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

HAMZA LIDJICI, MOHAMED RGUITI**, FARIDA HOBAR*, CHRISTIAN COURTOIS**, ANNE LERICHE**

Laboratoire d'étude et de développement des matériaux diélectriques et semiconducteurs, Université de Laghouat, Route de Ghardaïa B.P.37G. Laghouat, Algérie
**Laboratoire des microsystèmes et instrumentation, Département d'électronique, Université Mentouri de Constantine, Route Ain El bey, Constantine, Algérie*
***Laboratoire des Matériaux et Procédés, Université de Valenciennes et du Hainaut-Cambrésis, Z.I. du Champ de l'Abbesse 59600 Maubeuge, France*

E-mail: h.lidjici@mail.lagh-univ.dz

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The effects of sintering temperature on structure, microstructure, dielectric and piezoelectric properties of $0.935(Bi_{0.5}\,Na_{0.5})TiO_3$ -0.065$BaTiO_3$ (BNT6.5BT) lead free ceramics prepared by solid sintering technique at 1150-1200°C were investigated. The X-ray diffraction patterns showed that all of the BNT6.5BT ceramics exhibited a single perovskite structure with the co-existence of the rhombohedral and tetragonal phase. A fine and homogeneous grains were observed for samples sintered at 1150 and 1160°C and the increase of the sintering temperature up to 1180-1200°C induces significant grain growth with the appearance of coarse grains. The dielectric constant- temperature curves of the compositions exhibited strong dispersion with the increasing temperature, and the dielectric loss increased dramatically while the temperature over 230°C. The lowest value of depolarization temperature (T_d) was found at samples sintered at 1160°C. The values of remnant polarization P_r obtained at room temperature are 31 and 29 µC/cm^2 for specimens sintered at 1160°C and 1200°C respectively. At room temperature, BNT6.5BT ceramics sintered at 1180°C exhibited good performances: dielectric constant was 833 at 1 KHz, thick coupling factor k_t was 0.52 and the k_t/k_p ratio was 2.08. Therefore, the ceramics can be suitable for ultrasonic transducers in commercial applications.

INTRODUCTION

The lead-based piezoelectric materials like (Pb,Zr) TiO_3 (abbreviated as PZT) are the most widely used in piezoelectric applications [1, 2]. However, these materials cause serious environmental problems because of the toxicity of the lead oxide and its high vapor pressure during the sintering process, which is adversative to the sustainable development and the environmental protection [3]. Consequently, many researches are today carried out to develop lead-free piezoelectric materials that would present so good piezoelectric properties such as PZT ceramics.

Bismuth sodium titanate $(Bi_{0.5}\,Na_{0.5})TiO_3$ (abbreviated as BNT) is considered to be an excellent candidate of lead-free piezoelectric ceramics [4]. The BNT ceramic exhibits a large 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 = 200°C. 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 [5-10]. Among these solid solutions, $(1\text{-}x)(Bi_{0.5}\,Na_{0.5})TiO_3$ -$x BaTiO_3$ (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 = 0.6 - 0.7 [11].

Compared with pure BNT, the BNT-xBT ceramics reveal relatively high piezoelectric properties and low coercive field near the MPB. However, it is appeared that dielectric and piezoelectric properties depend on the ceramic process conditions and particularly on the sintering temperature.

In this paper, the dielectric and piezoelectric properties of $0.935(Bi_{0.5}\,Na_{0.5})TiO_3$ -0.065$BaTiO_3$ (BNT6.5BT) lead-free ceramics sintered at different tempe-ratures are studied.

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, 99.0 %),and oxides Bi_2O_3 (Aldrich, 99.9 %) , and TiO_2 (Riedel-dehaen). 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 air atmosphere. After calcining, the powders were rehomogenised by planetary milling in ethanol using agate balls for 1 h and then isostatically pressed. The preparation procedure can be seen in Figure 1.

The compacted samples were sintered between 1150 to 1200°C for 4 h in air atmosphere. The as- prepared samples were cut in disks shape of 12 mm in diameter and 1 mm in thickness.

The crystal structures of sintered ceramics were determined by means of 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 and after were poled in a silicone oil bath at 60°C under a DC field of 5 kV/mm for 10 min for piezoelectrics measurements. 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.

