

# Synthesis of Bismuth Sodium Titanate Nanosized Powders by Solution/Sol-Gel Process

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(Bi<sub>1/2</sub>Na<sub>1/2</sub>)TiO<sub>3</sub> (BNT) is a prominent candidate for a leadfree piezoelectric material. In this study, BNT was synthesized using the solution/sol-gel method, in which a solution of Bi<sub>2</sub>O<sub>3</sub> and Na<sub>2</sub>CO<sub>3</sub> was dissolved in HNO<sub>3</sub> as starting materials. The solution then was mixed with ethylene glycol and titanium tetraisopropoxide. The obtained BNT powder was analyzed using FT-IR, DTA-TG, Raman spectroscopy, and hightemperature XRD. Results showed that BNT crystallization occurred above 600°C. TEM investigation showed that 100-200 nm BNT particles were formed by heat-treating the sol-gel-derived BNT sol at 700°C for 6 h.

#### I. Introduction

EAD-FREE piezoelectric and pyroelectric ceramics have atatracted attention recently because PbO is volatile and detrimental to human health and the environment. Bismuth sodium titanate ((Bi<sub>1/2</sub>Na<sub>1/2</sub>)TiO<sub>3</sub>, BNT) is considered to be an excellent candidate for lead-free piezoelectric materials: BNT is ferroelectric, with remnant polarization ( $P_r$ ) of 38  $\mu$ C/cm<sup>2</sup>, Curie temperature ( $T_{\rm C}$ ) of 320°C, and coercive field ( $E_{\rm c}$ ) of 73 kV/cm at room temperature.<sup>1-4</sup> The crystal structure of BNT is rhombohedral, of which the solid solution with tetragonal perovskite can have a rhombohedral and tetragonal morphotropic phase boundary (MPB).<sup>5,6</sup> Ferroelectric ceramics with compositions approximating the MPB are known to have high piezoelectricity. Takenaka et al.<sup>6</sup> have reported that BNT-BaTiO<sub>3</sub> has a piezoelectric constant  $(d_{33})$  of 125 (10<sup>-12</sup> C/N). There are reports of BNT superstructure,<sup>7,8</sup> (Bi<sub>1/2</sub>K<sub>1/2</sub>)TiO<sub>3</sub>–(Bi<sub>1/2</sub>Na<sub>1/2</sub>)TiO<sub>3</sub> system phase relations,<sup>9</sup> (Bi<sub>1/2</sub>Na<sub>1/2</sub>)TiO<sub>3</sub>–PbTiO<sub>3</sub> system,<sup>10</sup> and BNT single crystals and (Bi<sub>1/2</sub>Na<sub>1/2</sub>) $(I_{1-1.5x}La_xTiO_3$ .<sup>11,12</sup>

For aspects of practical application, BNT is considered to be a prominent candidate for surface acoustic wave (SAW) substrates, ultrasonic generators, ferroelectric random access memory (FRAM), and so on. For these applications, it is necessary to fabricate a thin-film form of BNT, although few studies have been reported on film synthesis. The sol-gel method is thought to be one of the prominent techniques for this purpose. Therefore, detailed investigation on sol-gel processing and powder synthesis of BNT might be required.

This study specifically addresses BNT nanosized powder synthesis using a solution/sol-gel process. Potential advantages of sol-gel-derived powders over conventional powders (i.e., physical mixing of minerals and chemicals) are controlled size and shape, molecular scale homogeneity, and lower processing temperature.

Synthesis of BNT powder has been approached using a modified sol-gel method, which is called the solution/sol-gel (SSG) method. This study intends to show that BNT sol synthesis is possible using bismuth oxide (Bi2O3) and sodium carbonate  $(Na_2CO_3)$  solution in HNO<sub>3</sub>, titanium tetraisopropoxide, and ethylene glycol as precursors. Use of metal oxide or carbonate solution in acids is helpful to decrease costs of ceramic powder synthesis using the sol-gel method. Crystallization of BNT by heat-treating the prepared sol is studied using differential thermal analysis and thermogravimetry (DTA-TG) and high-temperature X-ray diffractometry (XRD) analysis. Morphology and BNT powder size is observed using transmission electron microscopy (TEM).

