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# Dielectric, ferroelectric and piezoelectric properties of $Bi_{0.5}Na_{0.5}TiO_3$–$(Ba_{0.7}Ca_{0.3})TiO_3$ ceramics at morphotropic phase boundary composition

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## ABSTRACT

$(1-x)Bi_{0.5}Na_{0.5}TiO_3$–$x(Ba_{0.7}Ca_{0.3})TiO_3$ (BNT–$x$BCT, $0 \le x \le 0.15$) solid solutions have been synthesized by a conventional solid state sintering method for obtaining a morphotropic phase boundary (MPB) with good piezoelectric properties. X-ray diffraction patterns reveal that a MPB of rhombohedral and tetragonal phases is formed at compositions $0.09 \le x \le 0.12$. Addition of BCT into BNT greatly lowered coercive field $E_c$ without degrading remanent polarization $P_r$. The specimen with $x = 0.09$ has the good piezoelectric properties: $d_{33} = 125$ pC/N and $k_p = 0.33$. A modified Curie–Weiss law was used to fit the dielectric constant of BNT–$x$BCT ceramics, and a frequency dispersion was observed during the phase transitions from antiferroelectric to paraelectric in specimens with $x$ exceeding 0.06.

## 1. Introduction

Even today, lead is used as an essential material for some long-term highly precise passive and active electronic components as well as for piezoelectric sensors and actuators. However, the use of lead-containing materials has caused serious lead pollution and environmental problems because of the high toxicity of lead oxide. Therefore, it is necessary to develop environment friendly lead-free ferroelectric and piezoelectric materials.

$Bi_{0.5}Na_{0.5}TiO_3$ (BNT) is a perovskite-structured ferroelectric having $Bi^{3+}$ and $Na^{+}$ complex on the A site of $ABO_3$-type compounds with a rhombohedral symmetry at room temperature. Because of its strong ferroelectricity ($P_r = 38\ \mu C/cm^2$), the BNT ceramic has been considered as one of the promising candidates for lead-free piezoelectric ceramics [1], however, its coercive field is as high as $E_c = 7.3$ kV/mm [1], resulting in the difficulty in the poling of the ceramics. Therefore, pure BNT ceramic exhibits much weaker piezoelectric properties ($d_{33} \sim 73$–$80$ pC/N) [2,3], compared with $Pb(Zr_{0.58}Ti_{0.42})O_3$ ceramics ($d_{33} = 223$ pC/N) [4]. To solve these problems and improve the electric properties, various types of compounds were added into BNT to form solid solutions. It is found that the piezoelectric properties of these "modified" BNT-based materials were effectively enhanced when a morphotropic phase boundary (MPB) composition was attained. It is generally accepted that, the composition-induced ferro–ferro transition at MPB causes the instability of the polarization state so that the polarization direction can be easily rotated by external stress or electric field [5,6], thereby resulting in a high piezoelectricity and permittivity [7–11]. Binary material systems, such as BNT–$PbTiO_3$ [12], BNT–$BaTiO_3$ [1], and BNT–$(Bi_{0.5}K_{0.5})TiO_3$ [13], and ternary systems, such as BNT–$BaTiO_3$–$(Bi_{0.5}K_{0.5})TiO_3$ [14], BNT–$(Bi_{0.5}K_{0.5})TiO_3$–$KNbO_3$ [15], and BNT–$(Bi_{0.5}K_{0.5})TiO_3$–$(Na_{0.5}K_{0.5})NbO_3$ [16], are typical systems with MPB compositions. Recently, it was reported that non-Pb piezoelectric system $Ba(Zr_{0.2}Ti_{0.8})O_3$–$x(Ba_{0.7}Ca_{0.3})TiO_3$ exhibits a very high piezoelectric coefficient at MPB, where $(Ba_{0.7}Ca_{0.3})TiO_3$ (BCT) is tetragonal symmetry at room temperature [17]. In this report, we fabricated novel (BNT–$x$BCT, $0 \le x \le 0.15$) solid solutions with a MPB, and investigated the dielectric, ferroelectric, and piezoelectric properties of binary ceramics BNT–BCT system.

