Ceramics International 44 (2018) 7877–7882

Contents lists available at ScienceDirect

Ceramics International

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

Effect of MnO_2 addition on the structure and electric properties of $(Ba_{0.94}Ca_{0.06})(Ti_{0.9}Sn_{0.1})O_3$ ceramics

Haizhu Song, Congfei Peng, Rongxia Huang*, Youliang Wu, Hua-Tay Lin

School of Electromechanical Engineering, Guangdong University of Technology, Guangzhou 510006, China

A R T I C L E I N F O

Keywords:
Perovskite structure ceramics
Piezoelectric ceramics
Microstructure
Electric properties

A B S T R A C T

The $(Ba_{0.94}Ca_{0.06})(Ti_{0.9}Sn_{0.1})O_3$ (BCTS) ceramics with pure perovskite structure were prepared by conventional solid-state reaction route with the addition of 0–0.8 mol% MnO_2. The crystal structure, microstructure, and electric properties were investigated systematically. X-ray diffraction patterns showed that the addition of MnO_2 changed the ratio of the coexistence of orthorhombic and tetragonal phases, which had apparent influences on the piezoelectric properties of ceramics. When the addition amount is 0.2 mol%, the average grain size increases from ~41.88–52.24 µm, and, however, the average grain size decreases with further addition > 0.2 mol%. A good combination of properties and performance could be achieved with the addition of 0.4 mol% MnO_2. The mechanical quality factor Q_m, dielectric loss $tan\delta$, piezoelectric constant d_{33}, and planar electromechanical coefficient k_p measured are 216, 0.011, 578 pC/N, and 0.39, respectively. Therefore, results of this study suggest that the BCTS-Mn ceramics synthesized could exhibit a great potential for piezoelectric component applications.

1. Introduction

Piezoelectric ceramic is classified as the one of the functional ceramic materials, which can convert mechanical and electric energy from each other. Thus, the piezoelectric ceramic has been widely used in sensors, ultrasonic transducers, actuators, buzzers, and other industrial applications [1,2]. At present, the commercially available piezoelectric ceramics are mainly the lead-based piezoelectric ceramics, which contain a large amount of lead, leading to serious environmental pollution. Therefore, developing environmentally friendly lead-free piezoelectric ceramics has become an urgent and important task for the ceramic community around the world. So far, $BaTiO_3$ (BT), (K, Na)NbO_3 (KNN), and (Bi, Na)TiO_3 (BNT) based ceramics have been mainly considered as potential candidates to replace lead-based piezoelectric ceramics [3–5]. The BT-based ceramics have been widely studied by many researchers due to its excellent piezoelectric properties [6–8]. A lot of researchers focused on BT's A, B site substitution, such as (Ba,Ca)(Ti,Sn)O_3 (BCTS) ceramics. In the study of the effect of substituting $BaTiO_3$-$CaTiO_3$ (BCT) with $BaSnO_3$ (BS) by Mayamae et al., the polymorphic phase composition showed outstanding piezoelectric values of k_p = 41.7%, and d_{33} = 469 pC/N [9]. Zhu et. al. reported the influence of Sn content on the properties of BCTS ceramics. It was found that the piezoelectric constant d_{33} could reach 670 pC/N when the Sn content was 0.11 [10]. Accordingly, BCTS ceramics has broad prospects to potentially replace the lead-based piezoelectric ceramics at room temperature.

