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Microstructure and electrical properties of $(Ba_{0.98}Ca_{0.02})(Ti_{0.94}Sn_{0.06})O_3$-modified $Bi_{0.51}Na_{0.50}TiO_3$ lead-free ceramics

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Abstract

$(Ba_{0.98}Ca_{0.02})(Ti_{0.94}Sn_{0.06})O_3$-modified $Bi_{0.51}Na_{0.5}TiO_3$ [(1 − x)BNT–xBCTS] ceramics were prepared by the normal sintering. A stable solid solution is well formed between BNT and BCTS, and the morphotropic phase boundary of (1 − x)BNT–xBCTS ceramics is identified in the compositional range of $0.05 \leq x \leq 0.06$. The temperature dependence of the dielectric loss and the poling temperature dependence of the d_{33} value are used to determine the depolarization value (T_d). The T_d value of these ceramics gradually decreases with increasing BCTS content, together with the gradual increase of the dielectric constant. An enhanced electrical behavior of $d_{33} \sim 170$ pC/N, $k_p \sim 32.8\%$, $P_r \sim 38.5$ μC/cm^2, and $E_c \sim 34.3$ kV/cm is demonstrated for the ceramic with x = 0.06, which is double than that of pure BNT ceramic.

Keywords: C. Piezoelectric properties; Lead-free ceramics; Piezoelectric materials; $Bi_{0.5}Na_{0.5}TiO_3$; (Ba, Ca)(Ti, Sn)O_3

1. Introduction

Piezoelectric ceramics become one kind of very important smart materials because of their good dielectric, ferroelectric, pyroelectric, and piezoelectric properties, promising as a candidate material in the field of microelectronic and microelectromechanical devices. However, some environmental issues have arisen, and restricted some applications of lead-based piezoelectric ceramics because of their toxicity and high vapor pressure during processing [1]. In 1960, sodium bismuth titanate ($Bi_{0.50}Na_{0.50}TiO_3$, BNT) is first investigated by Smolenskii and Aganovskaya [2]. In the past of several years, considerable attention has been given to these BNT-based ceramics for the replacement of lead-based piezoelectric ceramics because of a dense microstructure and a relatively high piezoelectric behavior [3–9].

BNT has been recently considered as a promising candidate of lead-free piezoelectric ceramics because of its strong ferroelecricity, an electric field-induced strain, and a high Curie temperature of ∼320 °C [3–9]. However, a high coercive field and a high conductivity become a serious barrier for the development and application of BNT-based ceramics [3–9]. Some methods have been used to resolve these barriers of BNT-based ceramics. Among these methods, the formation of BNT solid solutions with other ferroelectrics is to help improve their electrical properties [10–19], for example, BNT–$Ba(Cu_{1/2}W_{1/2})O_3$ [10], BNT–$K_{0.5}Bi_{0.5}TiO_3$ [11], BNT–$Bi_{0.5}K_{0.5}TiO_3$–$BaTiO_3$ [12], and BNT–$Bi(Mg_{2/3}Nb_{1/3})O_3$ [13]. However, piezoelectric properties of BNT-based ceramics are relatively low [10–13]. Recently, Ca and Sn-modified $BaTiO_3$ ceramics have a high d_{33} value of >500 pC/N by constructing a phase boundary at room temperature [20,21]. It may be highly expected that an enhanced piezoelectric behavior is induced by forming the solid solution of BNT and $BaTiO_3$ with Ca and Sn modification. However, there are few reports on the piezoelectric properties of BNT ceramics combined with $(Ba_{0.98}Ca_{0.02})(Ti_{0.94}Sn_{0.06})O_3$ (BCTS). Moreover, the Bi excess can improve the electrical properties of BNT-based ceramics by compensating the loss of Bi during preparation [22–24]. In the present work, we tried to improve the electrical properties of BNT ceramics by introducing BCTS, and $(1 - x)Bi_{0.51}Na_{0.5}TiO_3$–$x(Ba_{0.98}Ca_{0.02})(Ti_{0.94}Sn_{0.06})O_3$ [(1 − x)BNT–xBCTS] ceramics were prepared by a conventional solid reaction method. Effects of BCTS content on the electrical properties of (1 − x)BNT–xBCTS ceramics were systematically investigated, and some related physical mechanisms are also studied.

