J Mater Sci (2007) 42:9750–9755
DOI 10.1007/s10853-007-2005-z

The effects of CuO-doping on dielectric and piezoelectric properties of $Bi_{0.5}Na_{0.5}TiO_3$–Ba(Zr,Ti)O_3 lead-free ceramics

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Received: 7 May 2007 / Accepted: 18 July 2007 / Published online: 20 August 2007

Abstract CuO-doped lead-free ceramics based on bismuth sodium titanate ($Bi_{0.5}Na_{0.5}TiO_3$, BNT) and barium zirconate titanate ($Ba(Zr_{0.07}Ti_{0.93})O_3$, BZT) were prepared via a multi-step solid-state reaction process. The BNT–BZT with CuO dopant ceramics sintered at 1150–1180 °C for 2 h in air showed a pure perovskite structure. SEM images reveal that a small amount of CuO (<2 mol%) play a significant role on the microstructure to improve its sintering attributes, while it will degrade when the dopant is added beyond 2 mol%. The dielectric and piezoelectric properties of CuO-doped BNT–BZT ceramics were evaluated. At room temperature, the sample doped with 2 mol% CuO shows quite good properties such as a high piezoelectric constant (d_{33} ~156.5 pC/N) and a high electromechanical coupling factor (k_t ~52%). The depolarization temperature increased dramatically and the maximum permittivity temperature decreased slightly.

Introduction

Due to the increasing demand for environmental protection, studies have been performed in depth on various lead-free ceramics for environmentally friendly applications (dielectrics for capacitors, actuators, etc). Bismuth sodium titanate ($Bi_{0.5}Na_{0.5}TiO_3$, BNT) is one of the most important lead-free piezoelectric materials with a perovskite structure [1]. It has a high Curie temperature (T_c = 320 °C) and a large remnant polarization (P_r ~38 μC/cm^2) at room temperature. BNT has been considered as a promising candidate to substitute for the widely used lead-based piezoelectric materials. Nevertheless, the large coercive field (E_c ~7.3 kV/mm), low depoling temperature, and high conductivity during poling are barriers for practical applications [2–4].

On the other hand, $BaTiO_3$ and its doped species, i.e. doped on A and B sites of the ABO_3 perovskite structure, have been investigated to develop high-quality lead-free ceramics to replace the toxic lead-based materials and components because of their very high level of strain (up to 1% along the (001) direction). Many studies show that the substitution of Ti^{4+} in $BaTiO_3$ with quadrivalence ions (such as Zr^{4+} and Ce^{4+}) can significantly improve the overall properties of the material [5, 6]. $Ba(Ti_{0.95}Zr_{0.05})O_3$ ceramics were reported to show a satisfactory piezoelectric response with the d_{33} value of 236 pC/N at room temperature [7]. We also investigated $Ba(Zr_xTi_{1-x})O_3$ (BZT) ceramics focusing on the relationship between the composition and piezoelectric parameters. A high valued piezoelectric parameter of d_{33} ~300 pC/N was obtained at $x = 0.07$ between the orthorhombic and rhombohedral phases in our work. Second, a small decrease in the Curie temperature was obtained for a low content of Zr in the BZT. i.e. T_c = 106 °C when $x = 0.07$ compared to T_c = 120 °C for $BaTiO_3$. Therefore this composition was used in this study. However, the large temperature dependence of the dielectric constant and a low Curie temperature for $BaTi_{1-x}Zr_xO_3$ (BZT) ceramics limit their practical applications. To make use of the merits of both materials a trade off is required between the high piezoelectric

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coefficient of BZT and the high Curie temperature of BNT. Several solid solutions of BNT with $SrTiO_3$ [8], $NaNbO_3$ [9], $BaTiO_3$ [10] have improved electrical properties to that of BNT.

The BNT–BZT system becomes dense at about 1180 °C, and the bismuth and sodium content may evaporate during the sintering process which can cause a deficiency in A-site ions. It is believed that the sintering attributes of BNT–BZT system can be improved considerably to enable practical industrial applications. Among the several sintering aids employed for dielectric ceramics, CuO is often used because of its low melting point and formation of the liquid phase [11–13].