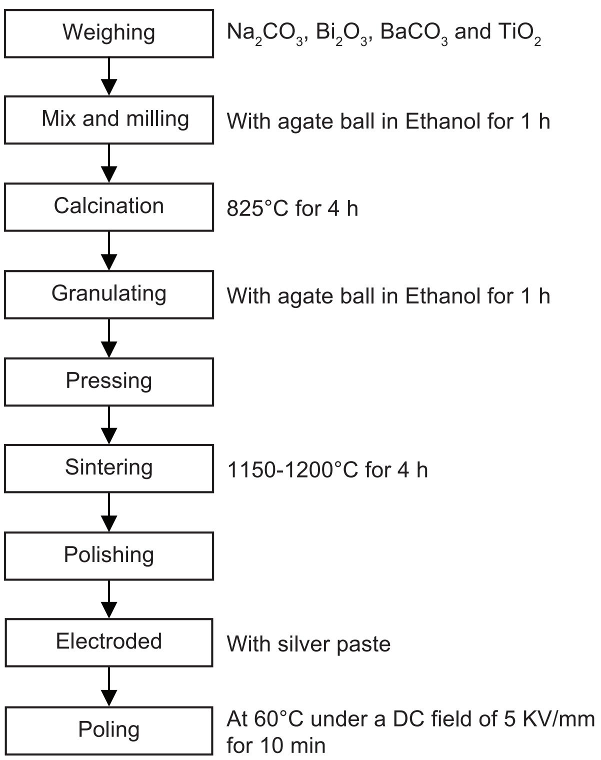


Figure 1. Flowchart of samples preparation.

Temperature dependence of dielectric properties of the unpoled samples was investigated using impedance analyzer (HP 4194A)in the temperature range of 30-450°C.

RESULTS AND DISCUSSION

The X-ray diffraction patterns of BNT-6.5BT ceramics sintered at 1150, 1160, 1180 and 1200°C respectively are shown in Figure 2.

These patterns show an almost pure perovskite structure phase whatever the temperatures with some slight amount of $Na_2Ti_3O_7$ phase. At room temperature, the $Bi_{0.5}$ $Na_{0.5}$ TiO_3 system is in rhombohedral phase and $BaTiO_3$ is in tetragonal phase.

According to the literature, there is a rhombohedral-tetragonal MPB in their solid solution near 0.935($Bi_{0.5}$ $Na_{0.5}$)TiO_3 -0.065$BaTiO_3$ composition. X-ray diffraction pattern of the composition at MPB is characterized with separated presence of two peaks to (003)/(021) at about 39.84° and splitting of the peak to (202) planes at around $46{,}51^0$. In this work, further XRD analysis performed in the 2 theta ranges of 39-41° and 45-48° is shown in the inset of Figure 2. Pattern exhibits the feature of peak splits at corresponding diffraction angles, indicating co-existence of tetragonal and rhombohedral angles phases in BNT-6.5BT ceramics.

Figure 3 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

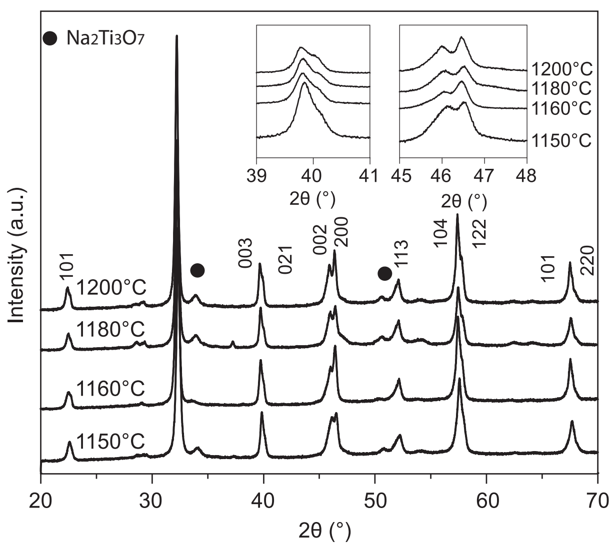


Figure 2. XRD patterns of 0.935($Bi_{0.5}Na_{0.5}$)TiO_3 -0.065$BaTiO_3$ ceramics sintered at different temperatures.

