Structure and electrical properties of $(Na_{0.5}Bi_{0.5})_{1−x}Ba_xTiO_3$ ceramics made by a citrate method

Qing Xu · Xin-Liang Chen · Wen Chen · Bok-Hee Kim · Su-Long Xu · Min Chen

Abstract $(Na_{0.5}Bi_{0.5})_{1−x}Ba_xTiO_3$ ($x=0–0.12$) powders were synthesized by a citrate method, and the structure and electrical properties of the resulting ceramics were investigated. A gradual change of crystal structure with the increase of $BaTiO_3$ concentration was detected together with a significant evolution in grain size and shape. A rhombohedral-tetragonal morphotropic phase boundary (MPB) near $x=0.06$ at room temperature was ascertained for the ceramics. The dielectric constant (ε_r) and dissipation factor ($\tan\delta$) attain maximum values at $x=0.08$ and $x=0.06$, respectively. The specimen of $x=0.06$ provides the maximum piezoelectric constant ($d_{33}=180$ pC/N) and electromechanical coupling factor ($k_p=0.28$), accompanied by a large remanent polarization of $P_r=37.1$ μC/cm^2 and a low coercive field of $E_c=42.7$ kV/cm.

Keywords Structure · Piezoelectricity · Ferroelectricity · $(Na_{0.5}Bi_{0.5})_{1−x}Ba_xTiO_3$ · Citrate method

1 Introduction

In recent years, there is an increasing interest of investigating lead-free piezoelectric ceramics from the viewpoint of environmental protection. Sodium bismuth titanate,

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$(Na_{0.5}Bi_{0.5})TiO_3$ (NBT), is a perovskite-type ferroelectric with a large remanent polarization ($P_r=38$ μC/cm^2) at room temperature and a high Curie temperature ($T_c=320$ °C) [1]. The desired ferroelectricity makes NBT a promising candidate material for lead-free piezoelectric ceramics. However, NBT suffers from a poling problem because of its large coercive field ($E_c=73$ kV/cm), leading to a difficulty in obtaining high piezoelectric properties. To solve this poling problem, various NBT based solid solutions have been developed [2–5]. Among them, $(Na_{0.5}Bi_{0.5})_{1−x}Ba_xTiO_3$ [NBT–BT(x)] system has attracted considerable attention due to the existence of a rhombohedral-tetragonal morphotropic phase boundary (MPB), where the compositions show substantially improved poling and piezoelectric properties [2, 6].
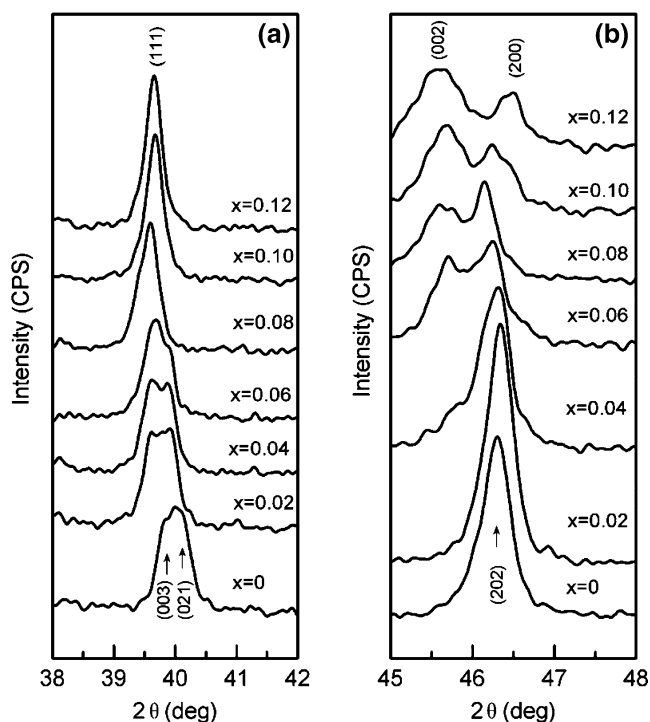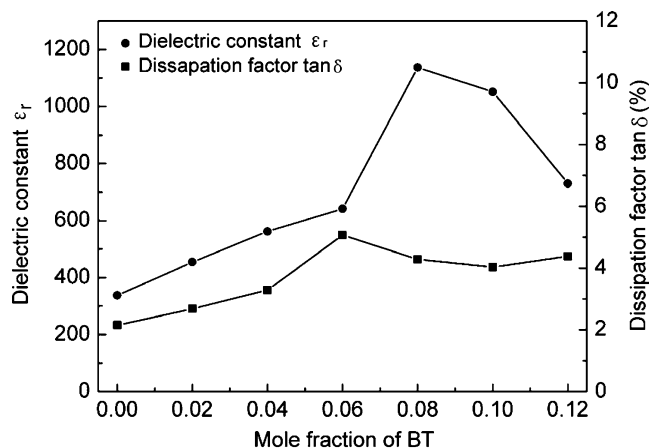
NBT based ceramics are usually produced by the conventional solid state method. Recently, research efforts have been devoted to the preparation of the material by various chemical methods, such as citrate method [7], hydrothermal process [8] and stearic acid gel route [9]. Our previous research demonstrated that the citrate method allows the production of fine and homogeneous NBT–BT (x) powders at relatively low calcining temperature [10]. In this work, we report the structure and electrical properties of NBT–BT(x) ceramics made by the citrate method.