#### **II. Experimental Procedure**

Bismuth oxide (Bi<sub>2</sub>O<sub>3</sub>, 99.9%, 1-2 µm, Kojundo Chemical Laboratory Co., Ltd., Saitama, Japan) and sodium carbonate (Na<sub>2</sub>CO<sub>3</sub>, 99%, anhydrous, Kojundo Chemical Laboratory) were dissolved in nitric acid (HNO<sub>3</sub>, 69%-70%, Wako Pure Chemical Industries, Ltd., Osaka, Japan). They then were added to ethylene glycol (HOCH<sub>2</sub>CH<sub>2</sub>OH, ≥99.5%, Wako Pure Chemical Industries). The solution was evaporated at 80°C to remove water contained in nitric acid. After the soluntion was distilled, the color of the remaining solution was pale yellow. A stoichiometric amount of titanium tetraisopropoxide  $(Ti(OCH(CH_3)_2)_4) \ge 95\%$ , Wako Pure Chemical Industries) then was added to the solution, and the mixture was stirred at 70°C for 2 h. The color then became transparent yellow. Viscosity of this clear sol was  $\sim 50$  cP. High-temperature XRD analysis (Scintag, Inc., Santa Clara, CA) with CuKa radiation was conducted to determine whether BNT crystal could be formed from the sol and at what temperature BNT crystallized. BNT sol was first dried at 170°C, then put on a platinum plate and analyzed using high-temperature XRD at room temperature, 300°, 500°, 700°, and 900°C after holding at each temperature for 30 min in air. DTA and TG (DTA50, Shimazu Corp., Kyoto, Japan) were performed to determine thermodynamic reaction of the sol; DTA and TG measurements were conducted at 10°C/min heating rate in air.

For further investigation, the obtained BNT sol was dried at 170°C and heat-treated at 500°, 600°, and 700°C for 6 h, Fourier-transform infrared spectroscopy (FT-IR; Model WIN-SPEC100, JEOL, Tokyo, Japan) was used to measure the heattreated powders. Raman spectroscopy (Model SPEX1482D, Spex Industries, Inc., Edison, NJ) of the obtained gel and BNT powders, which were heat-treated at 600°, 700°, and 900°C, was also measured using an argon laser (514.5 nm). TEM investigation (Model H-8100T, Hitachi Co., Ltd., Tokyo, Japan) was performed at 200 kV to distinguish crystal shape and size of powders heat-treated at 700°C for 6 h.

## **III. Results and Discussion**

## (1) Infrared Spectroscopy

Infrared spectra for dried gel and calcined powders are shown in Fig. 1. The bending mode of H–O–H appears at 1635  $cm^{-1}$ , and

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**Fig. 1.** FT-IR spectra of BNT powders (a) dried at  $170^{\circ}$ C and heat-treated at (b)  $500^{\circ}$ , (c)  $600^{\circ}$ , and (d)  $700^{\circ}$ C for 6 h.

the stretching mode of O-H is at 3415 cm<sup>-1</sup>. The sharp and intensive peak at 1384 cm<sup>-1</sup> is due to presence of nitrate, <sup>13,14</sup> which is added as HNO<sub>3</sub> as a solvent for Na<sub>2</sub>CO<sub>3</sub> and Bi<sub>2</sub>O<sub>3</sub>. Two peaks at 2854 and 2921 cm<sup>-1</sup> indicate the C-H stretching mode. Peaks at 1076, 908, and 790 cm<sup>-1</sup> are assigned to CO vibration.<sup>15</sup> When the specimen is heat-treated at 500°C, C-H and CO peaks disappear and the H-O-H bending mode peak diminishes. The nitrate peak remains, although it also becomes smaller. The peak at 1429  $\text{cm}^{-1}$  is assigned to COO vibration. Therefore, carbon remains when the specimen is heat-treated below 600°C. When the specimen is heat-treated at 700°C, nitrate and carbon peaks disappear. However, water is thought to exist in the form of OH because of remaining O–H bending and stretching peaks. Music *et al.*<sup>13</sup> have assigned 650–550 cm<sup>-1</sup> to Ti–O vibration, which is also observed in our experiment (Fig. 1). In addition, it has been confirmed that heat-treated powder at 600°C simultaneously contains yellow and black regions, which show there are two types of powders coexisting at this temperature.

