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Characterization of acceptor-doped (Ba, Ca)TiO_3 "hard" piezoelectric ceramics for high-power applications

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ABSTRACT

Acceptor Mn or Co-doped $Ba_{0.925}Ca_{0.075}TiO_3$ (abbreviated as BCT-Mn and BCT-Co) lead-free piezoelectric ceramics with high density and fine grains were synthesized by conventional solid-state reaction method. The phase structure and electrical properties of the ceramics were investigated. The acceptor-doped BCT ceramics were found to exhibit asymmetrical polarization-electric field hysteresis loops corresponding to the presence of an internal bias field E_i, indicating that the domain walls were pinned by preferentially oriented defect dipoles formed by the acceptors and oxygen vacancies. High mechanical quality factor Q_m and low dielectric loss $tan\delta$ were obtained for the ceramics due to the strong internal bias field (E_i =4–5kV/cm). In particular, BCT-Mn ceramics exhibited the best properties, with mechanical quality factor Q_m =1020, dielectric loss $tan\delta$=0.2% and piezoelectric coefficient d_{33} =190 pC/N. Furthermore, the planar electromechanical coupling factor k_p for BCT-Mn ceramics was found to be larger than 0.4 in the temperature range of 25 °C to 75 °C. These results indicate that the Mn-doped BCT lead-free ceramics material is a promising candidate for high-power piezoelectric applications.

1. Introduction

Lead-free $BaTiO_3$ (BT) ceramics were historically the first man-made polycrystalline ferroelectric materials and developed for various piezoelectric applications such as actuators, sensors and transducers [1]. With the discovery of high piezoelectric properties in $Pb(Zr_{1-x}Ti_x)O_3$ (PZT) ceramics at the morphotropic phase boundary (MPB), BT has been primarily investigated and commercialized as a base dielectric material owing to its superior dielectric properties [2,3]. However, because of the environmental regulations now days, it is desirable to develop lead-free piezoelectric materials with comparable properties to replace the lead-based counterparts [4–6]. In recent years, BT-based ceramics as a member of lead-free families have been intensively revisited and studied for piezoelectric applications [7–15]. High piezoelectric coefficients (d_{33} =350–519 pC/N) were reported for pure BT ceramics fabricated by ordinary, microwave and two-step sintering methods, revealing that the d_{33} can be enhanced by controlling the grain size and the corresponding domain structure [7,8]. Some elements (e.g. Ca, Zr, Sn, and Hf) were actively used to improve the piezoelectric properties by driving the formation of different phase boundaries in BT-based solid solutions [9–15]. Specially, a high d_{33} value on the order of 620pC/N was reported in the $Ba(Zr_{0.2}Ti_{0.8})TiO_3$-$(Ba_{0.7}Ca_{0.3})TiO_3$ (BZT-50BCT) solid solutions at the morphotropic phase boundary [9]. However, in the above cases, the high piezoelectric response is attributed to the existence of the polymorphic phase boundary or morphotropic phase boundary, and it exhibits strong temperature instability and thermal hysteretic effects [16]. On the other hand, there was limited work focusing on the "hard" BT-based piezoelectric ceramics with low mechanical loss (high mechanical quality factor Q_m) and dielectric loss tanδ for high-power applications [17]. These piezoelectric applications such as ultrasonic motors, transformers and high intensity focused ultrasound (HIFU) demand high Q_m and low tanδ to deliver high acoustic power without excess heat generation and increase the efficiency at resonance or off-resonance frequencies [18].

