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Letter

Enhanced d_{33} value of $Bi_{0.5}Na_{0.5}TiO_3$–$(Ba_{0.85}Ca_{0.15})(Ti_{0.90}Zr_{0.10})O_3$ lead-free ceramics

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ABSTRACT

$(1-x)Bi_{0.5}Na_{0.5}TiO_3$–$x(Ba_{0.85}Ca_{0.15})(Ti_{0.90}Zr_{0.10})O_3$ [$(1-x)$BNT–xBCTZ] lead-free piezoelectric ceramics were prepared by a conventional solid reaction method. A stable solid solution is well formed between BNT and BCTZ. The ε_r increases, and the T_m, T_d, and the density slightly decrease with increasing BCTZ content. Moreover, the d_{33} value of $(1-x)$BNT–xBCTZ ceramics with $x = 0.06$ demonstrates a temperature independence and a poling electric field dependence. $(1-x)$BNT–xBCTZ ceramics with $x = 0.06$ exhibit an optimum electrical behavior: $d_{33} \sim 158$ pC/N, $k_p \sim 31.2\%$, and $\varepsilon_r \sim 1165$, which is much better than that of pure BNT ceramic. As a result, $(1-x)$BNT–xBCTZ ceramics are a promising candidate material for the piezoelectric device.

1. Introduction

Lead-based piezoelectric ceramics have been used as an essential material for some electronic devices. However, the use of lead-containing materials has caused serious lead pollution and some environmental issues due to its high toxicity of lead oxide. Therefore, it is necessary to develop lead-free piezoelectric materials for the replacement of these lead-based ceramics [1–6].

In 1960, Smolenskii and Aganovskaya firstly reported that the $Bi_{0.5}Na_{0.5}TiO_3$ (BNT) composition is an important lead-free piezoelectric material with a rhombohedral perovskite structure [7]. It has been considered as one of the best candidates for the lead-free piezoelectric ceramics because of its high remanent polarization ($P_r \sim 38\ \mu C/cm^2$) at room temperature and a high Curie temperature (T_c) [8]. In contrast, BNT ceramics often exhibit poor piezoelectric properties because of a high coercive field ($E_c \sim 7.3$ kV/mm) [9]. A high d_{33} value has been recently demonstrated for the Ca and Zr-modified $BaTiO_3$ ceramics by constructing a tricritical point at room temperature, which is superior to the PZT materials [6,10], but a low Curie temperature seriously limits the practical application in the field of piezoelectric devices.

To improve the piezoelectric properties of BNT ceramics, BNT-based solid solutions with other ferroelectric materials have been formed, such as BNT–$Bi_{0.5}K_{0.5}TiO_3$ [11–13], BNT–$NaNbO_3$ [14], and BNT–$BaTiO_3$ [15–21]. However, there are few reports on the piezoelectric properties of BNT ceramics combined with BCTZ, and an improved piezoelectric behavior is highly expected in such a material system. In the present work, we have attempted to improve the piezoelectric properties of BNT ceramics by introducing BCTZ, and $(1-x)Bi_{0.5}Na_{0.5}TiO_3$–$x(Ba_{0.85}Ca_{0.15})(Ti_{0.90}Zr_{0.10})O_3$ [$(1-x)$BNT–xBCTZ] lead-free piezoelectric ceramics were prepared by a conventional solid reaction method. The effect of BCTZ content on the piezoelectric properties of $(1-x)$BNT–xBCTZ ceramics was systematically investigated, and some related physical mechanisms were studied.

2. Experimental procedure

$(1-x)$BNT–xBCTZ ceramics with $x = 0$, 0.02, 0.04, 0.05, 0.06, 0.07, 0.08, and 0.10 were prepared by the solid state reaction route. Raw materials were $BaCO_3$ (99%), $CaCO_3$ (99.9%), ZrO_2 (99%), Bi_2O_3 (99%), $NaCO_3$ (99.8%), and TiO_2 (99.99%). Raw powders were thoroughly ball mixed with ZrO_2 balls for 24 h using the ethanol as the medium. Homogenous 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 mm. All ceramics were sintered at ~1150 °C for 2 h in air after burning out the PVA binder at ~850 °C for 2 h, and the ceramic with $x = 0.02$ was sintered in the temperature range of 1115–1210 °C. Silver paste was fired at ~700 °C for 10 min on both sides of these samples as electrodes for electrical measurements. All samples were poled at a room temperature of ~25 °C in a silicone oil bath under a dc field of 5.0 kV/mm for 20 min. The phase structure in these ceramics was measured by using X-ray diffraction (XRD) (DX1000, PR China). The density of these ceramics was determined by the Archimedes method. Scanning electron microscopy (SEM) was employed to study the surface morphologies of these ceramics. The dielectric behavior as a function of measurement temperature of these ceramics was obtained using an LCR meter (HP 4980, Agilent, USA). The piezoelectric constant d_{33} of these ceramics was measured using a piezo-d_{33} meter (ZJ-3A, China).