## (2) DTA and TG Analyses

Figure 2 shows DTA and TG curves for dried BNT precursor. Complicated exothermic peaks and accompanied weight loss appear between 200° and 600°C. There is no weight loss above 600°C. Exothermic peaks and weight loss are thought to be caused by residual solvent and organics volatilization and BNT polymerization. More careful analysis for TG curves indicates that there



**Fig. 2.** DTA and TG curves of BNT dried at 170°C in air at a heating rate of 10°C/min.



**Fig. 3.** High-temperature XRD patterns of BNT powders after drying at 170°C. Platinum peaks marked by arrows correspond to platinum specimen holder and heating stage.  $HNO_3$  was used for dissolving  $Bi_2O_3$  and  $Na_2CO_3$ .

are four steps of weight degradation. There is ~20% weight loss up to 230°C, ~64.8% weight loss to 338°C, 80.8% weight loss to 484°C, and 94% weight loss to 600°C. This implies that BNT formation might undergo multiple stages of water and solvent evaporation as well as organics decomposition and polycondensation, which are similar to a previous report on barium titanium citrate thermal decomposition.<sup>16</sup>

BNT crystallization is thought to begin at  $\sim 600^{\circ}$ C or higher, because no weight loss is confirmed. However, it is difficult to determine crystallization temperature from this thermal analysis, because there is no DTA peak above 600°C.

## (3) High-Temperature XRD Analysis

High temperature XRD profiles of dried BNT gel, which were prepared using HNO<sub>3</sub> for dissolving Bi<sub>2</sub>O<sub>3</sub> and Na<sub>2</sub>CO<sub>3</sub>, are shown in Fig. 3. No peaks are evident until 500°C; BNT crystal peaks first appear at 700°C. Peak intensity increases with increasing test temperature up to 900°C. At 700°C, there is a broad peak around  $2\theta = 30^\circ$ , showing the remaining amorphous phase. Crystallization of BNT derived from the solution/sol–gel method thus is found to start below 700°C and finish below 900°C.



**Fig. 4.** High-temperature XRD patterns of dried (170°C) BNT powder prepared using HCl for dissolving  $Bi_2O_3$  and  $Na_2CO_3$  (( $\blacktriangle$ )  $Bi_2Ti_2O_7$ , ( $\blacksquare$ )  $Bi_4Ti_3O_{12}$ , and ( $\bigoplus$ ) BiOCl).



**Fig. 5.** Raman spectra of BNT powders that were heat-treated at 600°, 700°, and 900°C for 6 h. Spectrum of the BNT ceramic body that was sintered at 1150°C for 4 h using solid-state reaction and sintering method is also indicated for comparison.

