



Structure and piezoelectric properties of $(\text{Ba}_{1-x}\text{Ca}_x)(\text{Ti}_{0.95}\text{Hf}_{0.05})\text{O}_3$ lead-free ceramics

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ABSTRACT

Lead-free $(\text{Ba}_{1-x}\text{Ca}_x)(\text{Ti}_{0.95}\text{Hf}_{0.05})\text{O}_3$ ($x = 0.04\text{--}0.14$) (BCHT) ceramics with good piezoelectric properties were successfully prepared using solid state reaction method. The structural and electrical properties of the BCHT ceramics were systematically studied. The polymorphic phase transitions (PPT) from orthorhombic phase to tetragonal phase shifts towards low temperature with increasing Ca contents, and the PPT can be obtained at room temperature (RT) in the composition range of 0.08–0.10 for the BCHT ceramics. The tetragonality of the BCHT ceramics at PPT is increased after poling treatment as depicted in the XRD patterns and Raman spectroscopy. The BCHT ceramics at $x = 0.08$ exhibit good piezoelectric properties ($d_{33} = 380$ pC/N, $k_p = 50\%$ and $S_{\text{max}} = 0.19\%$ under the applied electric field of 50 kV/cm) and ferroelectric property ($P_r = 13.4$ $\mu\text{C}/\text{cm}^2$), due to the coexistence of tetragonal phase and orthorhombic phase. The aging rate of d_{33} values from 20 °C to 90 °C is lower than 20% in this work, indicating that the BCHT ceramics have good temperature stability. The high piezoelectric properties with good temperature stability indicate that the BCHT ceramics are promising candidates as lead-free piezoelectric ceramics.

1. Introduction

Nowadays, lead zirconate titanate (PZT-based) ceramics, have been widely utilized in various electromechanical devices such as buzzers, actuators, transducers, sensors, transformers and piezoelectric energy harvesting [1,2], attributing to their superior piezoelectric properties near the morphotropic phase boundary (MPB) between rhombohedral and tetragonal phases. Nevertheless, Pb element causes much serious environmental pollution during the manufacture process and the procedures of using. With the development of environment friendly, many researches have been focused on lead-free piezoceramic systems such as $(\text{K}_{0.5}\text{Na}_{0.5})\text{NbO}_3$ (KNN)-based [3], $(\text{Bi}_{0.5}\text{Na}_{0.5})\text{TiO}_3$ (BNT)-based [4] and BaTiO_3 (BT)-based [5] piezoceramics. Some of lead-free piezoceramics possess quite piezoelectric coefficient d_{33} values close to that of lead contained piezoceramics [6]. These lead-free ceramics are also deemed as promising substitutes for lead-free piezoelectric materials and possess great potential for electromechanical application of electricity and microelectronics.

Among these piezoceramics, BT-based ceramics exhibit good piezoelectric property ($d_{33} \geq 300$ pC/N) and relatively high dielectric constant [7]. Therefore, BT-based ceramics is considered as one of the

most promising candidate for the PZT systems because of its outstanding electrical properties and high degree of solid solution with other perovskites [8]. For example, the $\text{Ba}(\text{Ti}, \text{Zr})\text{O}_3$ [9], $\text{Ba}(\text{Ti}, \text{Hf})\text{O}_3$ – $(\text{Ba}, \text{Ca})\text{TiO}_3$ [10] and $\text{Ba}(\text{Ti}, \text{Sn})\text{O}_3$ – $(\text{Ba}, \text{Ca})\text{TiO}_3$ [11] systems. The excellent piezoelectric property is attributed to the PPT, which is the coexistence of tetragonal phase and orthorhombic phase or the coexistence of rhombohedral phase and orthorhombic phase. The free energy at PPT is isotropic and independent of polarization direction leading to none existence of energy barrier for polarization rotation [12]. However, the high sintering temperature (≥ 1400 °C) and the low Curie temperature (T_c) (~ 90 °C) are the disadvantages of BT-based ceramics. These also are barriers of the practical application of BT-based ceramics [13]. Hence, it is high time to put more attentions to investigation of optimizing the properties of BT-based ceramics.

