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X.X. WANG✉
H.L.W. CHAN
C.L. CHOY

# $(Bi_{0.5}Na_{0.5})_{0.94}Ba_{0.06}TiO_3$ lead-free ceramics with simultaneous addition of $CeO_2$ and $La_2O_3$

Department of Applied Physics and Materials Research Center, The Hong Kong Polytechnic University, Hunghom Kowloon, Hong Kong, P.R. China

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**ABSTRACT** $(Bi_{0.5}Na_{0.5})_{0.94}Ba_{0.06}TiO_3$ (BNBT-6) with simultaneous addition of 0.5 mol% $CeO_2$ and 0.25, 0.5 and 0.75 mol% $La_2O_3$, respectively, was prepared by a conventional ceramic fabrication technique. An addition of 0.5 mol% $CeO_2$ together with 0.5 mol% $La_2O_3$ enhanced the piezoelectric and dielectric constant of BNBT-6 ceramics significantly. At room temperature, this composition exhibits a high piezoelectric constant ($d_{33} = 162 \times 10^{-12}$ C/N) and relatively low dielectric loss ($\tan\delta = 2.0\%$) at 1 kHz. X-ray diffraction pattern shows that the coexistence of tetragonal and rhombohedral phases in the BNBT-6 composition was not changed by adding $CeO_2+La_2O_3$, and they diffused into the BNBT lattice during sintering. SEM observation indicates that a small amount of $CeO_2+La_2O_3$ almost does not affect the microstructure.

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## 1 Introduction

As we know, Pb(Zr, Ti)$O_3$ (PZT) ceramics play a dominant role in ongoing piezoelectric applications because of their superior piezoelectric properties. However, the high volatilization of PbO, a main composition of PZT ceramics, during firing and the disposal of PbO-contaminated materials cause crucial environmental pollution [1]. As one of the important eco-materials, lead-free piezoelectric ceramics are attracting considerable attention because of their outstanding advantages in free control atmosphere and no lead contamination.

The $(Bi_{0.5}Na_{0.5})TiO_3$ composition (abbreviated to BNT) is a perovskite ferroelectric with good potential to replace PZT piezoelectric ceramics because of its strong ferroelectricity. It has a high Curie temperature, $T_c = 320\,°C$, a relatively large remanent polarization of $P_r = 38\,\mu C/cm^2$ and a coercive field of $E_c = 73\,kV/cm$ at room temperature [2–4]. A low-temperature phase transition from the ferroelectric to the anti-ferroelectric phase at about 200 °C in the BNT composition leads to a very interesting anomaly in the dielectric properties. However, the high conductivity of pure BNT ceramics causes difficulty in the poling process. Furthermore, its piezoelectric properties are too low for practical use. To improve the poling process and the electrical properties, some modification of the BNT system has been carried out. It has been reported that BNT base compositions modified with $BaTiO_3$ (abbreviated as BT) [5], $NaNbO_3$ [6], $BiFeO_3$ [7], $Bi_2O_3Sc_2O_3$ [8], $La_2O_3$ [9] and $Ba(W_{1/2}Cu_{1/2})O_3$ [10], showed improved piezoelectric properties and were easier to pole compared with pure BNT ceramics. Among them, BNT–BT (abbreviated to BNBT) was more interesting because there is a rhombohedral ($F_R$)–tetragonal ($F_T$) morphotropic phase boundary (abbreviated to MPB) between BNT and BT. It has been reported that the $(Bi_{0.5}Na_{0.5})_{0.94}Ba_{0.06}TiO_3$(abbreviated to BNBT-6) composition near the MPB has relatively large piezoelectric properties [5]. Some further enhancements in the piezoelectric properties of BNBT ceramics were reported by adding $Nb_2O_5$ [10] and $CeO_2$ [11].

In this work, both $CeO_2$ and $La_2O_3$ are added to further enhance the piezoelectric properties of BNBT ceramics. The effects of simultaneous doping of $CeO_2+La_2O_3$ on the electrical properties and microstructure of the BNBT-6 ceramics were examined. The dielectric properties of the samples were also measured as a function of temperature.

