

# FABRICATION AND MECHANICAL PROPERTIES OF $\text{Na}_{0.5}\text{Bi}_{0.5}\text{TiO}_3\text{--BaTiO}_3$ LEAD-FREE PIEZOELECTRIC CERAMICS

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*Piezoelectric ceramics with  $0.94\text{Na}_{0.5}\text{Bi}_{0.5}\text{TO}_3\text{--}0.06\text{BaTiO}_3$  compositions were fabricated by solid state mixed oxide method and sintered at different temperatures varying from 1050°C to 1150°C to obtain dense ceramics. Phase analysis using X-ray diffraction showed tetragonal perovskite structure of  $\text{Na}_{0.5}\text{Bi}_{0.5}\text{TO}_3$ , with no  $\text{BaTiO}_3$  peak detected. The SEM observation revealed that the crystal grain size of the piezoelectric ceramics is on the nano-size dimensions under all the sintering temperature. The study on the compressive mechanical characteristics showed that the compressive strength of the  $0.94\text{Na}_{0.5}\text{Bi}_{0.5}\text{TO}_3\text{--}0.06\text{BaTiO}_3$  piezoelectric ceramics increases with the rise of sintering temperature and sintering time. The change behavior of the compressive strength with the rise of cold pressure presents increasing firstly and then decreases.*

## INTRODUCTION

Lead zirconate titanate (PZT) piezoelectric ceramics with perovskite structure display the excellent piezoelectric and ferroelectric properties and are widely used in many applications such as sensors, oscillators, actuators and transducers [1-4]. Furthermore, the piezoelectric or ferroelectric devices fabricated by PZT ceramics would be operated at relatively high temperature due to its high Curie temperature of about 390°C [5]. However, lead, titanium and zirconium oxides based piezoelectric ceramics generally have poor mechanical properties such as low bend strength and low fracture toughness [6, 7]. More importantly, owing to the effects of lead toxicity and environmental issues, the exclusion of electronic part including lead compounds is restricted gradually and will be prohibited in a near future [8]. Numerous works turn towards new promising lead free materials to improve their piezoelectric properties in order to progressively replace PZT devices [9-11]. Unfortunately, the piezoelectric and ferroelectric properties of the most alternative lead-free ceramics are inferior to that of PZT [12].

To date, a large number of studies on the lead free piezoelectric ceramics systems with morphotropic phase boundary (MPB) are mainly focused on the alkali niobates, modified bismuth titanates, bismuth ferrites and other systems [13]. Among the various lead-free piezoelectric ceramics systems, bismuth sodium titanate  $\text{Bi}_{0.5}\text{Na}_{0.5}\text{TiO}_3$  (BNT) and its solid solutions (1-x) BNT-x

BT are most attractive and intensively studied because of their superior ferroelectric and piezoelectric properties [14, 15]. It is considered as one of the most promising lead free piezoelectric ceramics to replace the PZT for piezoelectric applications.

BNT is a compound with strong ferroelectric and weak piezoelectric properties. The addition of BT to BNT improves the piezoelectric and sintering properties. The (1-x) BNT-x BT compositions exist as the MPB between the rhombohedral phase (BNT) and the tetragonal (BT) phase while x values varying between 0.06 and 0.08 [16,17]. Many recent studies have been focused on the ferroelectric, piezoelectric and dielectric properties and little investigation has been paid to the mechanical properties of BNT ceramics system. It is well known that the mechanical properties of polycrystalline ceramics not only depend on the composition but also on the microstructure, which determined by the preparation processes. Therefore, we focus on the mechanical properties of the  $0.94\text{Na}_{0.5}\text{Bi}_{0.5}\text{TO}_3\text{--}0.06\text{BaTiO}_3$  (abbreviated as BNT-BT<sub>0.06</sub>) ceramics in this study.