Based on our work, efforts were made to locate the morphotropic phase boundary (MPB). The xBNT-$(1-x)$BZT ceramics were studied and the MPB was found at $x = 0.075$ for BZT in the compounds. In this study, $0.925Bi_{0.5}Na_{0.5}TiO_3$–$0.075BaZr_{0.07}Ti_{0.93}O_3$ (BNT–BZT) acted as the host material and x mol% CuO ($x = 0.5$, 1, 2, and 5) as the addition. The influences of CuO doping on the microstructures and electrical properties are presented.

Experimental procedure

High purity Bi_2O_3 (99.9%), Na_2CO_3 (99%), TiO_2 (99%), $BaCO_3$ (99.5%), and ZrO_2 (99%) powders were used as starting materials. To prepare the $Bi_{0.5}Na_{0.5}TiO_3$ (BNT) raw powder, Bi_2O_3, Na_2CO_3, and TiO_2 were mixed and ground and then calcined at 850 °C for 4 h in air. $BaZr_{0.07}Ti_{0.93}O_3$ (BZT) powders were prepared through mixing $BaCO_3$, ZrO_2, and TiO_2 and calcined at 1200 °C for 4 h. BZT powders were ball milled again and dried before being mixed with BNT powders. The BNT and BZT as-calcined powders were then weighed and mixed according to the compositions of 0.925BNT–0.075BZT with x mol% CuO doping ($x = 0.5$–5). After ball-milling in alcohol for 4 h and drying, the powders were pressed into discs of 12 mm diameter by 1 mm thick. The discs were then sintered in air at temperatures of 1150–1180 °C for 2 h with multiple steps at different heating rates between 2.5 and 5 °C/min. X-ray diffraction (XRD) using a Philips Diffractometer with CuK_α radiation ($\lambda = 0.15406$ nm) was performed to check the phases of the powders and ceramics. The morphology was observed by field emission scanning electron microscopy (SEM, JSM-6335F). The ceramic discs for electrical characterization were electroded with silver paste screen-printed on both sides followed by a heat treatment at 650 °C for 20 min. The dielectric constant and loss tangent of the ceramics were measured as a function of temperature (room temperature to 500 °C) in a frequency range from 1 kHz to 1 MHz using impedance analyzers HP 4192A and HP 4194A. To measure the piezoelectric properties, the ceramic samples were poled in silicone oil at 80–100 °C under a d.c. electric field of 4–6 kV/mm for 30 min. The piezoelectric charge coefficient d_{33} was measured at 110 Hz using a piezo d_{33} meter (ZJ-38, Institute of Acoustics Academia Sinica). The electromechanical coupling coefficients (k_p, k_t) were determined using the resonance method from the impedance data measured by an impedance analyzer (HP 4294A) as a function of frequency.

Results and discussion

Figure 1 shows the X-ray diffraction patterns of BNT powder, BZT powder, and a BNT–BZT ceramic in the 2θ range of 20–60°. The BNT powder was pure perovskite phase after calcining the ball-milled raw materials of Bi_2O_3, Na_2CO_3, and TiO_2 at 850 °C for 4 h. The solid-state reaction between TiO_2, ZrO_2, and $BaCO_3$ was almost complete at 1200 °C forming a pure perovskite structure, as shown in Fig. 1b. The BNT–BZT ceramic was sintered at different temperatures, resulting in a splitting of peak (111) in the sample sintered at 1150 °C for 2 h. The (110) peak was detected at $2\theta = 32.62°$ for the BNT powder, at 31.51° for the BZT powder, and merged into a single peak located at 32.24° for BNT–BZT ceramic. However, the (111) peak was detected at 40.16° for the BNT powder, 38.83° for the BZT powder, and 38.45°/39.81° for BNT–BZT ceramic. The split peaks of 38.45° and 39.81° were almost matched with BNT(111) and BZT(111). This suggested that the solid solution reaction between BNT and BZT was incomplete at this temperature (see Fig 1c), showing two peaks from BNT(111) and BZT(111),