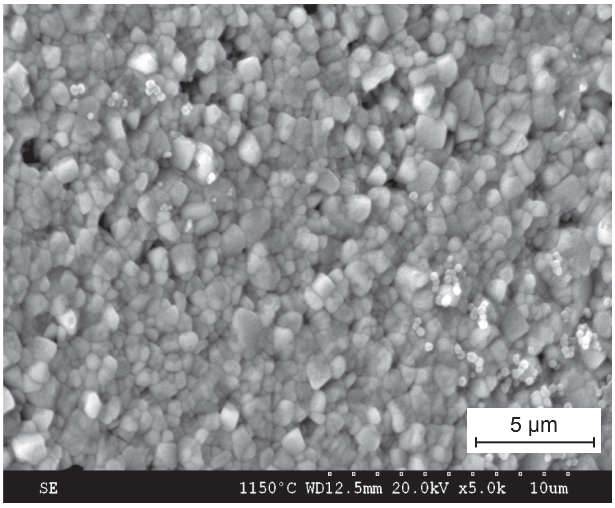
1160°C the microstructures consist of fine and homogeneous grains with an average grain size close to 1 µm. Some slight porosity is observed and consists of small intergranular pores. This porosity is consistent with the value of the apparent density *r* measured by Archimedes' method. An increase of 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 (~3-4µm). The density of all specimens is between 97.1 and 97.6 % (see Table 1).

Figure 4 shows the P-E hysteresis loops of BNT-6.5BT ceramics sintered at different temperatures. These hystereses were achieved at room temperature. The saturated loops confirm the ferroelectric nature of the specimens.

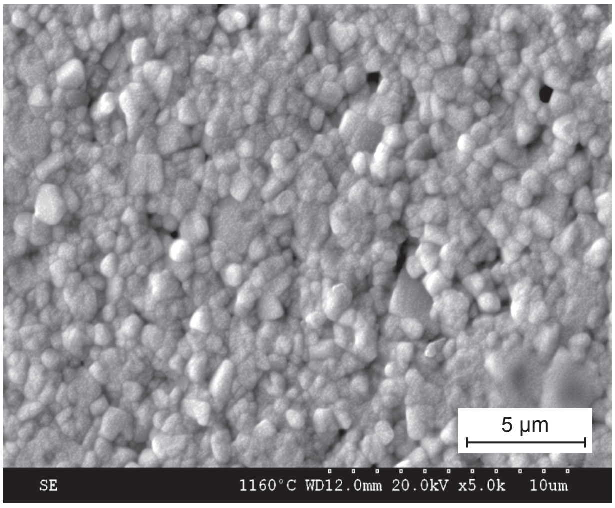
The values of remnant polarization P_r are 27, 31, 27 and 29 $\mu C/cm^2$ for specimens sintered at 1150, 1160, 1180 and 1200°C respectively. The specimen sintered at 1160°C exhibits the maximum value and has the good squareness loops. The high values of remnant polarization P_r in the system can be attributed to increase in domain wall motion that switches domains and hence affects the polarization. The coercive field of all samples is between 31.98 and 33.75 kV/cm. These values are lower than the value of the $Bi_{0.5}$ $Na_{0.5}$ TiO_3 ceramics (about 73 kV/cm) at room temperature.

Table 1. Density, dielectric, piezoelectric and mechanical properties of BNT-6.5BT ceramics sintered at different temperatures.

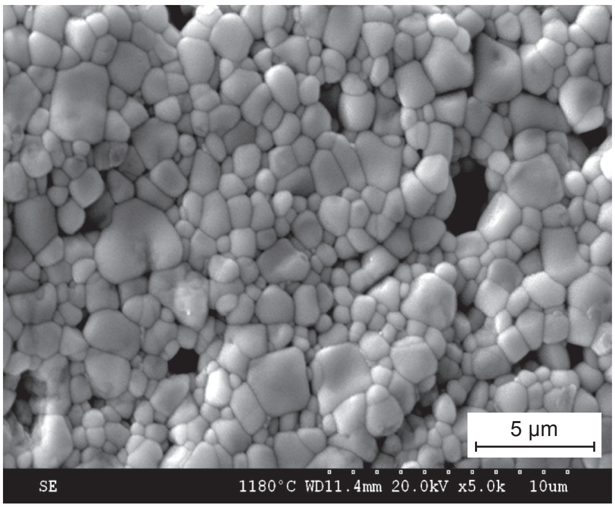
Sintering temperature (°C)	1150	1160	1180	1200
Density (%)	97.3	97.6	97.3	97.1
Dielectric Constant ε_r (at 1 KHz)	830	910	833	864
Dielectric loss tg(δ) (at 1 KHz)	0.036	0.035	0.037	0.032
Depolarization temp. (T_d) (°C)	160	155	166	162
Piezoelectric constant d_{33} (pC/N)	141	145	148	155
Planar coupling factor K_p	0.24	0.26	0.25	0.28
Thick coupling factor K_t	0.40	0.45	0.52	0.51
The ratio of K_t/K_p	1.62	1.73	2.08	1.78