## 2 Experimental

The conventional mixed-oxide technique was used to prepare $(Bi_{0.5}Na_{0.5})_{0.94}Ba_{0.06}TiO_3$ (BNBT-6) ceramics. The starting materials were $Bi_2O_3$ (99.9%, Acros Organics), $Na_2CO_3$ (99.5%, Wako Pure Chemical Industries Ltd.), $BaCO_3$ (99.9%, Wako Pure Chemical Industries Ltd.) and $TiO_2$ (99.9%, Aldrich Chem. Co.). The powders were milled in alcohol using $Y_2O_3$-stabilized zirconia balls for 6 h. Calcination was conducted at 800 °C for 2 h. Then, 0.5 mol% $CeO_2$ (99.9%, Aldrich Chem. Co.) together with 0.25, 0.5 and 0.75 mol% $La_2O_3$ (99.9%, Aldrich Chem. Co.) were added to the calcinated BNBT-6 base powders, respectively. The powders were milled again for 6 h, dried and granulated by adding PVA (Wako Pure Chemical Industries Ltd.) as a binder. The

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✉ Fax: +852/2333-7629, E-mail: xx.wang@polyu.edu.hk

granulated powders were pressed into discs with diameter of 22 mm and thickness of 2 mm. The compacted discs were sintered at 1180 °C for 2 h in air. Silver paste (Guangzhou Luxing Tech. Ltd.) was fired on both faces of the discs at 650 °C as electrodes. The samples for the measurement of the piezoelectric properties were poled in silicone oil at 50 °C under 4.5 kV/mm for 10 min.

The density of the sintered samples was measured using the Archimedes method. After poling, a $d_{33}$ meter (ZJ-30 Piezo $d_{33}$ Meter) was used to measure the $d_{33}$ coefficient at 100 Hz. The dielectric properties of the samples were determined at room temperature using an impedance analyzer (Agilent 4294A precision impedance analyzer) at 1 kHz. The temperature dependence of the dielectric constant and the dissipation factor of the unpoled samples were measured at a step of 5 °C using a Hewlett–Packard 4192A impedance analyzer in a temperature-programmable tube furnace at different frequencies. The XRD pattern was obtained, to identify the crystal phase of the samples, using an X-ray diffractometer (XRD–Philips Expert System). A scanning electron microscope (SEM-Leica Stereoscan 440) was used to observe the microstructure of the sintered samples.

## 3 Results and discussion

Table 1 shows the electrical properties of BNBT-6 ceramics and BNBT-6 ceramics with $CeO_2+La_2O_3$. The results indicate that simultaneous addition of an optimal amount of $CeO_2$ and $La_2O_3$ into BNBT-6 enhances the piezoelectric and dielectric constants significantly at room temperature. With 0.5 mol% $CeO_2$ and 0.5 mol% $La_2O_3$, the piezoelectric constant $d_{33}$ increases from 129 to $162 \times 10^{-12}$ C/N. The dielectric constant also increases from 625 to 831. The dissipation factor slightly varies with the relative amount of $CeO_2$ and $La_2O_3$ within the tested range. It has been reported that $CeO_2$ has the dual effect of improving the piezoelectric properties of BNBT-6 ceramics and decreasing the dissipation factor at the same time, as it does in lead-based Pb(Zr, Ti)$O_3$ ceramics [12]. The mechanism for the effect of $CeO_2$ is considered to be concerned with its two valence states: $Ce^{4+}$, with a radius of 0.94 Å, and $Ce^{3+}$, with a radius of 1.18 Å. $Ce^{3+}$ occupies the A site as $Ba^{2+}$ in the BNBT lattice and functions as a donor, leading to some A-site vacancies, which facilitates the movement of the domain wall so as to improve the piezoelectric properties. Meanwhile, $Ce^{4+}$ may go into the $Ti^{4+}$ site and change the space charge, which suppresses the domain movement, resulting in a decrease in the dissipation factor. $La_2O_3$ is a typical soft additive for PZT ceramics [12] and is also effective for enhancing the piezoelectric properties of BNT ceramics [9]. $La_2O_3$ goes into A sites in the BNBT lattice by occupying a $Bi^{3+}$ site or a $Ba^{2+}$ site. The former results in deformation of the lattice and the latter leads to some vacancies in A-sites of the lattice, which makes the movement of the domain walls easier, so as to increase the piezoelectric and dielectric constants. The $P$–$E$ loop measurement, as shown in Fig. 1, reveals an increase in the remanent polarization $P_r$ and a decrease in the coercive field $E_c$ of BNBT-6 ceramics by the addition of 0.5 mol% $CeO_2$ and 0.5 mol% $La_2O_3$ simultaneously, which implies the enhancement of the ferroelectric and piezoelectric effects and the facilitation of domain movement, leading to an increase in piezoelectric properties. However, a suitable addition amount is important. Addition of 0.75 mol% $La_2O_3$ may cause too many defects to result in a decrease in the piezoelectric properties. We have reported recently that BNBT-6 ceramics with $CeO_2$ have a piezoelectric constant $d_{33}$ of $152 \times 10^{-12}$ C/N [11]. It is thus seen that simultaneous addition of $CeO_2+La_2O_3$ has a complex effect of modification.

