The enhancing performance of $(\text{Ba}_{0.85}\text{Ca}_{0.15}\text{Ti}_{0.90}\text{Zr}_{0.10})\text{O}_3$ 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 $(\text{Ba}_{0.85}\text{Ca}_{0.15})(\text{Ti}_{0.90}\text{Zr}_{0.10})\text{O}_3$ (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: $d_{33} = 590 \text{ pC/N}$, $k_p = 0.46$, $\varepsilon_r = 2810$, $\tan\delta = 0.014$ and $T_c = 91^\circ\text{C}$, which was obviously superior to BCZT ceramics with anatase titanium dioxide.

Keywords: A. Ceramics C. X-ray diffraction D. Electrical properties D. Microstructure D. Piezoelectricity

1. Introduction

Barium calcium zirconate titanate $(1-x)\text{Ba}(\text{Zr}_{0.2}\text{Ti}_{0.8})\text{O}_3-x(\text{Ba}_{0.7}\text{Ca}_{0.3})\text{TiO}_3$ (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 $\text{Ca}^{2+}/\text{Zr}^{4+}$ to replace $\text{Ba}^{2+}/\text{Ti}^{4+}$ in $(\text{Ba}_{1-x}\text{Ca}_x)(\text{Zr}_y\text{Ti}_{1-y})\text{O}_3$ ($\text{BC}_x\text{Z}_y\text{T}$) 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 $(\text{Ba}_{0.85}\text{Ca}_{0.15})(\text{Ti}_{0.90}\text{Zr}_{0.10})\text{O}_3$ 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 $(\text{Ba}_{0.85}\text{Ca}_{0.15})(\text{Zr}_{0.10}\text{Ti}_{0.90})\text{O}_3$ 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.

2.2 Characterization

The sintered ceramics were examined by X-ray powder diffraction analysis using a Cu $K\alpha$ 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 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 (CaCO₃). 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 (BaCO₃). The first and second mass loss is the similar with carbon dioxide (CO₂) 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]:

the occurrence of endothermic peak is probably due to phase change. TiO₂ 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 TiO₂ will be transformed into rutile-type TiO₂ when anatase-type TiO₂ is calcined at ~915 °C. Therefore, the endothermic peak indicates that the phase change of TiO₂ 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 TiO₂ 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 [BaO₁₂] clusters. Both Ti (Zr) atoms are bonded to six oxygen atoms, forming the [TiO₆] and [ZrO₆] clusters. This distortion can be arising from the covalent character between the O-Ti-O bonds with change structure [3]. Moreover, BCZT solid solution accompanied with the phase change process is

formed by high temperature solid state reaction, which would effects grain growth of the ceramics. As shown in Figs. 2(c) and (d), the grain of the BCZT_a ceramics is obviously smaller than that of the BCZT_r ceramics. When anatase-type structure TiO₂ is calcined at high temperature (~915 °C) and transform into rutile-type structure TiO₂, powder demonstrate poor activity due to its small specific surface areas [10, 12, 13]. The rutile-type structure TiO₂ display much higher activity comparing with anatase-type structure TiO₂ that result in faster growth rate, bigger and fuller grain of the BCZT_r ceramics.

The phase structure and microstructure possessed by tailoring anatase-type and rutile-type TiO₂ influence apparently the electrical properties of the ceramics. Fig. 3(a) depicts piezoelectric ceramics d_{33} and electromechanical coupling factor k_p of the BCZT_a and BCZT_r ceramics. It can be seen that the BCZT_r ceramics displays perfect performance of d_{33} and k_p comparing with the BCZT_a ceramics. Fig. 3(b) gives P - E and I - E loops of the BCZT_a and BCZT_r ceramics. Moreover, the ferroelectric properties of the ceramics are also strongly impacted by changing anatase-type and rutile-type TiO₂. It can be found that remnant polarization P_r of the BCZT_r ceramics reveal higher value than that of the BCZT_a ceramics. The coercive field E_c can be identified as the electric field correspondent to the current peak and in this case it coincides with the electric field correspondent at $P=0$ in the P - E loop in Fig. 3(b) [14]. As shown in Fig. 3(b), E_c changes slightly. The BCZT_r ceramics calcined at 1200 °C and sintered at 1440 °C indicates the favorable properties, which are listed as follows: $d_{33} = 590$ pC/N, $k_p = 0.46$, $P_r = 11.18$ $\mu\text{C}/\text{cm}^2$ and $E_c = 2.06$ kv/cm. Other electrical