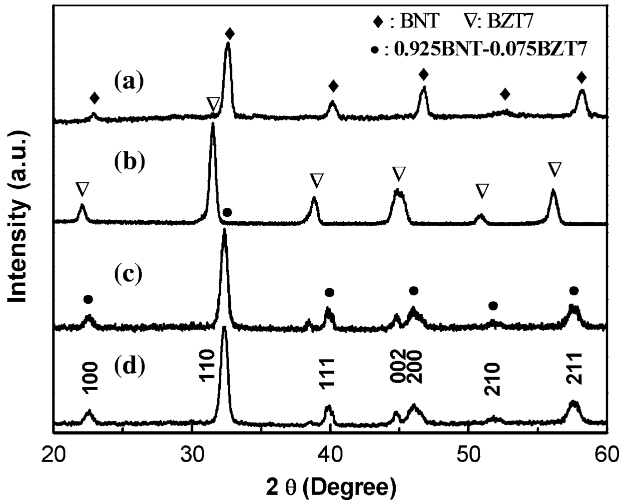

Fig. 1 XRD pattern of (**a**) BNT powder calcined at 850 °C for 4 h; (**b**) BZT powder calcined at 1200 °C for 4 h; and (**c**) 0.925BNT–0.075BZT ceramic sintered at 1150 °C for 2 h. (**d**) 0.925BNT–0.075BZT ceramic sintered at 1180 °C for 2 h

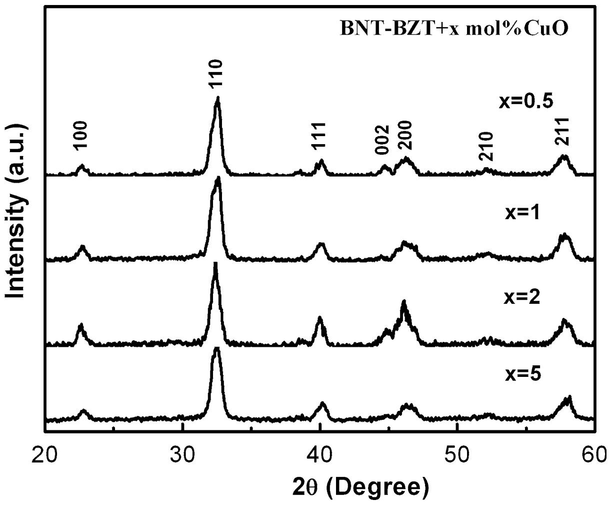

Fig. 2 X-ray diffraction patterns of BNT–BZT ceramics doped with x mol% CuO (x = 0.5–5) sintered at 1180 °C for 2 h

respectively. As the temperature was increased the peak at 38.45° is reduced significantly and the (111) peak for the solid solution remains, as shown in Fig. 1d.

Figure 2 shows the X-ray diffraction patterns of BNT–BZT ceramics doped with x mol% CuO (x = 0.5–5) sintered at 1180 °C for 2 h. The XRD patterns show a pure perovskite phase and no individual phases from BNT or BZT can be seen, implying the formation of a solid solution rather than a mixed compound. The fact that peaks split at about 40° and 46° indicates the co-existence of rhombohedral and tetragonal phases in the CuO-doped BNT–BZT ceramics. The (002) and (200) peaks are separated for the samples with low CuO concentration and merged gradually into one broad peak with the increased amount of dopants. Moreover, the intensity of (002) peak decreased and that of (200) increased with increasing CuO amount.