Recently, lead-free $(\text{Ba}, \text{Ca})(\text{M}, \text{Ti})\text{O}_3$ (BCMT, $\text{M} = \text{Zr}, \text{Sn}$) systems were reported with a special focus on their high piezoelectric performance near the PPT around RT. Large piezoelectric response suggests that they might be the promising alternatives for lead-based piezoelectric materials. Moreover, there are little literature reports on confirming the substitution of Ti^{4+} in BaTiO_3 with quadrivalence ions (such as Hf^{4+} or Ce^{4+}), which can largely improve the overall

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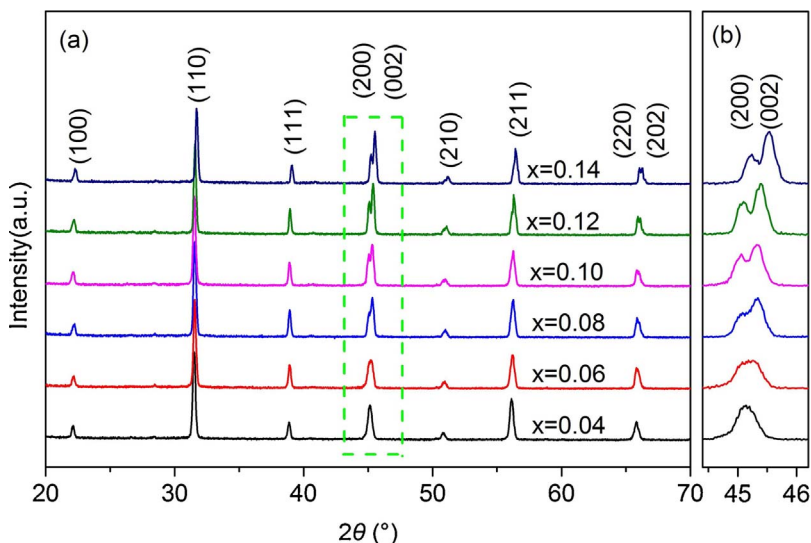


Fig. 1. The XRD patterns of the BCHT ceramics in the 2θ range: (a) $20\text{--}70^\circ$ and (b) $44.5\text{--}46.5^\circ$.

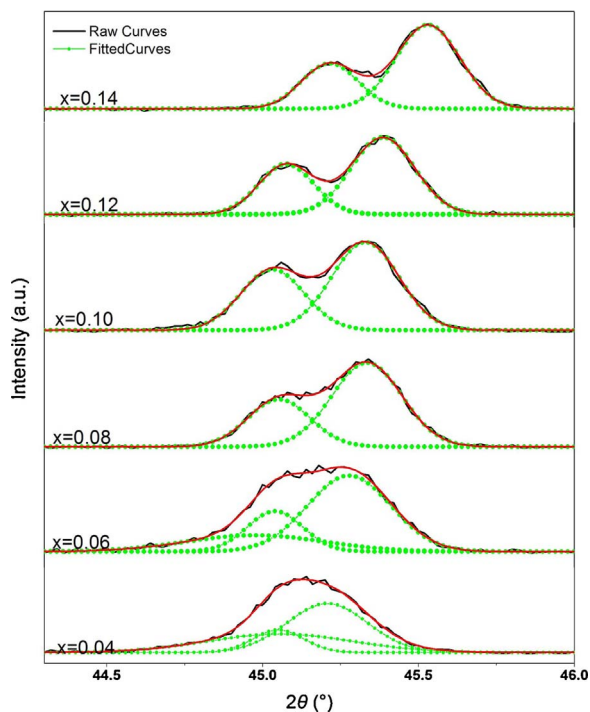


Fig. 2. Gaussian fitting curves of the BCHT ceramics in the 2θ range: $44.5\text{--}46.5^\circ$.

properties of the material. In the present work, $(\text{Ba}_{1-x}\text{Ca}_x)(\text{Ti}_{0.95}\text{Hf}_{0.05})\text{O}_3$ (BCHT) ($x = 0.04, 0.06, 0.08, 0.10, 0.12$ and 0.14) ceramics, were prepared by the conventional solid state reaction method. The structural, dielectric, ferroelectric, and piezoelectric properties were systematically investigated in this research. Particularly, the structural and electrical properties of the BCHT ceramics were measured at unpoled and poled states, for searching for high-performance lead-free piezoelectric materials as well as expanding the range of the lead-free BCMT systems.

