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Effect of Sintering Temperature on the Electromechanical Properties of $0.945Bi_{0.5}Na_{0.5}TiO_3$-$0.055BaZrO_3$ Ceramics

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In this work, lead-free $0.945B_{0.5}N_{0.5}TiO_3$-$0.055BaZrO_3$ (BNT-BZ) ceramics were synthesized by using conventional solid-state reaction method and the effect of different sintering temperatures (1145 − 1200 °C) on its structure and electromechanical properties were investigated. XRD patterns revealed single a phase-perovskite structure for all samples sintered at different temperatures. An optimum sintering temperature enhanced densification, promoted grain growth, and improve the dielectric and piezoelectric properties. However, at low (1145 °C) and high (1200 °C) sintering temperatures, the BNT-BZ ceramics showed inferior electromechanical properties. BNT-BZ ceramics sintered at an optimum temperature (1175 °C) showed an enhanced strain (0.39%) response at an applied electric field of 7 kV/mm with a high dynamic piezoelectric coefficient (d^*_{33} = 557 pm/V). These results can be attributed to the high density of the BNT-BZ ceramics sintered at 1175 °C.

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I. INTRODUCTION

Several synthetic ceramic materials have been described to exhibit piezoelectric effect. Among synthetic piezoelectric materials, lead-based ceramics, such as lead zirconium titanate $Pb(Zr,Ti)O_3$ (PZT), lead lanthanum zirconate titanate (PLZT), lead magnesium niobate (PMN) *etc.*, possess high a piezoelectric response [1–3]. However, the large amount of toxic lead can cause serious environmental pollutions, so the rapid development of lead free materials is urgently needed in the piezoelectric industry to find the substitutes for lead based ceramics [4,5].

As a replacement for lead-based piezoelectric materials, lead-free bismuth sodium titanate $Bi_{0.5}Na_{0.5}TiO_3$ (BNT) is considered to be an excellent alternative. BNT has rhombohedral symmetry at room temperature and is strongly ferroelectric with a large remnant polarization of $P_r = 38\ \mu C/cm^2$ and a high Curie temperature of T_c = 320 °C [6]. Nevertheless, the evaporation of bismuth at high sintering temperature is believed to increase the conductivity of the material and make its poling difficult. Therefore, various BNT-based solid solutions have been developed to enhance the poling and piezoelectric properties [7–11]. The physical properties of ceramic material, in addition to their compositional modification, strongly depend on the sintering temperature. The sintering temperature strongly effects densification and the particle size of the materials and play important roles in the enhancement of the electromechanical properties [12–15].

Recently, we have developed $(1-x)Bi_{0.5}Na_{0.5}TiO_3$-$xBaZrO_3$ (BNT-BZ100x) ceramics with enhanced piezoelectric properties [16]. If the electromechanical properties of this system are to be optimized and reproducible and high-quality BNT-BZ ceramics are to be obtained, it is necessary to study its sintering performance. In this work, lead-free $0.945Bi_{0.5}Na_{0.5}TiO_3$-$0.055BaZrO_3$ (BNT-BZ ceramics) were synthesized and sintered at different temperatures, and their crystal structure, microstructure, and electrical properties (dielectric, ferroelectric and field induced strain) were investigated.

II. EXPERIMENTAL PROCEDURE

A conventional mixed oxide route was utilized to prepare $0.945B_{0.5}N_{0.5}TiO_3$-$0.055BaZrO_3$ (BNT-BZ) ceramics. Commercially-available reagent-grade $BaCO_3$ (99%), Na_2CO_3 (99.95%), Bi_2O_3 (99.90%), ZrO_2 (99%), and TiO_2 (99.90%) from Sigma Aldrich Co were used as starting raw materials. Prior to measuring their weights, the powders were dried in an oven at 100 °C for 24 h. The dried powders were weighed according to the stoichiometric formula and ball-milled for 24 h in ethanol. The dried slurries were calcined at 850 °C for 2 h and ball

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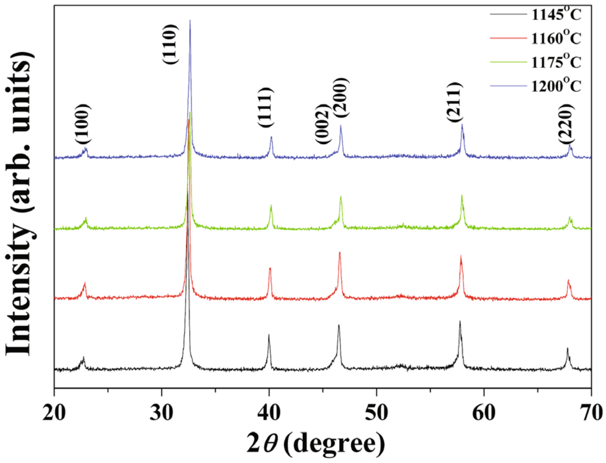

Fig. 1. (Color online) X-ray diffraction patterns of BNT-BZ ceramics.