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2. Experimental procedure

$(1-x)$BNT–xBCTS piezoelectric ceramics with the composition of $x=0$, 0.02, 0.04, 0.05, 0.06, 0.07, 0.08, and 0.10 were prepared by the solid state reaction route. $BaCO_3$ (99%), $CaCO_3$ (99.9%), TiO_2 (99%), SnO_2 (99%), Bi_2O_3 (99%), and Na_2CO_3 (99.8%) were used as raw materials of this work. These powders weighed according to the chemical formula of $(1-x)$BNT–xBCTS materials. These raw powders were ball mixed with ZrO_2 balls for 24 h using ethanol as the medium. These mixtures were calcined at ~850 °C for 6 h, and then these calcined powders were mixed with a polyvinyl alcohol (PVA) binder solution and compacted into disk samples with a diameter of ~1.0 cm and a thickness of ~1.0–1.3 mm. All ceramics were sintered at ~1160 °C for 2 h in air after burning out the PVA binder at ~850 °C for 2 h. Silver pastes were fired at ~700 °C for 10 min on both sides of these samples as electrodes for electrical measurements. All samples were poled at ~25–180 °C in a silicone oil bath under a dc field of ~5.0 kV/mm for 20 min. The phase structure of these ceramics was measured by using X-ray diffraction (XRD) (DX1000, PR China). Scanning electron microscopy (SEM) was employed to study the surface morphologies of these ceramics. The dielectric behavior as a function of the measurement temperature of these ceramics was measured by using an *LCR* meter (HP 4980, Agilent, USA), and their piezoelectric constant d_{33} of the ceramics was measured using a piezo-d_{33} meter (ZJ-3A, China). The polarization versus electric field (P–E) hysteresis loops of the ceramics were measured using a Radiant Precision Workstation (USA).

3. Results and discussion

Fig. 1(a) plots the XRD patterns of $(1-x)$BNT–xBCTS ceramics. A pure phase is observed for these ceramics, confirming that there is a stable solid solution between BNT and BCTS. Fig. 1(b) shows the expanded XRD patterns in the 2θ range of 45–48° of $(1-x)$BNT–xBCTS ceramics. A single peak of (2 0 2) is observed for these ceramics with $x<0.05$, confirming the involvement of a rhombohedral symmetry [10,11,13]. The (0 0 2)/(2 0 0) peak splitting gradually appears with increasing BCTS content, which is corresponding to a tetragonal symmetry. As a result, the MPB of rhombohedral and tetragonal phases is identified in the compositional range of $0.05 \le x \le 0.06$ at room temperature. Moreover, the position of the diffraction peaks is shifted to a lower angle with increasing BCTS content, suggesting an expansion of the unit cell volume because of the part substitution of Ba^{2+}/Ca^{2+} ($r_{Ba^{2+}} \sim 1.61$ Å and $r_{Ca^{2+}} \sim 1.34$ Å) and Sn^{4+} ($r_{Sn^{4+}} \sim 0.69$ Å) respective for the $(Bi_{0.5}Na_{0.5})^{2+}$ ($r_{Bi^{3+}} \sim 1.40$ Å and $r_{Na^{+}} \sim 1.39$ Å) and Ti^{4+} ($r_{Ti^{4+}} \sim 0.605$ Å) sites. Fig. 2(a)–(d) shows the surface morphologies of $(1-x)$BNT–xBCTS ceramics with $x=0$, 0.04, 0.06, and 0.08, respectively. All the ceramics exhibit a dense microstructure, independent on the composition of these ceramics. Moreover, the average grain size of $(1-x)$BNT–xBCTS ceramics almost keeps unchanged with increasing BCTS content, and the inhomogeneous grain size may be attributed to the inhibition of the grain growth because of the introduction of BCTS.