Figures 2 and 3 show the temperature dependence of dielectric constant $\varepsilon_r$ and dissipation factor $\tan\delta$ of the unpoled BNBT-6 ceramics and BNBT-6 ceramics containing 0.5 mol% $CeO_2$ and 0.5 mol% $La_2O_3$ at different frequencies, respectively. The temperature-dependent dielectric constant shows relaxor-like behavior, probably due to cation disorder, as $Na^+$ and $Bi^{3+}$ are randomly distributed in A-sites of the lattice [13]. Comparing with the results reported by Takenaka [5], both samples are characterized by the existence of three phases of ferroelectric, anti-ferroelectric and paraelectric states in different temperature ranges. Here, $T_d$ refers to the temperature of the transition between the ferroelectric

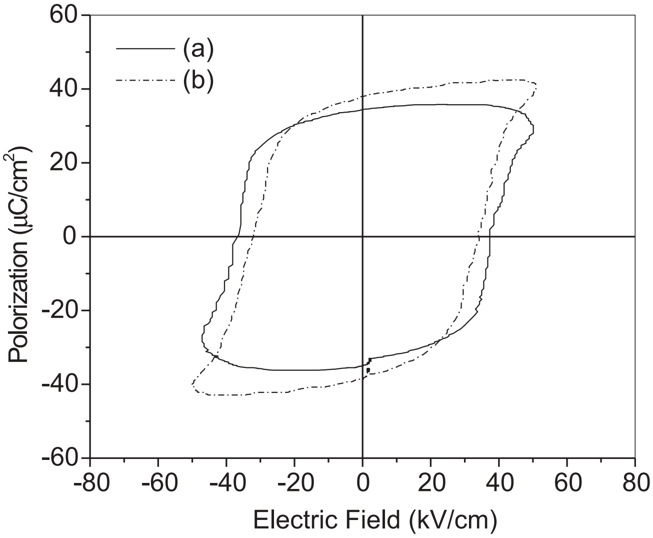

**FIGURE 1** $P$–$E$ hysteresis loops of (a) BNBT-6 ceramics and (b) BNBT-6 ceramics containing 0.5 mol% $CeO_2$ and 0.5 mol% $La_2O_3$ at room temperature

| Composition | $d_{33}$ ($10^{-12}$ C/N) | $\varepsilon_r$ | $\tan\delta$ (%) | $\rho$ (g/cm$^3$) |
|---|---|---|---|---|
| BNBT-6 | 129 | 625 | 1.9 | 5.69 |
| BNBT-6+0.5 mol% $CeO_2$+0.25 mol% $La_2O_3$ | 158 | 787 | 1.7 | 5.67 |
| BNBT-6+0.5 mol% $CeO_2$+0.5 mol% $La_2O_3$ | 162 | 831 | 2.0 | 5.68 |
| BNBT-6+0.5 mol% $CeO_2$+0.75 mol% $La_2O_3$ | 65 | 310 | 2.4 | 5.69 |