In addition to the different BT systems formed by various substituents, there were many studies on Mn-doped piezoelectric ceramics in recent years. It was reported that the doping of MnO_2 could reduce the sintering temperature and increase the Q_m value [11–14]. In addition, the MnO_2-doped BCT system was also studied. The results showed that adding more Mn could inhibit the grain growth and thus achieve good piezoelectric properties (e.g., d_{33}~190 pC/N, $tan\delta^{<}$ 0.5%, and $Q_m{}^{>}$ 1200) [15]. Many researchers also studied the minor doping of Mn, which showed superior piezoelectric properties and temperature stability characteristics. The minor change in composition has an apparent influence on the phase structure, thus affecting the piezoelectric dielectric properties [16]. As mentioned earlier, it was reported that BCTS

* Corresponding author.
E-mail address: 9319484@qq.com (R. Huang).

https://doi.org/10.1016/j.ceramint.2018.01.223
Received 29 December 2017; Received in revised form 26 January 2018; Accepted 26 January 2018
Available online 31 January 2018

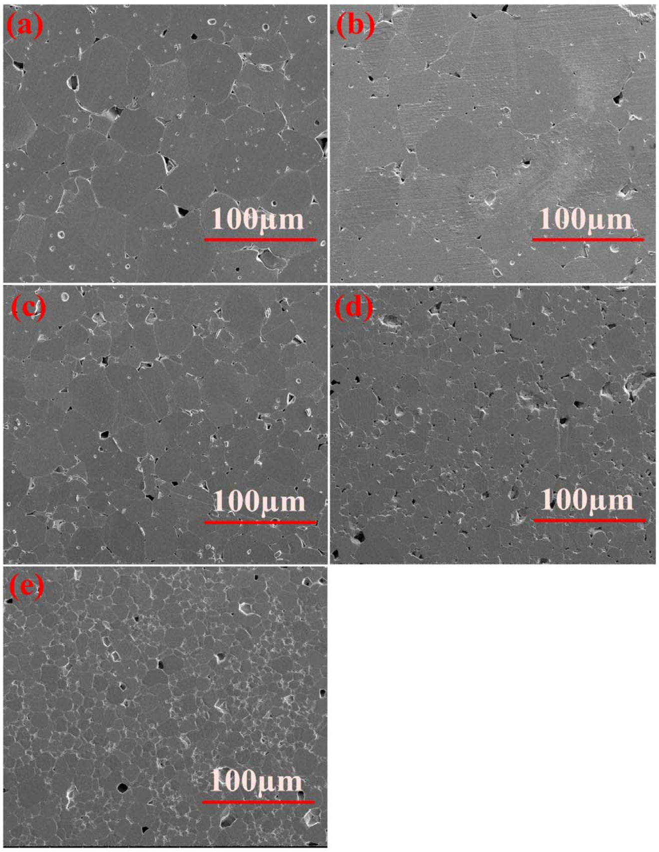

Fig. 1. Typical SEM pictures of the polished surfaces of BCTS ceramics as a function of Mn content, where (a) x = 0, (b) x = 0.2, (c) x = 0.4, (d) x = 0.6, (e) x = 0.8.

ceramics with O-T phase coexistence had higher values of properties [10,17], and MnO_2 doping had a great influence on the structure and properties of BT-based ceramics.

In this work, the effects of MnO_2 content on the crystal structure, microstructure, and electric properties of BCTS ceramics were systematically investigated in this study. The BCTS ceramics were prepared using the conventional solid-state reaction route. The insight of underlying physical mechanisms related to the microstructure and electrical properties are also discussed in this paper.

2. Experimental procedure

The $(Ba_{0.94}Ca_{0.06})(Ti_{0.9}Sn_{0.1})O_3$-xmol%$MnO_2$ (x = 0, 0.2, 0.4, 0.6, and 0.8) piezoelectric ceramics were prepared by the conventional solid-state reaction process. Raw materials of $BaCO_3$ (99.0%, Sinopharm Chemical Reagent Co., Ltd, China), $CaCO_3$ (99.0%, Sinopharm Chemical Reagent Co., Ltd, China), SnO_2 (99.5%, Sinopharm Chemical Reagent Co., Ltd, China), TiO_2 (98.0%, Sinopharm Chemical Reagent Co., Ltd, China) and MnO_2 (85.0%, Tianjin Fuchen Chemical Reagents Factory, China) were weighed according to the nominal stoichiometric ratio and then planetary milled with ZrO_2 balls for 24 h by using the ethanol as a medium. After milling, the powders are dried and calcined at 1200 °C. The calcined powder was mixed with a polyvinyl butyral (PVB) binder solution and pressed into ~ 12 mm in diameter pellets. The pellets were subsequently cold isostatic pressed at 200 MPa for 5 min. These final green pellets were first burnt out at 650 °C, and then sintered at 1440 °C for 2 h in air. The obtained ceramics were polished and coated with silver pastes at ~ 780 °C for 20 min on both sides of these samples as electrodes for electrical measurements. All samples were poled in a silicone oil bath under a dc field of ~ 5.0 kV/mm for 15 min.

