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Enhancement of the dielectric, piezoelectric, and ferroelectric properties in $BiYbO_3$-modified $(Ba_{0.85}Ca_{0.15})(Ti_{0.9}Zr_{0.1})O_3$ lead-free ceramics

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Abstract

Lead-free $(1-x)(Ba_{0.85}Ca_{0.15})(Ti_{0.9}Zr_{0.1})O_3-xBiYbO_3$ [$(1-x)$BCTZ$-x$BYO] piezoelectric ceramics in the range of BYO concentrations were prepared by the conventional oxide-mixed method, and the effect of BYO content on their microstructure, crystalline structure, density and electrical properties was investigated. A dense microstructure with large grain was obtained for the ceramics with the addition of BYO. The ceramics with $x=0.1\%$ exhibit an optimum electrical behavior of $d_{33}\sim580$ pC/N, $r\sim10.9\ \Omega$, $k_p\sim56.4\%$, and $\tan\delta\sim1.12\%$ when sintered at a low temperature of $\sim1350\ ^\circ$C. When the measuring electric field is 40 kV/cm, the well-saturated and square-like P–E loops for the ceramics were observed with $P_r\sim12.2\ \mu C/cm^2$ and $E_c\sim1.83$ kV/cm.

Keywords: C. Piezoelectric properties; C. Ferroelectric properties; D. Perovskite; Microstructure

1. Introduction

Recently, due to environmental concerns, lead-free piezoceramics have been given to much attention [1–10]. In the search for lead-free piezoceramics candidates, such as $Bi_{0.5}Na_{0.5}TiO_3$ [5,6,11] and $K_{0.5}Na_{0.5}NbO_3$ [7,8,12] materials have been extensively conducted to improve their piezoelectric properties, but their piezoelectric constants are lower than that of lead zirconate titanate (PZT) piezoelectric ceramics [13–15]. Therefore, it is necessary to develop lead-free piezoceramics systems with higher piezoelectric properties to replace PZT ceramics.

In recent years, an increasing amount of research has been done on the new piezoelectric materials of the $BaTiO_3$-based ceramics systems [1–4,16–18]. In these systems, Mn- and Cu-modified $(1-x)BiFeO_3-xBaTiO_3$ ceramics exhibited a high T_c of $\sim485\ ^\circ$C, but with a low-field piezoelectric properties of $d_{33}\sim170$ pC/N, $k_p\sim34.2\%$, which was reported by Zhou [1]. In 2009, a surprisingly high piezoelectric property of $d_{33}\sim620$ pC/N has been reported for the $BaTiO_3$-based ceramics by Ren [18]. Since then, a new piezoelectric system $(Ba_{0.85}Ca_{0.15})(Ti_{0.9}Zr_{0.1})O_3$ (BCTZ) with a super high d_{33} was extensively investigated [16,19–21]. Hao et al. [22] showed that the samples with grain size $>10\ \mu m$ exhibit excellent piezoelectric properties as $d_{33}\sim470$ pC/N, $k_p\sim48\%$ using different sintering methods for BCTZ piezoceramics. Damjanovic et al. [17] reported that the temperature-induced anomalies in the dielectric, piezoelectric, elastic coefficients and Raman spectroscopy of BCTZ ceramics. The $[(Ba_{1-3x/2}Bi_x)_{0.85}Ca_{0.15}](Ti_{0.9}Zr_{0.1})O_3$ ceramics with $x=0.75\%$ exhibits an optimum electrical behavior of $d_{33}\sim361$ pC/N and $k_p\sim40.2\%$ [23]. In our previous study, CeO_2-modified BCTZ ceramics exhibited improved electrical properties of $d_{33}\sim600$ pC/N, $k_p\sim51\%$, $\tan\delta\sim1.2\%$ [24]. In addition, Shi [25] found $(1-x)(0.36BiScO_3–0.64PbTiO_3)-xBiYbO_3$ piezoelectric ceramics to exhibit a good piezoelectric constant $d_{33}\sim443$ pC/N with a high Curie temperature of $T_c\sim450\ ^\circ$C. Feng et al. [26] stated that a very promising material of $xBiYbO_3–(1-x)PbTiO_3$ piezoelectric ceramics for a high Curie temperature (T_c up to $590\ ^\circ$C). And the BYO material has a high Curie temperature of $T_c\sim650\ ^\circ$C [27].

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In this present work, the microstructure, dielectric, piezoelectric, and ferroelectric properties of $(1-x)$BCTZ$-x$BYO ceramics were studied. With the optimized processing, the enhanced d_{33} and tan δ in the $(1-x)$BCTZ$-x$BYO system were obtained. These results show that the $(1-x)$BCTZ$-x$BYO ceramics with good electrical properties are induced by doping an optimum BYO content.

2. Experimental procedure

The $(1-x)(Ba_{0.85}Ca_{0.15})(Ti_{0.9}Zr_{0.1})O_3-x$BiYbO$_3$ [$(1-x)$ BCTZ$-x$BYO] (x=0, 0.05, 0.1, 0.2, 0.4, and 0.6%) ceramics were prepared by a conventional ceramics technique. The starting raw materials were TiO_2, Bi_2O_3, ZrO_2, Yb_2O_3, $BaCO_3$, and $CaCO_3$ (>99.5%, Analytically pure). The powders in the stoichiometric ratio of the compositions were mixed thoroughly in ethanol using ZrO_2 balls for 20 h, and then dried and calcined at 1250 °C for 4 h in air. After the calcination, the mixture was wet ball-milled again for 10 h dried and granulated with 5 wt% PVA as a binder, and then pressed into green disks with diameters of 12 mm and thickness 1 mm under a pressure of 100 MPa. After burning off PVA at 600 °C for 2 h the disk samples were sintered at 1350 °C for 4 h in the sealed Al_2O_3 crucibles. Silver paste was screen-printed on the surfaces as electrodes and then fired at 600 °C for 40 min.

