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Short communication

Effect of Ho doping on piezoelectric properties of BCZT ceramics

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Abstract

Lead-free $(Ba_{0.99}Ca_{0.01})(Ti_{0.98}Zr_{0.02})O_3$ (BCZT) + x mol% Ho (x = 0–0.6) ceramics were prepared using solid-state reaction technique. High piezoelectric coefficient of d_{33} = 330 pC/N and planar electromechanical coupling factor of k_p = 40% were obtained at x = 0.2%. Furthermore, greatly enhanced temperature stability of the piezoelectric properties was obtained in the temperature range from 20 to 100 °C, in which the Ho doped BCZT ceramics exhibited pure tetragonal phase. With the increase of Ho content, the orthorhombic–tetragonal phase transition shifted towards low temperature, while Curie temperature (T_c) remained at about 120 °C. The results indicate that Ho doped BCZT ceramics could be promising candidate as lead-free piezoelectric materials.

Keywords: C. Dielectric properties; C. Piezoelectric properties; D. $BaTiO_3$ and titanates

1. Introduction

Driven by global environmental concerns, there is currently a strong push to discover practical lead-free piezoelectrics for device engineering. Recently, several notable lead-free piezoelectric ceramics have been reported to exhibit promising piezoelectric properties [1–12]. In those lead-free ceramics, the enhanced piezoelectric properties are accompanied by the occurrence of a polymorphic phase transition (PPT) around room temperature [3,6–11], and they are thus considered to be closely associated with the coexistence of phases. The instability of the polarization state at the phase transition regions allows a significant polarization variation under external stress or electric field. As a result, the properties of materials related to polarization change, such as dielectric permittivity and piezoelectric coefficients, can be enhanced significantly. Consequently, the polymorphic phase transition (being different with composition-induced MPB) is largely temperature-dependent, which is a severe shortcoming for practical application.

Recent studies further reveal that the $BaTiO_3$ (BT) based system has a high piezoelectric coefficient of $d_{33} > 300$–600 pC/N [10–12], while their optimal composition with high d_{33} value exhibits low T_C and large temperature dependent degradation in the common usage temperature range. Therefore, research efforts to improve the piezoelectric temperature stability and to clarify the related mechanism are urgently needed. In the present study, we report our results on the efforts in Ho doped $(Ba_{0.99}Ca_{0.01})(Ti_{0.98}Zr_{0.02})O_3$ lead-free ceramics.

2. Experimental procedure

The $(Ba_{0.99}Ca_{0.01})(Ti_{0.98}Zr_{0.02})O_3$ + x mol% Ho (x = 0, 0.2, 0.4 and 0.6) ceramics were prepared by conventional solid–state reaction technique. Raw materials of $BaCO_3$ (99.0%), $CaCO_3$ (99.0%), ZrO_2 (99.0%), TiO_2 (99.5%) and Ho_2O_3 (99.0%) were mixed according to a predetermined ratio with addition of alcohol, which were then dried and calcined at 1200 °C for 4 h. Thereafter, calcined powders were remixed, pressed into 12 mm-diameter pellets and sintered at 1450 °C for 4 h in air. Phase structure was examined using an X-ray diffraction meter with a Cu K_α radiation (λ = 1.54178 Å) (XRD, D8 Advance, Bruker Inc., Germany). Dielectric properties were measured using the precision impedance analyzer (4294A Agilent Inc., USA) at 100 kHz. Ferroelectric hysteresis loops were measured at room temperature using an aix-ACCT TF2000FE-HV ferroelectric test unit (aix-ACCT Inc., Germany). Piezoelectric constant d_{33} was measured using a quasi-static d_{33} meter (YE2730 SINOCERA, China).

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Piezoelectric properties as a function of temperature were determined using an impedance analyzer and a temperature controlled chamber. Planar electromechanical coupling factor k_p were calculated following IEEE standards using the impedance analyzer.

