as primary factors contributing to their excellent piezoelectric performance [25,26]. Recent works have revealed that the mixed phase region is an intermediate orthorhombic phase, leading to high piezoelectric and electromechanical properties [27–29]. Very recently, Tan et al. [30] investigated the microstructural origin of the exceptionally high piezoelectric response of polycrystalline BCZT using *in situ* transmission electron microscopy, and the results demonstrated that the excellent piezoelectric properties of this lead-free ceramic are the result of the structural instability and elastic softening. Hence, the phase diagram and the underlying mechanism responsible for the high piezoelectricity of the system remain controversial.

At room temperature the BCZT system presents not only high piezoelectric coefficients but also an exceptionally large normalized strain $S_{max}/E_{max}=1100$ pm/V at 50 kV/cm [9], demonstrating that it is a potential lead-free candidate for actuator applications. Generally, the strain response for piezoelectric materials arises from two main contributions: (i) an intrinsic piezoelectric lattice strain; and (ii) an extrinsic ferroelastic strain [31]. On the other hand, the extrinsic strain is caused by the motion of ferroelastic, or non-180°, domain walls that increases the volume fraction of ferroelastic domains aligned in and around the direction of the applied electric field [31]. In addition, BNT-based materials exhibit a large electric-field-induced strain and have been reported to result from field-induced phase transition [6,32]. Acosta et al. [15] investigated the relationship between phase diagram and electromechanical properties for the BCZT system, and demonstrated that the strain response presents maximized values at both rhombohedral to orthorhombic and to tetragonal phase transitions. Ehmke et al. [27,31] explored the structural contributions to the electric-field-induced strain in BCZT ceramics using field-dependent *in situ* XRD measurements, and the results revealed that the large macroscopic strain response under an applied field originates from the combined effects of a lattice strain and a ferroelastic strain contribution. Also, the stress, temperature and electric field-dependent electromechanical properties have been investigated for compositions across the MPB in the (Ba, Ca)(Ti, Zr)O_3 ferroelectric system [16,17].

It has been demonstrated that doping is a common strategy to alter the material's sensitivity to external stimuli and optimize it for specific applications. In previous works, the investigations on $(Ba_{1-x}Ca_x)(Zr_yTi_{1-y})O_3$ systems were mainly focused on the ferroelectric and piezoelectric properties [23,29,33,34]. Only limited research exhibits on the electromechanical properties of BCZT [15–17,27,31], and currently there are no systematic studies of the electromechanical properties on the $(Ba_{0.85}Ca_{0.15})(Zr_xTi_{1-x})O_3$ (BCZT) system. Under these considerations, the objective of this work is characterize the effects of Zr content on phase transition and large-field electromechanical properties of $(Ba_{0.85}Ca_{0.15})(Zr_xTi_{1-x})O_3$ lead-free ceramics. Furthermore, the temperature-dependent strain response for the system is also investigated and discussed.

2. Experimental procedure

$(Ba_{0.85}Ca_{0.15})(Zr_xTi_{1-x})O_3$ ($x=0.03$–0.25) ceramics were prepared using a conventional solid-state reaction route. $BaCO_3$ (99.8%, Alfa Aesar), $CaCO_3$ (99.95%, Alfa Aesar), TiO_2 (99.6%, Alfa Aesar), and ZrO_2 (99%, Alfa Aesar) were used as starting raw materials. The powders were weighed according to the composite formula and then ball-milled in ethanol for 24 h. This mixture was calcined at 1300 °C for 4 h in a covered alumina crucible, and then pressed into 10 mm diameter pellets with 8 wt% polyvinyl alcohol (PVA) as a binder. After burning out PVA at 550 °C for 6 h, the pellets were finally sintered at 1500 °C for 2 h in air. Silver electrodes were formed on each side of sintered disk by firing at 600 °C for 10 min for the electrical measurements.

The crystalline structure of the prepared ceramic samples was determined by X-ray diffraction (XRD, Bruker D8 Advanced, Germany) with Cu Ka radiation. The relative density of the sintered samples was measured by the Archimedes method. The Surface morphologies of the as-sintered samples were characterized using a scanning electron microscopy (SEM) (JSM, EMP-800; JEOL, Tokyo, Japan). Temperature dependence of the dielectric constant and loss of the samples was measured under different frequencies with a high-precision LCR meter (Agilent E4980A). The FE hysteresis loops and strain curves of the samples were measured at 10 Hz using a FE test system (Precision Premier II; Radiant Technologies Inc, Albuquerque, NM) connected with a Miniature Plane-mirror Interferometer and the accessory Laser Interferometric Vibrometer (SP-S 120/500; SIOS Me β technik GmbH, llmenau, Germany). Before piezoelectric properties measurements, the samples were poled into silicone oil for 30 min. After 24 h aging of the poled sample, the piezoelectric constant d_{33} was measured using a quasi-static d_{33} meter (Institute of acoustic, Chinese Academic Society, ZJ-6A, Beijing, China). The electromechanical coupling coefficient k_p was determined using the resonance and antiresonance technique using an impedance analyzer (HP 4294A).

3. Results and discussion

The SEM micrographs of the free surface of $(Ba_{0.85}Ca_{0.15})(Zr_xTi_{1-x})O_3$ ceramics are presented in Fig. 1(a)–(c). Dense