The phase structure of these BCTS-based ceramics was characterized by using X-ray diffraction (XRD, D8 ADVANCE, BRUCKER AXS, Germany). The surface morphologies of these ceramics samples after polishing and thermal etching at 1250 °C were characterized by the scanning electron microscopy (SEM, Nova NanoSEM430, FEI, Netherlands). The piezoelectric constant d_{33} of the ceramics was measured using a piezo-d_{33} meter (ZJ-3AN, Institute of Acoustics Academic, China). Dielectric loss was obtained by the precision LCR meter (TH2816A, China). The polarization versus electric field (*P-E*) hysteresis loops of the ceramics were measured using a RADIANT Trek MODEL-609B standard ferroelectric analysis system. Planar electromechanical coefficient k_p and the mechanical quality factor Q_m were measured by the resonance and antiresonance method using a precision impedance analyzers (6500B,Wayne Kerr, UK) based on the IEEE standards [18].

3. Results and discussion

Fig. 1 shows the typical SEM images of the thermally etched surfaces of BCTS ceramics as a function of MnO_2 content. The grain size distribution plots and the average grain size plot as a function of MnO_2 content were also shown in Fig. 2. Results of grain size distribution and average grain size suggest that the addition of MnO_2 dopant strongly influences the microstructure of BCTS ceramics. When the addition amount is 0.2 mol. %, the average grain size increased from ~41.88–52.24 μm, suggesting that the addition of Mn could promote the grain growth. The observed grain growth might be attributed to the fact that the ionic radius of Mn [19], such as Mn^{2+} (r~0.67 Å, low spin; r~0.82 Å, high spin) and Mn^{3+} (r~0.58 Å, low spin; r~0.65 Å, high spin), might replace Ti^{4+} (0.61 Å)/Sn^{4+} (0.71 Å). As results many oxygen vacancies are then produced, which could facilitate the transport of mass, resulting in an increase in grain size [20–22]. However, when the added amount is ≥ 0.4 mol%, the grain size significantly decreases, and the grain size distribution also becomes much narrower (Fig. 2c-e). It is hypothesized that with the addition of higher content MnO_2, the grain growth mechanism may be hindered due to the excessive Mn ions pinning at the grain boundaries, thus resulting in a decrease in grain size [14,23].

The XRD patterns of BCTS ceramics as a function of MnO_2 content are shown in Fig. 3. There were no secondary phase peaks observed in all XRD results, and all samples showed a pure perovskite structure. By comparing the PDF card (05–0626, tetragonal, designated as T phase), the relative strength ratio of (112) and (211) is 3:7. However, for BCTS-0Mn samples, the peak intensity ratio of near 55.9° and near 56.1° is about 7:10. Therefore, XRD results suggest that the phase structure of BCTS-0Mn is not only the T phase, but the coexistence of orthorhombic (designated as O) and T phases. With the increase of Mn content, it was observed that the peaks of near 55.9° and 56.1° shifted to a higher degree. The shift of these two peaks might be hypothesized that the both Sn and Ti ions were substituted by the Mn ions in the BCTS crystal lattice, resulting in a certain degree of lattice distortion. Also, the addition of MnO_2 changed the ratio of the coexistence of O and T phases, and resulted in a slight increase in the proportion of T