

Microstructure and electrical properties of the rare-earth doped $0.94\text{Na}_{0.5}\text{Bi}_{0.5}\text{TiO}_3\text{-}0.06\text{BaTiO}_3$ piezoelectric ceramics

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Abstract Phase structure, microstructure, piezoelectric and dielectric properties of the 0.4 wt% Ce doped $0.94\text{Bi}_{0.5}\text{Na}_{0.5}\text{TiO}_3\text{-}0.06\text{BaTiO}_3$ (Ce-BNT6BT) ceramics sintered at different temperatures have been investigated. The powder X-ray diffraction patterns showed that all of the Ce-BNT6BT ceramics exhibited a single perovskite structure with the coexistence of the rhombohedral and tetragonal phase. The morphologies of inside and outside of the bulk indicated that the different sintering temperatures did not cause the second phase on the inside of bulk. However, the TiO_2 existed on the outside of the bulk due to the Bi_2O_3 and Na_2O volatilizing at higher temperature. The ceramics sintered at 1,200 °C showed a relatively large remnant polarization (P_r) of about $34.2 \mu\text{C}/\text{cm}^2$, and a coercive field (E_c) of about 22.6 kV/cm at room temperature. The permittivity ϵ_r of the ceramics increased with the increasing of sintering temperature in antiferroelectric region, the depolarization temperature (T_d) increased below 1,160 °C then decreased at higher sintering temperature. The resistivity (ρ) of the Ce-BNT6BT ceramics increased linearly as the sintering temperature increased below 1,180 °C, but reduced as the sintering temperature increased further. A maximum value of the ρ was 3.125×10^{10} ohm m for the Ce-BNT6BT ceramics sintered at 1,180 °C at room temperature.

Keyword ($\text{Bi}_{0.5}\text{Na}_{0.5}$) TiO_3 · Piezoelectrics · Sintering · Microstructure · Dielectric

1 Introduction

The piezoelectric devices currently used in various fields contain a large amount of lead, therefore, the volatilization of lead during the heat-treatment process and the final disposal of piezoelectric devices containing lead are issues that must be addressed. Recently some progress has been made to this end and the investigation and development of lead-free piezoelectric ceramics is of current research interest. Lead-free piezoelectric ceramics can be divided into three types: (a) perovskite, (b) tungsten bronze, and (c) bismuth layer in terms of their structures. Among them, ($\text{Bi}_{0.5}\text{Na}_{0.5}$) TiO_3 composition (abbreviated to BNT) with a rhombohedral perovskite structure has been considered a good candidate for lead-free piezoelectric ceramics because of its strong ferroelectricity, high Curie temperature ($T_C=320$ °C), and relatively large remnant polarization of $P_r=38 \mu\text{C}/\text{cm}^2$ and coercive field of $E_c=73$ kV/cm at room temperature [1–3]. In addition, it reveals a very interesting anomaly in dielectric properties as a result of low-temperature phase transition from the ferroelectric to the antiferroelectric phase at about 200 °C. However, there are some difficulties in poling BNT ceramics because of high leakage current. Thus, some modifications have been made to the BNT composition to improve the poling process and the electrical properties. It has been reported that BNT base compositions modified with BaTiO_3 [4], NaNbO_3 [5], BiFeO_3 [6], $\text{Bi}_2\text{O}_3\text{-Sc}_2\text{O}_3$ [7], or La_2O_3 [8], had improved piezoelectric properties and easier treatment in the poling process compared with pure BNT ceramics.

In many ferroelectrics, the studies of sintering behavior and electrical conductivity are very important since the associated physical properties like piezoelectricity, pyroelectricity and also strategy for poling are dependent on the order and nature of conductivity in these materials.