When BNT synthesis was conducted by dissolving Bi<sub>2</sub>O<sub>3</sub> and Na<sub>2</sub>CO<sub>3</sub> in HCl, mixing with ethylene glycol, and adding titanium tetraisopropoxide, BNT crystallization was not confirmed, as shown in Fig. 4. Figure 4 shows that BiOCl is first formed at 300°C,  $Bi_2Ti_2O_7$  appears at 500°C, and  $Bi_4Ti_3O_{12}$  begins to appear at 700°C. Prasada Rao *et al.*<sup>17</sup> have reported  $Bi_4Ti_3O_{12}$ synthesis from a coprecipitation route using  $TiCl_4$  and  $Bi(NO_3)_3$ ; however, Bi4Ti3O12 obtained from TiCl4 in their study shows contamination of BiOCl, which subsequently leads to formation of Bi<sub>2</sub>Ti<sub>4</sub>O<sub>11</sub>. Mao et al.<sup>18</sup> have reported that they have succeeded in solution/sol-gel synthesis of BiPbSrCaCuO powder by dissolution of metal oxides (Bi2O3, PbO, and CuO) and carbonates (SrCO3 and CaCO<sub>3</sub>) in HNO<sub>3</sub>. Therefore, the type of acid used as a solvent of oxide and carbonate is very important when their solutions are used as precursors for sol-gel synthesis. In the present investigation for BNT synthesis, we therefore infer that dissolution of Bi<sub>2</sub>O<sub>3</sub> and Na<sub>2</sub>CO<sub>3</sub> in HNO<sub>3</sub> enables a yield of an appropriate BNT single-phase compound, because HNO<sub>3</sub> forms no salt that affects formation of impure crystals, such as BiOCl, in the products.

## (4) Raman Spectroscopy

Raman spectroscopy of BNT powders heat-treated at 600°, 700°, and 900°C was measured at room temperature (see Fig. 5).

For comparison, sintered BNT ceramic was prepared using conventional powder mixing and a solid-state sintering method. The Raman spectrum of this sintered specimen was also measured at room temperature: A1(TO) absorption bands of rhombohedral BNT appear at 130, 269, and 541 cm<sup>-1</sup> and an E(TO) band appears at 52.5 cm<sup>-1.<sup>19</sup> In the case of the specimen heat-treated</sup> below 500°C, there is no Raman band, indicating that there is no Raman active mode. When the specimen is heat-treated at 600°C, A<sub>1</sub>(TO) Raman peaks begin to appear. As the heat-treatment temperature increases, Raman scattering intensity increases. Therefore, it is thought that rhombohedral crystals begin to form at 600°C and that BNT crystallization is almost completed at 900°C. Although there exists differences of each experimental condition, these Raman results agree well with DTA and high-temperature XRD investigations. Raman scattering intensity for the powders calcined at 900°C is almost the same as that of the sintered BNT specimen that is prepared using a conventional solid-state reaction sintering method.

## (5) TEM Observation of BNT Powder

TEM images and a corresponding electron diffraction pattern for calcined powder at 700°C are shown in Fig. 6. Figure 6 shows that BNT crystal size is on the nanometer scale ( $\sim$ 100–200 nm) with a polygonal shape when the specimen is heat-treated at 700°C for 6 h. The electron diffraction pattern (Fig. 6(b)) shows a spotty ring pattern, indicating that the powder is crystallized. Figure 6(c) shows the BNT crystal surface is covered with small particles and amorphous phase.

## IV. Conclusions

In this study, solutions of  $Bi_2O_3$  and  $Na_2CO_3$  in HNO<sub>3</sub> are used as precursors for BNT sol-gel synthesis. Nanosized BNT powders (100–200 nm) are first synthesized using the sol-gel method. Sol-gel synthesis of BNT is possible without using high-cost alkoxide. Results of high-temperature XRD, DTA and TG analyses, and Raman spectroscopy indicate that BNT crystallization occurs above 600°C. Moreover, DTA-TG and IR spectroscopy show that BNT crystals seem to be synthesized in multiple stages of solvent evaporation, organics volatilization, and condensation. TEM photography shows that 100–200 nm sized crystals of BNT are synthesized using the present sol-gel method when heat treatment at 700°C for 6 h is used. This method is considered to be useful to prepare a lead-free piezoelectric BNT material. This result implies that the present sol-gel process has advantages for



Fig. 6. (a) TEM photograph and (b) corresponding selected-area electron diffraction pattern for BNT powder that was heat-treated at 700°C for 6 h. (c) BNT crystal surface is covered with fine particles and amorphous phase.

preparation of thin films and as a starting powder for sintered BNT ceramics.

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