In this work, two methods of the temperature dependence of the dielectric loss (tan δ) and the poling temperature dependence of the d_{33} value are conducted to characterize the depolarization temperature (T_d). Fig. 3(a) shows the temperature dependence of the tan δ of $(1-x)$BNT–xBCTS ceramics with different BCTS content, measured at 100 kHz. A peak for the tan δ value is observed for all ceramics, which has been identified as the T_d. Moreover, the tan δ peak position of $(1-x)$BNT–xBCTS ceramics changes with increasing BCTS content, that is, the T_d value of $(1-x)$BNT–xBCTS ceramics gradually decreases with increasing BCTS content, and approaches a room temperature for these ceramics with $x \ge 0.07$ because of the introduction of BCTS [25]. This result also confirms that the T_d near room temperature results in a low piezoelectric behavior of $(1-x)$BNT–xBCTS ceramics in this work, which will be discussed later. In order to further confirm the T_d value of $(1-x)$BNT–xBCTS ceramics, the

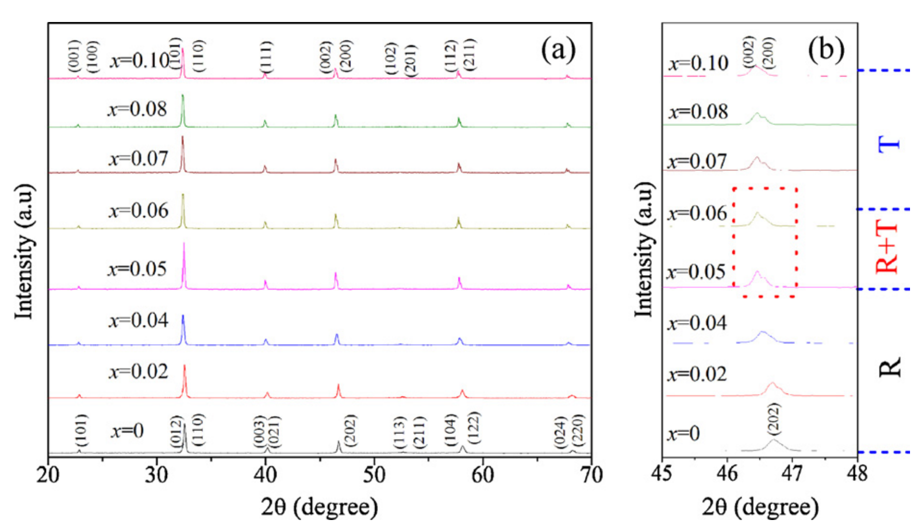

Fig. 1. (a) XRD patterns and (b) expanded XRD patterns of $(1-x)$BNT–xBCTS ceramics as a function of x.

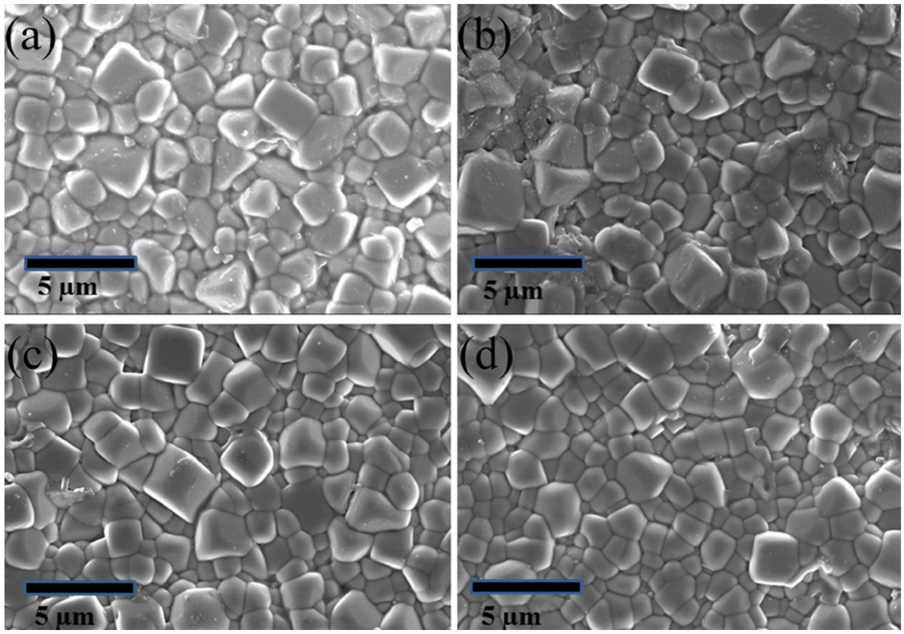

Fig. 2. SEM patterns of $(1-x)$BNT–xBCTS ceramics: (a) $x=0$, (b) $x=0.04$, (c) $x=0.06$, and (d) $x=0.08$.

poling temperature dependence on the d_{33} value of $(1-x)$BNT–xBCTS ceramics is conducted, as shown in Fig. 3(b). The d_{33} value of these ceramics dramatically decreases and approaches zero with the increase of the poling temperature. The poling temperature which results in a $d_{33} \sim 0$ value of $(1-x)$BNT–xBCTS ceramics is well in agreement with these results in Fig. 3(a). Therefore, the temperature dependence of the tan δ and the poling temperature dependence of the d_{33} value are two effective ways to identify the T_d value of $(1-x)$BNT–xBCTS ceramics in this work.

