

ISLAM TAKIUL<sup>1</sup>, SANGHAW LEE<sup>1</sup>, HAEJIN HWANG<sup>1\*</sup>

## SINTERABILITY, MICROSTRUCTURAL EVOLUTION, AND DIELECTRIC PERFORMANCE OF BISMUTH SODIUM TITANATE ( $\text{Bi}_{0.5}\text{Na}_{0.5}\text{TiO}_3$ ) LEAD-FREE FERROELECTRIC CERAMICS

In this study, lead-free bismuth sodium titanate (BNT;  $\text{Bi}_{0.5}\text{Na}_{0.5}\text{TiO}_3$ ) powder was synthesized using wet precipitation. The sintering behavior and dielectric properties of the BNT ceramics were investigated in terms of the sintering temperature. Titanium isopropoxide, sodium nitrate, and bismuth nitrate were used as starting materials. A titanium peroxo complex (TPC) solution was synthesized using titanium hydroxide, nitric acid, and hydrogen peroxide. A clear Bi-Na-Ti precursor solution was obtained by mixing the TPC, sodium, and bismuth nitrate solutions. The pH of the precursor solution was increased to 9 using NaOH and a white powder was precipitated. A spherical and pyrochlore phase-free BNT powders were obtained by calcining the white precipitate above 600°C for 3 h. Particle size analysis and SEM observations revealed that the BNT powder calcined at 700°C exhibited homogeneous distribution with particle size less than 300 nm. The sinterability of the BNT ceramic prepared through wet precipitation was significantly enhanced compared to that of the BNT powder prepared via the solid-state reaction of sodium carbonate, bismuth oxide, and titanium oxide powders.

*Keywords:* Bismuth sodium titanate; lead-free; ferroelectrics; sintering; dielectric constant

### 1. Introduction

Ferroelectric or piezoelectric ceramics, which can convert mechanical energy into electrical energy and vice versa, are technologically important materials widely used in actuators, sensors, capacitors, and transducers [1-3]. At present, the commonly used ferroelectric or piezoelectric ceramics are lead-containing perovskite-type ( $\text{ABO}_3$ ) materials such as lead zirconium titanate and  $\text{Pb}(\text{Zr},\text{Ti})\text{O}_3$  (PZT) solid solutions [4-6]. However, the use of lead causes environmental concerns; therefore, the development of alternative lead-free ferroelectric materials, is essential.

Bismuth sodium titanate (BNT;  $\text{Bi}_{0.5}\text{Na}_{0.5}\text{TiO}_3$ ) perovskites with rhombohedral symmetry ( $R3c$ ) have been extensively studied over the last decade and are considered among the most promising lead-free ferroelectric materials that can replace PZT-based materials [7-10]. BNT ceramics exhibit excellent ferroelectric and piezoelectric properties, such as large remanent polarization, high coercive field, high Curie temperature (320°C), and high strain by field-induced phase transformations [11,12].

In general, BNT ceramics can be fabricated by sintering the BNT powder at temperatures above 1200°C for several hours [13]. High-temperature sintering can facilitate significant grain growth (in addition to inhomogeneous grain size distribution) and Bi evaporation, which can lead to deteriorated ferroelectric and piezoelectric properties of BNT ceramics. Therefore, developing a powder synthesis technique to produce BNT powder with nanosized particles and a spherical morphology, is necessary. Various powder synthesis techniques, such as solid-state, sol-gel, hydrothermal, and combustion reactions, have been proposed [14-16]. Among these, solid-state reactions are straightforward and simple. However, it suffers from poor sinterability owing to producing particles with large particle size and inhomogeneous size distribution. Alternatively, wet synthesis techniques can produce nanosized BNT particles. However, tedious processing time and hardly agglomerated powders are major issues that need to be circumvented [16].

This study aimed to synthesize lead-free BNT powder using wet precipitation. Nanosized spherical BNT particles were prepared from a Bi-Na-Ti precursor solution by precipitation. The sinterability, microstructural evolution, and dielectric performance of the BNT ceramics were investigated.