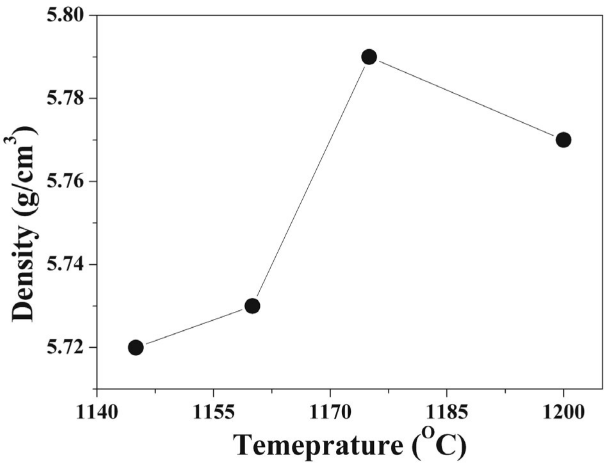

Fig. 2. Density of BNT-BZ ceramics sintered at different sintering temperatures (1145 – 1200 °C).

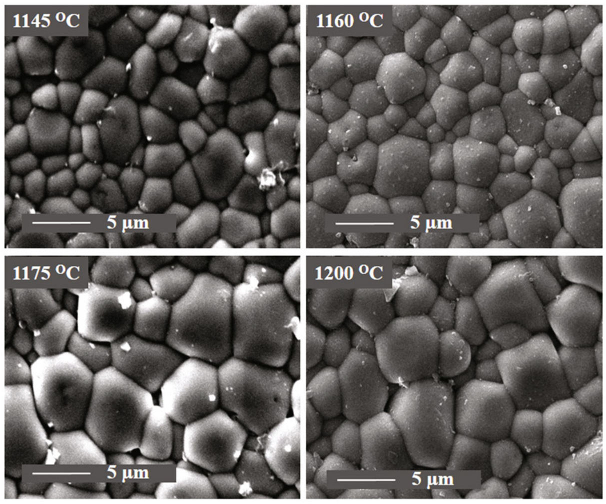

Fig. 3. SEM images of BNT-BZ ceramics for four sintering temperatures.

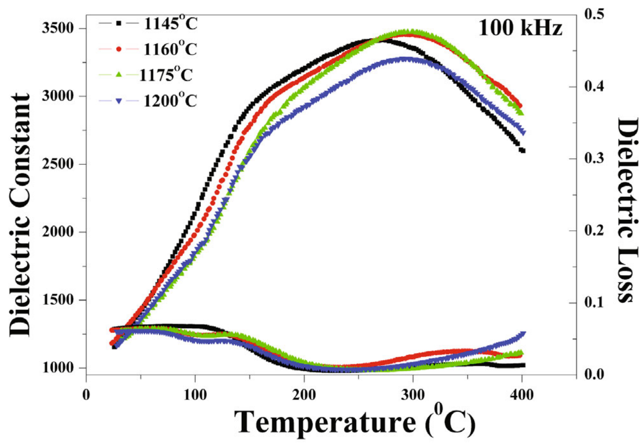

Fig. 4. (Color online) Temperature-dependent dielectric constant and dielectric loss of BNT-BZ ceramics measured at 100 kHz.

milled again to dissociate the agglomerates. After drying, the powders were pulverized, passed through a sieve of 150 μm mesh and mixed with an aqueous polyvinyl alcohol (PVA) solution as a binder for granulation. The granulated powders were subsequently pressed into green disks with diameter of 10 mm and thicknesses of 2 mm. To minimize the evaporation of the volatile elements (Bi, Na), we embedded the green disks in the same compositional powder and sintered at 1145 – 1200 °C for 2 h in air.

The crystal structure was characterized using an X-ray diffractometer (XRD, Miniflex II Rigaku) while the microstructure was examined through scanning electron microscopy (SEM) JP/JSM5200 (Japan). The density of the sintered specimens was measured by the Archimedes method. To measure the electrical properties, we coated the silver paste on both polished faces of the sintered samples and fired then at 650 °C for 0.5 h to form electrodes. The piezoelectric properties were measured after aging for a period of 24 h. The dielectric constant and loss of the specimens were measured using an automatic acquisition system using an impedance analyzer (Agilent HP4192A, USA) in 25 – 450 °C temperature range at different frequencies. The ferroelectric hysteresis loops were measured using a Precision Premier II equipment (Radiant Technology, Inc.). Field-induced strain curves were obtained by using a contact-type displacement sensor (Millitron: Model 1240).