Fig. 4(a) shows the dielectric properties of $(1-x)$BNT–xBCTS ceramics as a function of BCTS content, measured at 1 kHz and room temperature. The ε_r value of $(1-x)$BNT–xBCTS ceramics gradually increases with increasing BCTS content, as shown in Fig. 4(a), which could be attributed to the introduction of the BCTS with a high ε_r value [20,21]. Moreover, the tan δ of $(1-x)$BNT–xBCTS ceramics also gradually increases with increasing BCTS content because that the introduction of BCTS results in a higher processing temperature of $(1-x)$BNT–xBCTS ceramics [20,21]. Fig. 4(b) shows the piezoelectric properties (d_{33} and k_p) and the mechanical quality factor (Q_m) of $(1-x)$BNT–xBCTS ceramics as a function of BCTS content. The d_{33} value of $(1-x)$BNT–xBCTS ceramics increases with increasing BCTS content, reaches a maximum value of ~170 pC/N at $x=0.06$ because of the formation of MPB, and dramatically decreases to near zero with further increasing BCTS content owing to the involvement of a T_d value near room temperature. Similarity to the change of the d_{33} value, the k_p value of $(1-x)$BNT–xBCTS ceramics with $x=0.06$ reaches a maximum of ~32.8%. Low d_{33} and k_p values of $(1-x)$BNT–xBCTS ceramics with $x>0.06$ could be attributed to a lower T_d value near room temperature as confirmed by the double P–E loop in Fig. 5, where these $(1-x)$BNT–xBCTS ceramics with $x>0.06$ ceramics have a micro-domain structure at room temperature. Therefore, the involvement of the micro-domain into these ceramics leads to the poor piezoelectric effect for $(1-x)$BNT–xBCTS ceramics with $x>0.06$ [26]. However, the mechanical quality factor (Q_m) value of these ceramics gradually decreases with increasing BCTS content because of BCTS materials with a low Q_m value.

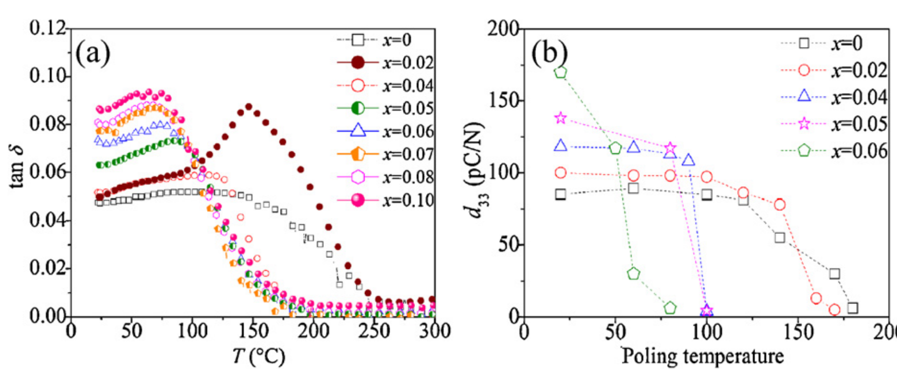

Fig. 3. (a) Temperature dependence of the dielectric loss and (b) poling temperature dependence of the piezoelectric constant of $(1-x)$BNT–xBCTS ceramics.