In this paper, the BNT-BT<sub>0.06</sub> piezoelectric ceramics were fabricated by solid state reaction and incorporation with non-pressurized sintering method. The microstructure and morphology were investigated by XRD and SEM technology. The influences of preparation conditions such as sintering temperature, cold pressure and sintering time on the compressive mechanical properties were systematically investigated.

## EXPERIMENTAL

### Preparation of ceramics

The solid state reaction method was used to prepare BNT-BT<sub>0.06</sub> piezoelectric ceramics.  $TiO_2$  (99 %),  $Bi_2O_3$  (99 %),  $NaCO_3$  (99 %) and  $BaCO_3$  (99 %) were used as starting materials. Poly vinyl alcohol (saponification degree: 99 %, number average polymerization:  $1750 \pm 50$ ) was used as dispersant and binder. All the materials were analytical reagents and supplied by Siopharm Chemical Reagent Co., Ltd., Shanghai, China. Firstly, the materials were weighed according to the compositions of BNT-BT<sub>0.06</sub>. Then the powders were mixed and vibratory milled in anhydrous ethanol for 8 h. After the milled powders dried at 80°C for 4 h to remove moisture, the powders were subsequently calcined at 900°C for 2 h. The calcined powders were granulated and pressed into cylinder blocks under different pressure at room temperature and maintained pressure for 5 min by tablet pressing machine. In order to improve the casting ability of the calcined powders, the 2 ml of 3 wt. % PVA solution used as binder was blended with calcined powders before cold pressing. Finally, the cylinder blocks were sintered at 1050°C, 1100°C and 1150°C for various times in air, respectively. The typical sintering temperature curve is shown in Figure 1.

In this paper, the influences of cold pressure, sintering temperature and sintering time on the microstructure and mechanical properties of the BNT-BT<sub>0.06</sub> piezoelectric ceramics were investigated. The main processing conditions are tabulated in Table 1.

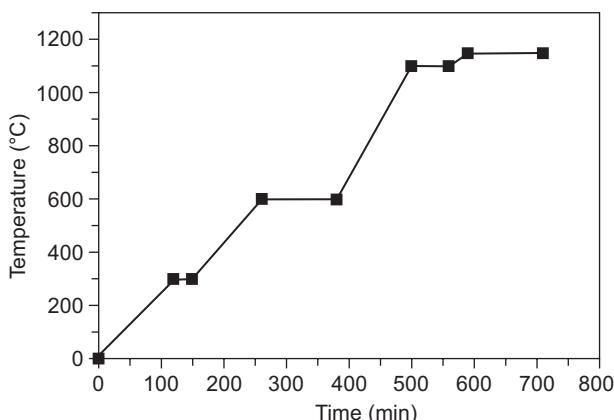


Figure 1. Sintering temperature curve of BNT-BT<sub>0.06</sub> lead-free ceramics.

Table 1. Main processing conditions.

| Cold pressure (MPa) | Sintering temperature (°C) | Sintering time (h) |
|---------------------|----------------------------|--------------------|
| 5                   | 1050                       | 1                  |
| 10                  | 1100                       | 2                  |
| 15                  | 1150                       | —                  |

### X-ray diffraction analysis

Chemical composition and structure of the BNT-BT<sub>0.06</sub> lead-free ceramics blocks were detected by X-ray diffraction (Model: XRD-600), using Cu K $\alpha$  radiation at 40 kV and current 30 mA. The samples were scanned over 20 range from 20° to 75° and the step size of the scanning is 0.02°. The size of sample is cylinder with 12 mm diameter and 2 mm height.

### Microstructure and morphology observation

Microstructure and morphological characterization of the lead-free ceramics were investigated by S-4800 SEM at 3.0 kV. To avoid charging during the electron irradiation, the BNT-BT<sub>0.06</sub> lead-free ceramics was sputtered with a thin gold layer in the evaporator before scanning observation.

