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The effects of sintering temperature and poling condition on the piezoelectric properties of $0.935(Bi_{0.5}Na_{0.5})TiO_3$ - $0.065BaTiO_3$ ceramics

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The $0.935(Bi_{0.5}Na_{0.5})$ TiO_3 $-0.065BaTiO_3$ (abbreviated as BNT6.5BT) lead-free ceramics were prepared by conventional solid state sintering technique. The effects of sintering temperature (1150–1200 °C) and poling condition on its piezoelectric properties were examined. Piezoelectric properties like the piezoelectric constant (d_{33}) and electromechanical factors (k_p, k_t) depend on the poling field and poling temperature, whereas different poling times, in the 5–30 min range, were not observed to have any significant effect on the piezoelectric properties. With respect to piezoelectric properties, the chosen sintering temperature range is suitable for BNT6.5BT ceramics.

Keywords: *lead free ceramics, sintering temperature, Poling condition, dielectric and piezoelectric properties*

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1. Introduction

Lead zirconate titanate, abbreviated as PZT, ceramics have been widely used in piezoelectric applications because of their excellent piezoelectric and electrical properties [1, 2]. However, because of the toxicity of lead oxide, the use of these ceramics has caused serious environmental problems [3]. Therefore, there is a great need to develop lead-free piezoelectric ceramics with good piezoelectric properties in order to substitute them for the lead-containing ceramics in various applications.

Bismuth sodium titanate $(Bi_{0.5}Na_{0.5})TiO_3$ (abbreviated as BNT) is considered to be an excellent candidate material for lead-free piezoelectric ceramics [4]. The BNT ceramic exhibits high remnant polarization P_r = 38 μC/cm^2, a high Curie temperature T_c = 320 °C and a phase transition point from ferroelectric to antiferroelectric T_d = 120 °C. However the use of BNT in piezoelectric applications is limited by the difficulty of poling this ceramic, due to its large coercive field (73 kV/cm).

To improve the piezoelectric and dielectric properties of BNT ceramics, various BNT-based solid solutions have been developed [5–9]. Among these solid solutions, $(1\text{-}x)(Bi_{0.5}Na_{0.5})TiO_3$ $-xBaTiO_3$ (BNT-xBT) system has been attracted a great deal of attention owing to the existence of a rhombohedral-tetragonal morphotropic phase

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boundary (MPB) near x = 0.06–0.07 [10]. Compared with pure BNT, the BNT-xBT ceramics reveal substantially improved poling and piezoelectric properties near the MPB.

A poling operation is a requisite process to yield desired piezoelectric performances of BNT-based solid compositions. Therefore it is interesting to investigate the influence of the poling and sintering conditions on the piezoelectric properties of these compositions.

In this paper, the influence of the poling condition and sintering temperature on the piezoelectric properties of $0.935(Bi_{0.5}Na_{0.5})TiO_3$ - $0.065BaTiO_3$(BNT6.5BT) lead-free ceramics prepared by solid state route was studied.

2. Experimental procedure

The ceramic samples were prepared by solid state sintering from carbonates Na_2CO_3 (reagent grade, Sigma-Aldrich, 99,5 %), $BaCO_3$ (reagent grade, Sigma-Aldrich, 99 %), and oxides Bi_2O_3 (Aldrich, 99,9 %), and TiO_2 (Riedel-de Haen). The powders were weighed respectively according to BNT6.5BT composition then mixed by planetary milling in ethanol using agate balls as milling media for 1 h. The milled powders were calcined at 825 °C for 4 h in an air atmosphere. After calcining, the powders were rehomogenised by planetary milling in ethanol using agate balls for 1 h and then isostatically pressed. The compacted samples were sintered between 1150 to 1200 °C for 4 h in air atmosphere. The as-prepared samples were cut into disk shaped samples 12 mm in diameter and 1 mm in thickness.