<sup>1</sup> INHA UNIVERSITY, DEPARTMENT OF MATERIALS SCIENCE AND ENGINEERING, 100 INHA-RO, MICHUHOL-GU, INCHEON 22212, KOREA

\* Corresponding author: [hjhwang@inha.ac.kr](mailto:hjhwang@inha.ac.kr)



## 2. Experimental

Bismuth sodium titanate (BNT;  $\text{Bi}_{0.5}\text{Na}_{0.5}\text{TiO}_3$ ) powder was synthesized via wet precipitation. Reagent-grade titanium tetraisopropoxide (TTIP;  $\text{Ti}(\text{OC}_3\text{H}_7)_4$ , 97%, Sigma-Aldrich), bismuth nitrate pentahydrate ( $\text{Bi}(\text{NO}_3)_3 \cdot 5\text{H}_2\text{O}$ , 98%, Sigma-Aldrich), and sodium nitrate ( $\text{NaNO}_3$ , > 99%, Sigma-Aldrich) were used as starting materials to prepare Bi-Na-Ti precursor solutions. TTIP was dissolved in isopropanol and hydrolyzed using distilled water at pH 9. A white precipitate ( $\text{Ti}(\text{OH})_4$ ) was obtained within a few minutes. The precipitate was washed several times with distilled water using filter paper and dried in the oven at  $100^\circ\text{C}$ .  $\text{Ti}(\text{OH})_4$  was converted into titanyl nitrate ( $\text{TiO}(\text{NO}_3)_2$ ) by adding nitric acid under continuous stirring. A reddish-brown titanium peroxo complex (TPC) solution was obtained after adding hydrogen peroxide to the  $\text{TiO}(\text{NO}_3)_2$  solution. The color of the TPC solution depends on the amount of hydrogen peroxide and the pH of the TPC solution.  $\text{Bi}(\text{NO}_3)_3 \cdot 5\text{H}_2\text{O}$  and  $\text{NaNO}_3$  were dissolved in distilled water and then added to the TPC solution. After stirring the resultant solution at  $25^\circ\text{C}$  for 1 h, concentrated sodium hydroxide solution was added to the Bi-Na-Ti precursor solution to adjust the pH to 9. The resultant white powder was precipitated and washed several times with distilled water and ethanol to remove unwanted salts and solvents. The BNT powder was obtained by drying the precipitate at  $100^\circ\text{C}$  for 3 h and subsequently calcining the dried gel powder at  $500^\circ\text{C}$ ,  $600^\circ\text{C}$ ,  $700^\circ\text{C}$ , and  $800^\circ\text{C}$  for 3 h. For comparison, the BNT powder was also prepared by solid-state reaction. Reagent-grade sodium carbonate ( $\text{Na}_2\text{CO}_3$ ), bismuth oxide ( $\text{Bi}_2\text{O}_3$ ), and titanium oxide ( $\text{TiO}_2$ ) powders were purchased from Sigma-Aldrich. Stoichiometric amounts of starting powders were mixed in a planetary ball mill (Pulverisette 6, Fritsch, Germany) using ethanol (99%, Wako, Japan) as the medium. Milling was performed using a powder mixture of zirconia balls ( $d = 5$  mm) in a zirconia jar (80 mL) at a rotational speed of 500 rpm for 2 h. The slurry was dried at  $100^\circ\text{C}$  for 2 h followed by calcination at  $700^\circ\text{C}$  in a box furnace for 3 h under an air atmosphere. The BNT powders prepared by wet precipitation and solid-state reaction techniques were uniaxially pressed into disks, followed by cold isostatic pressing at 200 MPa. The disk-type green bodies were sintered at  $900^\circ\text{C}$ ,  $950^\circ\text{C}$ ,  $1000^\circ\text{C}$ , and  $1050^\circ\text{C}$  for 5 h in air. The diameters and thicknesses of the sintered samples were 20 mm, and 0.2 mm, respectively.