properties are showed in Table.1. Although anatase-type TiO_2 own bigger the band gap energy (3.2 e.V) than rutile-type TiO_2 (3.0 e.V) so that it possesses better reaction activity, the phase change of TiO_2 changes covalent energy between the O-Ti-O bonds take place the transformation by calcining process [10, 12]. So, it is believed that the phase change of TiO_2 influence the phase structure of the ceramics with the different mixture intensity of orthorhombic and tetragonal phase, resulting in the improved electrical performances. Moreover, the BCZT_r ceramics have well-grown grains with lower porosity, uniform microstructure and higher relative density ($\rho_r=95\%$) which can also be conducive to improving electrical properties, as shown in Table.1.

4. Conclusions

Lead-free $(\text{Ba}_{0.85}\text{Ca}_{0.15})(\text{Ti}_{0.90}\text{Zr}_{0.10})\text{O}_3$ piezoelectric ceramics using the two various phase structure TiO_2 as the raw materials have been prepared by solid-state reaction. The origin of the two-phase structural state of the ceramics consisting of the tetragonal and orthorhombic phases is related to different type TiO_2 induced lattice and rotational distortions in a perovskite unit cell by XRD patterns. In same conditions, the grain growth of the BCZT_r ceramics is faster, more uniform and more evenly microstructure because the BCZT_a ceramics with anatase-type TiO_2 need external heat due to the phase change of the anatase/rutile-type TiO_2 . These results showed that the BCZT_r ceramics sintered at 1440 °C had the good electrical properties, which were $d_{33} = 590 \text{ pC/N}$, $k_p = 0.46$, $\varepsilon_r = 2810$, $\tan\delta = 0.014$, $T_c=91 \text{ }^\circ\text{C}$, $\varepsilon_r=2900$, $\varepsilon_m=14500$, $P_r=11.18 \text{ } \mu\text{C/cm}^2$ and $E_c=2.06 \text{ kv/cm}$. This finding implies that the electrical performance of the ceramics could be further improved by elaborately

designing the anatase/rutile-type TiO_2 .

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Figure captions

Fig.1. Thermogravimetric curve (a) of the BCZT_a and BCZT_r ceramics, (b) XRD patterns of anatase-type TiO₂ and (c) rutile-type structure TiO₂.

Fig.2. (a) XRD patterns of the BCZT_a and BCZT_r ceramics, (b) Schematic representation of crystalline BCZT_a and BCZT_r structure, SEM of (c) the BCZT_a and (d) BCZT_r ceramics.

Fig.3. (a) d_{33} and k_p , (b) P - E and I - E loops of the BCZT_a and BCZT_r ceramics.

Table. 1. The electrical properties of the BCZT_a and BCZT_r ceramics.

Graphical Abstract

Titanium dioxide (TiO_2) with different phase structure had interesting influence on the crystal structure, microstructure, the sintering temperature and electrical properties.

Figure

Fig.1. X. L. Chao, T. Zhang et al.

Fig.2. X. L. Chao, T. Zhang et al.

Fig.3. X. L. Chao, T. Zhang et al.

Table. 1 The properties of the ceramics prepared by different crystalline TiO₂

The composition	ρ_r	d_{33} (pC/N)	k_p	$\tan \delta$	ε_r	ε_m	T_C (°C)	P_r ($\mu\text{C}/\text{cm}^2$)	E_c (kv/cm)
BCZT _r	95%	590	0.46	0.0140	2900	14500	91	11.18	2.06
BCZT _a	93%	412	0.41	0.0158	2810	11920	91	8.875	2.26