3. Results and discussion

Fig. 1 shows XRD patterns of the Ho doped BCZT ceramics. As can be seen, all samples have a single phase of perovskite structure and no secondary phase is found. In $(Ba_{(1-x)}Ca_x)(-)(Ti_{(1-y)}Zr_y)O_3$ ceramics, the PPT (orthorhombic–tetragonal T_{O-T} and tetragonal–cubic T_C) move closer with increasing Zr content and the $Ba(Ti_{0.98}Zr_{0.02})O_3$ ceramics exhibit only orthorhombic phase at room temperature. The composition of $(Ba_{0.97}Ca_{0.03})(Ti_{0.98}Zr_{0.02})O_3$ ceramics has tetragonal phase. There is a transition from orthorhombic phase to tetragonal phase with increasing Ca content. Therefore, orthorhombic and tetragonal phase are confirmed to coexist in the $(Ba_{0.99}Ca_{0.01})(-Ti_{0.98}Zr_{0.02})O_3$ ceramic at room temperature [12]. The Ho doped BCZT ceramics exhibit pure tetragonal phase featured with obvious splitting of the (0 0 2)/(2 0 0) peaks at room temperature [13]. On the other hand, the diffraction peaks of Ho doped BCZT ceramics shift slightly to high angles with increasing Ho content. The values of 2θ angles of (2 0 0) peaks are 45.34 for the ceramics at $x = 0\%$, 45.36 at $x = 0.2\%$, 45.40 at $x = 0.4\%$ and 45.40 at $x = 0.6\%$, respectively. Shifting of 2θ angles and splitting of the (0 0 2)/(2 0 0) peaks imply that Ho doping induces the lattice distortion.

Temperature dependence of dielectric constant for the Ho doped BCZT ceramics is shown in Fig. 2. Two obvious phase transitions above 0 °C corresponding to the T_{O-T} and T_C, respectively, are observed for all the ceramics [12]. With increasing Ho content, the orthorhombic to tetragonal phase transition peak shifts to low temperature, and Curie temperature T_C remains at about 120 °C. It can be noted with the fact that Ho doping does not strongly affect the T_C, but pushes the T_{O-T} below room temperature. Therefore, the Ho doped BCZT ceramics exhibit pure tetragonal phase at room temperature.

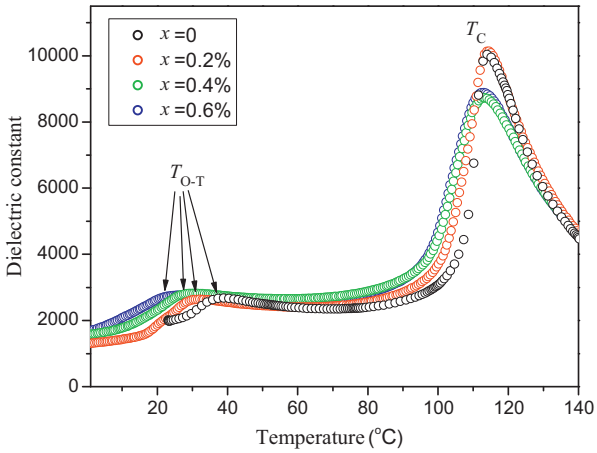

Fig. 2. Temperature dependence of dielectric constant for the Ho doped BCZT ceramics at $x = 0$, 0.2%, 0.4% and 0.6% measured at 100 kHz.

Fig. 3 shows the piezoelectric coefficient and planar mode electromechanical coupling coefficient as a function of temperature for the Ho doped BCZT ceramics from 20 °C to 130 °C. High piezoelectric coefficients of 378 pC/N, 330 pC/N, 280 pC/N and 230 pC/N are obtained at $x = 0$, $x = 0.2\%$, $x = 0.4\%$, and $x = 0.6\%$, respectively. The highest piezoelectric coefficient d_{33} of the BCZT ceramics in the previous study should be related to the phase coexistence [3,8–12] occurring near room temperature. With increasing Ho content, the T_{O-T} is pushed to low temperature and the piezoelectric coefficients decrease. But it still exhibits high piezoelectric properties ($d_{33} \sim 330$ pC/N and $k_p \sim 40\%$) for the Ho doped BCZT ceramics at $x = 0.2\%$. After annealing the samples at special temperature (every 10° in the range of 20–130 °C) for 20 min, the d_{33} and k_p values were measured at different temperature. It is known that strong temperature dependence of the dielectric and piezoelectric properties is usually observed in the materials