The crystal structures of the sintered ceramics were determined with an X-ray diffractometer (RIGAKU Miniflex) using Cu Kα radiation. The microstructure of the sintered ceramics was observed with scanning electron microscope (SEM, HITACHI, S-3500N).

The specimens were polished and electroded with a silver paste by a screen-printing technique. This silver paste was dried at 150 °C for 15 min and fired at 600 °C for 2 min. The samples were then poled for piezoelectric measurements. The poling apparatus consists of a silicone oil bath and an external power supply; the voltage was applied stepwise until the maximum field was reached. The different poling conditions (temperature, voltage, time) are detailed in the next paragraph. The piezoelectric coefficient d_{33} was measured using a piezoelectric d_{33}-meter (Piezotest PM 200) at a frequency of 100 Hz. The electromechanical coupling factors k_p and k_t were measured by the resonance and anti-resonance technique using an impedance analyzer (HP 4194A). P-E hysteresis loops were obtained by Radiant Precision Workstation ferroelectric testing system at room temperature.

3. Results and discussions

The X-ray diffraction patterns of BNT-6.5BT ceramics sintered at 1150, 1160, 1180 and 1200 °C respectively are shown in Fig. 1.

These patterns show an almost pure perovskite structure phase, whatever the temperatures, with a small amount of $Na_2Ti_3O_7$ phase. All the samples were sintered in a protective BNT bed in order to prevent Bi_2O_3 evaporation. X-EDS analysis did not reveal any significant defect of bismuth. It cannot be excluded that slight bismuth evaporation occurs, resulting in the appearance of $Na_2Ti_3O_7$ phase.

A fine scanning of ceramics in the 2 theta ranges 39–41° and 45–48° respectively is shown inset the Fig. 1. It can be clearly seen that the (003),(021) reflections of rhombohedral phase and (200),(002) reflections of tetragonal phase appear near 39.84° and 46.51° respectively. This result shows that all samples exhibit co-existence of a rhombohedral-tetragonal phase. The specific diffraction peaks of each phase are located at the same angles as the corresponding peaks of a homogeneous morphotropic composition. Thus, most probably, the observed two crystallographic phases are indicative of a second order transition.

Fig. 2 shows the SEM micrographs of BNT-6.5BT ceramics sintered for 4 hours at 1150, 1160, 1180 and 1200 °C respectively.

All the ceramics are almost fully densified whatever the temperature. At 1150 and 1160 °C, the microstructures consist of fine and homoge-

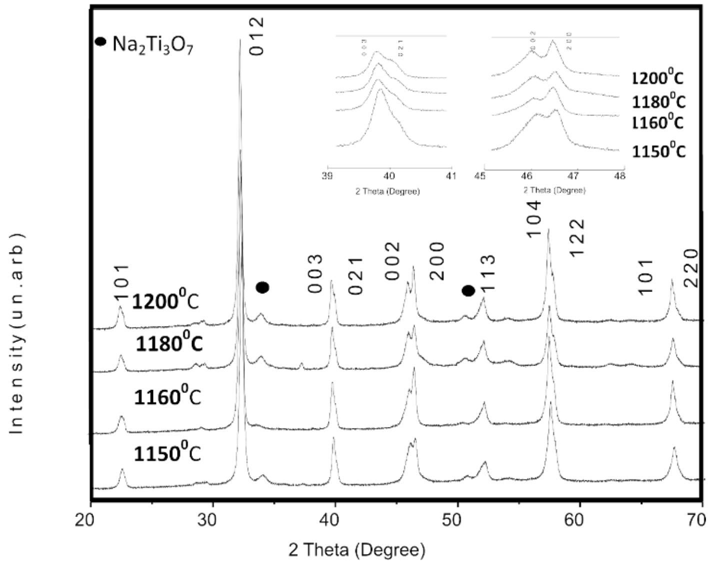

Fig. 1. XRD patterns of 0.935 $(Bi_{0.5}Na_{0.5})TiO_3$ -0.065$BaTiO_3$ ceramics sintered at different temperatures.

