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Sintering of $94Na_{0.5}Bi_{0.5}TiO_3$-$6BaTiO_3$ with SPS and conventional methods for crystal growth

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In this study, lead-free $94Na_{0.5}Bi_{0.5}TiO_3$-$6BaTiO_3$ (94NBT-6BT) piezoelectric ceramics and embedded single crystals in polycrystalline 94NBT-6BT matrix were sintered by conventional (CS) and spark plasma sintering (SPS) techniques. The effects of SPS and CS on the microstructure of the 94NBT-6BT ceramics were discussed and compared. Theoretical density of the CS and SPS treated samples were found to be 94% and almost 99.9%, respectively. High porosity and weak seed-matrix interaction at 1180 °C for 2 h were obtained from CS sintered ceramics. On the other hand, sintered samples with SPS showed non-porous polycrystalline matrix, and quite strong seed-matrix interface bonding at 950 °C for 5 min. Also, dielectric properties of sintered ceramics with SPS gave better results than CS. Therefore, SPS assisted 94NBT-6BT samples can be used to grow high quality and high performance single crystals using solid state single crystal growth.

Key words: 94NBT-6BT, Piezoelectric, Single crystal, SPS, Dielectric, Interface bonding.

Introduction

Lead-based perovskite oxides such as lead zirconate titanate (PZT), lead magnesium niobate-lead titanate (PMN-PT), and lead zinc niobate-lead titanate (PZN-PT) are extensively used in sensors, actuators, transducers, energy harvesting devices and other electronic devices due to their strong piezoelectric properties [1-3]. However, the PbO has a detrimental effect to the human health and environment due to toxicity of PbO during processing steps. Therefore, development of new lead free ceramics is urgent and essential to replace with lead-based ceramics. Therefore, the use of lead-based piezoelectric materials in the near future will be restricted by environmental regulations due to their toxicity during processing [4, 5]. Nowadays, sodium bismuth titanate-barium titanate (NBT-BT) based lead-free materials are considered to be excellent candidates to replace materials containing lead because of their high curie temperature ($T_c = 320$ °C) and high spontaneous polarization ($Pr = 38\ \mu C/cm^2$). However, their piezoelectric properties are still not superior due to their high volatilization, low densification and hard poling problems at high sintering temperatures [6-7].

Growing single crystal forms of NBT-BT is new way to enhance piezoelectric performance. Several different processes such as Bridgeman, Czochralski, flux growth, and top seeded solution growth (TSSG) are the most promising methods to improve piezoelectric properties. These techniques are high temperature melting processes. Therefore, they have some disadvantages such as a slow cooling rate, chemical inhomogeneity and high production costs. In recent years, the solid state crystal growth method (SSCG) has gained great interest in the growth of PMN-PT, NBT-BT based single crystals. It is not only quite cost-effective but also good for mass production of large single crystals [8-11]. This technique is very similar to the conventional sintering process, and is much simpler and more economical than the other crystal growth techniques. Single crystal seed is embedded by uniaxial and cold isostatic pressing. For crystal growth, pressed samples are placed in a hot press at high temperature (> 1100 °C). However, hot pressed or conventionally sintered samples contain small pores due to low density polycrystalline matrix during crystal growth. These pores transport into the grown crystal during hot pressing and crystal growth [12]. Spark plasma sintering (SPS) is a new technique designed to eliminate these problems. The SPS provides fully dense materials at low sintering temperatures in a much shorter sintering time (nearly 5 min) [9].

In recent years, only one paper has been published on the SSCG of NBT-BT single crystals. Kang et al. reported that many small pores were entrapped within crystal because of the residual pores in the polycrystalline 95NBT-5BT matrix [8]. An article on spark plasma sintering of lead-based PMN-35PT at 900°C for growing PMN-35PT single crystal by SSCG has just been published by Park et al. They report that the increase in density improved the dielectric and piezoelectric properties of ceramic [9]. Therefore, fully dense lead-free polycrystalline matrix and strong

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interface bonding between matrix and single crystal seed can be improved by SPS at lower temperature (< 1000 °C). Therefore, the aim of this work is to compare matrix density and matrix-single crystal interface bonding of sintered 94NBT-6BT samples with conventional sintering (CS) and SPS. According to our knowledge, this is the first report to be published on the microstructural comparison of the 94NBT-6BT matrix and matrix-seed interaction before crystal growth.