Phase purity and crystal structure were characterized using X-ray diffraction (XRD, Bruker D8-2-Advance, Bruker AXS, Germany). Volume density (ρ_v) and relative density (ρ_r) of the specimens were measured by the Archimedes method using deionized water as medium. Grain morphology of the samples was examined using scanning electron microscopy (SEM, JSM-5610LV/Noran-Vantage, JEOL, Tokyo, Japan). These ceramics were poled at 40 °C in a silicone oil bath under a dc field of 4 kV/mm for 20 min. The direct piezoelectric coefficient (d_{33}) was measured using a Berlincourt d_{33} meter (ZJ-3A, China) at 110 Hz. Piezoelectric and dielectric properties were measured using an impedance analyzer (Agilent 4294A, Agilent Technologies, America). The polarization–electric field (P–E) loops of ceramics were observed at different temperature and 1 Hz using a ferroelectric tester (Radiant Precision Work-station, America) with a programmable 9023 Delta Design oven (Delta Design, San Diego, CA).

3. Results and discussions

The XRD patterns of $(1-x)$BCTZ$-x$BYO ceramics are shown in Fig. 1a. These data show that all ceramics are consistent with a single phase perovskite and no secondary phases were detected [28]. This result indicates that a stable solid solution is formed between BCTZ and BYO in this work range of $0<x<0.6\%$. Fig. 1b shows the expanded XRD patterns in the 2θ range of 45–45.5° of $(1-x)$BCTZ$-x$BYO piezoelectric ceramics. At room temperature, there are different peak shapes for these ceramics with the increase of BYO content. The $(1-x)$BCTZ$-x$BYO ceramic exhibits a coexistence of tetragonal and rhombohedral phases with splitting of the (002) and (200) peaks [4,29]. As x increases, the $(1-x)$ BCTZ$-x$BYO ceramics have a feature with obvious splitting of the (002) and (200) peaks, and increase a intensity ratio of the tetragonal and rhombohedral (002)/(200). The $(1-x)$ BCTZ$-x$BYO ceramics with the increase of x to 0.1%, the integrated diffraction intensity of the (200) peak nearly increases to the value of the integrated diffraction intensity of the (002) peak, as shown in Fig. 1b. The morphotropic phase boundary (MPB) between rhombohedral and tetragonal is always obtained in this work range of $0<x<0.6\%$ [21,30].

Fig. 2 shows the effect of x on the Volume density (ρ_v) and relative density (ρ_r) of $(1-x)$BCTZ$-x$BYO ceramics sintered at 1350 °C for 4 h. With increasing BYO content, the ρ_v and ρ_r of the ceramics first increase evidently, reach their maximum value of $\rho_v \sim 5.612$ g/cm^3 and $\rho_r \sim 98.2\%$ at $x=0.1\%$ and then decrease slightly as $x>0.1\%$. Hence, we can see that a small amount of BYO content help to enhance the density of ceramics and lower the sintering temperature. The surface microstructure of $(1-x)$BCTZ$-x$BYO ceramics sintered at 1350 °C for 4 h are shown in Fig. 3. Grain size obviously was

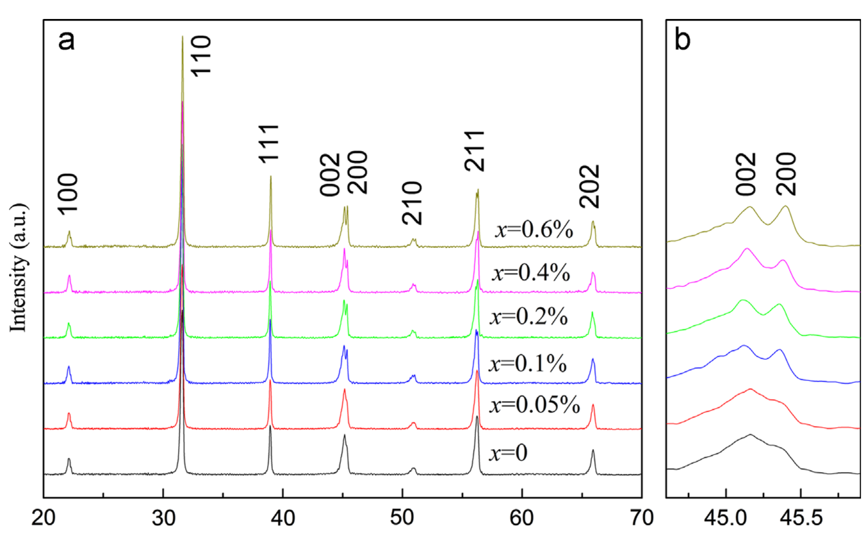

Fig. 1. (a) XRD patterns and (b) expanded XRD patterns of $(1-x)$BCTZ$-x$BYO ceramics as a function of x.