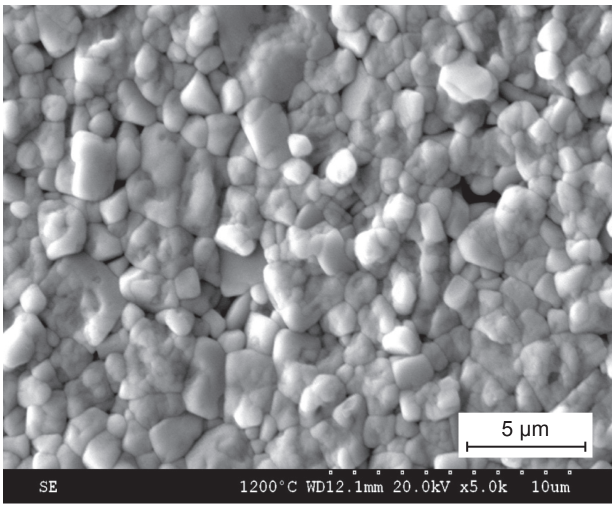
a) 1150°C



b) 1160°C



c) 1180°C



d) 1200°C

Figure 3. SEM micrographs of BNT-6.5BT ceramics sintered at a) 1150°C, b) 1160°C, c) 1180°C and d) 1200°C.

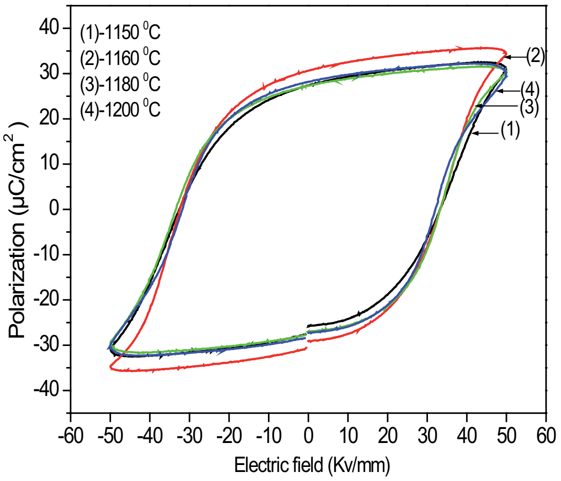


Figure 4. P-E hysteresis loops of $0.935(Bi_{0.5}Na_{0.5})TiO_3$ -0.065 $BaTiO_3$ ceramics sintered at different temperatures.

