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Structural and dielectric properties of (1-x)Bi($Ni_{1/2}Ti_{1/2}$)O_3-$x$$PbTiO_3$ ceramics with the morphotropic phase boundary composition

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Abstract (1-x)Bi($Ni_{1/2}Ti_{1/2}$)O_3-$x$$PbTiO_3$ (BNT-xPT, $0.42 \le x \le 0.52$) ceramics were prepared by the conventional mixed oxide method. With the increase of PT content, a change from rhombohedral phase to tetragonal phases, and while the morphotropic phase boundary (MPB) composition is located in the range of x=0.46–0.48. For x=0.46 sample, it exhibited a high Curie temperature (T_c) of 410 °C and good piezoelectric properties, d_{33} ~230pC/N, k_p ~40 % and k_t ~22 %. For $0.46 \le x \le 0.50$ samples, it can be found that depolarization temperature is around 350 °C by thermal depoling method.

Keywords Piezoelectric ceramics · High Curie temperature · Morphotropic phase boundary

1 Introduction

Recently, the piezoelectric ceramics, including $BiMeO_3$-$PbTiO_3$ (where Me=Sc^{3+}, Fe^{3+}, In^{3+}, Yb^{3+} …) [1–5] and Bi (Me1, Me2)O_3-$PbTiO_3$ (where Me1=Mg^{2+}, Zn^{2+}, Ni^{2+}, …, and Me2=Ti^{4+}, Nb^{5+}, W^{6+}…) [6–9], have attracted much attention, due to their high Curie temperature (T_c). The $BiScO_3$-$PbTiO_3$ (BS-PT) ceramics with morphotropic phase boundary (MPB) composition exhibit high Curie temperature (~450 °C) and excellent piezoelectric properties, d_{33}=460pC/N and k_p=56 % [1, 2], which were thought to be potential high temperature piezoelectric ceramics. (1-x)$BiFeO_3$-$x$$PbTiO_3$ [4, 9] (BF-PT) ceramics have high Curie temperature exceeding 600 °C at x= 0.30, while two drawbacks limited the application of these materials. Firstly, the conductivity and large dielectric loss were relatively high, which leads to poor dielectric properties. Secondly, it is hard to polarize the BF-PT ceramics because of the high coercive field (E_c), therefore the reported d_{33} is only ~9pC/N for BF-0.30PT ceramics [10].

Compared to BS-PT and BF-PT ceramics, (1-x)Bi ($Mg_{1/2}Ti_{1/2}$)-$x$$PbTiO_3$ (BMT-PT) and Bi($Ni_{1/2}Ti_{1/2}$)O_3-$PbTiO_3$ (BNT-PT) ceramics also possessed relatively high Curie temperature (>400 °C) and good piezoelectric properties (d_{33}>200 pC/N) near MPB. There are many reports about BMT-PT ceramics [11–13], but BNT-PT system was reported only by Choi et al. [14]. Thus, in this work, the phase structure, piezoelectric properties of BNT-PT ceramics were investigated. More important, the temperature dependent piezoelectric properties of BNT-PT ceramics with MPB composition were measured, which is valuable for the high temperature applications.

2 Experimental procedure

BNT-xPT ($0.42 \le x \le 0.52$) ceramics were synthesized using the conventional mixed oxide method. Bi_2O_3 (99.0 %),

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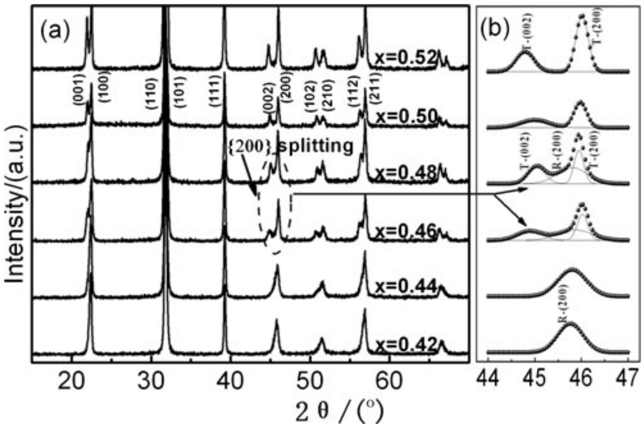


