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Short communication

The enhancing performance of $(Ba_{0.85}Ca_{0.15}Ti_{0.90}Zr_{0.10})O_3$ ceramics by tuning anatase–rutile phase structure

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ABSTRACT

To research effect of raw materials TiO_2 with the phase structures on the crystal structure, microstructure and electrical properties of lead-free $(Ba_{0.85}Ca_{0.15})(Ti_{0.90}Zr_{0.10})O_3$ (BCZT) ceramics, BCZT ceramics using either anatase or rutile as Ti source were synthesized by solid-state reaction. Titanium dioxide (TiO_2) with anatase/rutile phase structures had interesting influence on the crystal structure, microstructure and the sintering temperature by the X-ray diffraction and SEM, which also played an important role in improved electrical properties. The BCZT ceramics with rutile titanium dioxide demonstrated optimal piezoelectric and dielectric properties: d_{33} = 590 pC/N, k_p = 0.46, ε_r = 2810, tanδ = 0.014 and T_c = 91 °C, which was obviously superior to BCZT ceramics with anatase titanium dioxide.

1. Introduction

Barium calcium zirconate titanate (1-x)$Ba(Zr_{0.2}Ti_{0.8})O_3$-x$(Ba_{0.7}Ca_{0.3})TiO_3$ (BZT-xBCT)-based solid solution, a perovskite structure, has attracted widely attention due to its promising and large piezoelectric properties which has been considered as potential candidates to replace lead based piezoelectric materials [1,2]. It could open up entirely new possibilities for designing novel applications of piezoelectric devices in the fields of actuators, transducers, sensors, filters, and switches [3].

Recently, BZT-xBCT based materials have been investigated as promising lead-free alternative piezoelectrics for the origins of the strong piezoelectric response observed by various techniques, such as different preparation technique, adjusting component, ion substitution and most additives [4,5]. For matrix BZT-xBCT ceramics, the substitution of Ca^{2+}/Zr^{4+} to replace Ba^{2+}/Ti^{4+} in $(Ba_{1-x}Ca_x)(Zr_yTi_{1-y})O_3$ (BC_xZ_yT) ceramics have been researched [6,7]. Moreover, calcination temperature, the sintering temperature and dwell time have been constructed in the BZT-xBCT ceramic, showing an enhanced piezoelectric behavior [8,9]. It is well-known that titanium dioxide occurs in nature as the rutile, anatase and brookite. The rutile and anatase TiO_2 contain six-coordinated titanium, which are also the stable equilibrium phase compared to the brookite-type TiO_2 [10–12]. However, the effect of titanium dioxide with different structure on the phase transition, microstructure and electrical behaviors in $(Ba_{0.85}Ca_{0.15})(Ti_{0.90}Zr_{0.10})O_3$ based ceramics is not well understood so far.

In this paper, we investigated the effects of TiO_2 with different phase structure on the phase structure, microstructure, electrical properties and the sintering behavior of BCZT ceramics. Moreover, the interfacial reaction mechanism in BCZT ceramics with rutile- and anatase-type TiO_2 was also discussed.

2. Experiment

2.1. Sample preparation

A conventional solid-state sintering reaction method was utilized to prepare $(Ba_{0.85}Ca_{0.15})(Zr_{0.10}Ti_{0.90})O_3$ ceramics with anatase- and rutile-type TiO_2 ($BCZT_a$ and $BCZT_r$). Commercially available reagent grade oxide of $BaCO_3$ (99%), $CaCO_3$ (99%), ZrO_2 (99%), anatase-type TiO_2 (D50 = 532 nm, 99.99%) and rutile-type TiO_2 (D50 = 614 nm, 99.99%) powders were used as starting raw materials. The powders were weighed according to the stoichiometry composite. Dried and sieved powders were then calcined at 1200 °C for 6 h. The samples were sintered in a covered crucible at 1400, 1420, 1440 and 1460 °C for 6 h in air, respectively.

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2.2. Characterization

The sintered ceramics were examined by X-ray powder diffraction analysis using a Cu Kα radiation (DMX-2550/PC, Rigaku, Japan) to determine the crystalline phase at room temperature. Temperature-dependent dielectric constant was obtained with an LCR meter (Agilent, E4980A) connected to a computer-controlled temperature chamber by measuring the capacitance at 1 kHz. For polarization-electric field (*P*–*E*) hysteresis measurements, the top electrode was connected to a high voltage amplifier (Model 610E, Trek, USA) for the electrical loading. For electrical measurements, the BCZT samples were poled for 30 min at room temperature under an electric field of 4 kV/mm. The poled samples were aged for 24 h before conducting any electrical measurements. The piezoelectric coefficient d_{33} was measured by a quasistatic piezoelectric meter (ZJ-3d, Institute of Acoustics Academic Sinica, Beijing, China). The electromechanical coupling coefficient k_p was determined by the resonance and anti-resonance technique using an impedance analyzer (HP/Agilent Model 4294A).