Figure 3 shows SEM images of polished and thermally etched BNT–BZT + x mol% CuO ceramics, which depict the doping effect of CuO on the grain size. The grain size of the undoped BNT–BZT ceramic sintered at 1180 °C for 2 h is between 1 and 3 μm with several voids approximately 2 μm in size labeled as “A” and “B” in Fig. 3a. The average grain size increased from 3 to 5 μm for a 0.5 mol% CuO-doped sample, indicating that the CuO dopants enhance the grain growth with more regular square shaped grains, as shown in Fig. 3b. With the increased amount of CuO, a much easier densification of BNT–BZT ceramics is revealed, as shown in Fig. 3c and d. The size distribution of the BNT–BZT ceramics was predominantly determined by the amount of CuO addition and sintering temperature. For the 1 mol% CuO doped sample, larger grains were found with grain sizes ≥ 10 μm. When the amount of CuO dopant is over 5 mol%, the microstructures of BNT–BZT ceramics become more porous. The dense ceramics with a density >90% of the theoretical density were obtained by sintering at 1180 °C with CuO-doping. A small increase in densities was found by increasing the content of CuO, but the density reaches saturation value when the CuO doping was >2 mol%. The relative density is about 94% of the theoretical density for the sample with 2 mol% CuO-doping.

Figure 4 shows the temperature dependence of the relative permittivity (ε_r) of undoped BNT–BZT ceramic at

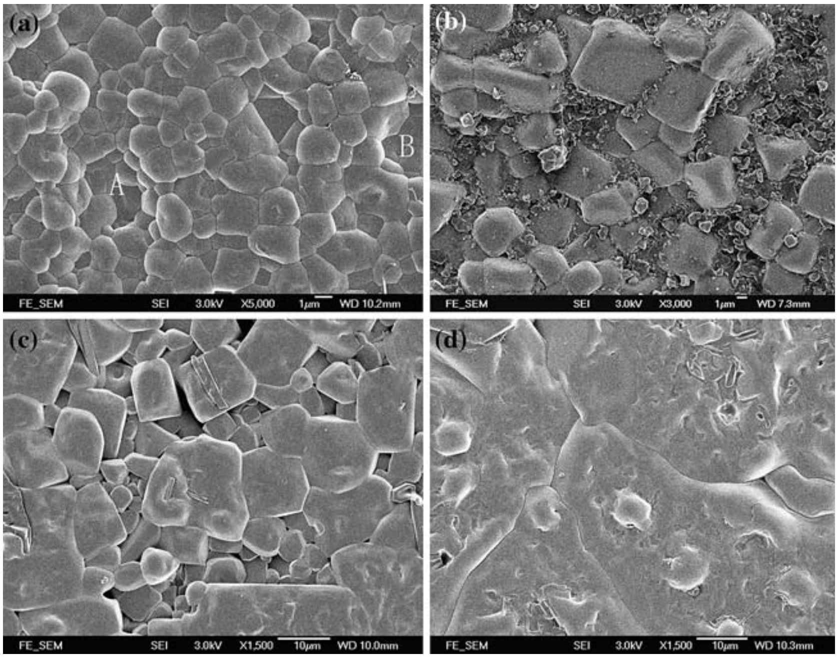

Fig. 3 SEM images of polished and thermally etched BNT–BZT doped with x mol% CuO ceramics. (**a**) x = 0, (**b**) x = 0.5, (**c**) x = 1, and (**d**) x = 2. Labels “A” and “B” in (**a**) denote the voids in the ceramic

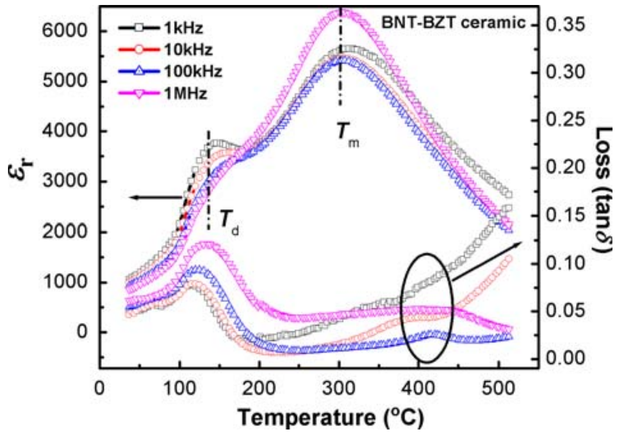

Fig. 4 Temperature dependence of the relative permittivity of undoped BNT–BZT ceramics at different frequencies ranging from 1 kHz to 1 MHz