### Mechanical properties testing

The compressive mechanical properties of BNT-BT<sub>0.06</sub> lead-free ceramics were investigated at room temperature by electronic universal testing machine (Model: WDW-50). Cylindrically shaped samples with 12 mm in diameter and 8 mm in height were used. Specimens were loaded in compression at a crosshead speed of 1 mm/min, and the compressive strength at failure was calculated in MPa.

## RESULTS AND DISCUSSIONS

### XRD analysis

Figure 2 shows the XRD diffraction patterns of BNT-BT<sub>0.06</sub> ceramics obtained at 1050°C, 1100°C, and 1150°C. It can be seen from Figure 2 that the characteristic peaks of BNT were located at 22.76°, 32.58°, 40.24°,

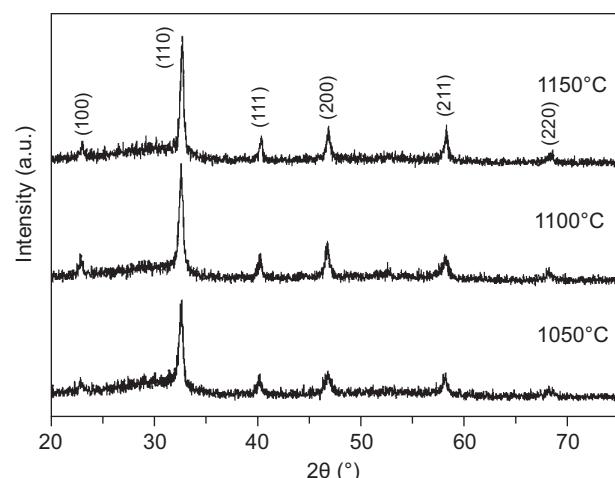


Figure 2. X-ray diffraction profiles of the BNT-BT<sub>0.06</sub> piezoelectric ceramics under different sintering temperatures (sintering time: 2 h, cold pressure: 10 MPa).

46.72° and 57.93° correspond to the crystalline plane (*hkl*) of the BNT at (100), (110), (111), (200) and (211), respectively. It should be noted that the pure tetragonal structure is characterized by a single peak (111) at 40° and a single peak corresponding to two crystal planes (112) and (211) at 57.9° [18,19]. Therefore, X-ray diffraction measurements show that all the sintering samples under different temperature present a tetragonal structure and no impurity phase was observed.

#### SEM observation

Figure 3 shows the effect of sintering temperature on the morphology of the BNT-BT<sub>0.06</sub> lead-free ceramics. It can be obviously seen from Figure 3 that the defects and micro-pores in the functional ceramics present decreasing trend with the rise of sintering temperature (From Figures 3a to 3c). These results indicated that the BNT-BT<sub>0.06</sub> piezoelectric ceramics become more and more compact with the rise of sintering temperature. It should be noted that the improvement of the densification of the BNT-BT<sub>0.06</sub> piezoelectric ceramics is beneficial to improve the mechanical properties of the materials. Further careful observation, it can be seen that the crystal grain size of the BNT-BT<sub>0.06</sub> piezoelectric ceramics is on the nano-size dimensions. The morphology of the crystal grain presents long rode-like structure with approximate 200-300 nm in diameter under low sintering temperature (Figure 3a). On the other hand, the rod-like structure of the piezoelectric ceramic broadens in diameter and shortens in the length with the rise of sintering temperature (Figures 3b and 3c). Furthermore, the crystal grain size obviously grows up with the rise of sintering temperature.

The effect of sintering time on the microstructure of the BNT-BT<sub>0.06</sub> ceramics is shown in Figure 4. It can be concluded from Figure 4 that the sintering time has greatly influence on the microstructure of the BNT-BT<sub>0.06</sub> ceramics. Firstly, the micro-pores in the piezoelectric ceramics obviously decreased with the rise of sintering time (Figures 4a and 4b). Secondly, the crystal grain size presents growing up trend and its distribution is more uniform with the rise of sintering time (Figures 4c and 4d). Furthermore, the arranging and contacts between the crystal grains become closer and the grain boundary defects obviously decreased with the sintering time prolonged. It should be noted that the change behavior of the microstructure with the rise of sintering time is beneficial for the mechanical properties improvement of the piezoelectric ceramics.

