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Role of Cu and Y in sintering, phase transition, and electrical properties of BCZT lead-free piezoceramics

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ABSTRACT

Lead-free $(Ba_{0.85}Ca_{0.15})(Ti_{0.9}Zr_{0.1})O_3$-xwt%CuOywt%$Y_2O_3$ (BCZT-Cu_xY_y) ceramics with high piezoelectricity were synthesized by the conventional solid-state reaction method. The role of Cu and Y (Cu/Y) in sintering, phase transition, and electrical properties of such ceramics was systematically studied. The results indicated that the sintering temperatures of BCZT-Cu_xY_y decreased by at least 100 °C due to the low melting point of CuO. The promotion effect of Cu/Y on phase transition lied in the improvement of T_C by 5–15 °C and the coexistence of O +T phase near room temperature. The contribution of Cu/Y to electrical properties was mainly ascribed to the grains growth, the formed oxygen vacancies and lattice distortions, and the donor doping effect of Y^{3+}. Adding 0.10 wt% Cu^{2+} and 0.06 wt% Y^{3+} into BCZT dramatically improved the electrical properties as following: d_{33} = 552 pC/N, ε_m = 10175, ε_r = 4546, tanδ = 0.016, T_C = 100 °C, k_p = 0.475, Q_m = 157.2, P_r = 10.82 μC/cm^2 and E_C = 2.33 kV/cm. A plausible mechanism was obtained to explain the reaction process and the favorable performances of BCZT-Cu_xY_y. Co-doping Cu^{2+} and Y^{3+} into BCZT could be a promising method to improve and balance the sintering, phase transition, and electrical properties for potential practical applications of lead-free piezoceramics.

1. Introduction

$Pb(Zr_{1-x}Ti_x)O_3$ (PZT), the dominating piezoceramic used in electronic devices, has attracted great attention due to its high lead content bringing huge damage to human health and the environment during calcination and sintering processes [1,2]. Over the past years, numerous efforts have been made to substitute PZT with lead-free piezoelectric ceramics, with $Bi_{0.5}Na_{0.5}TiO_3$ (BNT), $K_{0.5}Na_{0.5}NbO_3$ (KNN) and $BaTiO_3$ (BT) being considered the most potential substitutes [3–5].

Considering BNT and KNN as the promising lead-free alternatives is mostly because of their high Curie temperature (T_C) and large remnant polarisation (P_r) [6,7]. However, unstable alkali components and evaporation at high temperature make it hard to ensure accurate chemical ratios and good electrical properties [8]. Therefore, most recent studies have focused on BT system which has higher piezoelectric coefficient (d_{33}) and electromechanical coupling factor (k_p), such as $(Ba,Ca)TiO_3$ (BCT) [9], $Ba(Zr,Ti)O_3$ (BZT) [10], $(Ba,Ca)(Zr,Ti)O_3$ (BCZT) [11,12], $(Ba,Ca)(Ti,Sn)O_3$ (BCTS) [13,14].

Among them, BCZT has been extensively studied in recent years since Liu and Ren reported [15] that BCZT ceramic has a large piezoelectric coefficient d_{33} (620 pC/N) that is comparable to that of PZT. However, it is worth noting that the practical applications of BCZT ceramics are seriously limited by their high sintering temperature (T_{sin}) of 1500 °C and low Curie temperature of 93 °C. Hence, many researchers have paid much attention to improving the sinterability and Curie temperature of BCZT ceramics [16–23]. On the one hand, metallic oxides like Li_2CO_3 [16,17], CuO [18,19], and MnO [20] are often used as the sintering aids and introduced into BCZT ceramics to lower the sintering temperature. As Chen et al.'s reported [17], the appropriate addition of Li^+ significantly enhanced the sinterability of BCZT by reducing the sintering temperature to 1350 °C while keeping the piezoelectricity high at 493 pC/N. Whereas, all the obtained properties were at the cost of a low Curie temperature of 70 °C. Similarly, Wang et al. [18] found that a small amount of Cu^{2+} can lower the sintering