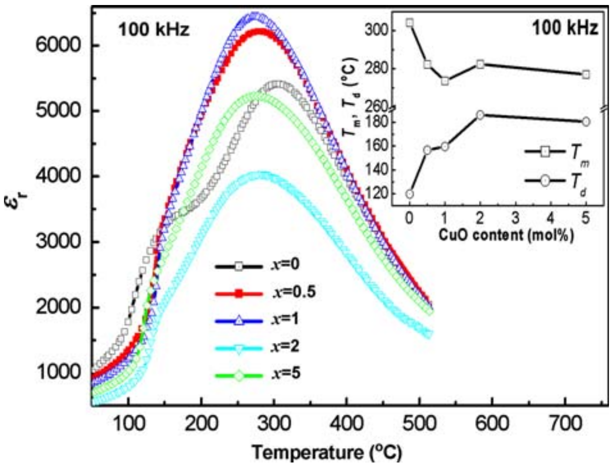

Fig. 5 Temperature dependences of relative permittivity and loss tangent for the samples with various amount of CuO dopant from $x = 0$ to 5 mol% for temperatures ranging from room temperature to 500 °C at a frequency of 100 kHz. The inset shows the compositional dependence of the two transition temperatures in BNT–BZT + x mol% CuO ceramics at 100 kHz

different frequencies ranging from 1 kHz to 1 MHz. Three phases of ferroelectric, anti-ferroelectric, and paraelectric exist in all samples at different temperatures [14]. The depolarization temperature (T_d), referred to the transition temperature between ferroelectric phase and anti-ferroelectric phase increased to 135.3 °C (120 °C for pure BNT ceramic). The maximum permittivity temperature (T_m) is 314.8 °C, which is slightly lower than that of pure BNT (320 °C).

The temperature dependence of the relative permittivity for samples with different amounts of CuO-dopant was measured to determine phase transitions. Two transition points (T_d and T_m) are clearly seen in the ε_r–T plot, as shown in Figs. 4 and 5. The ferroelectric to paraelectric phase transition temperature decreased after doping with CuO. The relative permittivity increased except for the sample doped with 5 mol% CuO, which is probably due the microstructures containing more voids. The loss tangent increased slightly, especially for the samples with greater CuO-doping. The depolarization temperatures were determined from the temperature dependence of the dielectric constants (ref. in Figs. 4, 5), as shown in inset of Fig. 5. The depolarization temperature increased sharply from 120 °C ($x = 0$) to 156.7 °C ($x = 0.5$) for the samples with low CuO content and reached a maximum value of 186.1 °C for $x = 2$. Meanwhile, the T_m dropped dramatically from 304.1 °C ($x = 0$) to 282.3 °C ($x = 0.5$) and remained almost constant after a slight increase to 282.4 °C for $x = 2$. The improvement in T_d from 120 to 186.1 °C is beneficial for practical applications. The depolarization temperature results from a transition to an antiferroelectric state from a ferroelectric state [10, 15]. Some researchers suggested that there is a coexistence of rhombohedral and tetragonal phases instead of an anti-ferroelectric phase [16]. The results show that the CuO-doping effectively suppressed the rhombohedral-to-tetragonal phase transition, giving rise to an increase in T_d.

Figure 6 shows relative permittivity (ε_r) and loss tangent (tanδ) of poled and unpoled BNT–BZT + x mol% CuO. It can be seen that the unpoled samples have higher values of ε_r and tanδ than those of the poled samples. The decrease in ε_r and tanδ after poling were attributed to the movement of domains in the piezoelectric ceramics [17]. The increase of tetragonality in the samples with a low CuO content also causes a decrease of the differences in relative permittivity between the unpoled and poled samples. It is evident that the (002) and (200) peaks become broad and merge into one peak, when the amount of CuO-doping is increased to 5 mol%. This has the effect of decreasing the tetragonal structure (see Fig. 2). The relative permittivity (ε_r) of both poled and unpoled samples increases with increasing amounts of CuO. The maximum value of ε_r appears in the sample doped with 1 mol% CuO, while the loss tangent has an inverse trend with relative permittivity. The loss tangent of the unpoled samples decreased slightly at low percentage of CuO and then increased, but decreases for the poled samples when the amount of CuO is beyond 2 mol%.

