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Ceramics International 38 (2012) 4761–4764

CERAMICS INTERNATIONAL

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Lead-free $(Ba_{0.85}Ca_{0.15})(Ti_{0.9}Zr_{0.1})O_3$–$CeO_2$ ceramics with high piezoelectric coefficient obtained by low-temperature sintering

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Received 15 January 2012; received in revised form 22 February 2012; accepted 22 February 2012
Available online 3 March 2012

Abstract

Lead-free $(Ba_{0.85}Ca_{0.15})(Ti_{0.9}Zr_{0.1})O_3$–$x\%CeO_2$(BCZT–$x$Ce) piezoelectric ceramics have been prepared by the traditional ceramic process and the effects of CeO_2 addition on their phase structure and piezoelectric properties have been studied. The addition of CeO_2 significantly improves the sinterability of BCZT ceramics which results in a reduction of sintering temperature from 1540 °C to 1350 °C without sacrificing the high piezoelectric properties. X-ray diffraction data show that CeO_2 diffuses into the lattice of BCZT and a pure perovskite phase is formed. SEM images indicate that a small addition of CeO_2 greatly affects the microstructure. Main piezoelectric parameters are optimized at around $x = 0.04$ wt% with a high piezoelectric coefficient ($d_{33} = 600$ pC/N), a planar electromechanical coefficient ($k_p = 51\%$), a high dielectric constant ($\varepsilon_r = 4843$) and a low dissipation factor ($\tan\delta = 0.012$) at 1 kHz, which indicates that the BCZT–xCe ceramics are promising for lead-free practical applications.

Keywords: A. Sintering; C. Piezoelectric properties; Dielectrics; Lead-free ceramics

1. Introduction

It is well known that lead zirconate titanate (PZT) ceramics have widely been used for piezoelectric actuators, sensors and transducers due to their excellent piezoelectric properties close to the morphotropic phase boundary (MPB) between rhombohedral and tetragonal. Nevertheless, they are not environmental friendly for their lead oxide toxicity. With recent growing demand of global environmental protection, many researchers have greatly focused on lead-free ceramics to replace the lead-based ceramics [1–3].

The newly discovered lead-free $Ba(Zr_{0.2}Ti_{0.8})O_3$–$x(Ba_{0.7}Ca_{0.3})TiO_3$ ceramics by Liu and Ren have attracted great attention due to the excellent piezoelectric properties (with $d_{33} = 350$–650 pC/N) [4–11]. A d_{33} of 650 pC/N is obtained for the composition of $(Ba_{0.85}Ca_{0.15})(Ti_{0.9}Zr_{0.1})O_3$ (BCZT) by optimizing sintering temperature at 1540 °C [9]. However the optimal composition with high d_{33} value is sintered at high temperature. It is well known that CeO_2 is commonly used as an additive for lead-free ceramics to further improve density and piezoelectric properties, such as BNT ceramics [12–14]. Therefore the purpose of this paper is to present the effect of CeO_2 addition on improving the sinterability and the electrical properties of BCZT ceramics. The dielectric properties of $(Ba_{0.85}Ca_{0.15})(Ti_{0.9}Zr_{0.1})O_3$–$x\%CeO_2$ (BCZT–xCe) ceramics are measured as a function of temperature. The modification mechanism of added CeO_2 has also been discussed.

2. Experimental

Using conventional solid-state reaction technique BCZT ceramics and CeO_2 ($x = 0$–0.1 wt%) doped BCZT–xCe ceramics were prepared. Systems were prepared by using a two-step method. Raw materials of $BaCO_3$ (99.8%), $CaCO_3$ (99.0%), ZrO_2 (99.5%), and TiO_2 (99.9%) were weighed and mixed in a centrifugal mill, as well as wet-homogenized with ethanol for 8 h. The obtained powders were dried in an oven, and then calcined at 1250 °C for 2 h. Different amounts of CeO_2

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doi:10.1016/j.ceramint.2012.02.063

were added into the calcined powders, respectively. The resulting mixtures were further mixed with 5% poly vinyl alcohol (PVA) solution thoroughly. The obtained powders were pressed into disks specimens with a diameter of 18 mm and a thickness of 1 mm only by uniaxial pressing with a pressure of 100 Mpa. After burning off PVA, sintering was carried out at the temperature of 1350 °C for 4 h.