**TABLE 1** The electric properties and density of BNBT-6 with simultaneous addition of $CeO_2+La_2O_3$

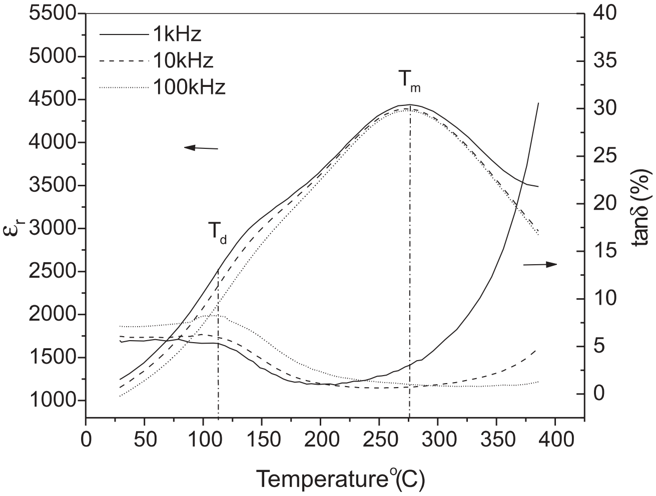

**FIGURE 2** Temperature dependence of dielectric constant and dissipation factor of BNBT-6 ceramics at different frequencies

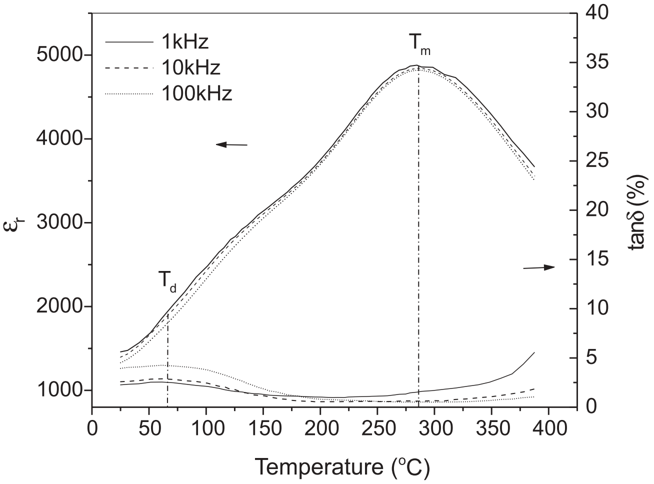

**FIGURE 3** Temperature dependence of dielectric constant and dissipation factor of BNBT-6 ceramics containing 0.5 mol% $CeO_2$ and 0.5 mol% $La_2O_3$ at different frequencies

phase and anti-ferroelectric phase and $T_m$ stands for the temperature corresponding to the maximum value of dielectric constant. An obvious decrease in $T_d$ and a slight increase in $T_m$ are observed by adding $CeO_2$+$La_2O_3$. Furthermore, the dielectric constant and dissipation factor at $T_m$ increase with the addition of $CeO_2$+$La_2O_3$. At 1 kHz and at a temperature higher than $T_m$, the dissipation factor of BNBT-6 compositions increases abruptly with increasing temperature (Fig. 2), which may be attributed to high conduction. It is evident that the addition of $CeO_2$+$La_2O_3$ can decrease the conductivity of BNBT-6 ceramics at high temperature to reduce the dissipation factor (Fig. 3). Also, it should be noted that the $T_d$ and $T_m$ of both samples are almost independent of the measurement frequencies. Below $T_d$ and above $T_m$, the dielectric constant of BNBT-6 ceramics varies with the measuring frequencies. However, the addition of $CeO_2$+$La_2O_3$ results in the dielectric constant of BNBT-6 ceramics being almost independent of the measurement frequencies over the whole temperature range.

