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Effects of Mn-doping on the properties of $(Ba_{0.92}Ca_{0.08})(Ti_{0.95}Zr_{0.05})O_3$ lead-free ceramics

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ABSTRACT

Lead-free piezoelectric ceramics $(Ba_{0.92}Ca_{0.08})(Ti_{0.95}Zr_{0.05})O_3$–*x*mol%Mn (BCTZ–*x*Mn) were synthesized by a traditional solid-state reaction. Effects of Mn addition on the microstructure and electrical properties of ceramics were investigated in the composition range of $0 \leqslant x \leqslant 2.2$. High mechanical quality factor of $Q_m = 921$ and low dielectric loss of $\tan\delta = 0.3\%$ have been obtained at $x = 2.0$. With the increase of Mn content, the piezoelectric constant d_{33} and planar electromechanical coupling coefficient k_p decrease with deviation from the polymorphic phase transition (PPT) region, and the Curie temperature T_C gradually decreases. The relative high d_{33}, k_p and T_C still maintain about 224 pC/N, 33.6% and 102 °C at $x = 2.0$, respectively. These results indicate that the BCTZ–*x*Mn ceramics are promising candidate for the lead-free piezoelectric applications.

1. Introduction

Barium titanate ($BaTiO_3$, BT) is the earliest known perovskite-type ferroelectric material [1], and it has played an important role in various electronic components,such as positive temperature coefficients of resistivity (PTCR) thermistor, energy storage devices, transducers and multilayer capacitors (MLCs) piezoelectric device [2,3]. However, because of the superior piezoelectric properties of lead zirconate titanate (PZT) ceramics near the morphotropic phase boundary (MPB) between rhombohedral and tetragonal phases, the BT ceramics have been replaced by PZT ceramics and the PZT ceramics became a major piezoelectric material. Nevertheless, they are not environmental friendly for their lead oxide toxicity. Due to environmental concerns, many studies are intended for producing lead-free ferroelectric systems with electrical properties comparable to those of the lead-based ones, and most of them have involved the consideration of systems based on perovskite-structured BT ceramics.

Recently, BT-based lead-free piezoelectric ceramics have been given to much attention, since Liu and Ren [4] reported that the piezoelectric constant d_{33} of 620 pC/N for the $Ba(Zr_{0.2}Ti_{0.8})O_3$–$(Ba_{0.7}Ca_{0.3})TiO_3$ which is even higher than that of some lead-based ceramics. However, the optimal composition of this ceramic with high d_{33} values exhibits low Curie temperature ($T_C = 93$ °C). At present, there have been many reports about the $(Ba,Ca)(Ti,Zr)O_3$ (BCTZ) ceramics, but most of these ceramics exist low mechanical quality factor (Q_m: 200–400) [5–9,12]. Consequently, the low T_C and Q_m of BCTZ ceramics are not suitable for practical piezoelectric application. It is well know that Mn has been used as an additive for lead-free ceramics to further improve the Q_m properties, such as NBT-based [10] and KNN-based [11] ceramics. Moreover, it seems that Mn-doping does not strongly reduce T_C [10]. Besides, the $(Ba_{1-x}Ca_x)(Ti_{0.95}Zr_{0.05})O_3$ ceramics have been prepared by Li et al. [12], which shows good properties at the polymorphic phase transition (PPT) from orthorhombic to tetragonal phase ($x = 0.08$). However the Q_m of $(Ba_{0.92}Ca_{0.08})(Ti_{0.95}Zr_{0.05})O_3$ ceramics is only about 130. In this paper, The relative high Q_m and T_C of the $(Ba_{0.92}Ca_{0.08})(Ti_{0.95}Zr_{0.05})O_3$ lead-free ceramics were obtained after Mn doping, and the effect of Mn addition on the microstructure and electrical properties of $(Ba_{0.92}Ca_{0.08})(Ti_{0.95}Zr_{0.05})O_3$ ceramics were investigated in detail.

