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Structural and Electrical Properties of BNT-BT0.08 Ceramics Processed by Spark Plasma Sintering

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***Abstract*—**$(Bi_{0.5}Na_{0.5})TiO_3$ doped with 8 mol % $BaTiO_3$ powder ($BNT\text{-}BT_{0.08}$), prepared by sol-gel method was compacted and sintered by Spark Plasma Sintering (SPS) process. The influence of SPS temperature on the densification of BNT-BT0.08 ceramic was investigated. Starting from sol-gel nanopowder of BNT-BT containing 8 mol % $BaTiO_3$ with an average particles size of about 30 nm, were obtained ceramics with density around 98 % of the theoretical density value when the SPS temperature used was about 850 °C. The average grain size of the resulting ceramics was 80 nm. The $BNT\text{-}BT_{0.08}$ ceramic sample obtained by SPS method has shown good electric properties at various frequencies.

***Keywords*—**$(Bi_{0.5}Na_{0.5})TiO_3$ doped with $BaTiO_3$, Spark Plasma Sintering (SPS), dielectric properties

I. Introduction

The modern tendencies to replace the toxic lead in various applications have imposed BNT-BT based ceramics as a viable alternative. Pure perovskite BNT ceramics are rhombohedral at room temperature,[1]. Around 320 ^oC a diffuse phase transition change the structure to a tetragonal one. The strong frequency dispersion places these ceramics in the relaxors category, [2]. The BNT material also show good ferroelectric properties with large values remnant of polarization $P_r = 38\ \mu C/cm^2$ with coercive field $E_c = 73$ kV/cm and high leakage current which make difficult to pole the structure, [3]. Poor, than those of the classical lead-based ferroelectrics such as PZT, piezoelectric properties do not recommend BNT to be used in applications. Unpurified BNT ceramics lead to the improvement of the piezoelectric properties in the vicinity of the morphotropic phase boundaries, [4].

Among various compositions, $(Bi_{0.5}Na_{0.5})TiO_3$ containing suitable quantities of $BaTiO_3$ seems to be a good candidate to replace the classical PZT based components in applications. Ceramics $BaTiO_3$ usually are in the paraelectric phase at room temperature for grains dimension larger than 100 nm. A typical ferroelectric first order transition around 130 ^oC Curie temperature, change in a cubic state the crystallographic structure. Other tetragonal-orthorhombic and orthorhombic to rhombohedral transitions appeared around 11 ^oC, respectively around 80 ^oC, [5]. Less than 100 nm the structure tend to be in a cubic state as a grains size effect, [6].

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II. Experimental

Raw material was obtained by a sol-gel method, [7]. All reagents (Aldrich) are of analytical grade purity. Sodium acetate [$Na(CH_3COO)$] and barium acetate [$Ba(CH_3COO)_2$] were dissolved in distilled water, and bismuth(III) acetate [$Bi(CH_3COO)_3$] was dissolved in acetic acid at 100 ^oC. Titanium (IV) isopropoxide, 97 % solution in 2-propanol [$Ti(OCH(CH_3)_2)_4$] was mixed with isopropanol in ratio of 1:10. The solutions of sodium, bismuth and barium, prepared as shown above, were added to the titanium isopropoxide solution to produce a Bi–Na–Ba–Ti complex solution. As-obtained sol was maintained under continuous stirring at 75 ^oC, for 4 h, to obtain the gel. After drying the gel around 200 ^oC, the resultant powder was treated at different temperatures to obtain the desired single-phase powder. $(Bi_{0.5}Na_{0.5})TiO_3$ doped with 8 mol % $BaTiO_3$ powder prepared by sol-gel was further compacted and sintered by SPS method in pellets having thickness of about 1.5 mm and diameter of 10 mm. It was used powder treated at 700 °C, 1.5 h in air with nanometer grains of about 30 nm and crystallized on the structure of rhombohedral $(Bi_{0.5}Na_{0.5})TiO_3$ phase. The pellets were sintered for 5 min by SPS method at 800 °C, 850 °C and 900 °C, under mechanical pressure of 65 MPa. Voltage and peak current used were below 5 V and 2000 A. Further, SPS samples were annealed at 800°C for 5 h to remove the carbon contamination. SPS method is a very good choice because it permits a shortening of the time to obtain BNT-BT ceramics at lower sintering temperatures. SPS method is also a convenient method because the BNT-BT ceramics exhibits great electrical conductivity. Thus high values of the DC current can be passed through ceramics in the sintering procedure. Through the uniform heating of the samples, in few minutes it can be obtained the samples, avoiding the classical sintering methods problem, concerning especially with the Bi and Na loss during the materials preparation. In the same time because of the shortening of the sintering time the grain dimensions do not increase too much, and nanometric grains can be obtained. This way carefully controlled, SPS method can be used to control grains dimension of the final product.Densities of the pellets were measured by Archimedes method using a density balance. Their values, related as percent from theoretical density of the material, are presented in Table 1. The fracture