The crystalline structure of sintered ceramics was examined by X-ray diffraction (XRD) (Bruker D8 Advance) with Cu-Kα radiation (step: 0.02°). Surface microstructure was observed by scanning electron microscopy (SEM) (JEOL, JSM-5610LV). Dielectric properties of the specimens were obtained together using an impedance analyzer (Agilent 4294A) by measuring the capacitance and loss (Cp–D) of the specimen homogenously from 20 °C to 150 °C, using with a heating rate of 60 °C h^{-1}. The planar coupling coefficient (k_p) was determined by the resonance–anti-resonance method, using Agilent 4294A impedance analyze. The piezoelectric coefficient (d_{33}) was recorded from 24-h-aged polarized samples using a quasi static piezoelectric d_{33} meter (ZJ-3AN, Institute of Acoustics, Chinese Academy of Sciences, China).

3. Results and discussion

Fig. 1 shows the X-ray diffraction (XRD) patterns of BCZT–*x*Ce ceramics with different contents of CeO_2 sintered at 1350 °C. As can be seen from Fig. 1(a), a single perovskite structure is observed for all sintered samples and there is no trace of second phase, which implies that Y ions diffuse into the BCZT lattices and a solid solution forms in the ceramics. Further XRD analysis is performed in the 2θ ranges from 44° to 47° as shown in Fig. 1(b). The XRD patterns exhibit the feature of peak which splits at about 44° and 47°, which indicates that coexistence of rhombohedral and tetragonal phases in the BCZT–*x*Ce ceramic samples with 0.0–0.1% CeO_2 at room temperature [4,9]. Meanwhile, the diffraction peaks of CeO_2 doped BCZT ceramics shift slightly to higher angles with increasing CeO_2 content. It is expected from the tolerance factors that small ions [$r(R^{3+}) < 0.087$ nm] will occupy the B site, large ions [$r(R^{3+}) > 0.094$ nm] will occupy the A site, and intermediate ions will occupy both sites with different partitioning for each ion [8]. Ce ions possibly exist in the BCZT structure in two valence states: Ce^{4+} in a radius of 0.094 nm, Ce^{3+} in a radius of 0.107 nm. Taking Ce ions into consideration, Ce ions should occupy the A-site of Ca^{2+} ($r = 0.1$ nm) and Ba^{2+} ($r = 0.135$ nm). According to the peaks shift to higher angles, the lattice parameter should decrease, and it is assumed that Ce ions occupy the A-site of Ba^{2+}.

As shown in Fig. 2, the SEM surface micrographs of the BCZT–*x*Ce ceramics modified with CeO_2 were sintered at 1350 °C for 4 h. It is evident that CeO_2 addition causes a large change in the grain size. The pure BCZT ceramics have a porous microstructure with small grains, as shown in Fig. 2(a). However, when a small amount of CeO_2 is added, a dense microstructure with enlarged grains is developed [see Fig. 2(b)]. The non-uniformity of grains seems to be slightly improved with the further addition of CeO_2, as seen from Fig. 2(c)–(f). The addition of CeO_2 promotes the mobility of grain boundary to a certain degree so that a relative non-uniformity of grain can be obtained. Therefore, it is believed that a small amount of CeO_2 adding to BCZT ceramics can modify the microstructure and the grain size of the BCZT ceramics, and result in a reduction of sintering temperature.