## 2. Experimental procedure

### 2.1. Sample preparation

Ceramic powders with nominal formula $(1-x)Bi_{0.5}Na_{0.5}TiO_3$–$x(Ba_{0.7}Ca_{0.3})TiO_3$ (BNT–$x$BCT) ($x = 0$, 0.03, 0.06, 0.09, 0.12, 0.15) were prepared by a conventional solid-state reaction. The powders

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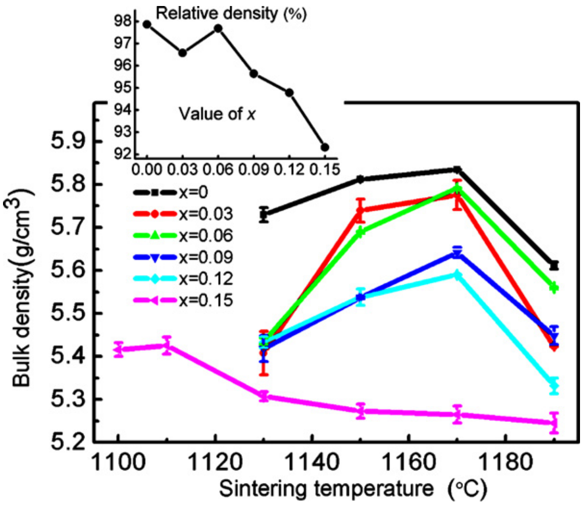

**Fig. 1.** Bulk density of NBT–*x*BCT ceramics as a function of sintering temperature. The inset shows relative density of the NBT–*x*BCT ceramics sintered at respective optimum sintering temperature.

of $Bi_2O_3$ (99%), $CaCO_3$ (99.99%), $Na_2CO_3$ (99.8%), $BaCO_3$ (99.92%) and $TiO_2$ (99.99%) were weighed according to the stoichiometric ratio and then milled in a polyethylene jar with $ZrO_2$ balls for 24 h using alcohol as a medium. Mixtures were dried and calcined at 850 °C for 3 h. Then the calcined powders were re-milled for 24 h and ground with PVA solution as a binder. Pellets 11.5 mm in diameter were pressed under 160 MPa using uniaxial pressing. The ceramics were submerged in powder of the same composition and sintered at 1100–1190 °C for 2 h in covered alumina crucibles. Then, the sintered ceramics were polished. Silver paste was fired on both faces of the disks at 650 °C as electrodes.

### 2.2. Characterization techniques

Bulk density of the ceramics was measured by Archimedes method and relative density was calculated. X-ray powder diffraction (XRPD, Rigaku D/max 2250, Tokyo, Japan) with Cu Kα radiation (40 kV and 50 mA) was used for the identification of phases. The microstructures of the sintered ceramics were observed using a scanning electron microscope (Quanta 200 SEM, FEI Co., Eindhoven, the Netherlands). The dielectric measurement was performed by using an Agilent E4980A precision LCR in a temperature range from 30 °C to 510 °C and a frequency range of 100 Hz to 1 MHz. Piezoelectric constant $d_{33}$ of the ceramics was measured using a quasistatic $d_{33}$ meter (ZJ-3A Institute of Acoustics, Chinese Academy of Sciences, Beijing, China). Piezoelectric properties were measured by means of the resonance–antiresonance method [18] using a precision impedance analyzer (HP4294A, Agilent Co., Santa Clara, CA). The remanent polarization $P_r$ was determined from *P*–*E* hysteresis loops obtained by Radiant Precision Workstation ferroelectric testing system at 1 Hz.