The crystal structure of the BNT powders was analyzed by X-ray diffraction (XRD; RU-200B, Rigaku Co., Ltd., Japan) technique with Ni-filtered  $\text{Cu-K}\alpha$  radiation of 600 mm/sec in 60 s. The microstructure of the samples was examined using field-emission scanning electron microscopy (FE-SEM; JSM-6700F, JEOL). The size of the BNT particles was measured using a Zeta Potential Analyzer (Model: ELS-Z). To measure the dielectric properties, a silver paste was applied to both surfaces of the sintered disk-type sample, and the capacitance and temperature dependence were measured using an LCR meter (Agilent HP4284). To measure the capacitance, the two electrode probes of the LCR meter were connected to both surfaces of the disk sample, and the capacitance was measured at three different

frequencies. The dielectric constant ( $\epsilon$ ) was calculated using the formula:  $\epsilon = Cd/\epsilon_0 A$ , where  $C$  is the capacitance,  $d$  is the thickness of the pellet,  $A$  is the cross-sectional area of the pellet, and  $\epsilon_0$  is the permittivity of free space.

## 3. Results and discussion

Fig. 1 shows the XRD patterns of powder samples prepared by wet precipitation and calcined at various temperatures. The powder sample calcined at  $400^\circ\text{C}$  showed a broad peak with low intensity at  $20^\circ$ - $30^\circ$  and no peaks are attributed crystalline phases. This indicates that the prepared sample is amorphous. In the case of powder samples calcined above  $500^\circ\text{C}$ , peaks corresponding to the crystalline phase appeared, and all the peaks could be ascertained as  $\text{Bi}_{0.5}\text{Na}_{0.5}\text{TiO}_3$  [16]. The precipitate comprising Bi, Na, and Ti precursors prepared by wet precipitation crystallized between  $400^\circ\text{C}$  and  $500^\circ\text{C}$ . Although a small peak at approximately  $29^\circ$  attributed to the presence of the pyrochlore phase ( $\text{Bi}_2\text{Ti}_2\text{O}_7$ ) [17], is confirmed in the powder sample calcined at  $500^\circ\text{C}$ , it disappeared in the sample calcined at  $600^\circ\text{C}$ . This result suggests that a single-phase BNT with no pyrochlore phase can be obtained by calcining the dried gel powder above  $600^\circ\text{C}$ . The intensities of the crystalline peaks increased with increasing calcination temperature. Further, in the case of the solid-state reaction, the single-phase BNT was obtained by calcining the powder mixture of  $\text{Na}_2\text{CO}_3$ ,  $\text{Bi}_2\text{O}_3$ , and  $\text{TiO}_2$  at  $700^\circ\text{C}$ ; however, this result is not reported in this paper. Therefore, wet precipitation is effective for reducing the temperature at which single-phase BNT can be obtained.

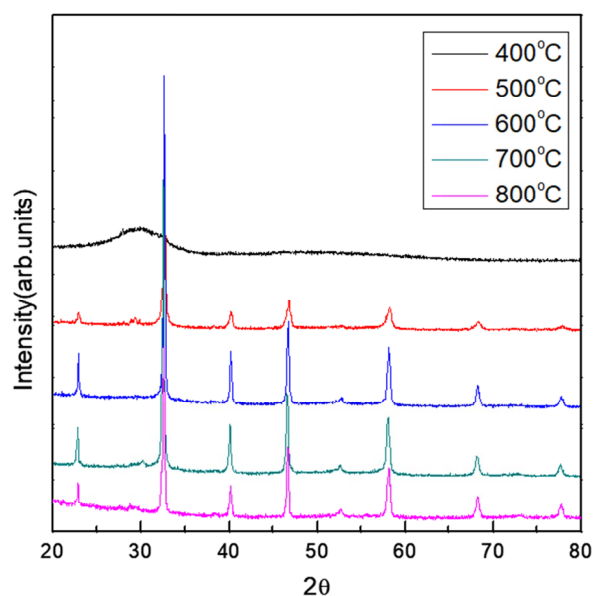


Fig. 1. XRD patterns of the BNT powders prepared by wet precipitation and calcined at  $400^\circ\text{C}$ ,  $500^\circ\text{C}$ ,  $600^\circ\text{C}$ ,  $700^\circ\text{C}$ , and  $800^\circ\text{C}$  for 3 h