2. Experimental

The $(Ba_{0.92}Ca_{0.08})(Ti_{0.95}Zr_{0.05})O_3$–*x*mol%Mn (abbreviated as BCTZ–*x*Mn) ceramics at $x = 0.0$, 0.6, 1.0, 1.6, 2.0 and 2.2 were prepared by the traditional solid-state reaction method, respectively. Reagent-grade metal oxide or carbonate powders of $BaCO_3$ (99%), $CaCO_3$ (99%), TiO_2 (99%), ZrO_2 (99%) and MnO_2 (97.5%) were used as starting row materials. The powders were weighed and mixed by ball-milling in alcohol for 12 h. After drying, the powers were calcined at 1200 °C for 2 h. The calcined powders were ground and mixed with 5 wt.% polyvinyl alcohol (PVA) binder. Thereafter, the powders were mixed again and pressed into discs 15 mm in diameter and about 1.3 mm in thickness. The disc samples were sintered at 1450 °C for 2 h in oxygen atmosphere. Both surfaces of the sample were coated with silver paste as electrodes and polarized under a dc field of 3.5 kV/mm at room temperature in silicone oil for 15–20 min.

The crystalline structure of sintered samples was identified by an X-ray diffractometer (D8 Advanced, Bruker). The microstructure evolution was observed using a scanning electron microscope (SEM, Model JSM-6700F, Japan). The temperature dependence of the dielectric properties was carried out by using an Agilent

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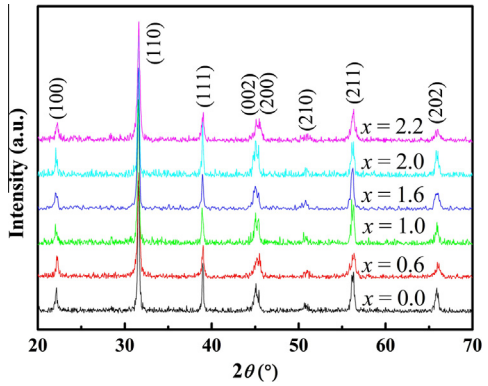

Fig. 1. X-ray diffraction patterns of BCTZ–*x*Mn ceramics in the range of 2θ from 20° to 70°.

4294A precision impedance analyzer. The mechanical quality factor Q_m and the planar electromechanical coupling factor k_p of the samples were measured by resonance f_r and anti-resonance f_a frequencies using an impedance analyzer (Agilent 4294A, Agilent Technology Inc.). The piezoelectric constant d_{33} was measured using a piezo-d_{33} meter (ZJ-3A, Chinese Academy of Acoustics). The *P*–*E* hysteresis loops were measured by a standard Sawyer–Tower circuit at room temperature with a frequency of 1 Hz.

3. Results and discussion

Fig. 1 shows the XRD patterns of BCTZ–*x*Mn ceramics. All the ceramics possess a pure perovskite structure and no secondary phase is observed. This suggests that Mn has completely diffused into the BCTZ lattices to form a homogeneous solid solution. At room temperature, it is known to be true that the orthorhombic phase and tetragonal phase coexist in pure BCTZ ceramics [12]. With increasing Mn content, the BCTZ–*x*Mn ceramics become tetragonal phase, featured with splitting of the (002)/(200) peaks at around 2θ of 45°.

It is reported that the valence of Mn ions exist in the state of +2 or +3 sintering in air [10,13]. And the ionic radius of Mn^{2+} (0.83 Å) and Mn^{3+} (0.645 Å) is much smaller than that of A-site ions (Ba^{2+}: 1.61 Å, Ca^{2+}: 1.35 Å), while the radius of Mn^{2+} and Mn^{3+} close to that of Ti^{4+} (0.605 Å) and Zr^{4+} (0.72 Å). Therefore, Mn ions are more likely to substitute into B-site ions. It is well known that the substitution of the lower valence cation in higher valence B-site induces the oxygen vacancies [14]. These oxygen vacancies are believed to play a major role in the hardening effect.