2 Experimental procedures

$(Na_{0.5}Bi_{0.5})_{1−x}Ba_xTiO_3$ [NBT–BT(x), $x=0–0.12$] powders were synthesized by a citrate method. Reagent grade $NaNO_3$, $Bi(NO_3)_3 \cdot 5H_2O$, $Ba(NO_3)_2$, tetrabutyl titanate and citric acid were used as starting materials. Tetrabutyl titanate was first dissolved into a citric acid solution and various nitrates were then added, followed by a stirring to yield a transparent aqueous solution. The mole ratio of

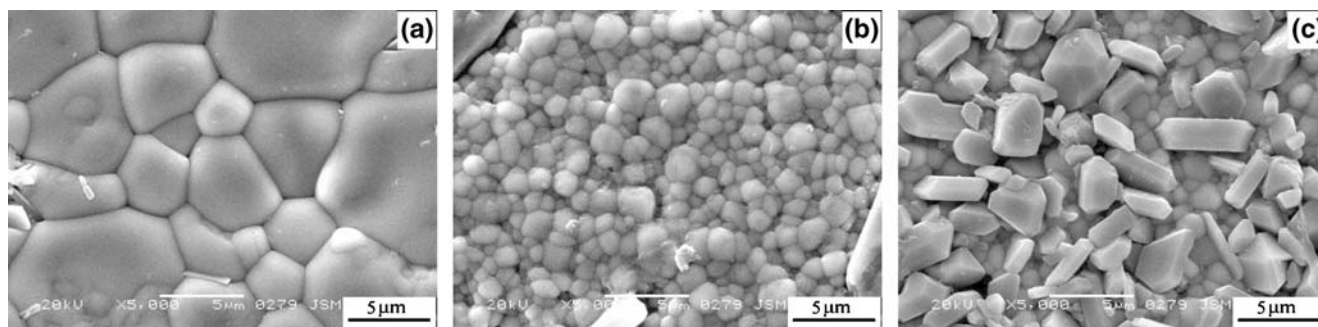**Fig. 1** XRD patterns of NBT–BT(x) ceramics in the 2θ ranges of (**a**) 38°–42° and (**b**) 45°–48°

Fig. 3 Dielectric properties of NBT–BT(x) ceramics as a function of BT concentration

measured by the resonance–antiresonance method using the impedance analyzer. The piezoelectric constant (d_{33}) was measured using a quasistatic d_{33} meter based on the Berlincourt method at 110 Hz. The polarization versus electrical field (P–E) loop was measured at room temperature using a Radiant precision workstation.

3 Results and discussion

NBT–BT(x) powders with a pure perovskite structure were produced by the citrate method, showing uniform particles around 100 nm [10]. A pure perovskite structure was also identified for the resulting ceramics. Figure 1 shows the X-ray diffraction (XRD) patterns of NBT–BT(x) ceramics in the 2θ ranges of 38°–42° and 45°–48°, respectively. The rhombohedral symmetry of NBT at room temperature is characterized by a (003)/(021) peak splitting between 38°–42° and a single peak of (202) between 45°–48°. In Fig. 1(a), the (003)/(021) peak splitting is obvious until x=0.06 and combines into a slightly asymmetric peak at x=0.08. In Fig. 1(b), the (202) peak became broad and asymmetric at x=0.04. A distinct peak splitting can be seen when x≥0.06, referring to a tetragonal symmetry. The result indicates that the rhombohedral-tetragonal MPB of NBT–

citric acid to the total metal cation content was 1.25. The precursor solution was heated to form a sol and subsequently a gel. The gel was calcined at 600 °C for 1 h in air. The detail of the synthesis process has been reported elsewhere [10]. The calcined powders were pressed into discs (19 mm in diameter and 1 mm in thickness) and sintered at 1150 °C for 2 h in air.