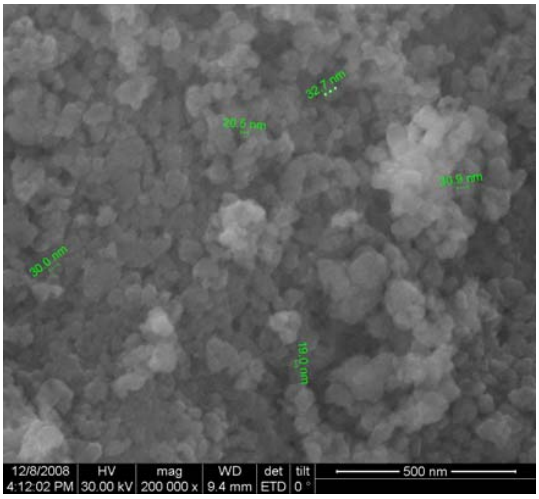
surface structures were investigated with a FEI Quanta Inspect F with EDAX scanning electron microscope (SEM). A Bruker-AXS tip D8 ADVANCE diffractometer with $CuK_{\alpha 1}$ radiation, at wavelength 1.5406 Å, a LiF crystal monochromator and Bragg-Brentano diffraction geometry were used to investigate the structure byX-ray diffraction. Dielectric measurements at fixed frequencies in the 120 Hz÷1 MHz frequency intervals have been performed on a large temperature range between room temperature of about 23 ^{o}C and 400 ^{o}C. A Hioki 3532-50 type automatic RLC bridge and Kethley 2000 voltmeter, with chromel–alumel thermocouple type for temperature measurements, were controlled by a computer through the GPIB interfaces for automatic experimental data registration and further investigations. Silver paste used as the electrodes, was painted on both surfaces of pellets.

III. Results and Comments

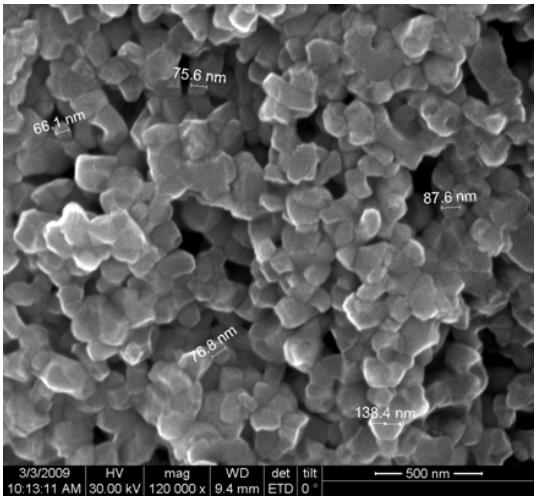
Samples densities show increased values, as a consequence of the sintering temperature increases, Table 1.

SEM images reveal the influence of the sintering temperature on the grains morphology of the ceramics, Fig.1.

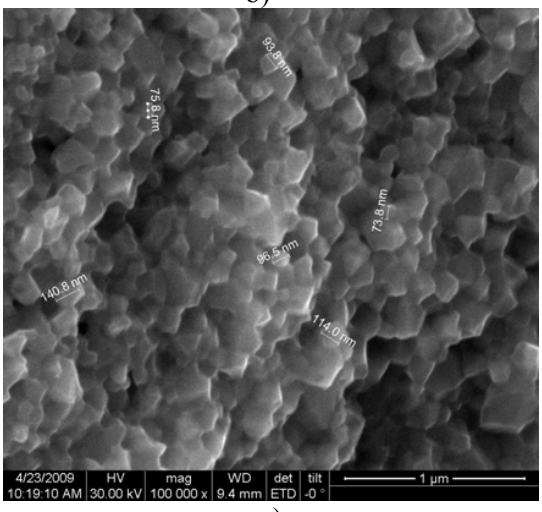
Raw material resulted from sol-gel synthesis, calcinated at 700 ^{o}C, shows a relative uniform distribution with mean granular grains size of about 30 nm, Fig.1a. Some intergranular pores can also be observed at 800 ^{o}C, which tend to disappear at 900 ^{o}C high sintering temperatures, Fig.1b-d. Well defined grains can be viewed at the 900 ^{o}C sintering temperature, Fig.1d.