To achieve the "hardening" effects (high Q_m and low $tan\delta$ values), lead-based piezoelectric ceramics such as PZTs are usually acceptor doped, e.g, with $Mn^{3+,2+}$ and $Fe^{3+,2+}$ substitution on the Zr^{4+}/Ti^{4+} sites, resulting the development of acceptor-oxygen vacancy defect dipoles (e.g., Mn_{Ti}''-$V_O^{\bullet\bullet}$). These defect dipoles can align along the spontaneous polarization direction through diffusion of oxygen vacancies during aging process, leading to internal bias fields as evident in the horizontal shifted and constricted polarization-electric field loops for the poled and unpoled ceramics, respectively [19]. The internal bias field effectively increases the coercive field (E_c) and thus stabilizes the domain-wall motion. Consequently, the acceptor dopants decrease the

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piezoelectric activity of the ceramics, but result in a considerable decrease of mechanical loss and dielectric loss by reducing the extrinsic contribution from domain-wall motion [20–22]. Therefore, analogue to the acceptor-doped "hard" PZT ceramics, it is predictable that high Q_m and low $tan\delta$ can be obtained in the acceptor-doped lead-free BT ceramics. It should be noted that there is an orthorhombic-tetragonal phase transition near room temperature for pure BT ceramics, which is also undesirable for practical applications due to the temperature instability of piezoelectric properties [1,16]. It was reported that, in (Ba,Ca)TiO3 solid solutions, partial substitution of Ba^{2+} with Ca^{2+} causes a negligible change of Curie temperature T_c, but a strong decrease of orthorhombic-tetragonal phase transition temperature T_{o-t}, leading to improve temperature reliability of tetragonal phase and inhibit formation of the hexagonal phase of BT [1,23]. Our preliminary studies also revealed that the T_{o-t} could be shifted from near room temperature to −35 °C but with Curie temperature T_c maintained at about 133 °C by substituting Ba with 7.5% mol Ca. Therefore, our studies were focused on the acceptor-doped (Ba, Ca)TiO_3 sold solutions.

In this paper, the phase structure, dielectric, piezoelectric and ferroelectric properties of the 0.75% mol Mn or 0.75 mol% Co-doped (Ba,Ca)TiO_3 ceramics were investigated to obtain a new type of lead-free piezoelectric ceramics for high-power applications, meanwhile the pinning and depinning of domain walls in the poled ceramics were investigated in terms of the internal bias field E_i.

2. Experimental

0.75% mol Mn-doped $Ba_{0.925}Ca_{0.075}TiO_3$ and 0.75% mol Co-doped $Ba_{0.925}Ca_{0.075}TiO_3$ ceramics (denoted as BCT-Mn and BCT-Co) were prepared by the conventional solid-state reaction method. High purity $BaCO_3$ (99.8%), $CaCO_3$ (99.9%), TiO_2 (99.99%), MnO_2 (99%) and $CoCO_3$ (99%) were selected as raw materials. The powders were weighed according to the nominal compositions of $Ba_{0.925}Ca_{0.075}TiO_3$ and then were milled using zirconia ball media in ethanol for 24 h. In order to prevent the abnormal grain growth and achieve microstructure with fine grains, 1% mol extra $BaCO_3$ was added to the powders [24]. After milling, these powders were dried and calcined at 1100 °C for 4 h. Then MnO_2 or $CoCO_3$ powders were added into the calcined powders and milled for 12 h again, subsequently granulated and pressed into pellets under 200 MPa. Then the pellets were sintered at 1300 °C for 4 h. The obtained ceramics were polished and silver pastes were fired on the surfaces at 700 °C for 20 min as electrode. The ceramics were poled under a dc field of 3 kV/mm in silicon oil for 20 min at room temperature and aged for 24 h prior to the electrical measurements.

The phase structure was examined by X–ray powder diffraction (XRD) with CuK_α radiation (PANalytical X'pert PRO, Phillips, Eindhoven, the Netherlands). The microstructure of the polished and thermally etched ceramics was investigated using a scanning electron microscopy (SEM; S-3500, Hitachi, Tokyo, Japan). The dielectric constant at room temperature was measured using a capacitance meter (HP4278A; Hewlett-Packard, Palo Alto, USA) at 1 kHz. The dielectric constant and loss tangent as a function of temperature was determined using multifrequency LCR meter (4284A, Agilent, Santa Clara, USA) in a temperature controlled furnace. The high field measurements including polarization hysteresis (P–E) loops and strain-electric field curves (S-E) were measured by using a modified Sawyer-Tower circuit and linear variable differential transducer (LVDT), driven by a lock-in amplifier (SR830, Stanford Research Systems Inc., Sunnyvale, USA). The electromechanical coupling factors and mechanical quality factor Q_m were determined by a resonance method according to the IEEE standards using an impedance analyzer (4194 A, Agilent, Santa Clara, USA). The planar electromechanical coupling factor k_p and thickness mode coupling k_t were measured using the disk samples with large diameter to thickness ratios ($\varphi/t \geq 10$). The longitudinal electromechanical coupling factor k_{33} was measured using the rod samples with large length to width ratios ($l/w \geq 10$). The piezoelectric coefficient d_{33} was measured using a piezo–d_{33} meter (ZJ–4A, Institute of Acoustics, Chinese Academy of Science, Beijing, China).