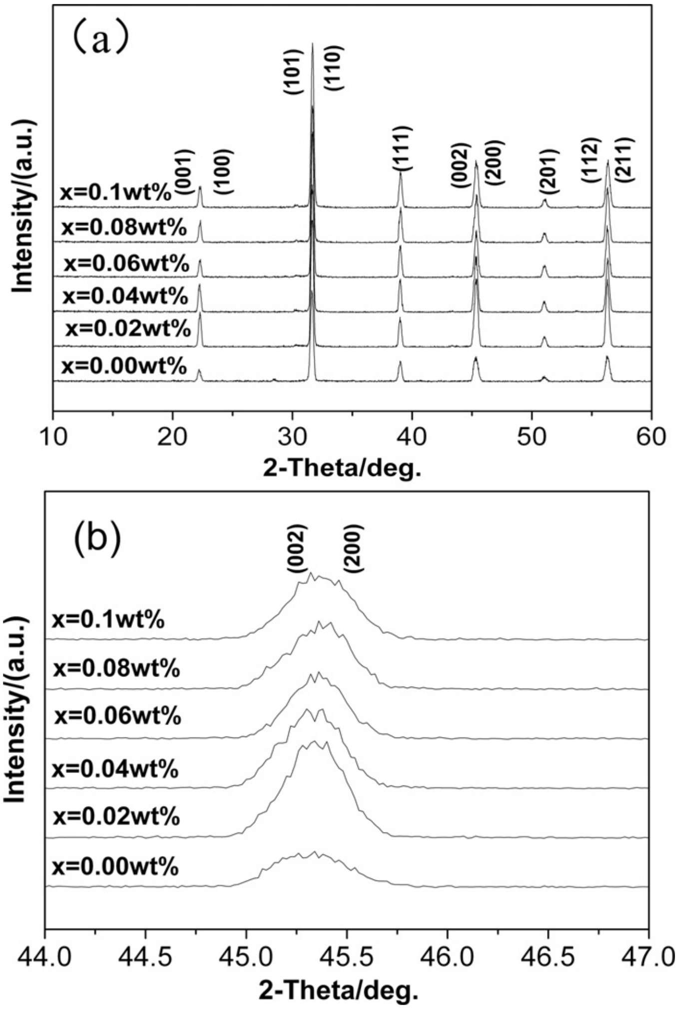

Fig. 1. X-ray diffraction patterns of BCZT–*x*%CeO_2 ceramics sintered at 1350 °C.

Fig. 3 shows the piezoelectric coefficient d_{33} and planar mode electromechanical coupling coefficient k_p of the BCZT–*x*Ce ceramics as a function of CeO_2 content. It can be seen from Fig. 3 that with the increasing of CeO_2 content, the piezoelectric constant d_{33} and the planar coupling factor k_p increase slowly up to a maximum value 600 pC/N at 0.04% CeO_2 and 0.54 at 0.08% CeO_2, and then decrease sharply with further increase of CeO_2. It is believed that the observed high piezoelectric properties should be ascribed to the phase coexistence [4,9] and the first-order PPT occurring near room temperature should be the origin of this phase coexistence. However, with the increasing of CeO_2 content to 0.1%, Ce ions should occupy the A-site of Ba^{2+}, which cause deformation in the ABO_3 lattice to make a phase transition completed at a lower temperature, resulting in a reduction of piezoelectric