Fig. 1 X-ray diffraction patterns of BNT-*x*PT ceramics

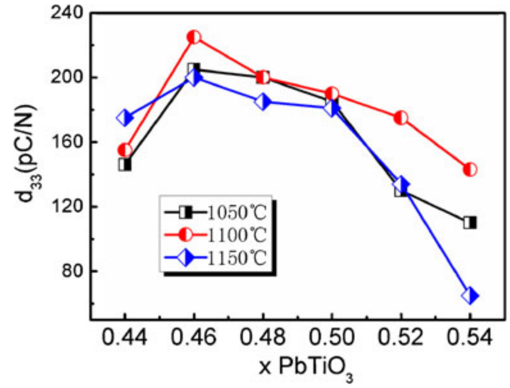


Fig. 3 Piezoelectric coefficient d_{33} for BNT-*x*PT ceramics sintered at different temperatures

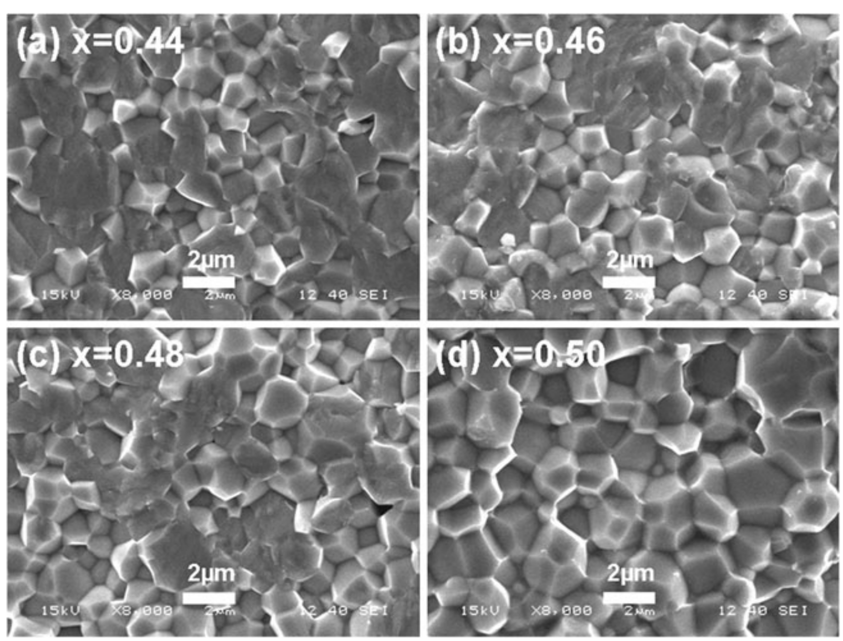
NiO_2 (99.0 %), TiO_2 (99.0 %), and PbO (99.9 %) powders were used as starting raw materials. The mixtures were ball-milled for 5 h in alcohol following by an oven drying, and the powders were calcined at 850 °C for 2 h in an alumina crucible. And then the calcined powders were pressed into disks of 10 mm in diameter and about 1 mm in thickness, with polyvinyl alcohol (PVA) as binder. The pellets were sintered at 1050–1100 °C for 2 h in a sealed alumina crucible to avoid the loss of PbO, Bi_2O_3 caused by sublimation.

Phase structure of the sample was characterized using X-ray diffraction (XRD) (Rigaku D/MAX-2400, Rigaku, Tokyo, Japan). The microstructure of the fracture surface of BNT-xPT ceramics was observed by scanning electron microscopy (SEM) (JSM-6360, JEOL, Tokyo, Japan). The d_{33} value was measured using a piezo-d_{33} meter (ZJ-3A) and the resonance frequency f_r and antiresonance frequency f_a were measured using a HP4294 (Hewlett-Packard, Palo Alto, CA) impedance analyzer. Dielectric measurements were performed with a HP4284A LCR meter from room temperature to 700 °C. The thermal depoling experiments were conducted by holding the poled samples at various high temperatures for 10 h, cooling to room temperature, measuring their d_{33}, f_r and f_a after 24 h [15].