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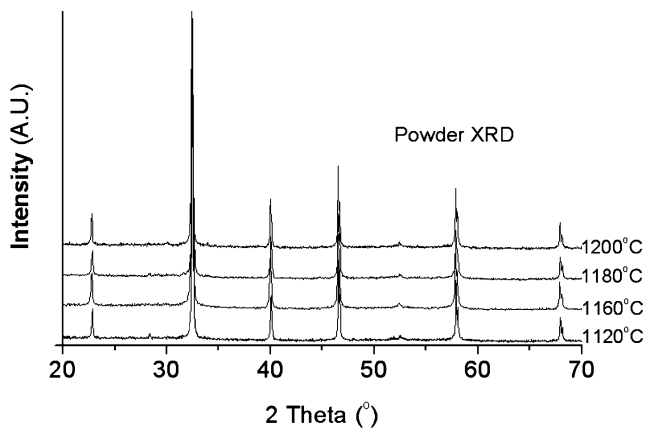


Fig. 1 X-ray diffraction patterns of Ce-BNT6BT ceramics powder sintered at different temperatures

In view of the increased interest in BNT and BNT based solid solutions, the present work has undertaken detailed studies of the sintering behaviors in the temperature range from 1,120 to 1,200 °C and the electrical conductivity at room temperature.

2 Experimental

The 0.4 wt% Ce-doped $0.94\text{Bi}_{0.5}\text{Na}_{0.5}\text{TiO}_3\text{-}0.06\text{BaTiO}_3$ (abbreviated as Ce-BNT6BT) ceramics were prepared by a solid sintering technique for commercial products. Reagent-

grade oxide or carbonate powders of Bi_2O_3 , Na_2CO_3 , BaCO_3 , TiO_2 and CeO_2 were used as the starting materials. The powders of these raw materials were mixed by a vibrating mill with hard steel ball for 6 h and calcined at 900 °C for 1.5 h. After calcined, the powders were mixed by the vibrating mill with iron ball for 6 h again, then added into 25 wt% binder and rolled into square platelet of $12 \times 12 \times 0.5$ mm. The binder was removed from the green platelets going through a complicated heating processing, then dwelling 30 min at 800 °C. After removing binder, the platelets were sintered at 1,120–1,200 °C for 1 h in the air atmosphere.

The surface morphologies and sections of the sintered specimens were observed by a scanning electron microscope (SEM; JSM-5610, JEOL, Tokyo, Japan). X-ray diffraction patterns were obtained using an automated diffractometer (XRD; X'Pert PRO MPD, Philips, Eindhoven, Netherlands) with Cu $K\alpha 1$ radiation. The powder and the fresh surface and the grinded surface of the samples were affirmed by XRD. Fired-on silver paste was used for the electrodes for the dielectric and piezoelectric measurements. Specimens for piezoelectric measurements were poled at 160–170 °C in a silicone oil bath by applying a DC electric field of 3–4 kV/mm for 20 min. The piezoelectric coefficient (d_{33}) was measured using a piezoelectric d_{33} -meter (ZJ-4NA, Institute of Acoustics Academic Sinica, Beijing, China) at a frequency of 100 Hz. The

Fig. 2 SEM micrographs of Ce-BNT6BT ceramics sintered at different temperatures on the grinded surface (*inside*) and fresh surface (*outside*) of the bulk sample: (a) 1,120 °C outside, (b) 1,140 °C outside, (c) 1,180 °C outside, (d) 1,180 °C inside