Material and Methods

Na_2CO_3, Bi_2O_3, Ba_2CO_3 and TiO_2 (> 99.9% purity) were used as the starting raw materials. The powders were weighted according to the stoichiometric ratio of formula $94Na_{0.5}Bi_{0.5}TiO_3$-$6BaTiO_3$, and then ground using a ball mill in ethanol medium using zirconia balls for 15 h. Milled and dried 94NBT-6BT polycrystalline powders were calcined at 900 °C for 4 h in a muffle furnace. Powders were milled again and sieved under 100 μm. CS and SPS sintering techniques were used in order to obtain a dense structure. The 94NBT-6BT powders were sintered in disk shape at 900 and 950 °C, for 5 min. under 50 MPa pressure in SPS. Also, granulated powders were pressed in disk shape. The compacted samples were conventionally sintered between 1130 to 1180 °C for 2 h. Density of the sintered samples with CS and SPS were compared using Archimedes methods.

Moreover, 94NBT-6BT seed crystal was embedded in polycrystalline powder and heat treated by CS and SPS to observe matrix-seed interactions. Crystal structures of the samples were characterized by X-ray diffraction (XRD, Rikagu Rint 2200, CuKα λ = 1.5406 Å, scan speed 2 °/min) technique. Fracture surfaces and grain morphology of sintered samples were analyzed using scanning electron microscopy (SEM, Zeiss Evo 50EP). Energy dispersive X-ray (EDX, Bruker AXS XFlash) and X-ray fluorescence (XRF, Rikagu ZSX Primus) were used to obtain elemental analyses. Dielectric constant (ε_r) and dielectric loss (tanδ) were investigated depending on frequency (0.1-1000 Hz) with Agilent 4294A impedance gain phase analyzer.

Results and Discussion

Fig. 1(a) shows the SEM image of calcined 94NBT-6BT powder at 900 °C for 4 h. The particles consist of three-dimensional round edge cubic particles. The XRD patterns for 94NBT-6BT ceramic are shown in Fig. 1(b). A pure perovskite structure without perceivable second phase (pyrochlore) is observed in 94NBT-6BT ceramic.

The compositional analyses of synthesized powders clearly indicate that the powders are composed of elements of Na, Bi, Ti, Ba and O. The experimental results are very close to the expected value. The amounts of the Na and Bi are slightly greater than the expected value due to excess Na and Bi content. It can be seen the Ba and BaO content is smaller than the expected value due to its evaporation during calcinations (Table 1).

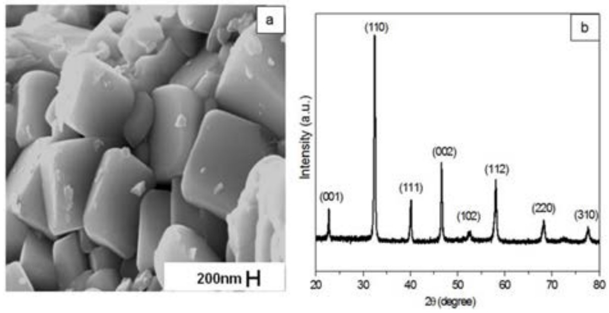

Fig. 1. SEM micrograph (a) and XRD analyses (b) of calcined 94NBT-6BT particles.

Table 1. EDX and XRF analysis of calcined 94NBT-6BT powder.