The crystal structure of the ceramics was examined by a Rigaku D/MAX2500 X-ray diffractometer using Cu K$_\alpha$ radiation. The microstructure of the ceramics was investigated by a Jeol JSM-5610LV scanning electron microscope (SEM) using thermally etched surfaces. The ceramics were painted with silver paste as electrodes. The dielectric properties were measured using a HP4294 impedance analyzer at 1 kHz. The ceramics for measuring piezoelectric properties were poled in a silicon oil bath at 80 °C under 3.5 kV/mm for 15 min. The piezoelectric properties were

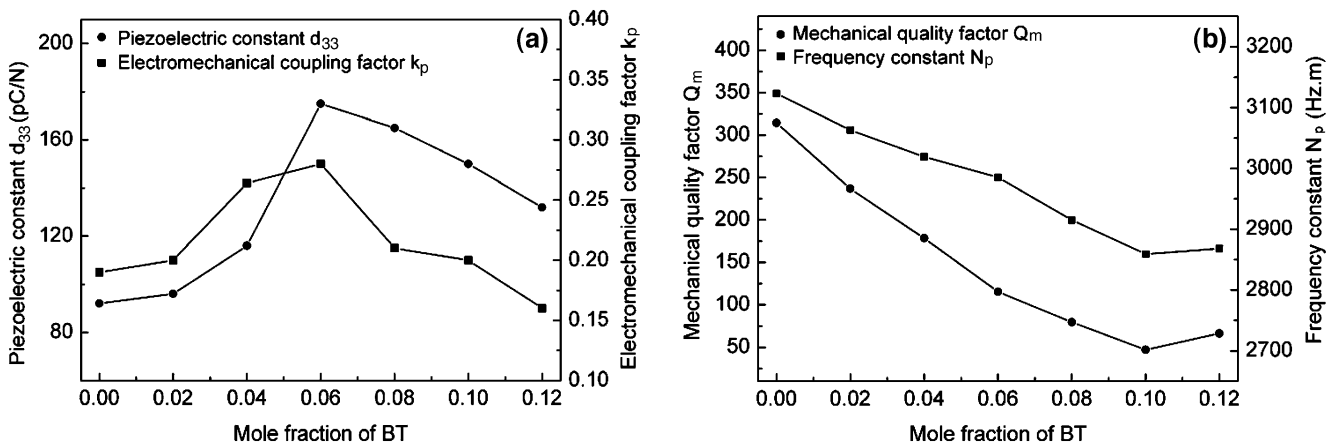**Fig. 2** SEM micrographs of NBT–BT(x) ceramics of (**a**) x=0, (**b**) x=0.06 and (**c**) x=0.12

Fig. 4 Piezoelectric properties of NBT–BT(x) ceramics as a function of BT concentration: (**a**) piezoelectric constant d$_{33}$ and electromechanical coupling factor k$_p$; (**b**) mechanical quality factor Q$_m$ and frequency constant N$_p$

BT(x) ceramics is near to $x=0.06$ at room temperature, which is consistent with an early report [2].

Figure 2 shows the SEM micrographs of NBT–BT(x) ceramics. It was observed that there is a significant evolution in grain size and shape, accompanying the diffusion phase transition with compositional change.

Figure 3 shows the dielectric properties of NBT–BT(x) ceramics as a function of BT concentration. The dielectric constant (ε_r) and dissipation factor (tanδ) enhance with the increase of BT concentration through maximum values at $x=0.08$ and $x=0.06$, respectively, and then decline. The piezoelectric constant (d_{33}) and electromechanical coupling factor (k_p) display a similar change with BT concentration, as shown in Fig. 4(a). Moreover, it can be seen that the mechanical quality factor (Q_m) and frequency constant (N_p) reach minimum values at $x=0.10$ [Fig. 4(b)]. The variation of dielectric and piezoelectric properties with BT concentration in the present work is generally in agreement with

the result obtained from NBT–BT(x) ceramics prepared by the conventional solid state method [6].

The specimen of $x=0.06$ provides the maximum piezoelectric constant ($d_{33}=180$ pC/N) and electromechanical coupling factor ($k_p=0.28$). This is probably due to the fact that the MPB compositions posses more possible spontaneous polarization directions than those in the rhombohedral or tetragonal side of the phase boundary [11]. In the case of an identical composition, the piezoelectric constant of the specimen of $x=0.06$ is much more larger than that of the specimen made by the conventional solid state method ($d_{33}=122$ pC/N), while its electromechanical coupling factor is comparable with the previous result ($k_p=0.29$) [6]. This reveals the advantage of the citrate method as an alternative route to the conventional method in improving the piezoelectric properties of NBT–BT(x) ceramics. It is presumably attributed to the desired morphology and high chemical homogeneity of the powders synthesized by the citrate method.

