SOLID STATE SINTERING PREPARED $0.935(Bi_{0.5}Na_{0.5})TiO_3$-$0.065BaTiO_3$ LEAD FREE CERAMICS: EFFECT OF POLING CONDITIONS

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In this work , the influence of poling conditions (poling field, poling temperature and poling time) on the piezoelectric properties of $0.935(Bi_{0.5}Na_{0.5})$ TiO_3-$0.065BaTiO_3$ (BNT6.5BT) lead-free ceramics was examined. Piezoelectric properties like piezoelectric constant (d_{33}) and electromechanical factors (K_p ,K_t) depend on poling field and poling temperature, whereas different poling times, in the 5-30 min range, were not observed to have significant effect on the piezoelectric properties.

INTRODUCTION

Bismuth sodium titanate $(Bi_{0.5}\ Na_{0.5}\ )TiO_3$ (abbreviated as BNT) is one of important lead-free piezoelectric ceramics with perovskite structure [1]. As BNT ceramic exhibits a strong ferroelectricity and high Curie temperature T_c = 320 °C, it has been considered to be a promising candidate of lead-free piezoelectric materials to replace the widely used PZT-based piezoelectric ceramics. However the use of BNT in piezoelectric application is limited by the difficulty to pole this ceramic due to its large coercive field (73 kV/cm).

To improve piezoelectric and dielectric properties of BNT ceramics, various BNT-based solid solutions have been developed [2-6]. Among these solid solutions, (1-x) $(Bi_{0.5}Na_{0.5}\ )TiO_3$-$x$$BaTiO_3$ (BNT-xBT) system has been attracted a great deal of attention owing to the existence of a rhombohedral-tetragonal morphotropic phase boundary (MPB) near x = 0.06-0.07 [7]. Compared with pure BNT, the BNT-xBT ceramics reveal substantially improved poling and piezoelectric properties near the MPB.

It is well known that piezoelectric ceramics do not have piezoelectricity until the random ferroelectric domains are aligned through the poling process. Therefore, the poling process significantly affected the piezoelectric properties of the ceramics. Namely the poling process is a very crucial step in processing of piezoelectric ceramics [8-9]. Therefore it is interest to investigate the influence of the poling condition on the piezoelectric properties of theses compositions.

The purpose of this paper is to investigate the influence of the poling conditions on the piezoelectric properties of $0.935(Bi_{0.5}Na_{0.5})TiO_3$-$0.065BaTiO_3$ (BNT6.5BT) lead-free ceramics.

EXPERIMENTAL

A conventional powder solid-state reaction method was used to prepare the samples: weighted powder of Na_2CO_3, $BaCO_3$, Bi_2O_3 and TiO_2 (at least of 99% purity) were ball-milled by planetary milling in ethanol for 1h. After calcining at 825°C for 4 h in air atmosphere, the powder was ball-milled again and then isostatically pressed at 3000 bars for 5 min. The compacted samples were sintered at 1160°C for 4 h in air atmosphere. The as-prepared samples were cut in disks shape of 12 mm in diameter and 1mm in thickness.

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 (voltage, temperature and time) are detailed in the next paragraph.

The piezoelectric coefficient d_{33} was measured using a piezoelectric d_{33}-meter (Priestest 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).

RESULTS AND DISCUSSION

Figures 1 and 2 show the X-ray diffraction (XRD) pattern and microstructure of BNT-6.5BT ceramics respectively [10].

The XRD pattern was determined by means of X-ray diffractometer (RIGAKU Miniflex) using Cu Kα radiation in the 2θ range of 20-70°. From figure.1, it can be seen that the sample displays a pure perovskite structure phase. 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 the sample exhibit co-existence of a rhombohedral-tetragonal phase.