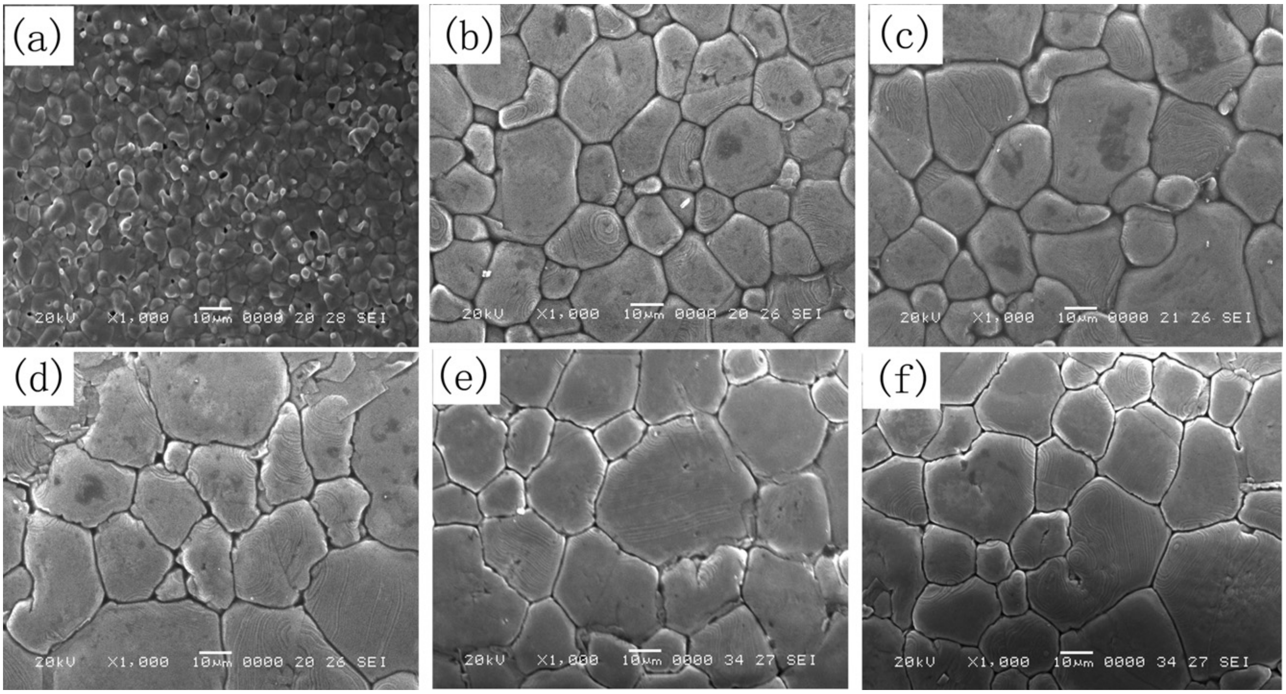

Fig. 2. SEM images of the BCZT–x%CeO$_2$ ceramic sintered at 1350 °C: (a) $x = 0.00$, (b) $x = 0.02$, (c) $x = 0.04$, (d) $x = 0.06$, (e) $x = 0.08$ and (f) $x = 0.1$.

coefficient d_{33}. This shows that a proper addition of CeO$_2$ induces a more significant piezoelectric activity, which can be mainly attributed to grain size, the densification and morphology of the ceramics.

The dielectric constant ε_r and dielectric loss (tan δ) for BCZT–xCe ceramics measured at 1 kHz are shown in Fig. 4. As we can see from Fig. 4, with increasing CeO$_2$ content the relative dielectric constant ε_r (1 kHz) first decreases to a peaked value of 4464 at 0.08% CeO$_2$ and then descends rapidly to 3866 at 0.1% CeO$_2$, the maximum ε_r (4923) is obtained at 0.02% CeO$_2$. Moreover the tan δ (at 1 kHz) distinctly decreases at first and reaches a minimum value of 0.9% at 0.08% CeO$_2$ addition. Generally speaking, the values of ε_r and tan δ decrease with increasing of CeO$_2$ content.

Fig. 5 shows the temperature dependence of the relative dielectric constant for BCZT–xCe ceramics measured at 10 kHz. One peak is observed on the dielectric constant versus temperature curves in the measured temperature range (20–150 °C). It is considered that the peak corresponds to the polymorphic phase transitions from tetragonal to cubic phase [4,9] the transition temperature (T_c) is around 90 °C. Besides, with the increasing CeO$_2$ content to 0.1%, the curie temperature T_c decreases from 90 °C to 85 °C because the Ce ions [r(Ce^{4+}) = 0.094 nm, r(Ce^{3+}) = 0.107 nm] are substituted for A-site of Ba^{2+} ($r = 0.135$ nm), resulting in the change of the ceramics lattice which cause deformation in the ABO$_3$ lattice. When the content of CeO$_2$ is low, the deformation is weak and the structure of the ceramic is

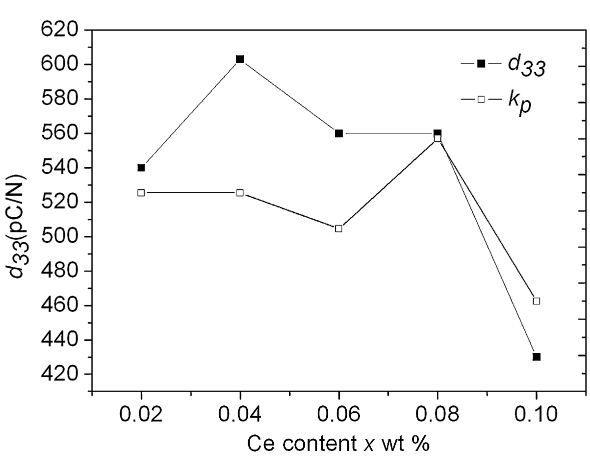

Fig. 3. The piezoelectric constant d_{33} and the planar electromechanical coefficient k_p of the BCZT–x%CeO$_2$ ceramics.