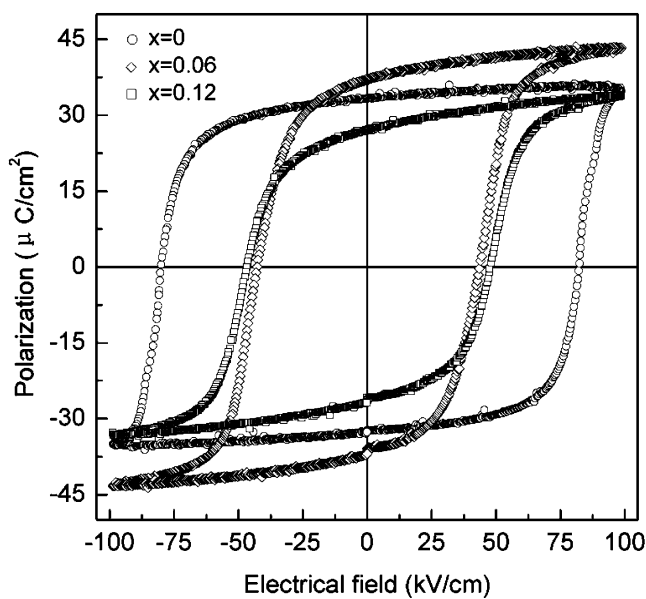The ferroelectric properties of NBT–BT(x) ceramics were examined in terms of their P–E hysteresis loops at

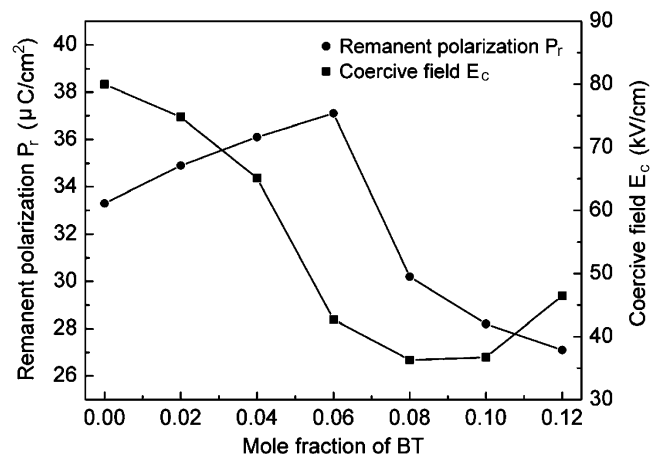**Fig. 5** P–E hysteresis loops of NBT–BT(x) ceramics

Fig. 6 Ferroelectric properties of NBT–BT(x) ceramics as a function of BT concentration

room temperature. Saturated loops were obtained over the whole investigated composition range under an electrical field of 100 kV/cm, confirming the ferroelectric nature of the specimens. Figure 5 shows the typical P–E hysteresis loops of NBT–BT(x) ceramics. The values of remanent polarization (P_r) and coercive field (E_c) were derived from measured loops. Figure 6 shows the remanent polarization and coercive field of NBT–BT(x) ceramics as a function of BT concentration. The specimen of x=0.06 exhibits the maximum remanent polarization of P_r=37.1 μC/cm^2 and a relatively low coercive field of E_c=42.7 kV/cm. It is noteworthy that NBT–BT(x) ceramics show the preferred piezoelectric properties at x=0.06 with respect to both the piezoelectric constant and electromechanical coupling factor. Therefore, an essential relation between the ferroelectric nature and piezoelectric properties can be reasonably suggested for NBT–BT(x) ceramics. It is regarded that the superior piezoelectric properties of the specimen of x=0.6 are closely associated with its desired ferroelectric characteristics.

4 Conclusions

The structure and electrical properties of $(Na_{0.5}Bi_{0.5})_{1-x}Ba_xTiO_3$ (x=0–0.12) ceramics made by a citrate method have been investigated. A diffusion rhombohedral-tetragonal phase transition and a significant microstructural evolution with the increase of BaTiO$_3$ concentration were detected. It was determined that the rhombohedral-tetragonal morphotropic phase boundary (MPB) of the ceramics is close to x=0.06 at room temperature. The dielectric properties attain maximum values at compositions near the MPB. The maximum piezoelectric constant (d_{33}=180 pC/N) and electromechanical coupling factor (k_p=0.28) were obtained in the specimen of x=0.06, attributed to its large remanent polarization of P_r=37.1 μC/cm^2 and low coercive field of E_c=42.7 kV/cm.

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