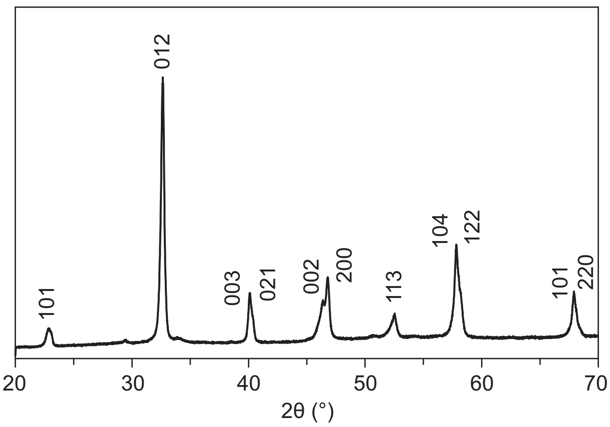

Figure 1. XRD patterns of 0.935($Bi_{0.5}Na_{0.5}$)TiO_3-0.065$BaTiO_3$ ceramic sintered at 1160°C.

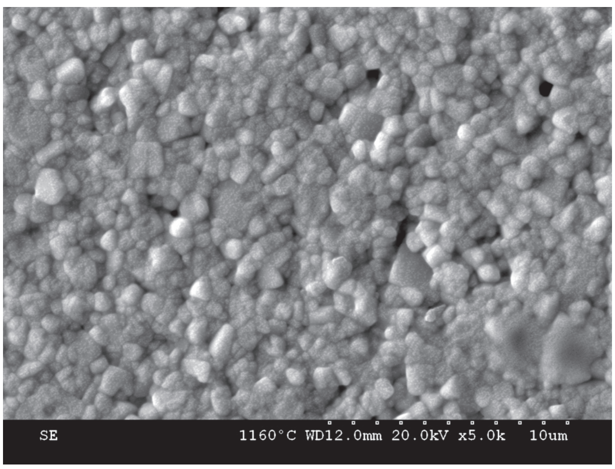

Figure 2. SEM micrograph of BNT-6.5BT ceramic sintered at 1160°C.

The SEM micrograph of BNT-6.5BT ceramics indicated in figure 2 was observed with scanning electron microscope (SEM, HITACHI,S-3500N). It can be seen that the ceramic was densified. The microstructure consists of fine and homogeneous grains with an average grain size close to 1µm. Some slight porosity is observed and consists of small intergranular pores. The density was measured by Archimedes' method and was about 97.6 %.

Figure 3 shows typical (P-E) hysteresis loop of the ceramics obtained by Radiant Precision Workstation ferroelectric testing at room-temperature. The saturated P-E loop confirms the ferroelectric nature of the specimens. It can be seen that the values of remnant polarization P_r and coercive field E_c are about 31 µC/cm^2 and 33 KV/cm respectively.

For revealing the influence of poling condition on the piezoelectric properties of the ceramics, we have started by poling the ceramics under poling field in the range of 30-50 KV/cm at temperature poling of 60°C

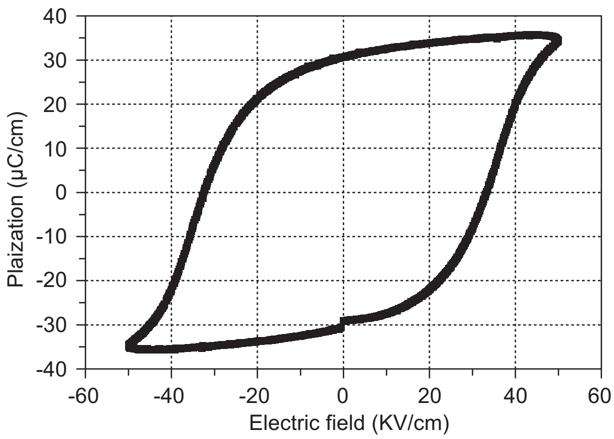

Figure 3. Hysteresis loop of BNT-6.5BT ceramic measured at room-temperature.