Component	EDX Analysis Atom% (expected)	Atom% (experimental)
Na	9.4	10.03
Ba	1.2	1.04
Ti	20	19.72
Bi	9.4	10.20
O	60	59.11
Total	100	100

Component	XRF Analysis wt% (expected)	wt% (experimental)
Bi_2O_3	51.62	53.10
Na_2O	6.84	7,03
TiO_2	37.60	37.42
BaO	3.94	3.55
Total	100	100

SEM images of conventionally sintered samples at 1130-1150 and 1180 °C for 2 h are shown in Fig. 2(a-b-c), respectively. It can be seen from Fig. 2(a)-(b) and (c) that porosity is observed for all samples. It is known that fabrication of the high density 94NBT-6BT materials is difficult under the air atmosphere by CS because of the high evaporation behavior of alkaline elements. Therefore, microstructure strongly affects the dielectric and piezoelectric properties of the ceramics, which depend on the sintering temperatures [13, 14]. Fig. 2(d)-(e) shows the microstructure of sintered 94NBT-6BT by SPS under 30 MPa at 900 °C for 5 min. The microstructure consists of micro crack and porosity due to the low SPS pressure. On the other hand, Fig. 2(f)-(g) shows the SEM images of sintered 94NBT-6BT specimens by SPS under 50 MPa, at 950 °C for 5 min. It can be clearly seen that the non-porous, fully dense microstructures are observed with increasing pressure and temperature when compared with CS. Fig. 2(h) compares the theoretical density of sintered samples with CS and SPS. Through the

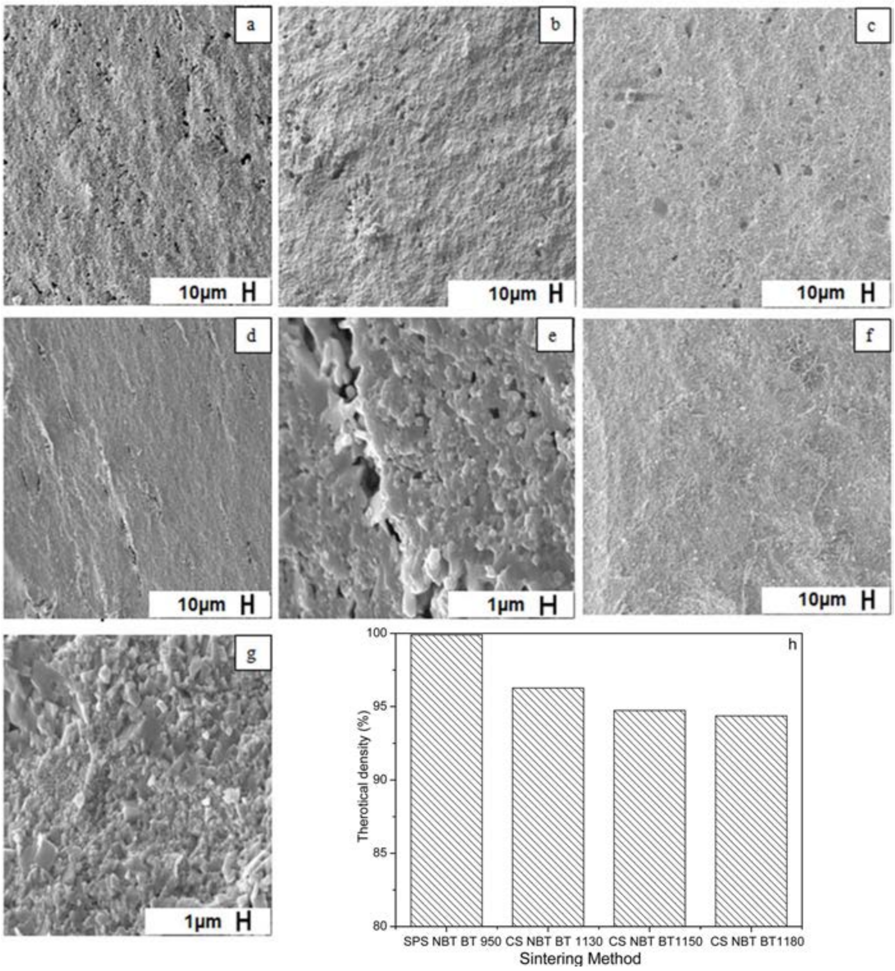

Fig. 2. SEM micrographs and theoretical density of sintered 94NBT-6BT ceramics with CS and SPS: (a) 1130 ºC, (b) 1150 ºC and (c) 1180 ºC for CS, (d)-(e) under 30 MPa at 900 ºC for 5 min, (f)-(g) under 50 MPa at 950 ºC for 5 min for SPS, (h) theoretical density measurement.