3. Results and discussion

Fig. 1(a) plots the XRD patterns of $(1-x)$BNT–xBCTZ ceramics as a function of BCTZ content. All ceramics are of a pure peroviskite

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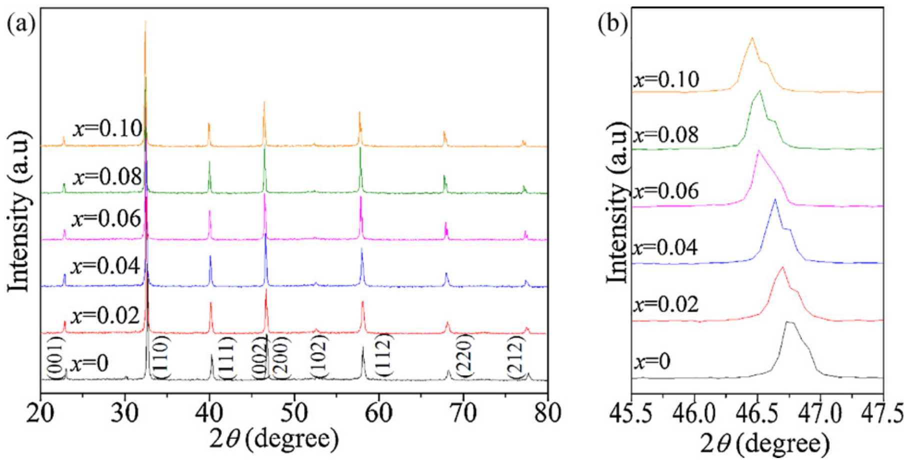

Fig. 1. (a) XRD patterns and (b) expanded XRD patterns of $(1-x)$BNT–xBCTZ ceramics with different BCTZ content.

phase, and secondary phases are not observed in the measurement range of XRD, confirming that the stable solid solution between BNT and BCTZ is formed in the investigated range of this work. Fig. 1(b) shows the expanded XRD patterns in the 2θ range of 45.5°–47.5° of $(1-x)$BNT–xBCTZ ceramics. The peaks position of BCTZ ceramics is shifted to a lower angle with an increase of BCTZ 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 Zr^{4+} ($r_{Zr^{4+}} \sim 1.45$ Å) respective for the $(Bi_{0.5}Na_{0.5})^{2+}$ ($r_{Bi^{3+}} \sim 1.4$ Å and $r_{Na^{+}} \sim 1.39$ Å) and Ti^{4+} ($r_{Ti^{4+}} \sim 1.32$ Å) sites in BNT [22].

Fig. 2(a)–(d) indicates the SEM patterns of surface morphologies of $(1-x)$BNT–xBCTZ ceramics as a function of BCTZ content ($x = 0$, 0.04, 0.06, and 0.08). It was observed that the average grain size of $(1-x)$BNT–xBCTZ ceramics decreases with increasing BCTZ content, which may be due to the BCTZ acting as a grain growth inhibitor. Moreover, some small grain are emerged into larger ones, resulting in the dense microstructure of $(1-x)$BNT–xBCTZ ceramics. Fig. 3 shows the densities ρ of $(1-x)$BNT–xBCTZ ceramics as a function of BCTZ content. The ρ value of these ceramics is in the range of 5.77–5.94 g/cm^3. The ρ value of these ceramics gradually decreases with increasing BCTZ content because of a lower density of BCTZ, while the dense microstructure is demonstrated for all ceramics, as shown in Fig. 2(a)–(d).

Fig. 4 shows the temperature dependence of the dielectric constant (ε_r) and dielectric loss ($\tan\delta$) of $(1-x)$BNT–xBCTZ ceramics, measured at 10 kHz. Two phase transitions are clearly observed for these ceramics, that is, the first one is the depolarization temperature (T_d) corresponding to the phase transition from ferroelectric to antiferroelectric and the second one is assigned to the temperature at maximum ε_r (T_m) corresponding to a phase transition from antiferroelectric to paraelectric order [19]. The insert of Fig. 4 plots the composition dependence of T_d and T_m values of $(1-x)$BNT–xBCTZ