Fig. 2 shows the SEM images of the BNT powder samples prepared by wet precipitation and calcined at  $600^\circ\text{C}$ ,  $700^\circ\text{C}$ , and  $800^\circ\text{C}$ . The BNT powder consisted of spherical nanoparticles

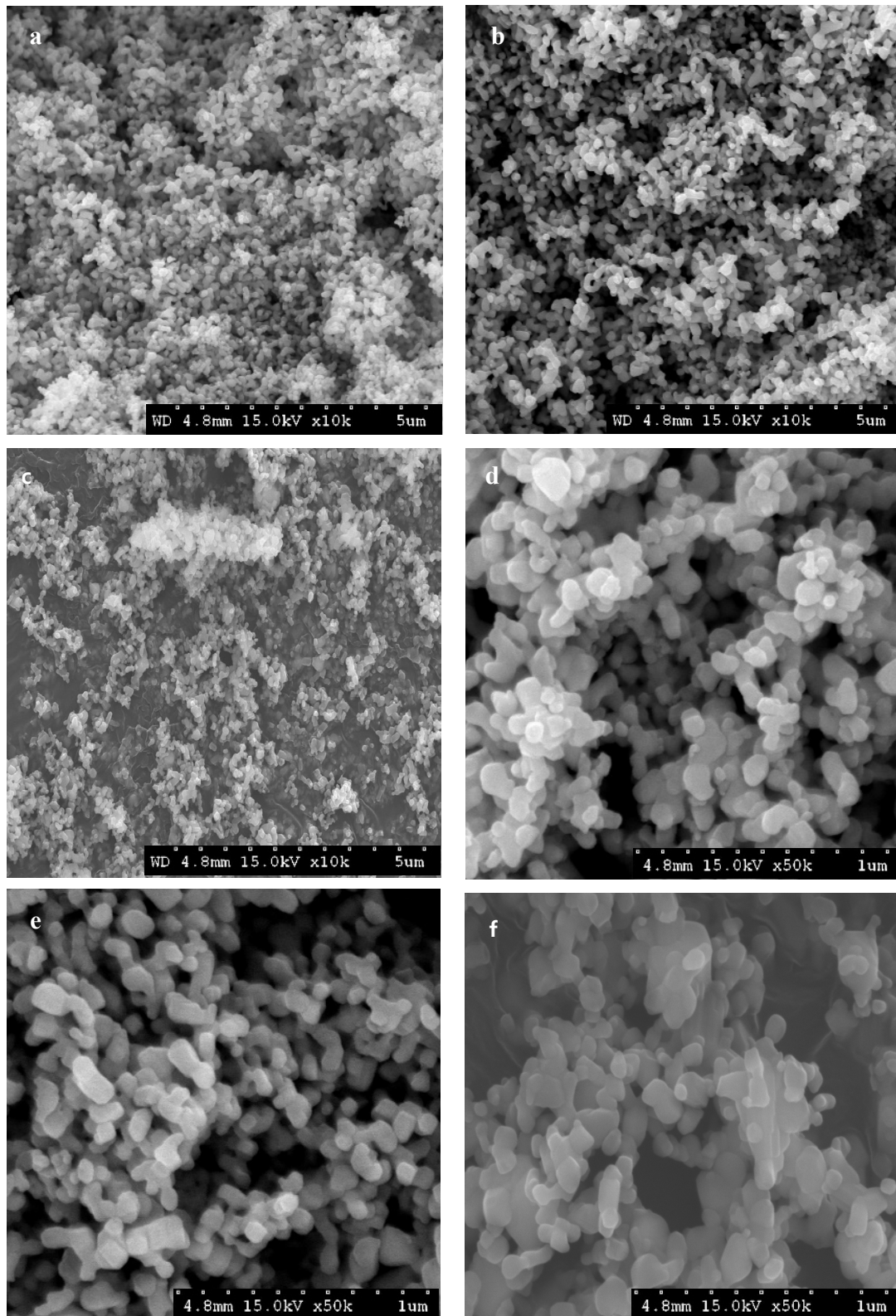


Fig. 2. SEM images of BNT powder samples prepared by wet precipitation and calcined at 600°C (a and d), 700°C (b and e), and 800°C (c and f)

at all calcined temperatures. Comparing Fig. 2(d) and Fig. 2(e) indicates that the effect of the calcination temperature on the particle size is not significant; in other words, high-temperature calcination did not result in accelerated particle growth. Fig. 2(f) shows that particles in the 800°C-calcined sample are more marginally agglomerated than those of the 600°C- and

700°C-calcined samples. The particle size of the BNT powder analyzed using a particle size analyzer was estimated to be approximately 400-500 nm (d<sub>50</sub>), as shown in Fig. 3. The particle sizes of 600°C- and 700°C-calcined powders are 475 and 402 nm (d<sub>50</sub>), respectively. As observed in Fig. 2, BNT primary particles form softly agglomerated secondary particles. This phenomenon

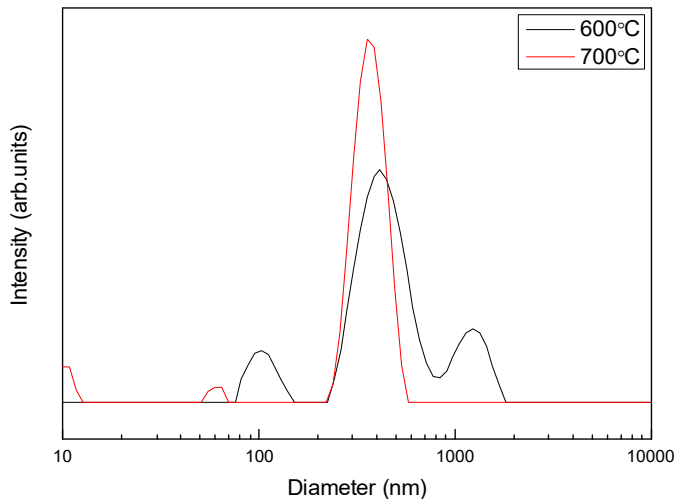


Fig. 3. Particle size analysis of BNT powders calcined at 600°C and 700°C

is closely related to the change in particle size as a function of calcination temperature, which may be associated with BNT crystallization. Further, Fig. 1 indicates that the peak intensi-

ties of the BNT powder sample calcined at 700°C are almost the same as that of the powder sample at 600°C. This can be attributed to the deterioration in crystallization with respect to the calcination temperature.

Fig. 4 shows the SEM images of the sintered BNT ceramic samples prepared by wet precipitation (a and b) and solid-state reactions (c and d). Figs. 4(a) and (c) show the SEM images of the BNT ceramic samples sintered at 1000 °C, while Figs. 4(b) and (d) depict that of the BNT ceramic samples sintered at 1050°C. SEM images show that dense BNT samples could be obtained by both wet precipitation and solid-state reactions. This suggests that sintering the sample at 1000°C is sufficient to obtain a fully dense BNT-sintered material. Fig. 4 shows that finer grain size and more homogeneous microstructure can be obtained by wet precipitation. The grain sizes of the BNT samples prepared by wet precipitation are 500 (1000°C) and 800 nm (1050°C), while those of the BNT samples prepared by solid-state reaction are 3-5 (1000°C) and 5-10  $\mu\text{m}$  (1050°C).