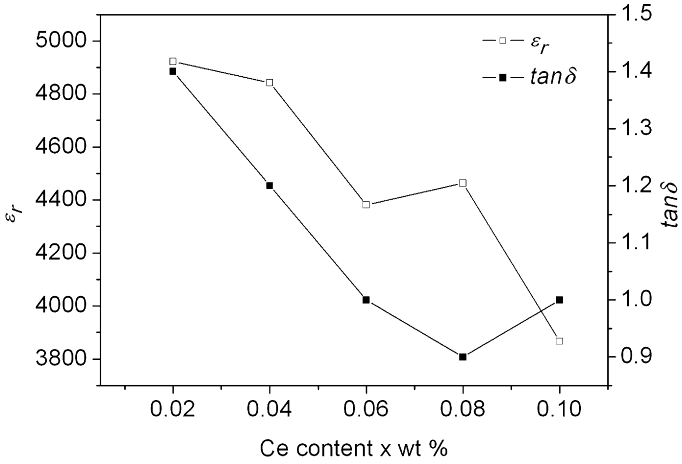

Fig. 4. The dielectric constant ε_r and the dielectric loss tan δ of the BCZT–x%CeO$_2$ ceramics.

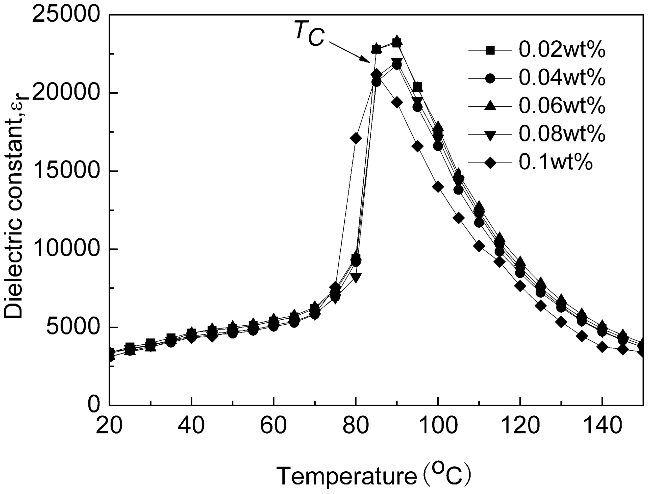

Fig. 5. Temperature dependence of dielectric constant for BCZT–x%CeO$_2$ ceramics measured at 10 kHz.

stable. However, when the content of CeO$_2$ become high, for example at 0.1%, the deformation cannot be ignored and the structure of the ceramic become non-stable. So when increasing the content of CeO$_2$, the structure change from tetragonal phase to cubic phase at lower temperature.

4. Conclusions

Lead-free BCZT–xCe piezoelectric ceramics have been prepared by the solid-state reaction technique. The crystalline phases, dielectric and piezoelectric properties have been studied in the paper. X-ray diffraction data show that CeO$_2$ diffuses into the lattice of BCZT with formation of a pure perovskite phase and reduction in sintering temperature. A small addition of CeO$_2$ can largely reduce the sintering temperature. Main piezoelectric parameters were optimized in the vicinity of $x = 0.04$ wt% with comparatively lower sintering temperature (1350 °C), showing a promising future as lead-free ceramics for low temperature applications.

Acknowledgments

The authors wish to acknowledge the financial support of the National Nature Science Foundations, grant No. 51102056, and Guangxi Nature Science Foundations, grant Nos. 2010GXNSFD013007, 2011GXNSFB018008.

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