Figure 5 shows the microstructure and morphology of the BNT-BT<sub>0.06</sub> piezoelectric ceramics under different cold pressure. It can be obviously seen from Figure 5 that the microstructures of the ceramics fabricated under various cold pressures are significantly different. The compactness of the piezoelectric ceramics prepared under 10 MPa is the best and that prepared under 5 MPa

is the worst. This result is mainly caused by two factors. On the one hand, the ceramic green body becomes more and more compact with the rise of cold pressure. Thus the micro-pores in the green body decrease and the mass diffusion becomes easy on the sintering processes.

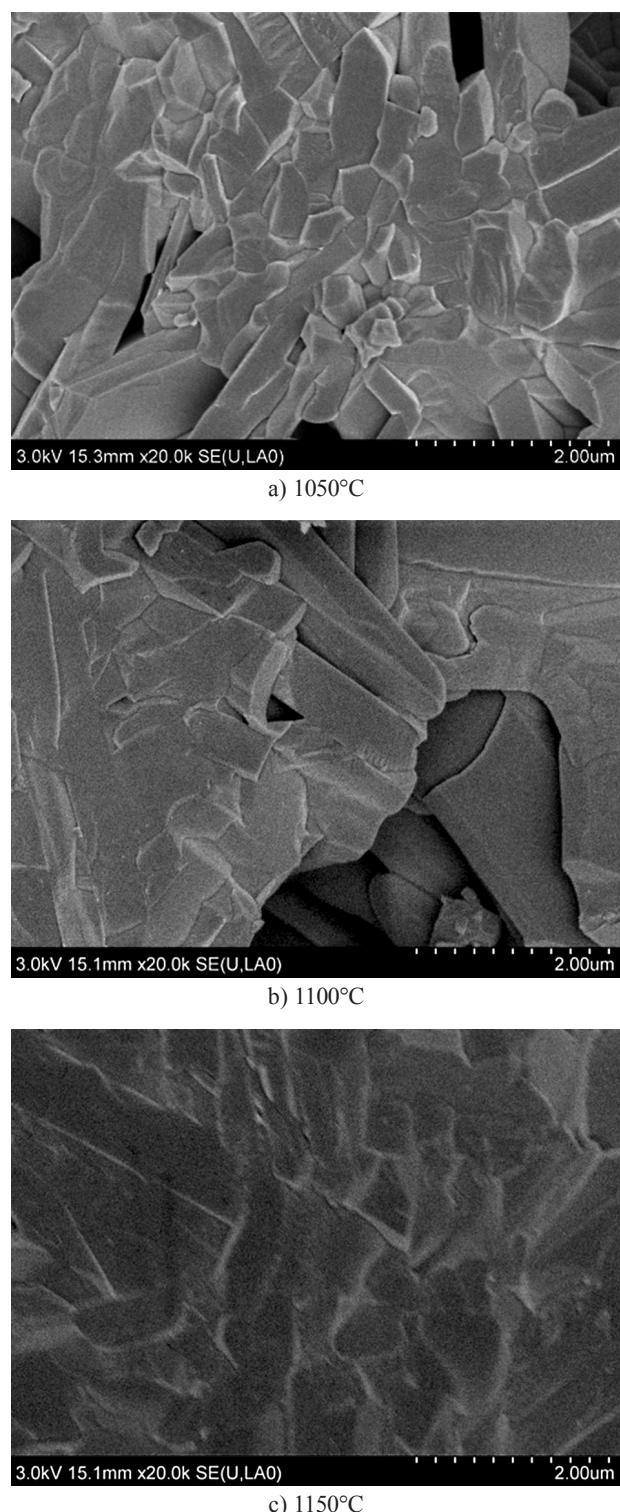


Figure 3. Microstructure and morphology of the piezoelectric ceramics under different sintering temperature: a) 1050°C, b) 1100°C, c) 1150°C (cold pressure: 10 MPa, sintering time: 2 h).