Abbreviations: Cu/Y, Cu and Y; T_{sin}, Sintering temperature

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temperature to 1230 °C, but the piezoelectric properties (382 pC/N) and Curie temperature (87 °C) are still relatively limited. On the other hand, changing the stoichiometric composition of BCZT from $(Ba_{0.85}Ca_{0.15})(Ti_{0.9}Zr_{0.1})O_3$ to $(Ba_{0.99}Ca_{0.01})(Ti_{0.98}Zr_{0.02})O_3$ or $(Ba_{0.98}Ca_{0.02})(Ti_{0.98}Zr_{0.02})O_3$ usually dramatically increases the Curie temperature from around 90–120 °C according to some studies [1,6,21–23]. However, the piezoelectric coefficients reported in most of these studies are below 400 pC/N despite the addition of some aids into the BCZT ceramics. These above results suggest that it is difficult to simultaneously improve and balance the sinterability, phase transition and electrical properties by only introducing one sintering agent or just changing the composition of BCZT. Therefore, co-doping oxides into BCZT ceramics, one serving as the sintering aids and the other used for promoting the phase transition and electrical performance, appears a feasible idea to satisfy the above three requirements and consequently, beneficially impact the possible practical applications.

Therefore, in this study, the co-doping idea was adopted in order to accelerate the academic and practical development of BCZT-based lead-free ceramics. Specifically, Cu^{2+} and Y^{3+} were co-added into BCZT to obtain $(Ba_{0.85}Ca_{0.15})(Ti_{0.9}Zr_{0.1})O_3$-xwt%CuOywt%$Y_2O_3$ (BCZT-Cu_xY_y) ceramics by the conventional solid-state reaction method. The role of Cu/Y in the sintering process was investigated to lower the sintering temperature and perfect the densification process. Meanwhile, the promoting effect of Cu/Y on phase transition and electrical properties was well analysed to elucidate the functional mechanism of Cu/Y in BCZT-based ceramics.

2. Experimental

2.1. Preparation of the BCZT-based ceramics

$BaCO_3$, $CaCO_3$, TiO_2, ZrO_2, CuO, and Y_2O_3 (≥ 99.0%, AR) were used as the raw materials to prepare $(Ba_{0.85}Ca_{0.15})(Ti_{0.9}Zr_{0.1})O_3$-xwt%CuOywt%$Y_2O_3$ (BCZT-Cu_xY_y) piezoelectric precursor powders and ceramics by the conventional solid-state reaction method. In accordance with the typical procedure, requisite quantities of raw materials were mixed in stoichiometric ratios and ball-milled for 1 h with the addition of ethanol. After being dried at 100 °C for 12 h, the mixtures were calcined at 1000 °C for 2 h. Subsequently, the calcined powders were remixed and pressed into pellets under 100 MPa (Ø20 mm × 1.8 mm), and then these pellets were sintered at 1250–1500 °C for 4 h. The samples in this study are denoted as BCZT-Cu_xY_y, where x = 0–0.15 wt% and y = 0–0.10 wt%.

2.2. Characterisation techniques

The crystalline phases of the ceramics were determined by X-ray diffraction (XRD, X′pert Pro MPD, PANalytical) with an Ni-filtered Cu Kα radiation source. The physical morphologies of the ceramics were collected by scanning electron microscopy (SEM, JSM 6700 M, JEOF). The microstructure and the elements distribution of the ceramics are confirmed by field emission electron microscope (FETEM, JEM-2100F, JEOL). The molecular structures of the ceramics were analysed by a laser microscopic confocal Raman spectrometer (Raman, LabRAM HR800, Horiba Jobin Yvon). The grain size of the ceramics was obtained by a Nano Measurer (an image analysis software, Version 2.1.5, Xiaomuchong Corporation, China), and five SEM images were chosen for each sample to minimise the measuring error. The linear shrinkage (S) was calculated by the equation: S (%) = (d_0-d/d_0)%, where d_0 and d represent the diameter of the original and sintered ceramics, respectively. Bulk density (ρ_b) of the ceramics was determined by the Archimedes method (ASTM C373). Relative density (ρ_r) was defined by the formula as follows: ρ_r (%) = (ρ_b/ρ_t) %, where ρ_t was the theoretical density of BCZT ceramics.