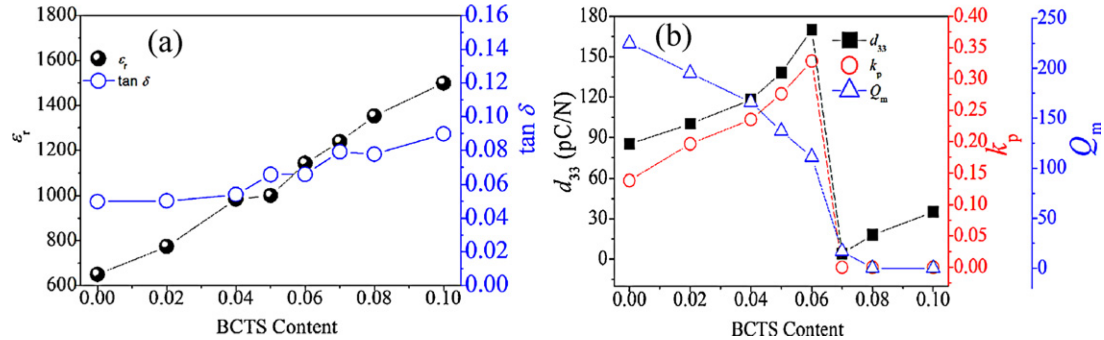

Fig. 4. (a) Dielectric and (b) piezoelectric properties of (1 − x)BNT–xBCTS ceramics as a function of BCTS content.

The polarization versus electric field hysteresis loops (P–E) for (1 − x)BNT–xBCTS ceramics were measured at 100 Hz, as shown in Fig. 5. Ferroelectric properties of (1 − x)BNT–xBCTS ceramics were significantly affected by the introduction of BCTS. Compared with the pure BNT ceramic with a high coercive field [2], these (1 − x)BNT–xBCTS ceramics were more easily switched at the same applied electric field in this work. Moreover, the remnant polarization (P_r) of (1 − x)BNT–xBCTS ceramics increases obviously with increasing BCTS content, reaches a maximum for these ceramics at $x = 0.06$, and then decreases with further increasing BCTS content. It is of great interest to note that a double P–E hysteresis loop is demonstrated for the ceramic with $x = 0.07$, confirming an obvious anti-ferroelectric feature. Therefore, it can be concluded that there exists a transition from ferroelectric to anti-ferroelectric phase for these ceramics with $x = 0.07$. In this work, the P_r value of (1 − x)BNT–xBCTS ceramics with $x = 0.06$ reaches a maximum value of ~38.5 μC/cm^2, together with a low coercive field (E_c) of ~34.3 kV/cm. Enhanced remnant polarizations indicate that ferroelectric properties of (1 − x)BNT–xBCTS ceramics have been improved because of the involvement of the MPB induced by the addition of BCTS with an optimum content.

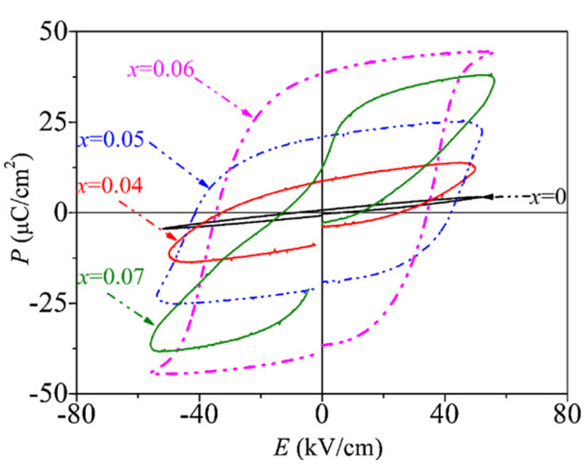

Fig. 5. P–E loops of (1 − x)BNT–xBCTS ceramics as a function of BCTS content.

4. Conclusions

$(1-x)Bi_{0.51}Na_{0.50}TiO_3$–$x(Ba_{0.98}Ca_{0.02})(Ti_{0.94}Sn_{0.06})O_3$ ceramics were prepared by the conventional solid-state method. The BCTS content strongly affects the phase structure and electrical properties of (1 − x)BNT–xBCTS ceramics, and a MPB of rhombohedral and tetragonal phases is well established for these ceramics at $0.05 \leq x \leq 0.6$. The T_d value of (1 − x)BNT–xBCTS ceramics is determined by using the temperature dependence of the dielectric loss as well as the poling temperature dependence of the d_{33} value. It is of great interest to note that the improved piezoelectric properties of $d_{33} \sim 170$ pC/N and $k_p \sim 32.8\%$ are observed for the 6% BCTS-modified BNT ceramics, together with enhanced ferroelectric properties of $P_r \sim 38.5$ μC/cm^2 and $E_c \sim 34.3$ kV/cm. Therefore, optimizing the BCTS content is an effective way to enhance the piezoelectric properties of BNT ceramics.

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