3 Results and discussion

Figure 1 shows the XRD patterns BNT-*x*PT (x=0.42–0.52) ceramics. For $x \leq 0.44$, asymmetry on the left-hand side of (111) reflection peak and the absence of (001) reflection peak splitting suggests that rhombohedral phase was remained. For $x \geq 0.50$, the asymmetry of (111) is absent and (001), (011) and (002) peaks are split, indicating a

Fig. 2 SEM photos of BNT-*x*PT samples sintered at 1100 °C



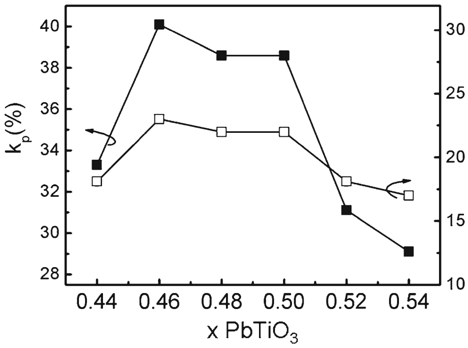


Fig. 4 Electromechanical coupling factor k_p and k_t for BNT-*x*PT ceramics sintered at 1100 °C

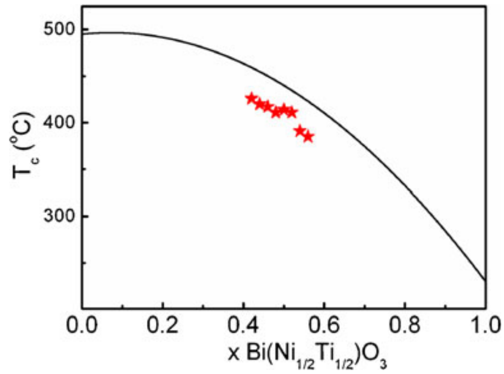


Fig. 6 T_c as function of BNT content

tetragonal phase. From $x=0.46$ to 0.48, (200) peaks undergo a change from gradually split to clearly split, demonstrating a phase transition from rhombohedral to tetragonal phases. It is indicated that the MPB composition is located in the range of $x=0.46$–0.48. The SEM photos of BNT-*x*PT ceramics are shown in Fig. 2. It can be seen that the microstructure of BNT-*x*PT ceramics were dense with fine grain size of 1.5–2.0 μm. For $x\leq0.50$, a little mixed intergranular and transgranular fracture phenomena is in the samples.

The room-temperature piezoelectric coefficients (d_{33}) and the electromechanical coupling factors (k_p and k_t) for BNT-*x*PT ceramics with different PT content are showed in Figs. 3 and 4. The piezoelectric coefficient d_{33} is found to reach a maximum about 230pC/N for $x=0.46$, while k_p and k_t are about 40 % and 22 %, respectively, indicating good piezoelectric properties near MPB region.

Dielectric permittivity and dielectric loss for BNT-*x*PT ($x=$ 0.46–0.52) ceramics as a function of temperature at 1–100 kHz were shown in Fig. 5. The Curie temperature is about 410 °C for BNT-PT ceramics. With increasing PT content, the maximal dielectric permittivity in phase transition temperature decreased. In addition, the anomaly dielectric permittivities were observed to be on the order of 300 °C for all samples. At temperatures above 300 °C, in the low-frequency (1~100 kHz), an increase dielectric loss is observed indicating conductivity problems at high temperature even with low ac field measurements, as discussed in Choi et al. [14].

Stringer et al. [16] found that there is a nonlinear relation between T_c and Bi(M′M″)O_3 content of (1-x)$PbTiO_3$-xBi(M′M″)O_3 systems, which can be namely,