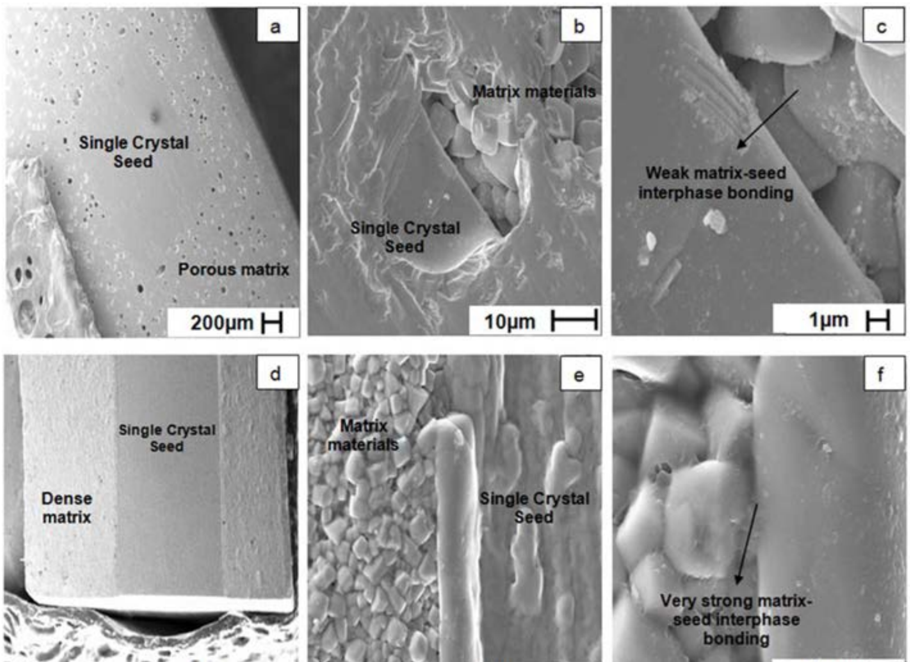

Fig. 3. SEM micrographs of embedded seed in matrix samples: (a)-(b)-(c) sintered ceramics at 1180 ºC with CS and (d)-(e)-(f) sintered ceramics with SPS at 950 ºC.

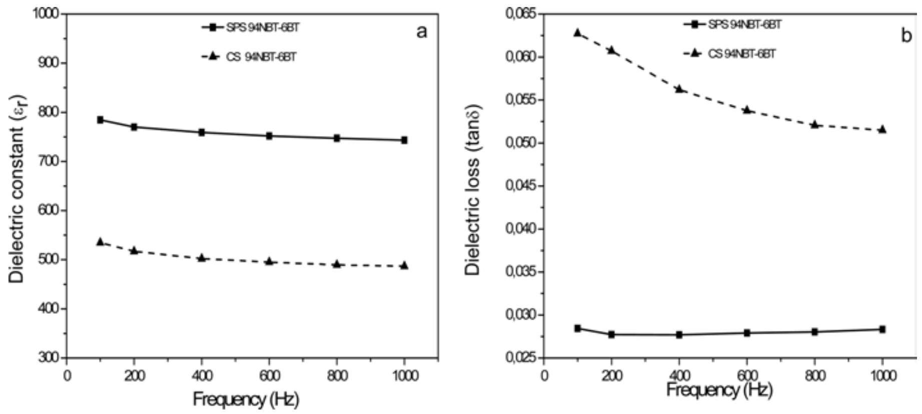

Fig. 4. Dielectric constant (a) and dielectric loss (b) of sintered samples with CS and SPS.