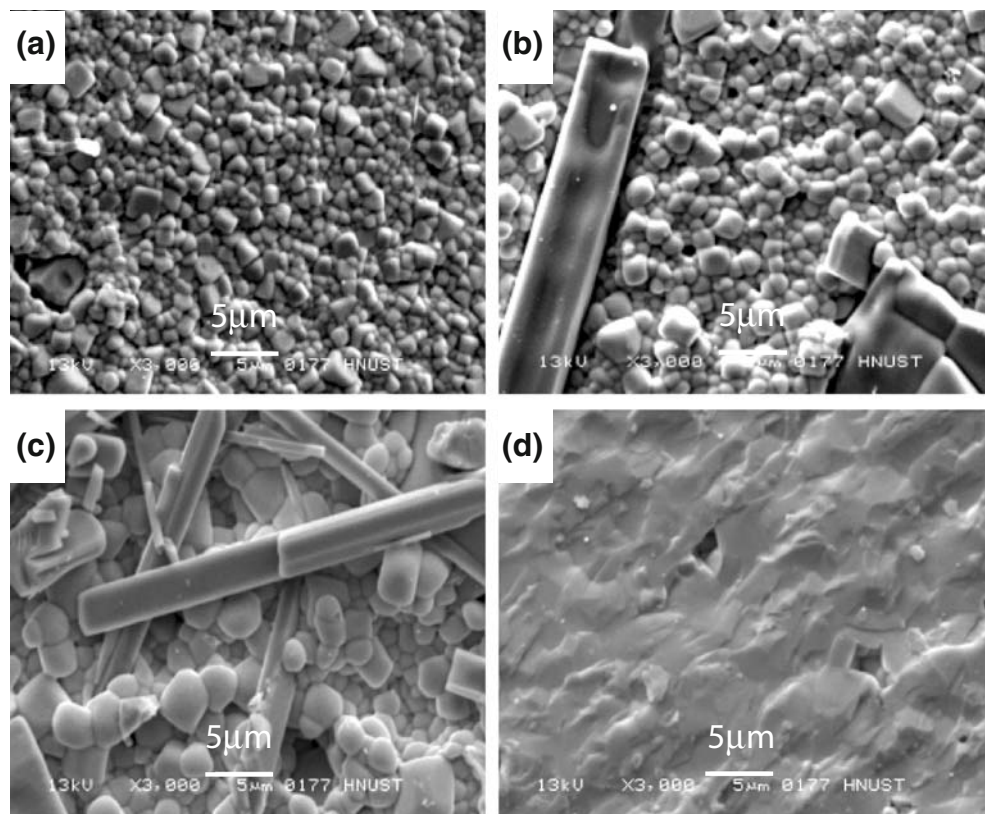
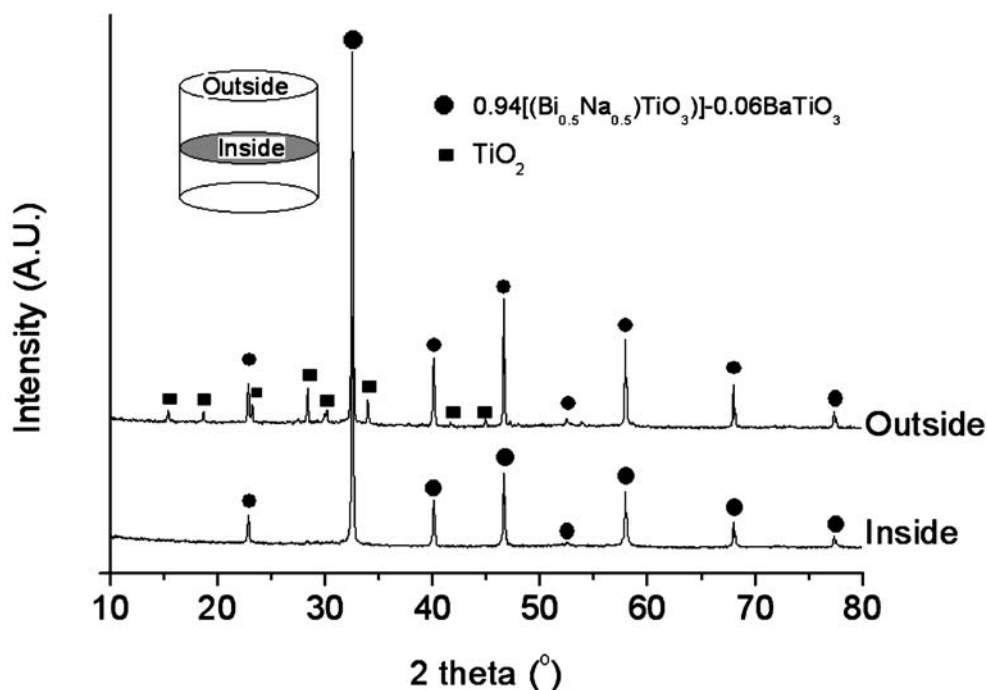


Fig. 3 X-ray diffraction patterns of Ce-BNT6BT ceramics sintered at 1,180 °C on the grinded surface (*inside*) and fresh surface (*outside*)



electromechanical coupling factors (k_p), was measured by the resonance and anti-resonance technique using an impedance analyzer (4294A, Agilent, Palo Alto, CA, USA). The electrical resistivity of the sintered specimens was measured using high-resistance analyzer (4339B, Agilent, Palo Alto, CA, USA), the loading voltage was 100 V, and holding time was 40 s.