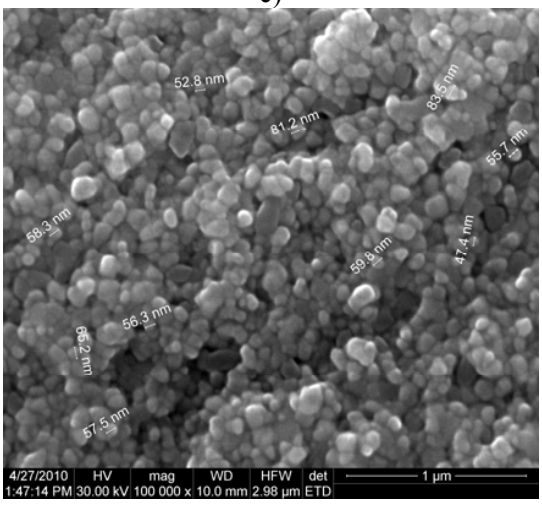
a)



b)



c)



d)

Fig.1 SEM photomicrographs of BNT-$BT_{0.08}$ powder obtained by sol-gel a) and ceramics obtained by SPS at b) 800, c) 850 and d) 900 °C

SEM images shows that the grains are well agglomerated suggesting a good density of the sintered pellets. In the same time it can be seen a tendency to form polyhedral grains increasing the sintering temperature from 800 to 900 °C.

Our estimations on the grains dimensions show an increase with the sintering temperature increase. It is suggested that the temperature and time of the sintering process can control the dimensions of the final product. In the same time, due to the short time of the sintering process at lower temperature, we can suppose a minimum loss of the volatiles Bi and Na.

Other investigations we performed (high resolution TEM and Selected area diffraction - data not shown here) shows the (300) planes of a rhombohedral structure of the ceramics sintered at 900 °C and also make evidence for the coexistence of the rhombohedral and tetragonal phases of $Bi_{0.5}Na_{0.5}TiO_3$ of the morphotropic phase boundary region, [8], [9].

X-ray diffraction patterns show the characteristic peaks of a perovskite structure, Fig.2. Other impurity phases, if exists are under the sensibility limits of the instruments.

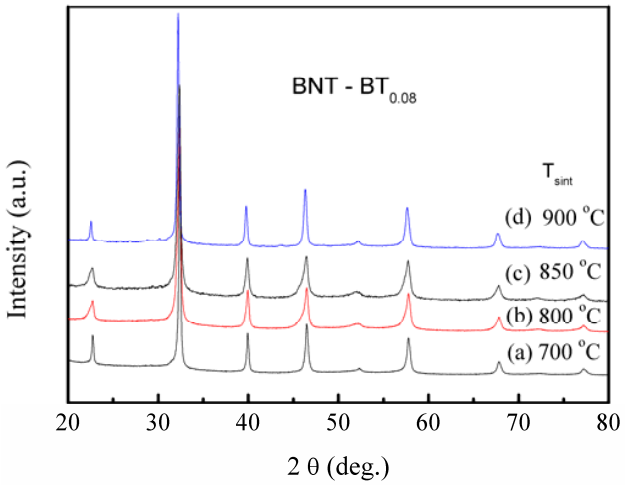


Fig. 2 X-ray diffraction patterns of the BNT-$BT_{0.08}$ powder calcinated at 700 °C a) and ceramics obtained by SPS at 800 °C b), 850 °C c), and 900 °C d)

TABLE I
DENSITIES OF THE SPS BNT-$BT_{0.08}$ SINTERED BY SPS AT 800 °C B), 850 °C C), AND 900 °C D)

Sintering SPS temperature (°C)	Density (% from theoretical density)
800	98.95
850	99.02
900	99.62

TABLE II
DIELECTRIC PROPERTIES OF BNT-BT0.08 CERAMICS AT 10 KHZ

Sintering SPS temperature (°C)	T_m (°C)	ε_r (at T_m)	tanδ (%)
800	265	1700	3.8
850	265	1860	2.7
900	285	2213	5.5