$$T_c(x) = A + Bx + Cx^2, \tag{1}$$

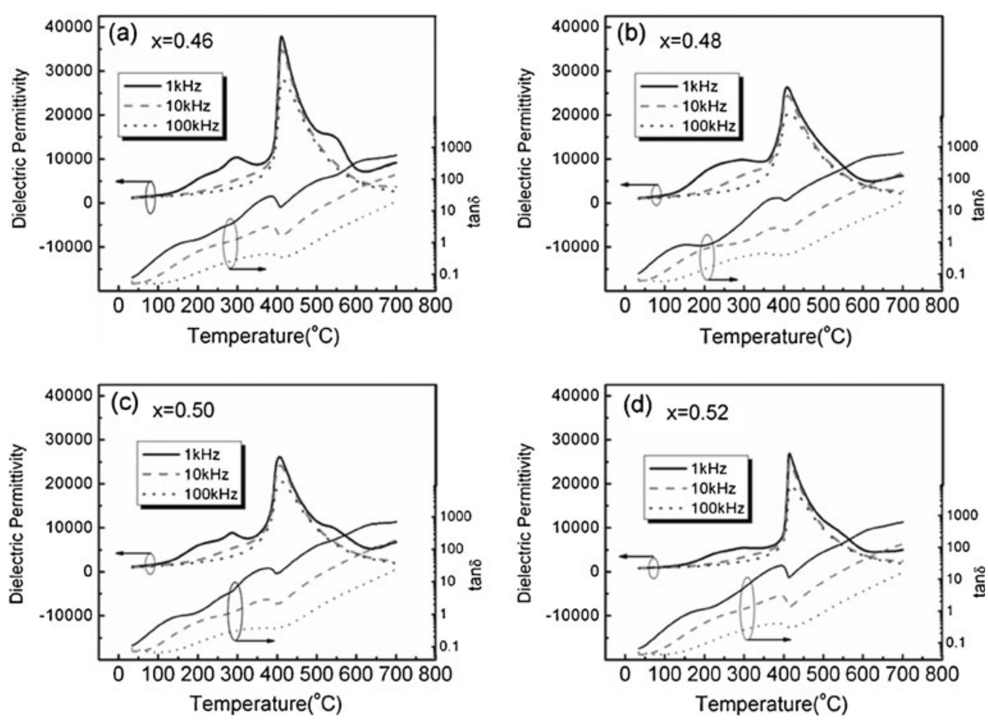


Fig. 5 Dielectric permittivity and dielectric loss as a function of temperature and frequency for BNT-*x*PT ceramics sintered at 1100 °C

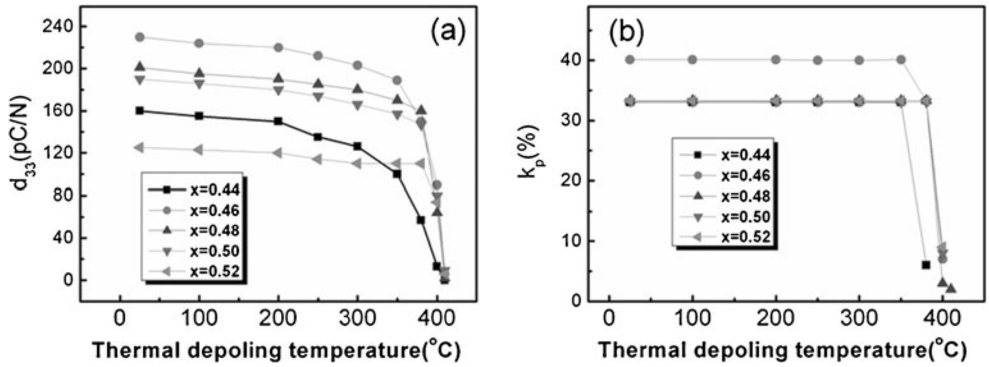


Fig. 7 Effect of thermal depoling on piezoelectric properties: (**a**) piezoelectric coefficient d_{33}; (**b**) electromechanical planar coupling factor k_p

where T_c is Curie temperature, A、B、C are constants, while $A=T_c(x=0)=495$ °C. From Stringer's reported, it can be found that, for BNT-PT system, this relation can be namely,

$$T_c(x) = 495 + 45x - 310x^2, \tag{2}$$

Figure 6 shows the contrast of T_c between our experimental value and value in Eq. (2). It can be found that the change of experimental value is accord with the value of Eq. (2), thus, it can infer that the maximum T_c is around $x=0.93$ for BNT-PT system.

Figure 7(a) and (b) show the effect of thermal depoling on the piezoelectric properties of BNT-xPT ceramics. In Fig. 7(a) and (b), for $x=0.44$, the d_{33} values slightly decreased with the temperature up to ~300 °C, and then sharply dropped. For $0.46 \leq x \leq 0.50$, d_{33} and k_p keep almost constant until 350 °C, and while for $x=0.66$, d_{33} and k_p keep almost constant until 400 °C. It indicated that it has excellent thermal stability for BNT-xPT ceramics.

4 Conclusion

(1-x)Bi($Ni_{1/2}Ti_{1/2}$)-$x$$PbTiO_3$ ceramics have been investigated, and the MPB was indicated from XRD patterns between $x=0.46$ and 0.48. For BNT-PT system, T_c is around 410 °C, and d_{33}, k_p and k_t is found to reach a maximum about 230pC/N, a 40 %, and 22 % for $x=0.46$ sample. The piezoelectric properties of BNT-xPT ceramics decreased slightly below 300 °C for $x=0.44$, while for $x=0.52$, d_{33} and k_p keep almost constant until 400 °C. The results of thermal depoling experiments indicated that BNT-xPT ceramics have excellent thermal stability, which would be provided for a proper solution for high-temperature applications.

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