3 Results and discussion

The powder X-ray diffraction patterns of the Ce-BNT6BT ceramics sintered at 1,120, 1,160, 1,180 and 1,200 °C, respectively, are shown in Fig. 1. The Ce-BNT6BT ceramics are all pure perovskite structure sintered at different temperatures. All of ceramics have high measured density ratio 90~99% to theoretical density. At room temperature, the BNT system is in rhombohedral structure and BaTiO₃ is in tetragonal structure. There is a rhombohedral–tetragonal MPB in their solid solution near 0.94Na_{0.5}Bi_{0.5}TiO₃-0.06BaTiO₃ composition. X-ray diffraction pattern of the composition at MPB is characterized with separated presence of two peaks to (003)/(021) at about 39.88 ° and splitting of the peak to (202) planes at around 46.58 ° [9]. Since BNT6BT composition used in this test is selected at MPB, its X-ray pattern exhibits the feature of peak splits at corresponding diffraction angles, indicating co-existence of tetragonal and rhombohedral phases in BNT6BT sample. The Ce-BNT6BT ceramics sintered at different temperatures all show the co-existence of the two phases, implying that different sintering temperatures (from 1,120

to 1,200 °C) do not lead to an obvious change in the phase structure.

Figure 2 shows the SEM micrographs of Ce-BNT6BT ceramics on the inside (grinded surface) and outside (fresh surface) of the bulk sample. The grain's shape of the Ce-BNT6BT ceramics is different between inside and outside of sample, and the outside of sample displayed a bar or plate shape. However, the grain's shape of the Ce-BNT6BT ceramics sintered below 1,140 °C was not like the bar or plate shape in both inside and outside of the sample. This implies that sintering temperature has an influence on the shape of grains in the outside of Ce-BNT6BT ceramics.

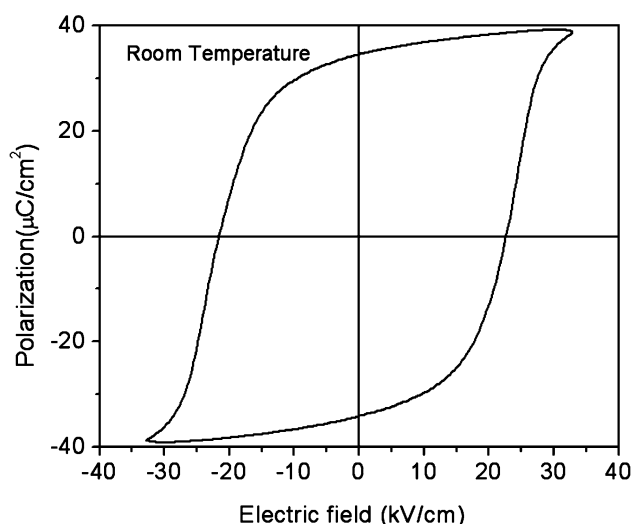


Fig. 4 P–E hysteresis loops of Ce-BNT6BT ceramics sintered at 1,200 °C

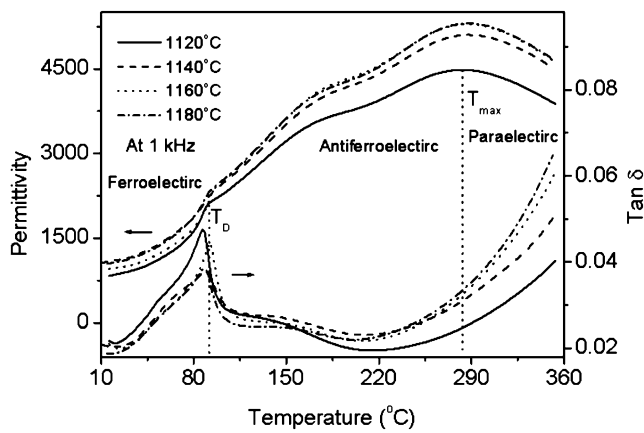


Fig. 5 Temperature dependence of permittivity and dielectric loss tangent at 1 kHz of Ce-BNT6BT ceramics sintered at different temperature