2. Experimental procedure

The $(\text{Ba}_{1-x}\text{Ca}_x)(\text{Ti}_{0.95}\text{Hf}_{0.05})\text{O}_3$ ($x = 0.04, 0.06, 0.08, 0.10, 0.12$ and 0.14 , BCHT) lead-free ceramics, were prepared by conventional solid state reaction method, using reagent-grade metal oxides or carbonate powders of CaCO_3 (99%), BaCO_3 (99%), TiO_2 (99.5%) and HfO_2 (99.99%) as starting materials. The raw materials made by Sinopharm

Chemical Reagent Co. Ltd. were weighed at stoichiometric proportion and then mixed homogeneously by planetary ball milling in a polyethylene with stabilized zirconia balls for 12 h, using anhydrous ethanol as liquid medium. After drying, the mixed powders were calcined at 1250°C for 4 h. After calcination, the mixture was milled again for 12 h. The powders were mixed with an appropriate amount of PVA, and pressed into pallets with diameter of 12 mm and thickness of 1.0 mm under the pressure of about 200 MPa. The pressure used to form pellets was uniaxial. After burning off PVA, the ceramics were sintered in an alumina crucible at 1450°C for 4 h. Poling process of the BCHT ceramics at $x = 0.08$ was performed in silicone oil under an applied electric field of 40 kV/cm for 20 min.

The ceramic crystallization behavior was examined with an X-ray diffraction (XRD) meter with a $\text{Cu K}\alpha$ radiation ($\lambda = 1.54178 \text{ \AA}$) (D8 Advance, Bruker Inc., Karlsruhe, Germany). Raman spectra were recorded on polished sintered pellets using 488-nm excitation with a Jobin-Yvon LabRam HR800 (Horiba Jobin Yvon Inc., Paris, France). The surface morphology of the ceramics was observed by a field-emission scanning electron microscope (FE-SEM, Carl Zeiss, merlin compact). Silver electrodes were coated on the top and bottom surfaces of the ceramics for the subsequent electrical measurements. The piezoelectric constant d_{33} was measured by a tester quasi-static d_{33} meter (YE2730 SINOCERA, Yangzhou, China). P - E loops, where P and E denote the polarization and the electric field, respectively, were measured by ferroelectric analyzer (TF2000 analyzer, Aixact, Germany). The temperature dependence of dielectric properties was measured by a capacitance meter (Agilent 4294A, Agilent Inc., American) at temperatures ranging from -20°C to 160°C with a heating rate of $3^\circ\text{C}/\text{min}$.

3. Results and discussion

The XRD patterns with 2θ ranging from 20° to 70° of the BCHT ceramics are shown in Fig. 1(a). As can be seen, all ceramics exhibit a pure perovskite structure, and no secondary or impure phases can be detected. This result indicates that a stable solid solution is formed by Ca^{2+} diffusion in A-site of perovskite structure. Fig. 1(b) illustrates an expanded XRD pattern in the 2θ range of $44.5^\circ\text{--}46.5^\circ$. The position of (200)/(002) peaks shifts to higher angle with increasing Ca contents. The reason for this phenomenon is that the smaller ionic radii Ca^{2+} (0.99 \AA , CN = 6) replaces Ba^{2+} (1.35 \AA , CN = 6), while the differences in ionic radius resulting in the lattice shrink at the same time [11]. The orthorhombic symmetry of BCHT ceramics at RT is characterized by an obvious peak of (200) at around 2θ of 45.5° , when $x < 0.08$. The splitting of the (200)/(002) peaks is observed for the BCHT ceramics at

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