## 3. Results and discussion

### 3.1. Sintering behavior and XRPD analysis

Fig. 1 shows the dependences of the bulk densities of the BNT–*x*BCT ceramics as a function of sintering temperatures. For all BNT–*x*BCT ceramics, the bulk densities increase to their maximum values as the sintering temperatures increased from 1100 °C to 1190 °C, and then drop with further increasing sintering temperatures. The optimum sintering temperature is 1170 °C for BNT–*x*BCT ceramics with $0 \leq x \leq 0.12$ and 1110 °C for the specimens with $x = 0.15$. As shown in the inset figure of Fig. 1, the relative density of the specimens with $0 \leq x \leq 0.12$ sintered at their optimum sintering temperatures are higher than 95% while that of $x = 0.15$ sample is only about 92%.

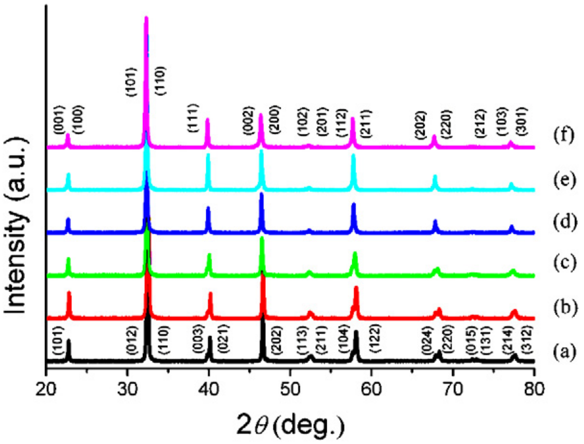

**Fig. 2.** XRPD patterns of NBT–*x*BCT ceramics in the 2*θ* range of 39.5–40.5° and 45.5–47.02°: (a) $x = 0.00$, (b) $x = 0.03$, (c) $x = 0.06$, (d) $x = 0.09$, (e) $x = 0.12$, (f) $x = 0.15$.

Fig. 2 shows XRPD patterns of the as sintered BNT–*x*BCT ceramics at room temperature. As can be seen from these patterns, all samples are indexed to be a pure perovskite phase, and no

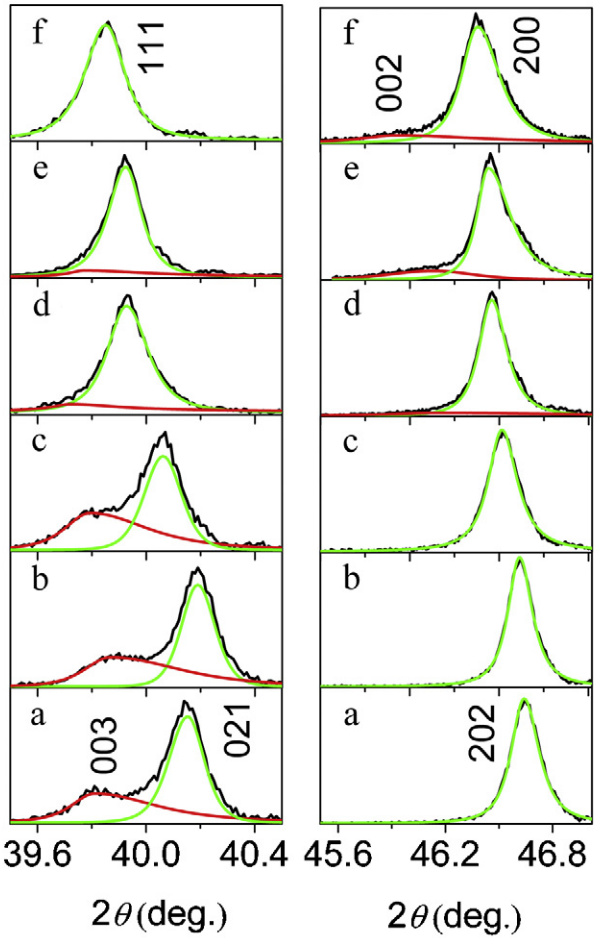

**Fig. 3.** XRPD patterns of NBT–*x*BCT ceramics in the 2*θ* range of 39.5–40.5° and 45.5–47.02°: (a) $x = 0.00$, (b) $x = 0.03$, (c) $x = 0.06$, (d) $x = 0.09$, (e) $x = 0.12$ and (f) $x = 0.15$.