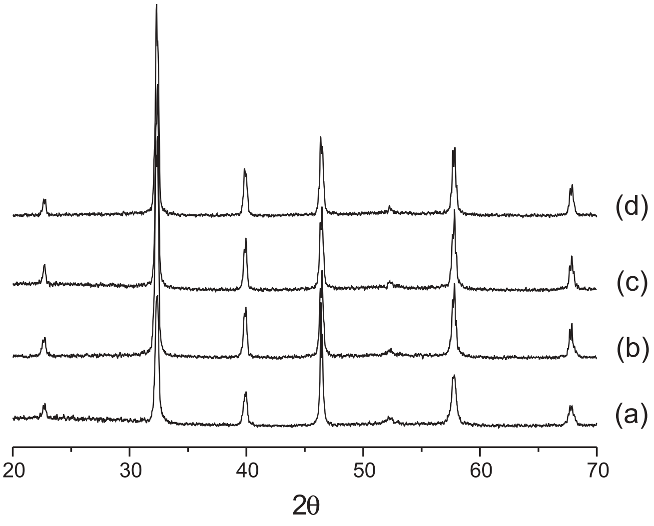

**FIGURE 4** X-ray diffraction patterns of BNBT-6 ceramics with: 0 mol% $CeO_2$+$La_2O_3$ (a); 0.5 mol% $CeO_2$ and 0.25 mol% $La_2O_3$ (b); 0.5 mol% $CeO_2$ and 0.5 mol% $La_2O_3$ (c); and 0.5 mol% $CeO_2$ and 0.75 mol% $La_2O_3$ (d)

XRD analysis was performed to examine the influence of 0.5 mol% $CeO_2$ + 0.5 mol% $La_2O_3$ addition on the structure of BNBT-6 ceramics. All samples showed a similar X-ray diffraction pattern (Fig. 4) and no second phase was observed. It is known that the BNT system is rhombohedral and that BT is tetragonal at room temperature. A rhombohedral–tetragonal morphotropic phase boundary (MPB) exists in their solid solution near the BNBT-6 composition. For the composition near to the MPB, the X-ray diffraction pattern is characterized by the presence of two separated peaks to (003)

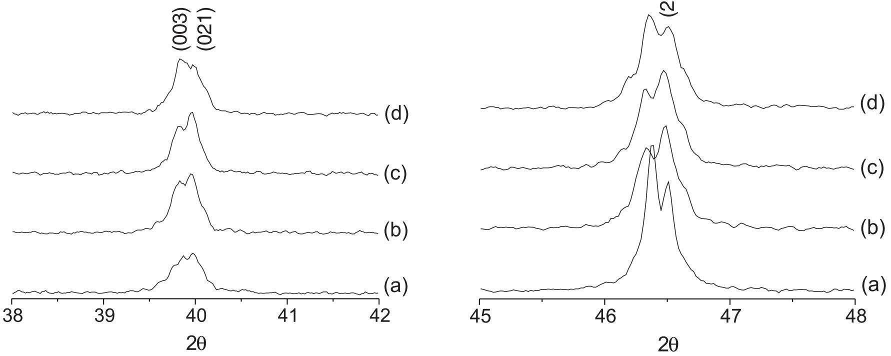

**FIGURE 5** Enlarged X-ray diffraction patterns of BNBT-6 compositions corresponding to (a), (b), (c), (d) shown in Fig. 4 at 2$\theta$ of 38° to 42° and 45° to 48°