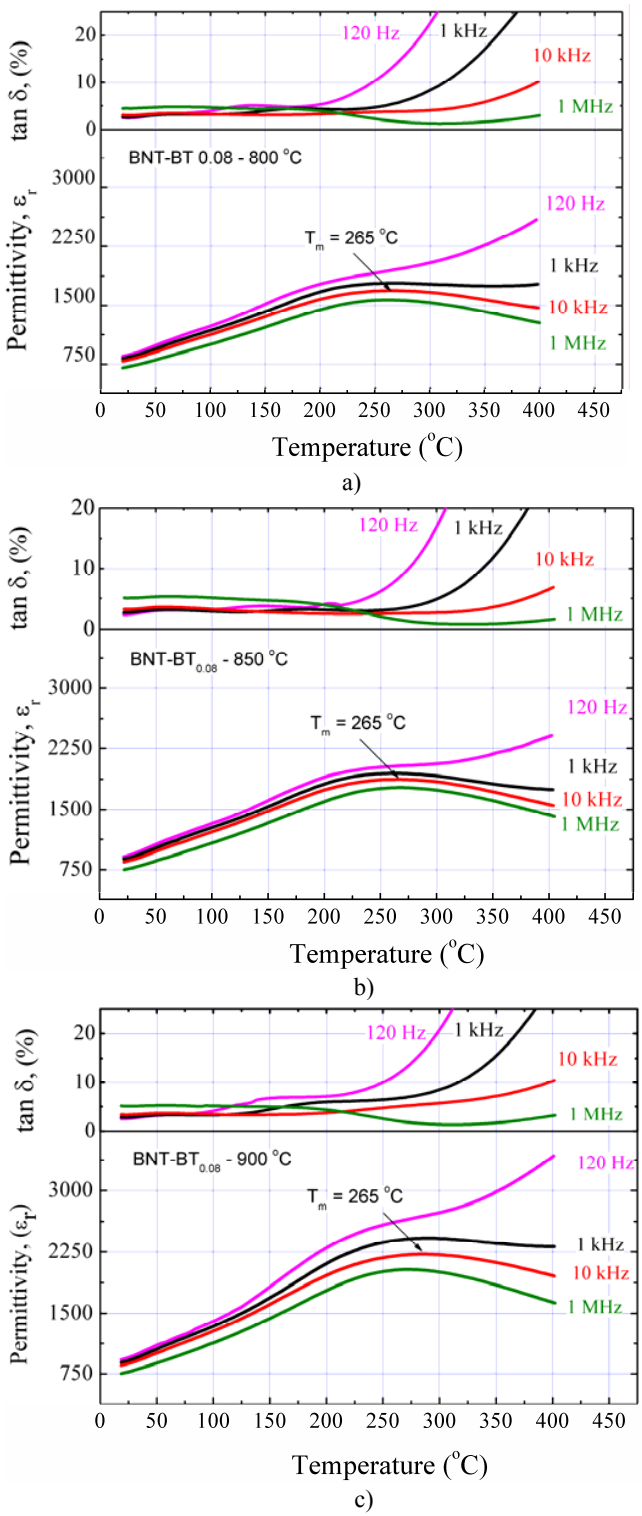


Fig. 3 Temperature and frequency dependence of dielectric properties for BNT-$BT_{0.08}$ ceramic sintered by SPS at a) 800 °C, b) 850 °C and c) 900 °C

Permittivity values showed increased values with the sintering temperature increase from 800 to 900 °C on the investigated temperatures and frequencies ranges, Fig.3,

tableII. This figure could be related to a better densification and to the higher values of the grains dimenssions of the ceramics increasing the sintering temperatures. Dielectric constant decreases its values with the frequencies increase for all sintering temperatures and frequencies. A more pronounced dispersion of the permittivity values can be observed for the 900 ^{o}C sintering temperature and also for higher samples temperatures at the same sintering temperature.This resembles the behavior of a relaxor ferroelectric, where the fluctuation of the randomly oriented nanodomains giving rise to the frequency dispersion is suppressed at low temperatures due to the lack of dynamics, [10],[11]. For 850 ^{o}C sintering temperature, we can observe the smallest frequencies dispersion for permittivity, increasing the samples temperature toward 400 ^{o}C. In the same time lower values of the permittivity, compared with other values reported by some authors, could be a consequence of the small grains dimensions. The loss behaviors also are affected by this. A not well defined depolarization temperature Td suggest a similar observed behavior for compositions ranging between 7 until 10 mol % BT in BNT in [9]. The authors suggest that the phase diagram of the unpoled BNT-BT ceramics shows a region where the ceramics belongs to the relaxor-antiferoelectric behavior. Some other aspects are responsible for loss increasing values. Among them, the free charges, oxygen vacancies, granular boundaries, defects, cracks can be remembered. Generally the structure of the granular limits being different from the core it is generally accepted that this one are barriers for the charge carriers which can be trapped in these regions. Also it is well known that the core of the grains is more conductive than their boundaries. In the low frequencies region (hundred of Hz) space charge in the ceramics are also responsible for the high losses values, [5]. Dielectric loss seems to decrease for the 850 ^{o}C sintering temperature. Above 200 ^{o}C, thermally activated conduction start to increase the loss values for lower frequency region and also for all compositions. Higher the frequency values, higher the temperatures from which losses begin to rapidly increase their values.

IV. Conclusions

BNT-$BT_{0.08}$ ceramics were successfully obtained by the SPS method at low sintering temperatures. The densities and grains dimensions of the SPS sintered ceramics increase with the sintering temperature increase. Permittivity values increase with the sintering temperature increase. Dielectric constant decreases their values with the frequency increase for all sintering temperatures. The dispersion of the permittivity and losses are characteristic to the relaxor behavior of the ceramics.

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