Figure 7 shows the piezoelectric coefficient (d_{33}) of the BNT–BZT + x mol% CuO ceramics as a function of the amount of CuO. The value of d_{33} increases from 120 pC/N for the pure BNT–BZT to a maximum value of 156.5 pC/N for $x = 2$ around the MPB region and then decreases to 136.5 pC/N for $x = 5$. Note that the d_{33} of BNT–BZT + x mol% CuO ceramics improves with low concentration of CuO doping due to an improvement in its sintering attributes (Ref. in Fig. 3). The maximum value of piezoelectric constant was higher than that of the BNT–BZT9 ceramics

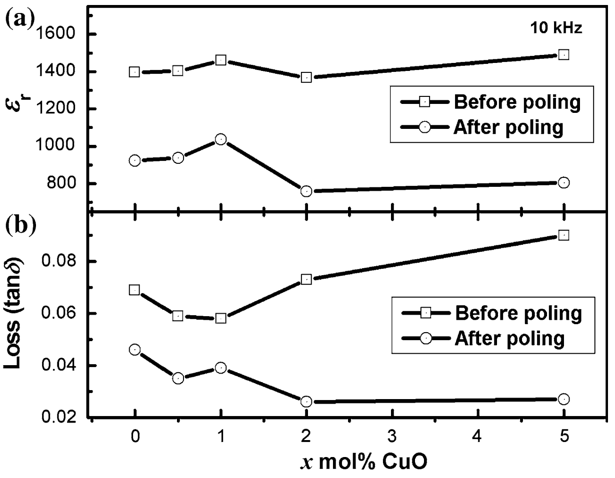

Fig. 6 The relative permittivity and loss tangent of BNT–BZT ceramics as a function of the amount of CuO-dopant

[18]. A further increase in the CuO-doping of the compounds will degrade the microstructure, leading to a decrease in d_{33}.

The mechanical coupling factors (k_p and k_t) are also affected by the CuO-doping. The value of k_t increases from 41% for the pure BNT–BZT ceramic to 52% for the sample doped with 2 mol% CuO and then decreases slightly to 48% for the sample doped with 5 mol% CuO. The value of k_p was 15.8% for the pure BNT–BZT ceramic, and this decreased to 14.8% for the sample with 1 mol% CuO. It was found that CuO dopant had less effect on the k_p value. The maximum values of k_p (~ 16.5%) and k_t (~ 52%) were obtained from the sample doped with 2 mol% CuO. It is obvious that the CuO-doping can improve the electric properties of BNT–BZT ceramics.

The mechanism for the effect of lattice distortion by addition of CuO is complicated. It is well known that Bi^{3+} and Na^+ are volatile at high temperature. The BNT–BZT ceramics may lose some Bi^{3+} during sintering resulting in some A-sites vacancies in the lattice. Thus, it is likely that the Cu^{2+} cations in the A-sites are formed by the Bi^{3+} deficiency. Bi^{3+} has a radius of 1.17 Å (6-coordinate) larger than 0.87 Å (6-coordinate) of Cu^{2+}, which acts as a donor. It is also possible for Cu^{2+} to fill in the sites of Na^+ (6-coordinate, r = 1.16 Å). Therefore, Cu^{2+} acts as both a donor and an acceptor in the BNT–BZT ceramics.

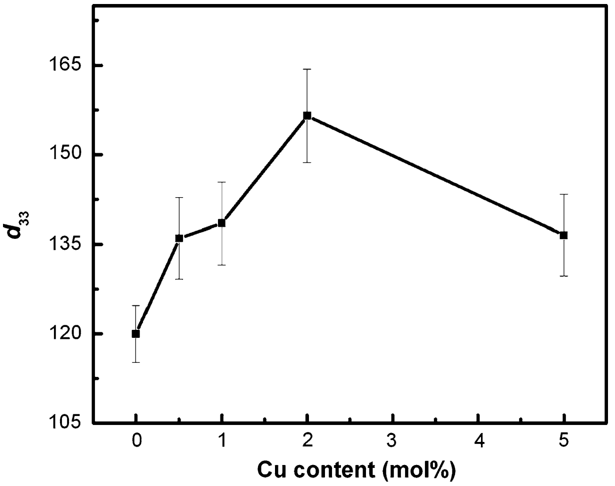

Fig. 7 The piezoelectric coefficient (d_{33}) of BNT–BZT + x mol% CuO as a function of the amount of CuO dopant