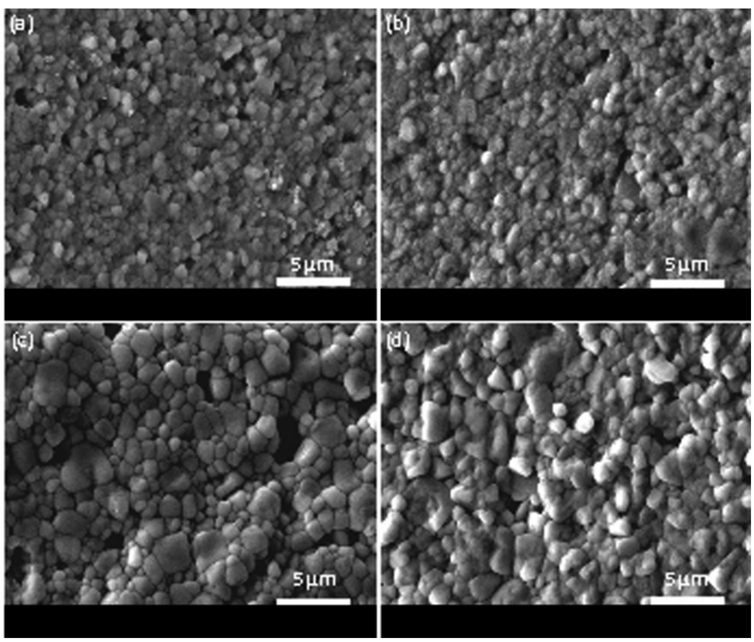

Fig. 2. SEM micrographs of BNT-6.5BT ceramics sintered at (a) 1150 °C, (b) 1160 °C, (c) 1180 °C and (d) 1200 °C.

neous grains with an average grain size close to 1 µm. Some slight porosity is observed and consists of small intergranular pores. This porosity is consistent with the value of the apparent density ρ measured by 'Archimedes' Principle. Increasing the sintering temperature up to 1180–1200 °C does not favor the densification state but induces significant grain growth. This last one conducts to the appearance of coarse grains (∼3–4 µm). The density of all specimens is between 97.1 and 97.6 %.

Fig. 3 shows the P-E hysteresis loops of BNT-6.5BT ceramics sintered at different temperatures.

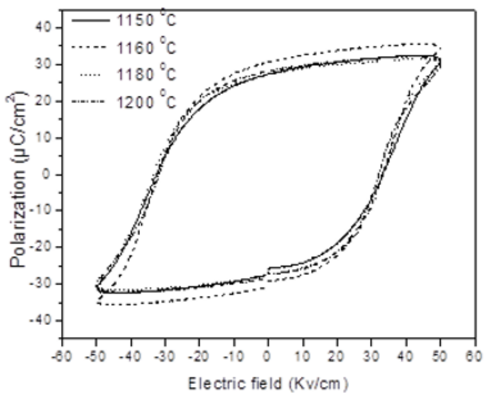

Fig. 3. P-E hysteresis loops of 0.935($Bi_{0.5}Na_{0.5}$)TiO_3 - 0.065$BaTiO_3$ ceramics sintered at different temperatures.

These hystereses were achieved at room temperature. The saturated loops confirm the ferroelectric nature of the specimens. The values of the remnant polarization P_r are 27, 31, 27 and 29 µC/cm^2 for specimens sintered at 1150, 1160, 1180 and 1200 °C respectively. The coercive field values of all samples are lower than these of the $Bi_{0.5}Na_{0.5}TiO_3$ ceramics (about 73 kV/cm) at room temperature.

If we are to understand how the poling condition influences the piezoelectric properties of the ceramics, we must first start by poling the ceramics under a DC field in the 30–50 kV/cm range at a poling temperature of 60 °C for 15 min. It was found that the poling field affected the piezoelectric properties. The piezoelectric constant d_{33} increases monotonically with the poling field. Increasing the strength of the poling field to 55 kV/cm did not enhance the piezoelectric properties.