The temperature dependences of the dielectric constant and loss of the BNT ceramics prepared by wet precipitation at 10 kHz, 100 kHz, and 1 MHz are shown in Fig. 5. The dielectric constant

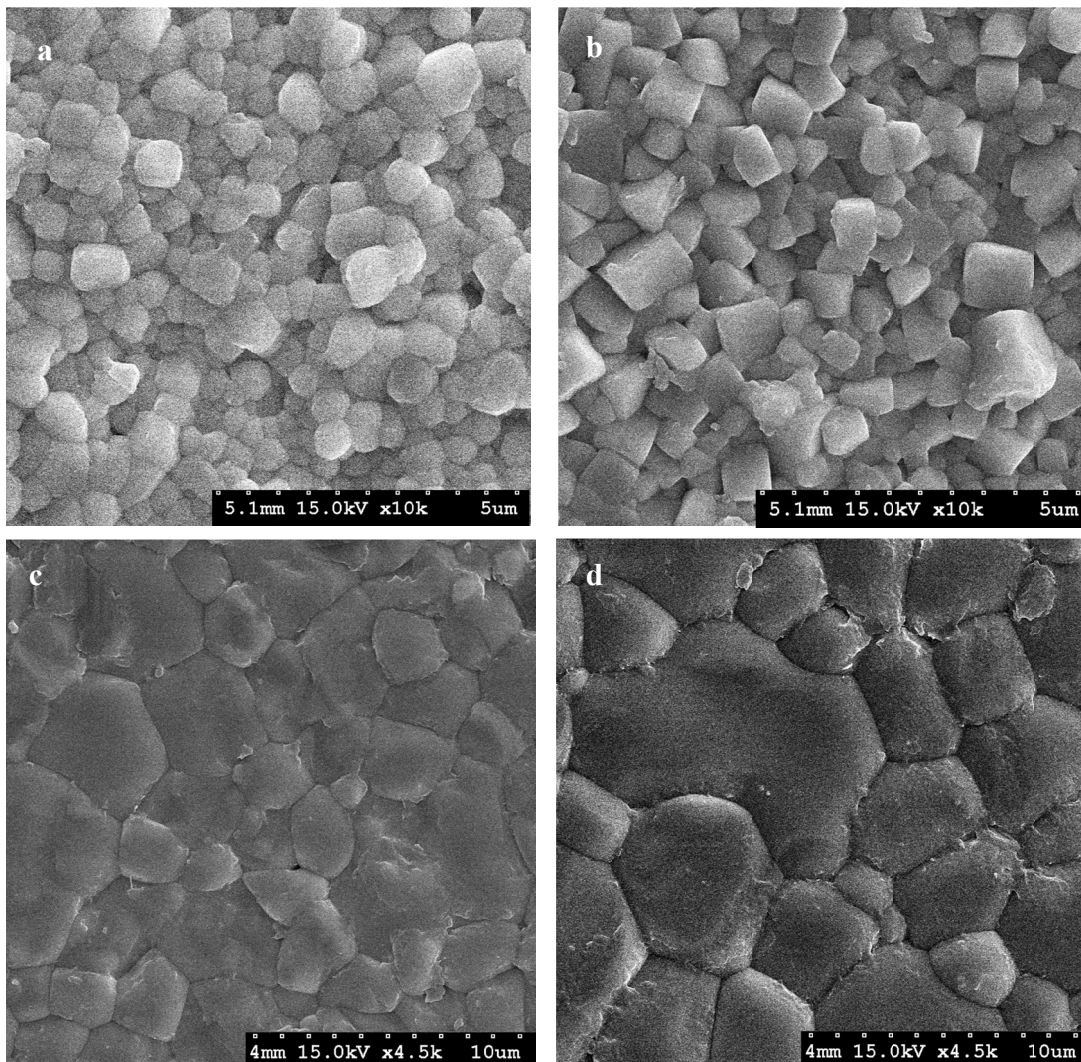


Fig. 4. SEM images of BNT samples prepared by wet precipitation (a and b) and solid-state reaction (c and d) and sintered at 1000°C (a and c) and 1050°C (b and d)