III. RESULTS AND DISCUSSION

Figure 1 shows the XRD patterns of BNT-BZ ceramics for various sintering temperatures. All ceramics exhibited a single phase perovskite structure, at all sintering temperature and no secondary phases were de-

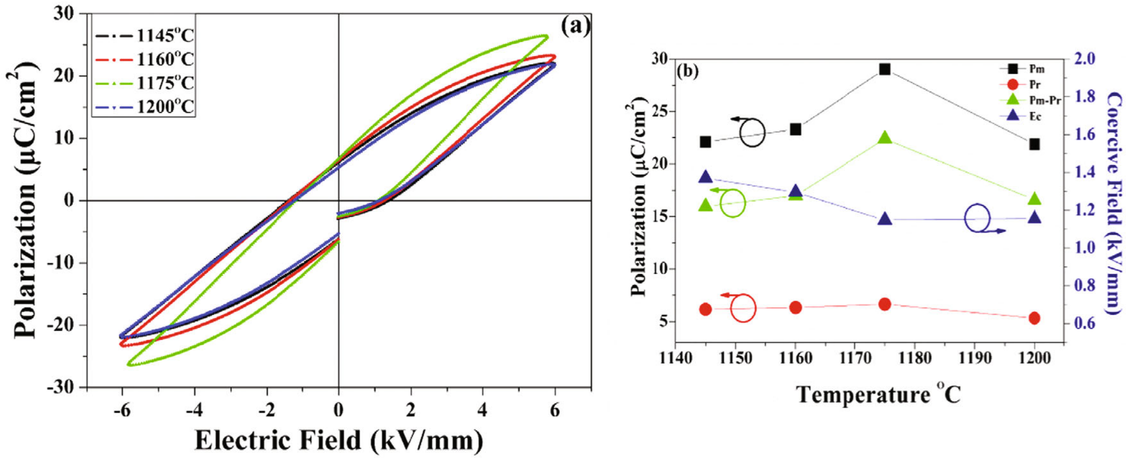

Fig. 5. (Color online) (a) P-E hysteresis loops and (b) P_m, P_r and E_c of BNT-BZ ceramics sintered at various temperatures.

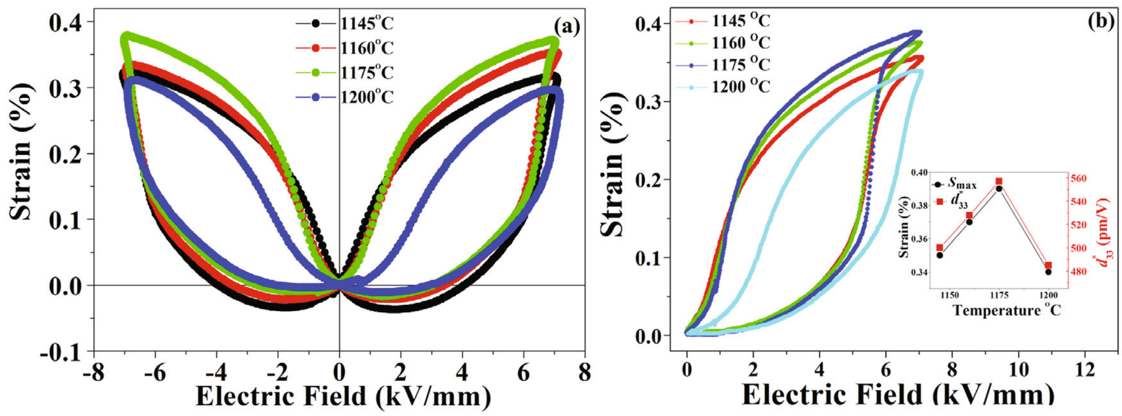

Fig. 6. (Color online) (a) Bipolar field-induced and (b) unipolar field-induced strain curves for BNT-BZ ceramics sintered at different temperatures.

tected. These results indicate that the different sintering temperatures (1145 – 1200 °C) do not change the crystalline structure of the BNT-BZ ceramics. A detailed XRD analysis revealed that slightly increasing the sintering temperature increase the (002) peaks intensity.

Figure 2 shows the density of BNT-BZ ceramics as a function of sintering temperatures. These ceramics have a low density when the sintering temperature is lower or higher than 1175 °C. The ceramics sintered at 1175 °C had the highest density, 5.79 g/cm^3. The densification behavior of the samples sintered at different temperatures yields an optimum sintering temperature for the studied BZ-modified BNT ceramics. At higher sintering temperature, the density of the materials decreased which may have been due to the evaporation of volatile alkali metal oxides [17–19].

Figure 3 shows the SEM patterns of BNT-BZ ceramics at various sintering temperatures. The sintering temperature obviously affects the surface morphology. All ceramics have closely packed and dense grain morphologies. However, with increasing sintering temperature, the average grain size increases. The average grain size of the ceramics sintered at different temperatures was found to vary from 3 to 4.5 μm.