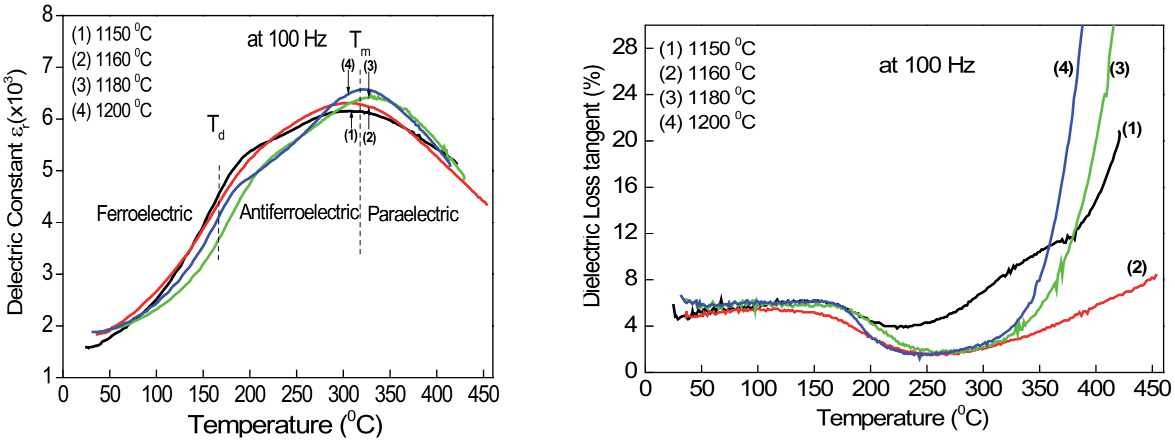
Figure 5 shows the temperature dependence of dielectric constant ε_r and dielectric loss tg(δ) at 100 Hz of 6.5 BNT-BT ceramics sintered at different temperatures. It can be seen that the three phases of ferroelectric, antiferroelectric and paraelectric exist in different temperature ranges for all samples which agrees with the result obtained by Takenaka et al [12].Here, the temperature where the transition between ferroelectric and antiferroelectric phase is called depolarization temperature (T_d) and the temperature corresponding to maximum value of dielectric constant is called maximum temperature (T_m). Above T_d, the ceramics will be depolarized. The values of the depolarization temperature have not an evident change with sintering temperature and the lowest value was observed for the ceramics sintered at 1160°C (see Table 1).

The dielectric constant at maximum temperature increases with increase of sintering temperature. The dielectric loss tg(δ) increases with the increase of temperature particularly beyond 230°C.The increase in dielectric loss tg(δ) at higher temperature might be due to increased electrical conductivity. The important mechanism of ionic conductivity in these ceramics is the movement of ions which are the current carriers. It has been long known that the alkali ion is a good current carrier in ceramics; therefore this ion plays an important role in the conductivity of BNT-BT ceramics, since the Na^+ ions move easily upon heating, resulting in the increase in conductivity with increasing temperature.

The detailed dielectric and electromechanical properties of BNT-6.5BT ceramics sintered at different temperatures are shown in Table 1. The 6.5 BNT-BT ceramics sintered at different temperatures all have applicable electrical properties. From the Table 1 the dielectric constant ε_r (1 KHz) and dielectric loss tg(δ) (1 KHz) do not have a remarkable change with sintering temperatures.

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 0.39 respectively for all sintering temperatures. The planar electromechanical coupling factor k_p has a small change when sintering temperature is below 1200°C. The larger value of thick electromechanical coupling factor k_t is obtained when BNT-6.5BT ceramics are sintered at temperature1180°C and 1200°C (0.51 and 0.52 respectively). We have calculated the ratio of k_t/ k_p because it is an important parameter for ultrasonic transducers [1]. The highest value of k_t/ k_p was found for the sample sintered at 1180°C.This ratio ranges from 1.62 to 2.08 for the sintered samples which satisfy well the requirement for applications.

These relatively high piezoelectric and electromechanical activities can be attributed to an increase in number of possible spontaneous polarization directions due to the co-existence of a rhombohedral-tetragonal phase [13-14].



a) at 100 Hz b) at 100 Hz

Figure 5. Temperature dependence of dielectric constant ε_r and dielectric loss tg(δ) of $0.935(Bi_{0.5}Na_{0.5})TiO_3$ -$0.065BaTiO_3$ ceramics sintered at different temperatures at 100 Hz.

Ceramics differs only by their microstructure (fine grained ceramics for 1150-1160°C sintering temperatures and slightly coarse grained ceramics (3-4mm) for 1180-1200°C sintering temperatures). One can estimate that coarse microstructures favour the polarization and depolarization behaviour due to a 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.

CONCLUSION

The phase structure, microstructure, piezoelectric and dielectric properties of BNT-6.5BT lead-free ceramics sintered at different temperatures (1150-1200°C) were investigated. X-ray diffraction pattern indicates a pure perovskite structure with the co-existence of the rhombohedral and tetragonal phase. The SEM micrographs show that the BNT-6.5BT ceramics are all almost fully densified and their density ranges between 97.1 and 97.6 %. At room temperature the sintered ceramics exhibit good piezoelectric and electromechanical properties: 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, 0.23 and 0,39 respectively and the k_t/ k_p ratio ranges from 1.62 to 2.08. It can be believed that these ceramics can be used in piezoelectric devices. This offered the opportunity to obtain a good candidate to replacing the lead-based ceramics.

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