Moreover applying a poling field strength greater than 55 kV/cm leads to electrical breakdown, for some specimens. Thus, the poling field of 50 kV/cm was found to be the optimal field for the specimens.

In second tests we set the strength of the poling field to 50 kV/cm and the poling temperature was varied from 25 to 100 °C for 10 min.The dependency of the piezoelectric constant d_{33} and electromechanical factors (k_p and k_t) on the poling temperature for the ceramics sintered at 1150, 1160, 1180 and 1200 °C are shown in Figs 4 and Fig. 5 respectively.

From Fig. 4(a)-(d), we can see that the piezoelectric constant d_{33} is almost constant in the 25–70 °C range, for the specimens sintered at 1150, 1160, 1180 and 1200 °C and then decreases in the 70–100 °C range of the poling temperature. As the poling field is not applied during the decrease of temperature, reorientation of ferroelectric domains is most likely to occur at the highest temperature values i.e. 70–100 °C. For poling temperatures in the 25–70 °C range, the electromechanical factors (k_p and k_t) seem almost unchanged but slightly decrease with the poling temperature between 70–100 °C, for all the samples (Fig. 5). In general they display the same variation like the piezoelectric constant d_{33}.

A low value of the piezoelectric constant was observed at a poling temperature of 120 °C (d_{33} = 37 and 45 pC/N), for the specimens sintered at 1150 and 1160 °C respectively. These low values of the piezoelectric constant can probably attributable to the relatively low depolarization temperature of the BNT-xBT solid solution near Morphotropic Phase Boundary (MPB) [11, 12]. 120 °C is a temperature that is close to a first allotropic transition of BNT-xBT materials (ferroelectric- antiferroelectric transition) which contributes to some moderate depolarisation and which explains why the measurement values for the piezoelectric constant are rather low. In addition the sample specimens are easily broken down when the poling temperature is over 100 °C, because of the increase of electrical conductivity. Therefore, 50–70 °C was choosen as the most suitable poling temperature range for our BNT-6.5BT ceramics.

Varying the poling time in the 5–30 min range did not enhance the piezoelectric properties under 50 kV/cm at 60 °C. For example, the dependency of the piezoelectric constant d_{33} on thepoling time for the specimen sintered at 1160 °C is shown in Fig. 6.

Under a poling field of 50 kV/cm, in the poling temperature range of 50–70 °C for 10 min, the ceramics sintered at 1150–1200 °C have good

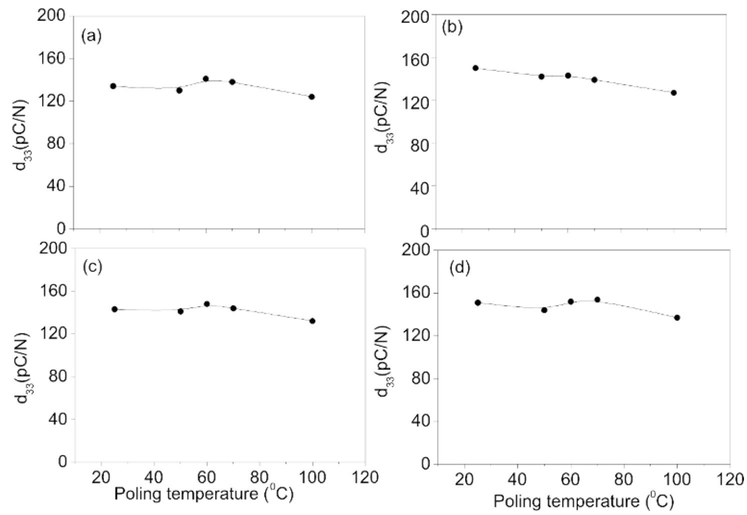

Fig. 4. Piezoelectric constant d_{33} vs poling temperature of BNT-6.5BT ceramics sintered at different temperature: (a) 1150 °C, (b) 1160 °C, (c) 1180 °C and (d) 1200 °C (Poling field = 50 kV/cm and poling time = 10 min)