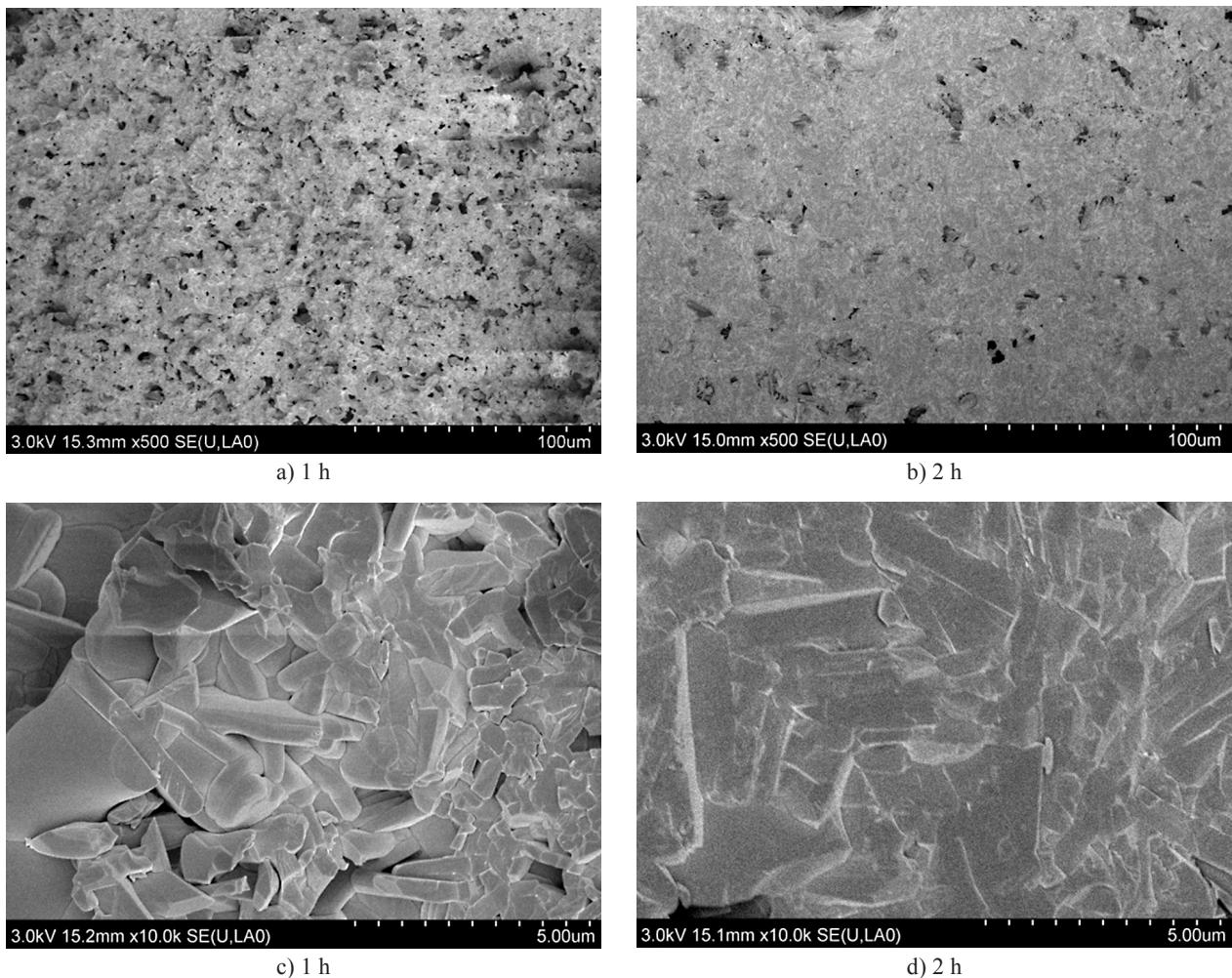


Figure 4. Effect of sintering time on the microstructure of the BNT-BT<sub>0.06</sub> ceramics: a) and c) 1 h, b) and d) 2 h (cold pressure: 10 MPa, sintering temperature: 1150°C).

Ultimately, the microstructure of the BNT-BT<sub>0.06</sub> piezoelectric ceramics becomes densification while the cold pressure rises from 5 MPa to 10 MPa. On the other hand, while the cold pressure rises further, the adhesive film which formed by PVA macromolecule binder was partly damaged under high cold pressure. This would result in the binding force between the ceramic particles decreasing and the micro-cracks would be formed after the ceramic green body releasing from mold. The existence of the micro-cracks in the ceramic green body would ultimately influence the densification of the piezoelectric ceramics on the sintering processes.

#### Compressive mechanical properties

Figure 6 shows the effect of sintering temperature on the compressive strength of BNT-BT<sub>0.06</sub> piezoelectric ceramics. It can be concluded from Figure 6 that the compressive strength of the ceramics obviously increased with the rise of sintering temperature. The compressive strength of the ceramics increased from 78 MPa to

210 MPa, almost increasing 2 times, while the sintering temperature rises from 1050°C to 1150°C. This result is mainly attributed to the improvement of densification in the microstructure of the ceramics with the rise of sintering temperature. It is well known that the diffusion rate of the mass transfer and grain growth during the ceramic sintering are mainly controlled by the sintering temperature. The mass diffusion would accelerate and simultaneously accompanied by the crystal grain growth with the rise of the sintering temperature. Ultimately, the densification of the ceramic increased with the improvement of sintering temperature. This change behavior of the piezoelectric ceramic densification with the sintering temperature is also verified by the SEM observation (from Figures 3a to 3c). It should be noted that the rise of densification of the BNT-BT<sub>0.06</sub> piezoelectric ceramics is beneficial for the compressive strength improvement of the ceramics.

Figure 7 shows the effect of sintering time on the compressive strength of the piezoelectric ceramics. It can be concluded from Figure 7 that the sintering time has greatly influenced the compressive strength of the

ceramics which increases from 76 MPa for sintering 1 h to 210 MPa for 2 h, almost increasing 2 times. The result of the compressive strength improvement with the sintering time is mainly attributed to the improving the densification of the ceramics and decreasing the defects.