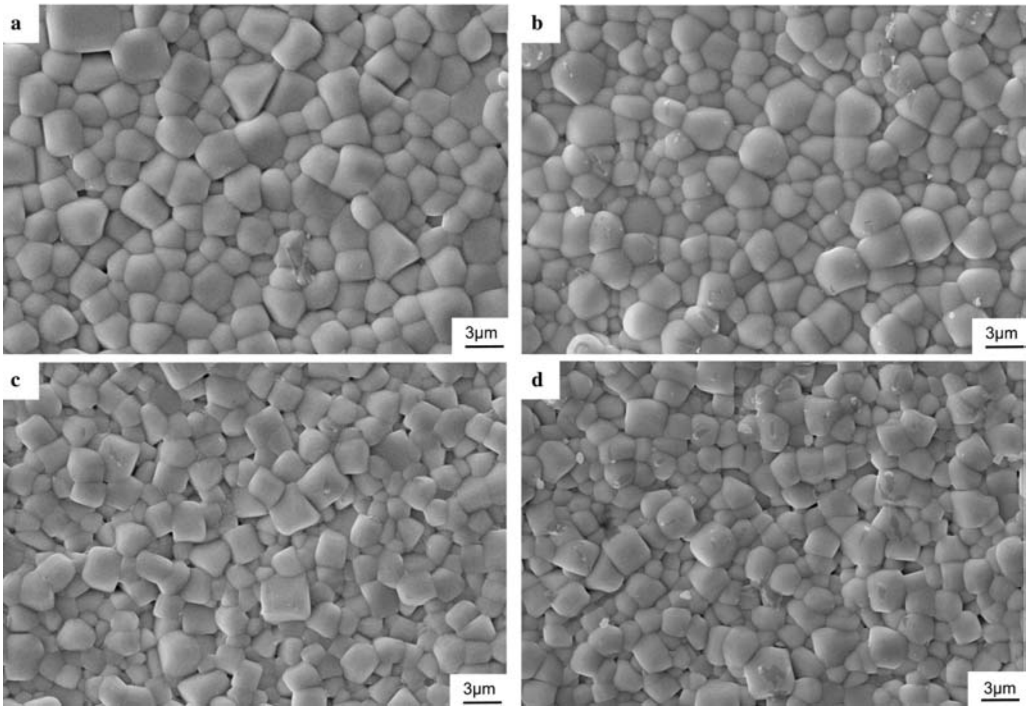

**FIGURE 6** SEM micrographs of BNBT-6 ceramics sintered at 1180 °C for 2 h with: 0 mol% $CeO_2+La_2O_3$ (**a**); 0.5 mol% $CeO_2$ and 0.25 mol% $La_2O_3$ (**b**); 0.5 mol% $CeO_2$ and 0.5 mol% $La_2O_3$ (**c**); and 0.5 mol% $CeO_2$ and 0.75 mol% $La_2O_3$ (**d**)

and (021) at about 39.8°, and the splitting of the peak to (202) planes at around 46.5° [10]. As the BNBT-6 composition used in this test was at the MPB, its X-ray pattern exhibited the feature of peak splitting at these diffraction angles, as shown in Fig. 5. This result indicates that tetragonal and rhombohedral phases coexist in both BNBT-6 and $CeO_2+La_2O_3$-added BNBT-6 ceramics. Therefore, it can be concluded that the addition of $CeO_2$ and $La_2O_3$ does not cause an obvious change to the phase structure.

The microstructures of the sintered BNBT-6 ceramics containing 0.5 mol% $CeO_2$ and 0.25, 0.5 and 0.75 mol% $La_2O_3$ were observed using SEM, and micrographs of the samples are shown in Fig. 6. All these samples are very dense. No obvious change in grain size is caused by adding $CeO_2+La_2O_3$ in the tested range. That is to say, the modification of $CeO_2+La_2O_3$, other than its effect on microstructure, plays a major part in affecting the piezoelectric properties of the BNBT-6 ceramics.

## 4 Conclusion

$(Bi_{0.5}Na_{0.5})_{0.94}Ba_{0.06}TiO_3$ (BNBT-6) ceramics with simultaneous addition of $CeO_2$ and $La_2O_3$ have been investigated. It was found that at 0.5 mol% $CeO_2$+0.5 mol% $La_2O_3$, both the piezoelectric and dielectric constants of BNBT-6 ceramics were increased significantly, but the dissipation factor was unaffected. The addition of $CeO_2+La_2O_3$ did not cause an obvious change in microstructure. BNBT-6 ceramics containing $CeO_2+La_2O_3$ still showed the coexistence of tetragonal and rhombohedral phases similar to the BNBT-6 ceramics and no second phase was observed.

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