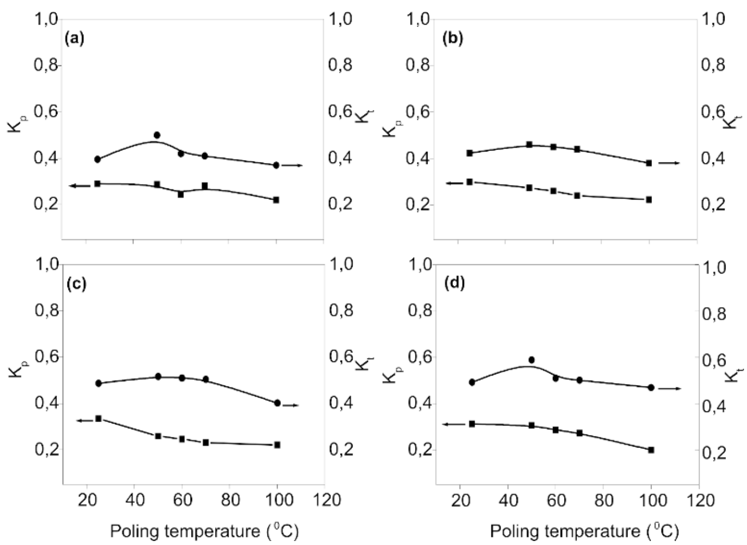

Fig. 5. Electromechanical factors (k_p and k_t) vs poling temperature of BNT-6.5BT ceramics sintered at different temperature : (a) 1150 °C, (b) 1160 °C, (c) 1180 °C and (d) 1200 °C (Poling field = 50 kV/cm and poling time = 10 min)

piezoelectric performances. The piezoelectric coefficient d_{33}, the planar coupling factor k_p and the thick coupling factor k_t are found to be over 130 pC/N, 0.24 and 0.41 respectively. These relatively high piezoelectric and electromechanical parameter values can be attributed to the MPB composition. Ceramics differ only in their microstructure (fine grained ceramics for sintering temperatures between 1150–1160 °C and slightly coarse grained ceramics (3–4 μm) for sintering temperatures between 1180–1200 °C). One can expect that coarse microstructures favour polarization and depolarization behaviour, due to less pining of domain walls. Piezoelectric characteristics do not seem to be affected by the sintering temperatures, indicating that piezoelectric domain structure is not affected by such microstructural modification.

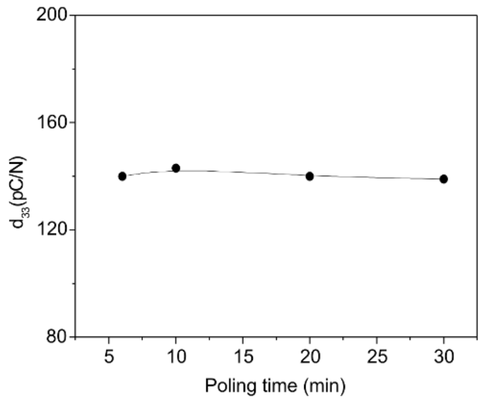

Fig. 6. Piezoelectric constant d_{33} vs poling time of BNT-6.5BT ceramics sintered 1160 °C.

4. Conclusions

In conclusion, the effects of poling condition on the piezoelectric properties of BNT-6.5BT ceramics were studied. It was found that the piezoelectric properties depend on both the poling field and the poling temperature. However, poling times in the 5-30 min range were not observed to be significant. For BNT-6.5BT ceramics, the preferred poling temperature range is 50-70 °C and the preferred poling field strength is 50 kV/cm. With respect to piezoelectric properties, the chosen sintering temperature range is suitable for BNT6.5BT ceramics.

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