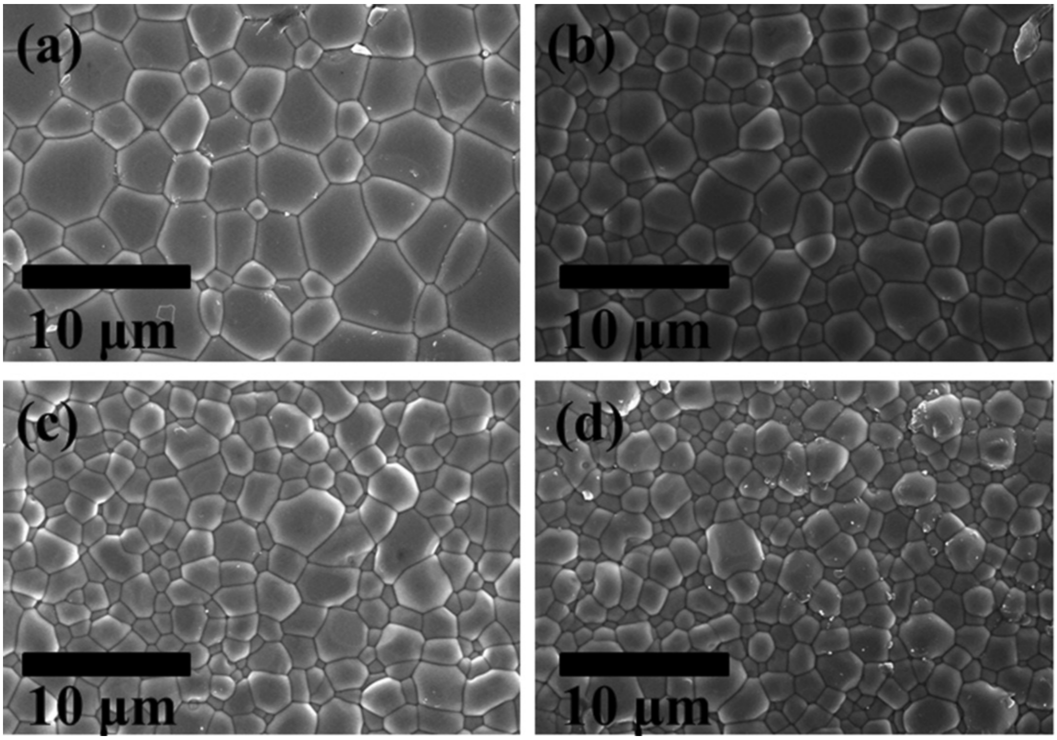

Fig. 2. Surface morphologies of $(1-x)$BNT–xBCTS ceramics: (a) $x = 0$, (b) $x = 0.04$, (c) $x = 0.06$, and (d) $x = 0.08$.

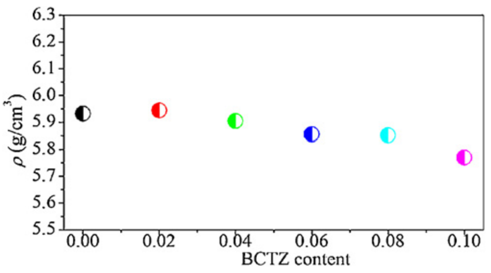

Fig. 3. Densities ρ of $(1-x)$BNT–xBCTZ ceramics with different BCTZ content.

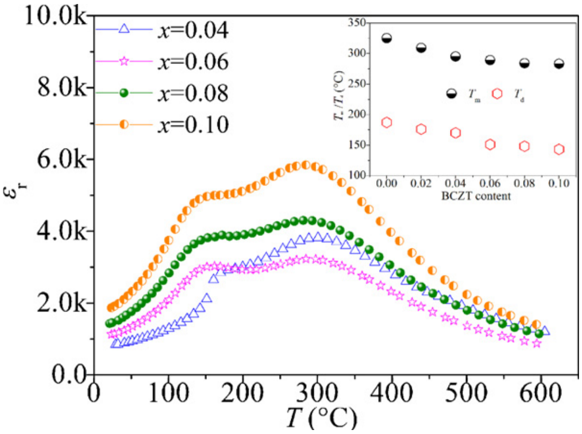

Fig. 4. Temperature dependence of the dielectric constant of $(1-x)$BNT–xBCTZ ceramics with different BCTZ content, where the insert is T_m and T_d values as a function of BCTZ content.

ceramics. It is well known that T_d and T_m values of pure BNT ceramic are ∼187 °C and 325 °C, respectively [23]. In the present work, the introduction of BCTZ simultaneously decreases these T_d and T_m values of $(1-x)$BNT–xBCTZ ceramics because of the introduction of BCTZ ceramics with a low Curie temperature [6,10].