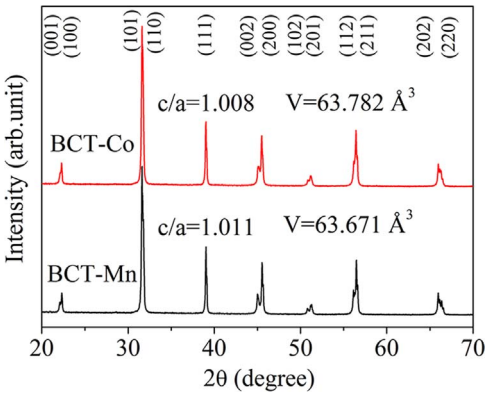

Fig. 1. XRD patterns for BCT-Mn and BCT-Co ceramics.

3. Results and discussion

The XRD patterns for BCT-Mn and BCT-Co ceramics are presented in Fig. 1. It can be seen that both BCT-Mn and BCT-Co ceramics exhibit the pure perovskite phase structure. The (002)/(200) peak splitting around 45° indicates that crystallographic symmetry of the ceramics is tetragonal. It is believed that the Mn and Co cations were incorporated into the B sites of the perovskite structure because the radii of $Mn^{2+,3+4+}$(r~0.67, 0.58 and 0.54 Å) and $Co^{2+,3+}$(r~0.65, 0.525 Å) are similar with that of Ti^{4+}(r~0.605 Å) [25]. The c/a ratios were caculated for BCT-Mn and BCT-Co ceramics, being 1.011 and 1.008, respectively. While the volume of unit cell for BCT-Mn and BCT-Co ceramics were calculated, being 63.671 $Å^3$ and 63.782 $Å^3$, respectively.

Fig. 2 shows the SEM micrographs of the polished and thermally etched fracture surfaces for the acceptor-doped BCT ceramics sintered at 1300 °C for 4 h. There were no obvious pores observed between the grain boundaries or within the grains, which indicates that the ceramics were well sintered under the high temperature. The relative densities of BCT-Mn and BCT-Co ceramics reach as high as 98%, due to

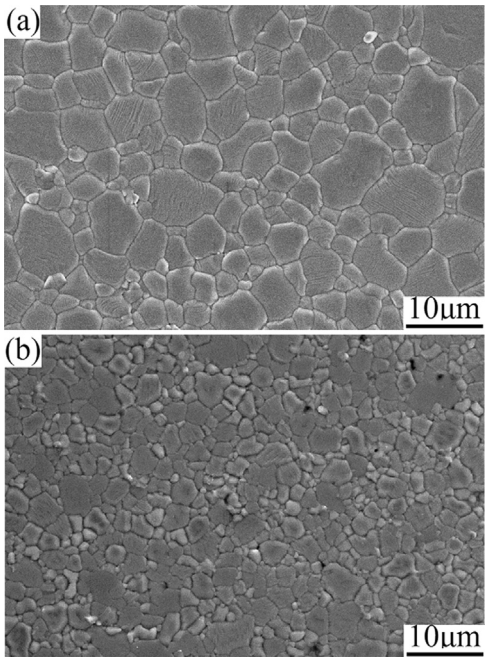

Fig. 2. SEM micrographs of the polished and thermally etched facture surfaces for the acceptor-doped BCT ceramics. (a) BCT-Mn and (b) BCT-Co.