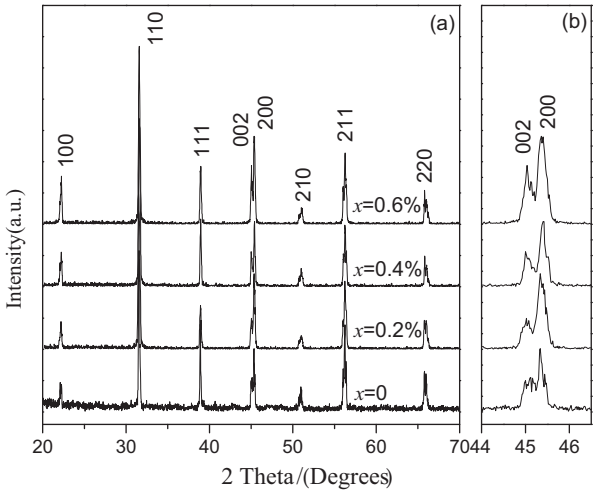

Fig. 1. X-ray diffraction patterns of the Ho doped BCZT ceramics at $x = 0$, 0.2%, 0.4% and 0.6%.

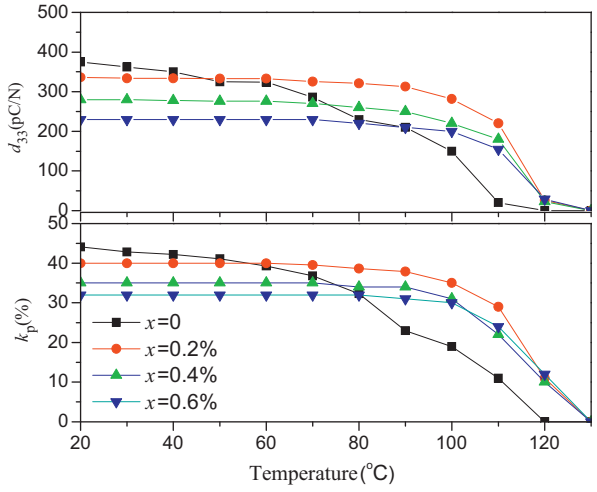

Fig. 3. Piezoelectric coefficient and planar mode electromechanical coupling coefficient as function of temperature for the Ho doped BCZT ceramics at $x = 0$, 0.2%, 0.4% and 0.6%.

with polymorphic phase transition (being different with composition-induced MPB) [8,9,14]. Consequently, for the BCZT ceramics, both d_{33} and k_p values decrease sharply with deviating from the PPT region, as shown in Fig. 3. However, greatly improved temperature stability of the piezoelectric properties is found in the temperature range from 20 to 100 °C for the Ho doped BCZT ceramics. Changes of d_{33} and k_p values are less than 5% between 20 and 90 °C. With increasing Ho content, temperature dependence of the piezoelectric response becomes weak and the d_{33} and k_p values of the Ho doped BCZT ceramics at $x = 0.6\%$ are nearly constant between 20 and 90 °C. The good temperature stabilities observed in the Ho doped BCZT ceramics is likely to be associated with pushing the T_{O-T} to lower temperature and pure tetragonal phase exhibiting in the temperature range from 20 to 100 °C. The Ho doped BCZT ceramics with excellent performance of piezoelectric properties are promising lead-free materials for practical applications.

4. Conclusions

Ho doping in BCZT ceramics does not strongly affect the T_C, but pushes the T_{O-T} to low temperature. The Ho doped BCZT ceramics show excellent piezoelectric performance with high piezoelectric coefficient of 330 pC/N and good temperature stability between 20 and 100 °C. Our work may provide a very effective lead-free piezoelectric material for practical application.

Acknowledgments

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