The SEM micrographs of BCTZ–*x*Mn ceramics are shown in Fig. 2. It can be seen that there is an inhomogeneous grain size distribution in pure BCTZ ceramics. After adding a small amount of MnO_2, the ceramics display a larger grain size compared with that of the pure BCTZ ceramics, indicating that the addition of Mn can

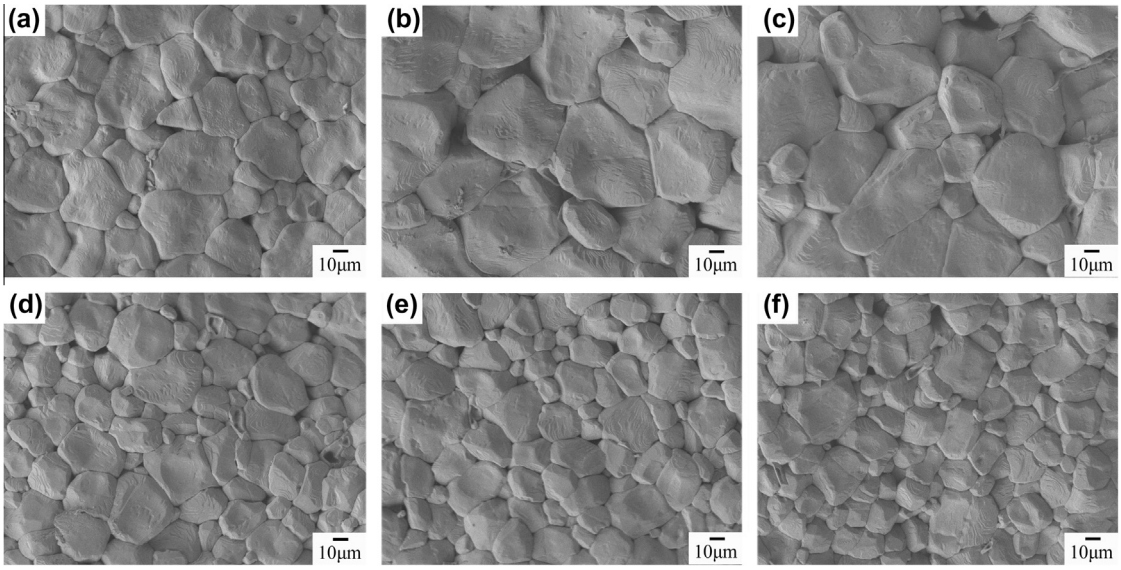

Fig. 2. SEM micrographs of BCTZ–*x*Mn ceramics: (a) *x* = 0.0, (b) *x* = 0.6, (c) *x* = 1.0, (d) *x* = 1.6, (e) *x* = 2.0, and (f) *x* = 2.2.

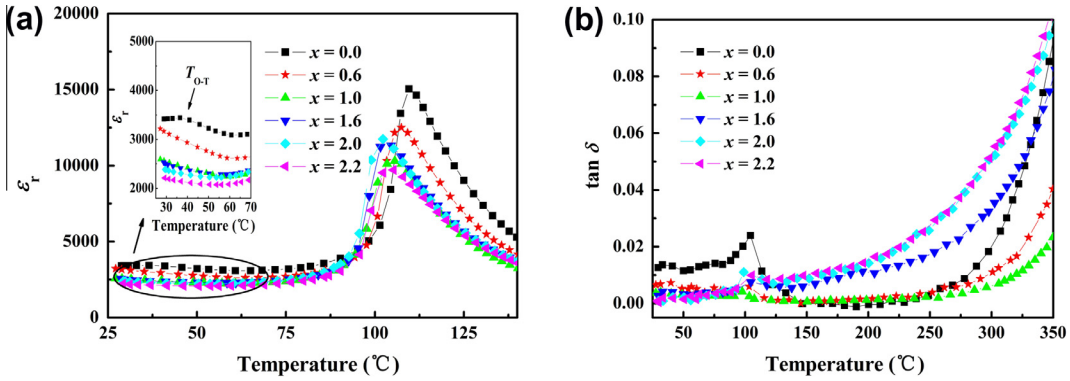

Fig. 3. Temperature dependence of dielectric constant ε_r and dielectric loss tanδ for the BCTZ–*x*Mn ceramics at 100 kHz.