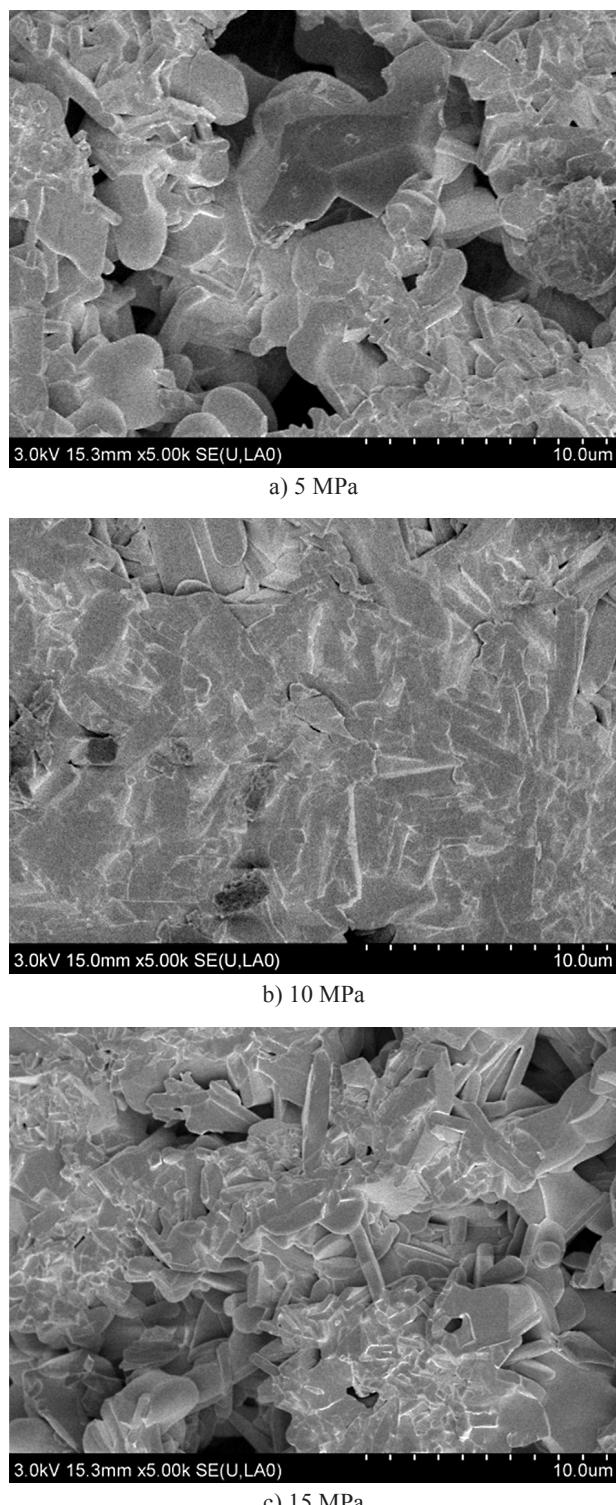


Figure 5. Effect of cold pressure on the microstructure of BNT-BT<sub>0.06</sub> piezoelectric ceramics: a) 5 MPa, b) 10 MPa, c) 15 MPa (sintering temperature: 1150°C, sintering time: 2 h).

The effect of cold pressure on the compressive strength of the BNT-BT<sub>0.06</sub> piezoelectric ceramic is shown in Figure 8. It can be concluded from Figure 8 that the compressive strength of the piezoelectric ceramic

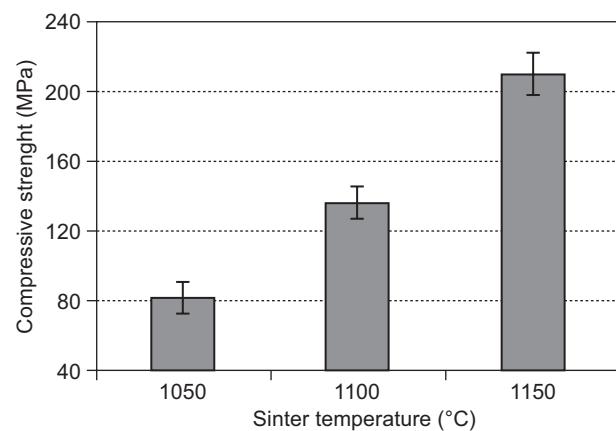


Figure 6. Effect of sintering temperature on the compressive strength of the BNT-BT<sub>0.06</sub> piezoelectric lead-free ceramics (cold pressure: 10 MPa, sintering temperature: 2 h).