The temperature dependences of the dielectric constant of the BNT-BZ ceramics at different sintering temperatures over a heating run at 100 kHz are shown in Fig. 4. The maximum temperature, T_m, value of the BNT-BZ ceramics almost stays constant for different sintering temperatures. Moreover, the ceramic sintered at 1175 °C is observed to have slightly higher dielectric constant (ε) then the ceramics sintered at 1145 °C, 1160 °C, and 1200 °C. This enhancement in the dielectric properties of the BNT-BZ sintered at 1175 °C can be attributed to the higher densities attained at that temperature.

Figure 5(a) shows the room-temperature P-E hysteresis loops of BNT-BZ ceramics sintered at temperature in the range 1145 – 1200 °C. The characteristic values of the maximum polarization (P_{max}), remanent polarization (P_r), and coercive field (E_c) were affected by the sintering temperature as shown in Fig. 5(b). The variations in the value of P_r and P_m of the ceramics with different sintering temperature were similar to the variation with the density of BNT-BZ ceramics. As the density cause a

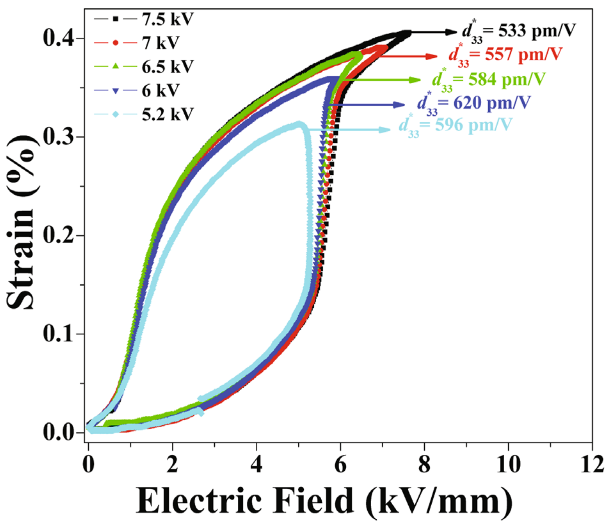

Fig. 7. (Color online) Unipolar strain curves of BNT-BZ sintered at 1175 °C under the application of different applied electric fields.

variation in the polarization, the polarization increases with increasing density of the ceramics [20].

Figure 6(a) and (b) show the bipolar and unipolar strain loops of the BNT-BZ ceramic samples sintered at different temperatures. Development of butterfly shape loops in the bipolar response hints at a relaxor ferroelectric nature of these samples. The maximum strain (S_{max}) level is affected by increasing the sintering temperature. Similar to the bipolar strain, the unipolar strain response was also enhanced and reached its maximum value (S_{max} = 0.39%) at an applied field of 7 kV/mm for ceramics sintered at 1175 °C, and the corresponding normalized strain ($d_{33}^* = S_{max}/E_{max}$) attained a maximum value of 557 pm/V. However, with further increase in the sintering temperatures the strain level decreased. The strain and the dynamic piezoelectric constant d_{33}^* are summarized in inset of fig. 6(b). The increased d_{33}^* at 1175 °C may be due to enhancements in the density and the grain size [21]. The decrease in the normalized strain at a higher sintering temperature of 1200 °C may be due to a decrease in the density and to the volatilization of alkali metals [19].

To estimate the suitability of the materials for actuator applications, we determined the strain curves for ceramics sintered at 1175 °C at different electric fields ranging 5.2 – 7.5 kV/mm, as shown in Fig. 7. A maximum electric field-induced strain response of 0.40% was obtained at an electric field of 7.5 kV/mm, which corresponds to S_{max}/E_{max} = 533 pm/V. However, when the applied field was reduced to 6 kV/mm and 5.2 kV/mm, the strain response were 0.36% and 31% with their corresponding normalized strains of 620 pm/V and 596 pm/V, respectively, which are higher than the value of other lead-free BNT-based binary system [8,10,22]. The high strain at low electric field makes this material a promising candidate for actuator applications.

IV. CONCLUSION

Lead-free $0.945Bi_{0.5}Na_{0.5}TiO_3$-$0.055BaZrO_3$ (BNT-BZ) ceramics were synthesized by using a conventional solid-state reaction method. The effect of different sintering temperatures (1145 – 1200 °C) on the crystal structure, microstructure, ferroelectric behavior, and field-induced strain behavior of BNT-BZ ceramics were investigated. BNT-BZ ceramics sintered at an optimum temperature of 1175 °C exhibited high density and good electrical properties. A high field-induced strain (0.39%) and a high dynamic piezoelectric coefficient (S_{max}/E_{max} = d_{33}^* = 557 pm/V) were obtained at an applied field of 7 kV/mm. The high dielectric constant, ferroelectric, and field-induced strain are believed to be due to the high density.

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