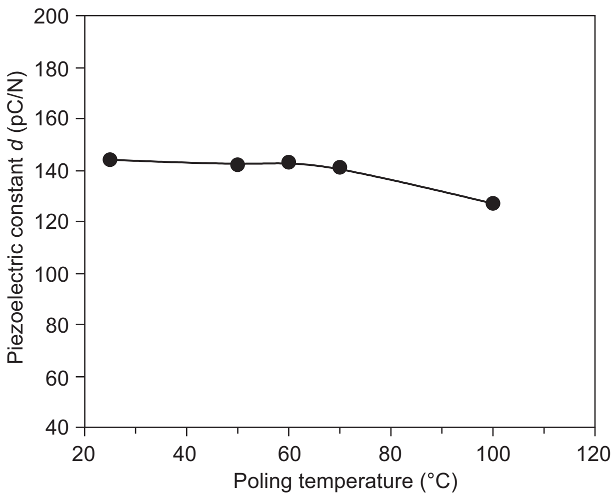

Figure 4. Piezoelectric constant d_{33} vs poling temperature (Poling field = 50 KV/cm and poling time = 10 min).

for 15 min. It was found that the poling field affected the piezoelectric properties. The piezoelectric constant d_{33} increases monotonously with poling field. Further increase of poling field did not enhance the piezoelectric properties. Moreover, the application of the poling field over 55 KV/cm leads to electrical break-down of some specimens. Thus, the poling field of 50 KV/cm was found to be the optimal field for the specimens.

In second time we have fixed a poling field at 50 kV/cm and the poling temperature ranges from 25 to 100°C for 10 min.The dependency of piezoelectric constant d_{33} and electromechanical factors (k_p and k_t) according the poling temperature for the ceramics are shown in figures 4 and 5 respectively.

From Figure 4, we can show that the piezoelectric constant d_{33} is almost constant in the range of 50-70°C for the specimens and then decreases in the range of 70-100°C of poling temperature. As the poling field is not applied during the decrease of temperature, re-orientation of ferroelectric domains likely occurs for the highest temperature values i.e. 70-100°C. In the range of 50-70°C of temperature poling, the electromechanical factors (k_p and k_t) seem almost unchanged but slightly decrease with the poling temperature from 70-100°C for the samples (Figure 5). In general they display the same variation like the piezoelectric constant d_{33}.

Also, it was found that the dielectric constant and the dielectric loss tangent display a similar variation like piezoelectric constant and electromechanical coupling factors, not obvious change shown in the poling temperature range of 50-70°C (see Figure 6).

A low value of the piezoelectric constant was observed at poling temperature of 120°C (d_{33}= 45 pC/N). This low value of the piezoelectric constant can probably allotted to the relatively low depolarization temperature of the BNT-xBT solid solution near Morphotropic Phase Boundary (MPB) [11-12]. 120°C is a value of temperature close to a first allotropic transition of BNT-xBT materials (ferroelectric-antiferroelectric transition) which one participates to some moderate depolarisation and then explains the slight low values of measured piezoelectric constant. In addition the specimens are easily broken down when the poling temperature is over 100°C because of the increase of electrical conductivity. With respect to that the poling temperature range 50-70°C is choosing for our BNT--6.5BT ceramics.

Table 1. Piezoelectric properties under 50 KV/cm at poling temperature of 60°C for 10 min.

Parameter	Symbol	Unit	Value
Piezoelectric constant	d_{33}	pC/N	144
Planar coupling factor	K_p	–	0.26
Thickness coupling factor	K_t	–	0.45