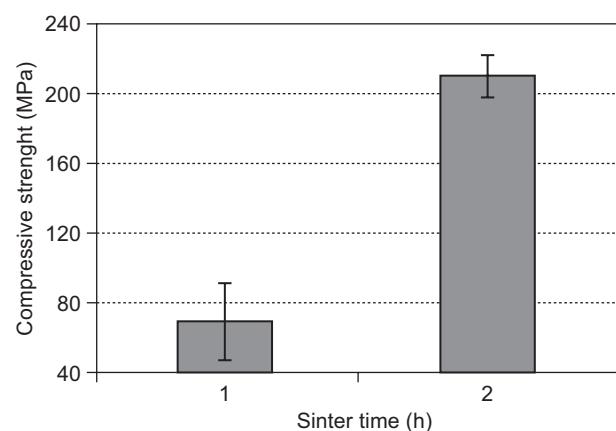


Figure 7. Effect of sintering time on the compressive strength of the BNT-BT<sub>0.06</sub> piezoelectric ceramics (cold pressure: 10 MPa, sintering temperature: 1150°C).

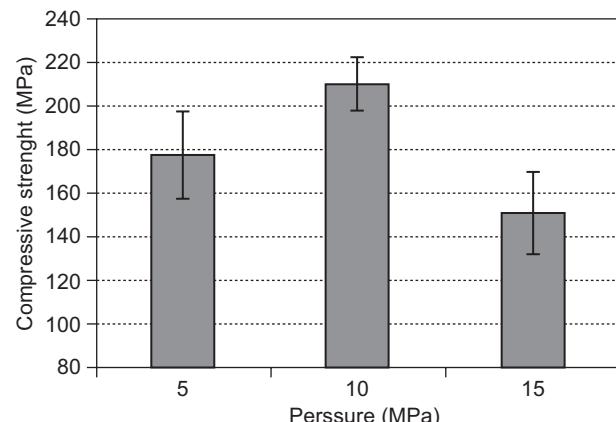


Figure 8. Effect of cold pressure on the compressive strength of the BNT-BT<sub>0.06</sub> piezoelectric ceramic (sintering temperature: 1150°C, sintering time: 2 h).

firstly increased and then decreased with the rise of the cold pressure. For example, the compressive strength of the piezoelectric ceramics increases from 177 to 210 MPa, increasing 15.7 %, while the cold pressure rises from 5 to 10 MPa, as the cold pressure increases further, the compressive strength of the ceramics presents a decreasing trend and dropping to 142 MPa.

The mechanical properties of the BNT-BT<sub>0.06</sub> piezoelectric ceramics are mainly depended on two aspects. On the one hand, the ceramic green body pressed more and more compacted with the rise of cold pressure. This compacted ceramic green body is beneficial for the densification improvement of the ceramic during the sintering processes. Ultimately, the compressive strength of the piezoelectric ceramic is expected to be improved effectively by the increasing of the cold pressure. On the other hand, while the cold pressure excesses a certain value, the ceramic green body is prone to cracking after mold releasing due to the damage of the adhesive film which formed by PVA macromolecule binder under high cold pressure. Furthermore, it can be seen from the morphology observation that the crystal grain size of the piezoelectric ceramic is nano-size dimensions. Due to its high surface energy, the ceramic is easy to crack during the sintering processes [20]. Ultimately, the compressive strength of the piezoelectric ceramics increased firstly and then decreased with the rise of cold pressure.

## CONCLUSIONS

In this study, the BNT-BT<sub>0.06</sub> piezoelectric ceramics were fabricated by solid state reaction method. The microstructure and morphology of the piezoelectric materials were detected by XRD and SEM characterization technologies. The results of XRD investigation showed that the BNT-BT<sub>0.06</sub> compositions present pure tetragonal structure. The SEM observation indicated that the crystal grain size of the piezoelectric ceramics is on the nano-size dimensions and the densification of the BNT-BT<sub>0.06</sub> ceramics increases with the rise of sintering temperature and time. The study on the compressive mechanical characteristics showed that the compressive strength of the BNT-BT<sub>0.06</sub> piezoelectric ceramics increases with the rise of sintering temperature and sintering time. The change behavior of the compressive strength with the rise of cold pressure presents increasing firstly and then decreases. It reaches the largest value at 10 MPa of cold pressure.

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