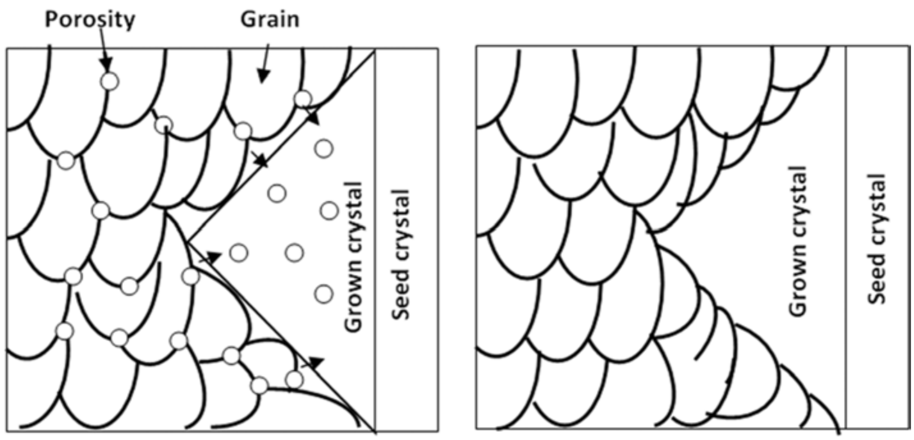

Fig. 5. Schematic representation of sintering with CS (a) and SPS (b) methods.

conventional sintering at 1130 °C for 2 h, the theoretical density of samples reaches 96%. Theoretical density decreases from 96% to 94% with increasing temperature due to its high alkaline evaporation. On the other hand, the theoretical density of the SPS treated 94NBT-6BT samples is nearly 99% at 950 °C for 5 min. The results show that SPS is an efficient sintering technique that provides high densification and lower alkaline evaporation due to its relatively low sintering temperature and short sintering time when compared to the CS method.

A capillary driving force is the main essential requirement to grow seed crystal in polycrystalline matrix. In order to obtain high quality single crystal using SSCG technique, grain size, density, and chemical homogeneity of polycrystalline matrix must be closely controlled during heat treatment. In particular, control of the matrix porosity is essential to grow non-porous and high density single crystals [9]. Embedded 94NBT-6BT seed crystal in polycrystalline matrix is given in Fig. 3. Low and high magnification SEM images of the sintered samples with CS are shown in Fig. 3(a)-(c). Matrix materials include porosity and weak seed-matrix interaction at 1180 °C for 2 h. On the other hand, the sintered sample with SPS at 950 °C shows highly dense polycrystalline matrix structure. Also, strong seed-matrix interface bonding is observed in Fig. 3(d)-(e)-(f). From the images, SPS technique may be the solution to the specified requirements for SSCG method. Fig. 4(a)-(b) shows the dielectric constants (ε_r) and dielectric loss (tanδ) of sintered 94NBT-6BT with CS and SPS as a function of measured frequencies. For the same measured frequency, dielectric constant of SPS samples is greater than CS samples. Also, dielectric loss of SPS samples is nearly two times less than CS samples due to higher density of SPS sintered ceramics. According to our approach, schematic images in Fig. 5(a-b) can explain why SPS process has better dielectric properties than CS method. In CS process, many small pores are transport and entrapped in grown crystal during crystal growth. On the other hand, the porous structure is eliminated during SPS process at lower sintering temperature. Therefore, sintered ceramics with SPS have better dielectric properties than CS due to their highly dense and non-porous structure.

Conclusions

The results point out that high density 94NBT-6BT ceramics were successfully sintered with SPS technique. The density was nearly 99% of the theoretical density for SPS treated 94NBT-6BT samples at 950°C.

Theoretical density was 94% for conventional sintered ceramics at 1180°C. Moreover, strong seed-matrix bonding and better dielectric properties were achieved by SPS before crystal growth. Also, SPS can be used as a new method to provide strong seed-matrix interface bonding and non-porous structures during SSCG.

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