3. Results and discussion

Thermal analysis technology is a kind of characterization methods, which can be used to study the phase transition and reaction temperature etc. of the materials. Fig. 1(a) presents the TG and DSC curves obtained from $BCZT_a$ and $BCZT_r$ powder. The $BCZT_a$ and $BCZT_r$ powders are heated from 30 °C to 1500 °C in air atmosphere with a heating rate of 10 °C/min using thermo-analyzer systems. TG data demonstrates that it takes place in two stages. The powder specimen mass decrease ~4% in the first obvious lengthy stage and temperature interval is from 30 °C to 725 °C. The occurrence of this stage is probably due to the decomposition of calcium carbonate ($CaCO_3$). The powder specimens mass markedly fall ~13% in second stage temperature range from ~730 °C to 970 °C. It is obvious that the maximum mass loss is related to decomposition of barium carbonate ($BaCO_3$). The first and second mass loss is the similar with carbon dioxide (CO_2) percentage of calcium carbonate and barium carbonate of the composition, accompanied by clear exothermic peak at 725 °C and 826 °C, respectively. In addition, a strongest exothermic peak appears at 1350 °C, which can be attributed to the solid state reaction and the initial crystallization in the DSC curves. Compared with the DSC curve of $BCZT_r$ powder, a quite endothermic peak appears between 826 °C and 1060 °C in the curve of $BCZT_a$ powder. According to the following chemical equation presented below: [13]

TiO_2 (anatase) → TiO_2 (rutile) − Q (Q = 1.26 kJ/mol),

the occurrence of endothermic peak is probably due to phase change. TiO_2 has two kinds of stable phase structure, which are anatase-type structure (a, PDF#89-4921) in Fig. 1(b) and rutile-type structure (r, PDF#21-1276) in Fig. 1(c), respectively. However, anatase-type TiO_2 will be transformed into rutile-type TiO_2 when anatase-type TiO_2 is calcined at ~915 °C. Therefore, the endothermic peak indicates that the phase change of TiO_2 happen here.

Fig. 2(a) shows the XRD patterns of $BCZT_a$ and $BCZT_r$ ceramics, measured at room temperature. $BCZT_a$ and $BCZT_r$ ceramics exhibit pure perovskite structure without any impurity. As shown in inset of Fig. 2(a), $BCZT_a$ and $BCZT_r$ ceramics displays the reflection intensity of $(002)/(200)_T$ and $(200)/(220)_O$, implying the coexistent phases of tetragonal and orthorhombic phases. While the reflection intensity of $(002)/(200)_T$ and $(200)/(220)_O$ shows difference perovskite phase structure, showing the formation of mixture phase and lattice deformation due to the TiO_2 structure change. Fig. 2(b) presents the schematic representation of the structure of $BCZT_a$ and $BCZT_r$ ceramics. As shown in Fig. 2(b), each Ba (Ca) atom is bonded to the twelve oxygen atoms and become $[BaO_{12}]$ clusters. Both Ti (Zr) atoms are bonded to six oxygen atoms, forming the $[TiO_6]$ and $[ZrO_6]$ clusters. This distortion can be arising from the covalent character between the O—Ti—O bonds with change structure [3]. Moreover, BCZT solid solution

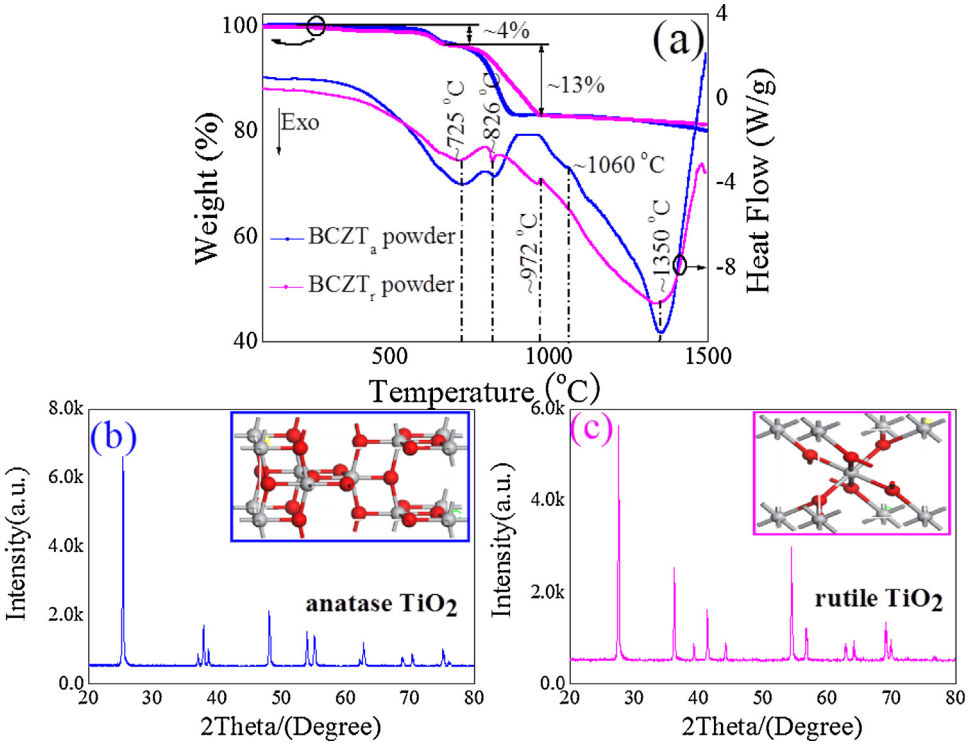

Fig. 1. Thermogravimetric curve (a) of the $BCZT_a$ and $BCZT_r$ ceramics, (b) XRD patterns of anatase-type TiO_2 and (c) rutile-type structure TiO_2.