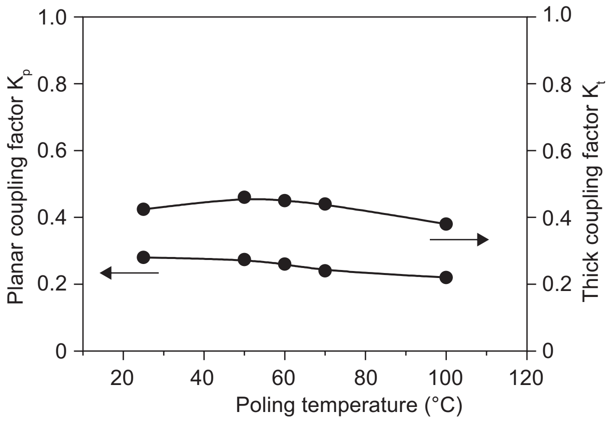

Figure 5. Electromechanical coupling factors (k_p and k_t) vs poling temperature of BNT-6.5BT ceramics (Poling field = = 50 KV/cm and poling time = 10 min).

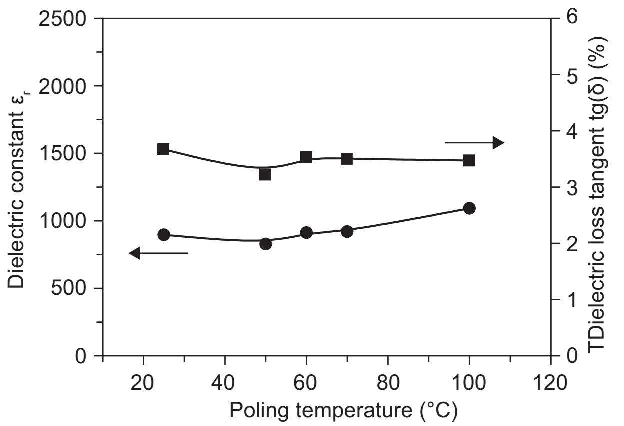

Figure 6. Dielectric constant and the dielectric loss tangent vs poling temperature of BNT-6.5BT ceramics (Poling field = = 50 KV/cm and poling time = 10 min).

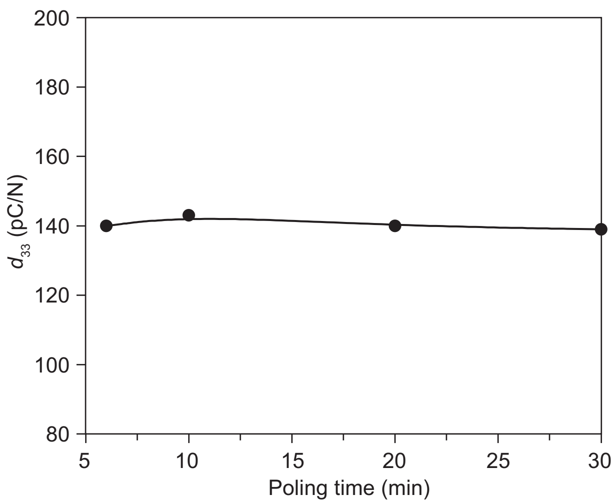

Figure 7. Piezoelectric constant d_{33} vs poling time of BNT--6.5BT ceramics (Poling field = 50 KV/cm and poling temperature = 60°C).

A variation on the poling time in the range 5-30 min. does not enhance the piezoelectric properties under 50 KV/cm at 60°C. For example the dependency of piezoelectric constant d_{33} on poling time is shown in Figure 7.

Under poling field of 50 KV/cm at poling temperature range of 50-70°C for 10 min the BNT-6.5BT ceramics have a good 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 140 pC/N, 0.24 and 0.44 respectively. For example, Tab. 1 summarizes the piezoelectric properties under 50 KV/cm at poling temperature of 60°C for 10 min.

These relatively high piezoelectric and electromechanical activities can be attributed to MPB composition [13].

CONCLUSION

In conclusion, the effect of poling conditions on the piezoelectric properties of BNT-6.5BT ceramics was studied. It was found that the piezoelectric properties depend on poling field and poling temperature, while no remarkable effect of the poling time was detected in the range of 5-30 min. The poling field of 50KV/cm, poling temperature range of 50-70°C and poling time of 10 min are the preferred poling conditions for BNT-6.5BT lead free ceramics.

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