and loss of the BNT ceramics indicate the presence of ferroelectrics, which can be observed in BNT ceramics. Generally, two dielectric peaks are observed for the BNT ceramics which are attributed to the ferroelectric to anti-ferroelectric transition at low temperatures (150-200°C) and anti-ferroelectric to paraelectric transition at high temperatures (300°C) [18]. In this study, the ferroelectric to anti-ferroelectric transformation with Curie temperature at 160°C is observed in the BNT sample sintered at 1050°C. However, in the case of the BNT sample sintered at 1000°C, no distinct transformation occurred up to 200°C. This result indicates that the transformation temperature is above 200°C and the BNT ceramic sample sintered at 1000°C is stabler than that sintered at 1050°C. Furthermore, the fine grain size could have caused the diffused phase transformation observed in the BNT sample sintered at 1000°C.

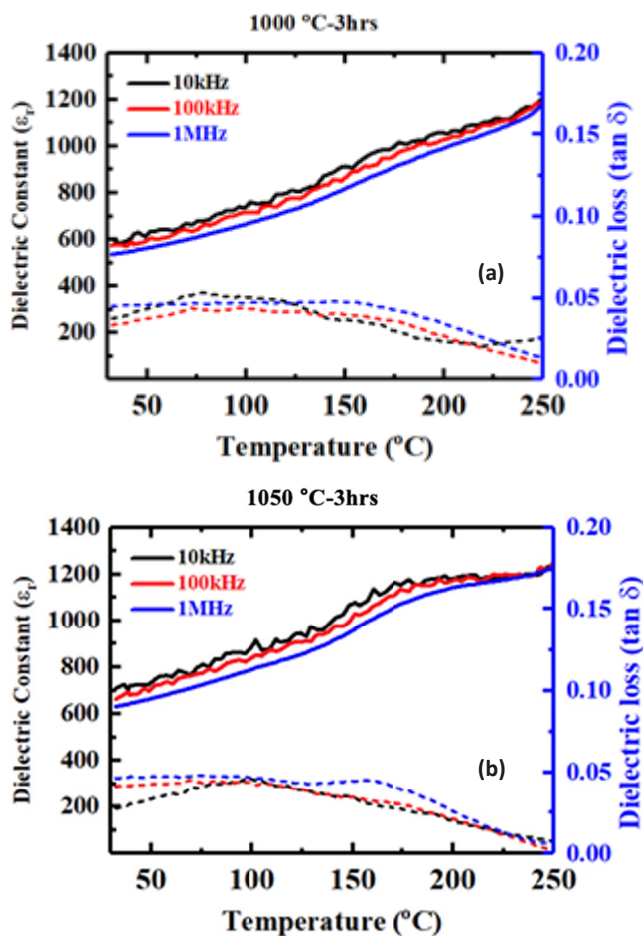


Fig. 5. Temperature dependence of the dielectric constant and dielectric loss ( $\tan \delta$ ) of BNT samples sintered at (a) 1000°C and (b) 1050°C for 3 h

#### 4. Conclusions

In this study, lead-free BNT powder was fabricated via wet precipitation. The microstructural evolution and dielectric properties of the BNT ceramics were investigated in terms of the sintering temperature. The precursor solution for precipitation was synthesized from a TPC solution containing bismuth nitrate and sodium nitrate. A white powder was precipitated by adding

NaOH to the Bi-Na-Ti precursor solution. Single-phase BNT powders were obtained by calcining the dried precipitate above 600°C. Particle size analysis and SEM observations revealed that the particle size of the BNT powder calcined at 700°C was less than 500 nm with homogeneous distribution. Further, a TPC solution containing bismuth and sodium is a crucial factor for obtaining nanosized BNT powder with spherical morphology. The microstructure of the samples showed that the grain size of the BNT ceramic prepared by wet precipitation was significantly finer than that of the BNT ceramic prepared by the solid-state reaction.

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