Fig. 5(a) plots the composition dependence of piezoelectric constant (d_{33}) and electromechanical coupling factor (k_p) of $(1-x)$BNT–xBCTZ ceramics. It has been reported that pure BNT ceramic has a lower d_{33} value [23]. However, the d_{33} value of $(1-x)$BNT–xBCTZ ceramics increases, reaches a maximum ($d_{33} \sim 158$ pC/N) for the ceramic with $x = 0.06$, and decreases with further increasing BCTZ content. Similarity to the change of d_{33} values, the k_p also obtains a maximum value for the ceramic with $x = 0.06$. In this work, piezoelectric properties of $(1-x)$BNT–xBCTZ ceramics with $x = 0.06$ have much better than these reported results (∼122 pC/N) by other authors [8,16], which could be attributed to the introduction of an optimum BCTZ content [6,10]. Fig. 5(b) shows the ε_r and $\tan\delta$ values of $(1-x)$BNT–xBCTZ ceramics as a function of BCTZ content. The ε_r value of $(1-x)$BNT–xBCTZ ceramics increases with increasing BCTZ content because of the introduction of the BCTZ composition with a high ε_r value [6,10], and a lower $\tan\delta$ value is also demonstrated for the ceramic with $x = 0.06$.

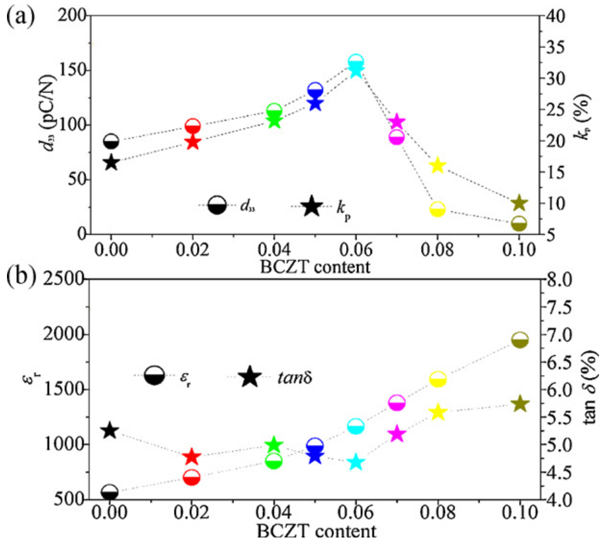

Fig. 5. (a) Piezoelectric and (b) dielectric properties of $(1-x)$BNT–xBCTZ ceramics as a function of BCTZ content.

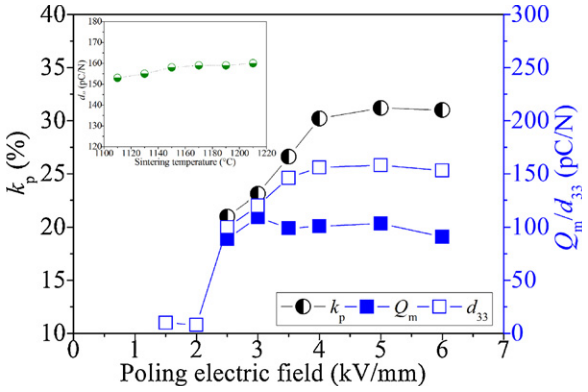

Fig. 6. (a) k_p, d_{33}, and Q_m values as a function of the poling electric field for the $(1-x)$BNT–xBCTZ ceramic with $x = 0.06$, where the insert is its d_{33} value as a function of sintering temperature.

The effect of the poling electric field (E_p) on the piezoelectric properties of $(1-x)$BNT–xBCTZ ceramics with $x = 0.06$ were conducted in the electric field range of 1.5–6.0 kV/mm, as shown in Fig. 6. k_p and d_{33} values for the ceramic is close to zero for $E_p < 2.5$ kV/mm, increases dramatically with increasing E_p value of 2.5–4.0 kV/mm, and then almost remains unchanged for $E_p \geq 4.0$ kV/mm, confirming that the E_p value is a very key factor to affect the piezoelectric properties of $(1-x)$BNT–xBCTZ ceramics. In this work, a too low E_p results in a low k_p and d_{33} values because that the domain is difficult to switch at such a low poling electric field. A higher poling electric field can reverse the domains completely, generating a better piezoelectric behavior. Moreover, the Q_m value of $(1-x)$BNT–xBCTZ ceramics is independent on the E_p value. In the present work, different sintering temperatures are also used to check the effect of the sintering temperature (1115–1210 °C) on the d_{33} value of $(1-x)$BNT–xBCTZ ceramics with $x = 0.06$, as shown in the insert of Fig. 6. Its d_{33} value is independent on the sintering temperature, confirming that the piezoelectric properties of $(1-x)$BNT–xBCTZ ceramic with $x = 0.06$ are insensitive to the sintering temperature.