2.3. Measurements of electrical properties

Prior to the measurement of electrical properties, both sides of the pellets were first coated with silver paste and then fired at 650 °C for 30 min to form Ag electrodes. The coated pellets were polarised by applying a DC field of 2.8 kV/mm for 30 min in a silicone oil bath at room temperature. After laying the polarised ceramics for 24 h, the piezoelectric coefficient d_{33} of these ceramics were measured by a quasi-static piezoelectric coefficient d_{33} testing meter (ZJ-3A, Institute of Acoustics, Chinese Academy of Sciences, China). The temperature dependence of the dielectric constant (ε_r) and dielectric loss (tanδ) was examined at 1 kHz using a LCR analyser (HP4284A, Agilent, America). The electromechanical coupling coefficient and the mechanical quality factor (Q_m) were calculated by a resonance antiresonance method with an impedance analyser (HP4294A, Agilent, America). The ferroelectric hysteresis loops (P-E) were carried out by a ferroelectric tester (WS-2000, Radiant, America).

3. Results and discussion

3.1. Promotion effect of Cu/Y on sintering

To investigate the possible promotion effect of Cu/Y on the sintering process as well as the crystalline phases of the ceramics, XRD measurements were carried out for BCZT-$Cu_{0.10}Y_{0.06}$ ceramics (The reason for choosing this component will be explained in Sections 3.2 and 3.3) at various sintering temperatures of 1250–1500 °C. It is evident in Fig. 1(a) that obvious impurity phases appear in the solid solutions when T_{sin} < 1350 °C, implying that the suitable sintering temperature of BCZT-$Cu_{0.10}Y_{0.06}$ should be at least 1350 °C. This is much lower than the temperature reported for pure BCZT ceramics (1500 °C) [15], and indicates the potential facilitating effect of Cu/Y additions on the sintering process. The main contributor for this effect might be CuO as its low melting point of 1026 °C. The fine scanning XRD in the 2θ range of 44.5°–46° (Fig. 1(b)) was measured to estimate the impact of various sintering temperatures on the phase transformation of BCZT-$Cu_{0.10}Y_{0.06}$ ceramics. Commonly, rhombohedral (200), orthorhombic (200)/(022), and tetragonal (002)/(200) are the three main phases corresponding to the peaks at around 45° in BT-based ceramics [18,24]. As plotted in Fig. 1(b), there is no significant change in the characteristic peaks at 45° and only orthorhombic (O) phase was found to form in the ceramics when T_{sin} ≤ 1350 °C. With further increase in sintering temperatures, however, the peaks at 45° gradually separated to two consecutive parts of (002) and (200), denoting the emergence of the tetragonal (T) phase and the coexistence of O and T phases. Moreover, only T phase was

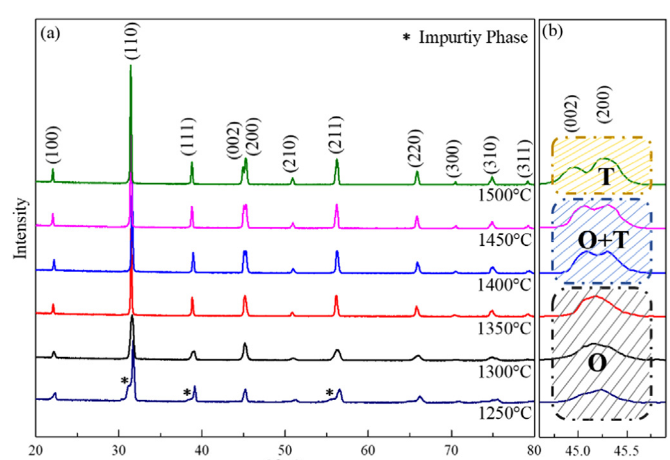

Fig. 1. XRD patterns of the BCZT-$Cu_{0.10}Y_{0.06}$ ceramics sintered at different temperatures in the 2θ range of (a) 20°–80°, and (b) 44.5°–46°.