Figure 3 shows the X-ray diffraction patterns of inside and outside for the Ce-BNT6BT ceramics sintered at 1,180 °C on the surface. The inside of the bulk is still single perovskite structure, but the outside of the bulk appears the second phase. The second phase TiO₂ is affirmed on the outside of the Ce-BNT6BT ceramics. When the bulk is ground into powder, it is difficult to find peaks of the second phase (Figs. 1 and 2), which suggests that a few TiO₂ grains only appear on the outside of the bulk. The reason may be the Bi₂O₃ and Na₂O volatilize when the sintering temperature increases.

Figure 4 shows the *P*–*E* hysteresis loop of Ce-BNT6BT ceramics sintered at 1,200 °C obtained at room temperature. The hysteresis loop has not reached to saturation due to leakage current during loading higher electric field. However, it is easy to observe a relatively large remnant polarization, *P*_r of about 34.2 μC/cm², which is higher than the value in 0.94Bi_{0.5}Na_{0.5}TiO₃–0.06BaTiO₃ system [5]. Meanwhile, the coercive field, *E*_c, of about 22.6 kV/cm, is lower than the value of Bi_{0.5}Na_{0.5}TiO₃ ceramics (about 73 kV/cm) at room temperature. The increase in *P*_r in the system can be attributed to the increase in the MPB nature of the system, due to dipole moments of the samples closed to the MPB being able to reorientate themselves more completely than those of the non-doped rhombohedral and tetragonal phase. The *P*_r increase can also be associated with

the increase in domain wall motion that switches domains and hence affects the polarization.

Figure 5 shows the temperature dependence of permittivity (ϵ_r) and dielectric loss tangent ($\tan \delta$) at 1 KHz of Ce-BNT6BT ceramics sintered at different temperatures. It can be seen that the three phases of ferroelectric, antiferroelectric and paraelectric exist in different temperature ranges for all samples, which agrees with the result obtained by Takenaka et al. [4]. Here, the temperature where the transition between ferroelectric phase and antiferroelectric phase is called depolarization temperature (T_d) and the temperature corresponding to maximum value of permittivity is called maximum temperature (T_m). There is a slope change in antiferroelectric region; it may be a 2nd phase transition or the end of ferroelectric and antiferroelectric transition. ϵ_r increases with the increase in sintering temperature in antiferroelectric region, but depolarization temperature (T_d) increases below 1,160 °C then decreases at higher temperature in the system (in Table 1). ϵ_r of any material, in general, is influenced by dipolar, electronic, ionic and interfacial polarizations [10]. Interfacial polarization increases due to the creation of crystal defects, and dipolar polarization decreases due to the increase in randomness of the dipoles with temperature. However, the temperature effect on ionic and electronic polarizations is very small. The increase in ϵ_r with sintering temperature suggests the increase in interfacial polarization. The increase in ϵ_r of the system is also due to the increase in density with sintering temperature. The increase in T_d with increasing sintering temperature can be attributed to the decrease in internal stress in the system. It can be seen in the SEM microstructures that the density increasing and grains rearranging of the samples lead to a decrease in internal stress in the samples with increasing sintering temperature. Because the phase transformation temperature is inversely proportional to the internal stress, consequently the decrease in depolarization temperature with increasing sintering temperature seems to be the result of increase in internal stress due to a decrease in porosity in the microstructure. Dielectric loss of the system decreases with the increase in sintering temperature. This can be explained by the decrease in space charge conduction in the system. Dielectric loss for the system sintered at different temper-

Table 1 The piezoelectric properties and resistivity of Ce-BNT6BT ceramics sintered at different temperatures.