In the MPB regions, enhanced dielectric and piezoelectric properties are obtained. This is attributed to the polarization vector being able to easily switch between the allowed polarization orientations [18]. The relationship between crystal phases and electrical properties requires further understanding that could lead to improved composition selection. It is believed that the electrical properties of BNT–BZT ceramics may be improved further.

Conclusions

This study aims to investigate the doping effect of CuO on the microstructure and electrical properties of BNT–BZT ceramics. BNT–BZT ceramics doped with x mol% CuO (x = 0–5) were prepared by a conventional solid-state reaction technique with a multi-step sintering process at 1180 °C for 2 h in air. The ceramics showed pure perovskite structures with the coexistence of rhombohedral and tetragonal phases. The grain size increases with an increasing amount of CuO. The maximum permittivity temperature is suppressed dramatically from 304.1 °C for pure BNT–BZT ceramic to 273.7 °C for the sample doped with 1 mol% CuO, and then increased gradually in the samples doped with further amounts of CuO. The depolarization temperature of the ceramics increased, which is beneficial for using the ceramics at higher temperatures. The maximum value of the piezoelectric constant d_{33} (156.5 pC/N) was obtained for the ceramic doped with 2 mol% CuO, which has a tetragonal phase near the MPB region. A high electromechanical coupling factor (k_t ~52%) was found in the sample doped with 2 mol% CuO. The BNT–BZT system is expected to be a new and promising lead-free dielectric and piezoelectric ceramics for practical applications.

Acknowledgements This work was supported by the Innovation and Technology Fund (ITF GHS/066/04) of the Hong Kong Polytechnic University.

References

1. Smolensky GA, Isopov VA, Argranovskaya AI, Krainic NN (1961) Sov Phys Sol Stat 2:2651
2. Wang XX, Or SW, Tang XG, Chan HLW, Choy PK, Liu PCK (2005) Solid State Commun 134:659

3. Wang XX, Chan HLW, Choy CL (2003) Solid State Commun 125:395
4. Takenaka T, Okuda T, Takegahara K (1997) Ferroelectrics 196:175
5. Yu Z, Guo RY, Bhalla AS (2000) Appl Phys Lett 77:1535
6. Ang C, Yu Z, Jing Z, Guo RY, Bhalla AS, Cross LE (2002) Appl Phys Lett 80:3424
7. Yu Z, Ang C, Guo RY, Bhalla AS (2002) J Appl Phys 92:1489
8. Sakata K, Masuda Y (1994) Ferroelectrics 7:347
9. Li Y, Chen W, Zhou J, Xu Q, Sun H, Xu R (2004) Mater Sci Eng B 112:5
10. Takenaka T, Muruyama K, Sakata K (1991) Jpn J Appl Phys 30(9B):2236
11. Matsubara M, Yamaguchi T, Sakamoto W, Kikuta K, Yogo T, Hirano S-I (2005) J Am Ceram Soc 88(5):1190
12. Kim DW, Ko KH, Hong KS (2001) J Am Ceram Soc 84(6):1286
13. Zhang YC, Yue ZX, Gui ZL, Li LT (2005) J Electroceram 14:67
14. Takennake T, Maruyama K, Akata K (1991) Jpn J Appl Phys 30(9B):2230
15. Suchanicz J, Roleder K, Kania A, Handerek J (1988) Ferroelectrics 77:107
16. Zhao SC, Li GR, Ding AL, Wang TB, Yin QR (2006) J Phys D: Appl Phys 39:2277
17. Wang XX, Choy SH, Tang XG, Chan HLW (2005) J Appl Phys 97:104101
18. Peng C, Li JF, Gong W (2005) Mater Lett 59:1576