4. Conclusions

$(1-x)Bi_{0.5}Na_{0.5}TiO_3$–$x(Ba_{0.85}Ca_{0.15})(Ti_{0.90}Zr_{0.10})O_3$ [$(1-x)$BNT–xBCTZ] lead-free piezoelectric ceramics were prepared by a conventional solid reaction method. The effect of BCTZ content on the piezoelectric properties of $(1-x)$BNT–xBCTZ ceramics was systematically investigated. The BCTZ diffuses into the BNT to form a stable solid solution, and T_m and T_d values slightly decrease with increasing BCTZ content, together with an increase in ε_r value. $(1-x)$BNT–xBCTZ ceramics with $x = 0.06$ exhibit an enhanced piezoelectric behavior: $d_{33} \sim 158$ pC/N and $k_p \sim 31.2\%$, and its d_{33} value is independent on the sintering temperature and strongly depends on the poling electric field.

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References

[1] L.E. Cross, Nature 432 (2004) 24.
[2] Y. Saito, H. Takao, T. Tani, T. Nonoyama, K. Takatori, T. Homma, Nature 432 (2004) 84.
[3] J. Rödel, W. Jo, K.T.P. Seifert, E.M. Anton, T. Granzow, D. Damjanovic, J. Am. Ceram. Soc. 92 (2009) 1153.
[4] S.J. Zhang, R. Xia, T.R. Shrout, J. Electroceram. 19 (2007) 251.
[5] J.G. Wu, Y.Y. Wang, D.Q. Xiao, J.G. Zhu, Appl. Phys. Lett. 91 (2007) 132914.
[6] W.F. Liu, X.B. Ren, Phys. Rev. Lett. 103 (2009) 257602.
[7] G.A. Smolenskii, A.I. Aganovskaya, Sov. Phys. Solid State 1 (1960) 1429.
[8] T. Takennaka, K. Maruyama, K. Sakata, Jpn. J. Appl. Phys. 130 (part) (1991) 2236.
[9] A. Herabut, A. Safari, J. Am. Ceram. Soc. 80 (11) (1997) 2954.
[10] J.G. Wu, D.Q. Xiao, Y.Y. Wang, W.J. Wu, B. Zhang, J. Li, J.G. Zhu, Scr. Mater. 65 (2011) 771.
[11] A. Sasaki, T. Chiba, Y. Mamiya, E. Otsuki, Jpn. J. Appl. Phys. 38 (1999) 5564.
[12] K. Yoshii, Y. Hiruma, H. Nagata, T. Takenaka, Jpn. J. Appl. Phys. 45 (5B) (2006) 4493.
[13] S. Zhao, G. Li, A. Ding, T. Wang, Q. Rui, J. Phys. D: Appl. Phys. 39 (2006) 2277.
[14] Y.M. Li, W. Chen, J. Zhou, Q. Xu, H.J. Sun, R.X. Xu, Mater. Sci. Eng. B 112 (2004) 5.
[15] Y. Bai, G.P. Zheng, S.Q. Shi, Mater. Res. Bull. 46 (2011) 1866.
[16] B.J. Chu, D.R. Chen, G.R. Li, Q.R. Yin, J. Eur. Ceram. Soc. 22 (2002) 2115.
[17] R. Ranjan, A. Dviwedi, Solid State Commun. 135 (2005) 394.
[18] X.Y. Zhou, H.S. Gu, Y. Wang, W.Y. Li, T.S. Zhou, Mater. Lett. 59 (2005) 1649.
[19] C. Xu, D. Lin, K.W. Kwok, Solid State Sci. 10 (2008) 934.
[20] W. Jo, J.E. Daniels, J.L. Jones, X. Tan, P.A. Thomas, D. Damjanovic, J. Rödel, J. Appl. Phys. 109 (2011) 014110.
[21] Y.S. Sung, J.M. Kim, J.H. Cho, T.K. Song, M.H. Kim, T.G. Park, Appl. Phys. Lett. 98 (2011) 012902.
[22] R.D. Shannon, C.T. Prewitt, Acta Crystallogr. B 25 (1969) 925.
[23] Y. Hiruma, H. Nagata, T. Takenaka, J. Appl. Phys. 105 (2009) 084112.