Sintering temperature	1,120 °C	1,140 °C	1,160 °C	1,180 °C	1,200 °C
Permittivity ϵ_r	1,023	949	920	914	851
Dielectric loss $\tan \delta$	0.021	0.024	0.018	0.020	0.019
Piezoelectric coefficient, d_{33} (pC/N)	83	126	116	120	127
Planar coupling factor, k_p	0.16	0.24	0.24	0.23	0.23
Depolarization temperature T_d (°C)	90	93	94	91	90
Resistivity ρ (10^{10} ohm m)	0.313	0.868	1.818	3.125	2.301

atures reaches maximum at a temperature smaller than Curie temperature T_c , which is a characteristic of relaxor ferroelectrics.

The piezoelectric properties and resistivity of Ce-BNT6BT ceramics sintered at different temperatures are shown in Table 1. The piezoelectric coefficients, d_{33} , are found to be above 115 pC/N for the system sintered at 1,140, 1,160, 1,180 and 1,200 °C, respectively. The planar coupling factors, k_p , are found to be over 0.23 for the system sintered at 1,140, 1,160, 1,180 and 1,200 °C, respectively, which are suitable for narrow-band filters. The resistivity, ρ , of the Ce-BNT6BT ceramics increases dramatically at room temperature. A maximum value of the ρ is 3.125×10^{10} ohm m for the Ce-BNT6BT ceramics sintered at 1,180 °C. Unfortunately, the resistivity drops while the sintering temperature increases to 1,200 °C. It may be that Bi_2O_3 and Na_2O volatilizing destroyed electric neutrality with increasing sintering temperature.

4 Conclusions

Phase structure, microstructure and resistivity of the Ce-BNT6BT ceramics have been investigated. The ceramics sintered at different temperatures all show the co-existence of rhombohedral and tetragonal phase. The sintering temperatures do not lead to an obvious change in the phase structure. The morphology of ceramic inside and surface indicated that a few TiO_2 grains existed on the outside of the bulk due to the Bi_2O_3 and Na_2O volatilizing at higher sintering temperature. The ceramics sintered at 1,200 °C obtained a relatively large remnant polarization, P_r of about

$34.2 \mu\text{C}/\text{cm}^2$, and a coercive field, E_c , of about 22.6 kV/cm at room temperature. The ϵ_r of the ceramics increased with the increase in sintering temperature, but depolarization temperature (T_d) increased below 1,160 °C ($T_d=94$ °C) then decreased at higher temperature. A maximum value of the resistivity ρ was 3.125×10^{10} ohm m for the Ce-BNT6BT ceramics sintered at 1,180 °C at room temperature.

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References

1. G.A. Smolenskii, V.A. Isupov, A.I. Agranovskaya, N.N. Krainik, *Sov. Phys., Solid State* **2**(11), 2651–2654 (1961) (Engl. Transl.)
2. J. Suchanicz, K. Roleder, A. Kania, J. Handerek, *Ferroelectrics* **77**, 107–110 (1988)
3. M.S. Hagiyeve, I.H. Ismaizade, A.K. Abiyev, *Ferroelectrics* **56**, 215–217 (1984)
4. T. Takenaka, K. Maruyama, K. Sakata, *Jpn. J. Appl. Phys.* **30** (9B), 2236–2239 (1991)
5. T. Takenaka, T. Okuda, K. Takegahara, *Ferroelectrics* **196**, 175–178 (1997)
6. H. Nakada, N. Koizumi, T. Takenaka, *Key Eng. Mater.* **169**, 37–40 (1999)
7. T. Takenaka, H. Nagata, *Jpn. J. Appl. Phys.* **36**(9B), 6055–6057 (1997)
8. A. Herabut, A. Safari, *J. Am. Ceram. Soc.* **80**(11), 2954–2958 (1997)
9. M. Onoe, H. Jumonji, *J. Acoust. Soc. Am.* **41**(4), 74–80 (1967)
10. A.K. Singh, T.C. Goel, R.G. Mendiratta, O.P. Thakur, C. Prakash, *J. Appl. Phys.* **91**, 6626 (2002)