Size-Controlled Hydrothermal Synthesis of Bismuth Sodium and Bismuth Potassium Titanates Fine Particles and Application to Lead-Free Piezoelectric Ceramics

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Cubic-shaped Bi₅₋ₓNaₓKₓTiO₃ (BNT) and BiₓK₃₋ₓTiO₃ (BKT) fine particles with narrow size distribution were directly prepared as a single phase from a suspension of TiO₂ anatase nanoparticles mixed with Bi(OH)₃ in aqueous alkaline metal hydroxides solutions by highly condensed hydrothermal method at 200–250°C for several hours. It was investigated that the effect of particle mean size on the piezoelectric properties of thus obtained BNT and BKT fine particles. [doi:10.2320/matertrans.M2010419]

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1. Introduction

Lead zirconium titanate, PbZrTiO₃ (PZT), is widely-used as piezoelectric ceramics; however, such lead-containing products evoked problems of human health and environment.¹⁻³ Thus, innovation of lead-free piezoelectric ceramics has attracted a great deal of attention in material science.⁴⁻⁵ Recently, piezoelectric properties and high Curie temperatures based on bismuth sodium titanate (BNT) and bismuth potassium titanate (BKT) derivatives have been considered to be an excellent candidate.⁶⁻⁸ In this regard, BNT and BKT derivatives are one of the most promising materials for alternative lead-free piezoelectric ceramics, hence it must replace PZT. The intensive efforts have been carried out to improve the characteristic piezoelectric properties of BNT and BKT by doping of metal ion species⁹,¹⁰ and changing of the sintering conditions.¹¹,¹² However, such efforts to obtain BNT- and BKT-based ceramics have been mainly investigated by solid phase sintering systems, expect for several examples.¹³⁻¹⁶ In contrast, generally speaking, liquid-phase synthesis of such ceramic particles has large advantages to obtain highly purified and homogeneous powders controlled in size, crystalline diameter, and morphology.¹⁷,¹⁸ This synthetic systems will be expected to control precisely nano-structures of BNT- and BKT-based novel-types of piezoelectric ceramics. Recently, we have developed preparation technique of BNT fine particles from aqueous solutions by applying the Gel-Sol method,¹⁹ which is one of a liquid phase particle synthesis system for the precise control of size, shape, composition, and structure of monodispersed particles in large quantities, developed by Sugimoto et al.²⁰ The synthesis method has a better record on the preparation of monodispersed hematite,²¹⁻²⁴ TiO₂,²⁵⁻³¹ and BaTiO₃ particles with perovskite-structure.³² We have been applying this method to the preparation of various shapes of BNT fine particles controlled in their size and shape, such as sphere, rod, and nanotube.²⁰ However, the problem at stake was the by-production of bismuth metal during this process. This serious problem of undesired change in Na/Bi/Ti ratio of as-prepared product as well as the contamination of Bi metal in ceramic materials causes unexpected trouble such as current leak and breakdown of the ceramics. In this regard, the further investigation to predominantly synthesize BNT and BKT fine particles without any impurities such as bismuth metal is essential for the development of lead-free piezoelectric materials with high performance.

In the present study, an efficient procedure for the predominant preparation of BNT and BKT fine particles has been developed with using a highly condensed hydrothermal method. In this procedure, the control in shape to cube and in crystallinity of BNT and BKT fine particles with a narrow size distribution has successfully been attained, where aqueous suspension mixture of anatase-type TiO₂: Bi(OH)₃, and alkaline metal hydroxides has been used as a precursor. The effect of particle mean size on the piezoelectric properties of thus obtained BNT and BKT fine particles will also be discussed.

2. Experimental

Titanium oxide (anatase, Cat. No: 205-01715), sodium hydroxide (NaOH, Cat. No: 198-13765), 8 mol/l sodium hydroxide solution (Cat. No: 194-09575), potassium hydroxide (KOH, Cat. No: 168-21815), and 8 mol/l potassium hydroxide solution (Cat. No: 169-20365) were purchased from Wako Pure Chemicals Inc. and used as-received. Bismuth hydroxide (Bi(OH)₃) from Kojundo Chemical Laboratory Co., Ltd was used as a bismuth source. Water was doubly distilled, deionized, and filtered prior to use. X-ray diffraction (XRD) measurements were carried out on a Rigaku Ultima-IV system using CuKα radiation (40 kV,
40 mA) equipped with a D/teX Ultra detector. FE-SEM images were taken by using a Hitachi S-4800 system with an acceleration voltage of 20 kV.

The preparation procedure of BNT or BKT fine particles was as follows. Initially, anatase-type TiO₂ powder (243 mg, 3.0 mmol) was mixed with Bi(OH)₃ (390 mg, 1.50 mmol) in alkaline metal hydroxides solutions (0–6 mL) with stirring. Then, the total volume was adjusted to 12 mL, and the resulting suspensions were further stirred for 10 min at room temperature. The concentrations of Ti⁴⁺ and Bi⁴⁺ in the suspension were 0.25 and 0.125 mol dm⁻³, respectively, and the alkaline metal hydroxides concentration was adjusted from 4.0 to 20 mol dm⁻³. Then the resulting suspension was placed into a Teflon-lined autoclave (Parr Instrument, 4749) and aged at 250°C for 3–24 h with stirring at 30 rpm in an oven made by HIRO COMPANY to nucleate and grow the BNT and BKT fine particles. Obtained powder was collected by centrifugation (18,000 rpm, 15 min), and the sediments were washed three-times with water, by dispersing followed by centrifuging. The resulting precipitates were dried at 60°C in an oven to obtain BNT and BKT fine particles. BNT powders by solid-phase synthesis, as a comparison, was prepared as follows. Initially, Bi₂O₃, Na₂CO₃, and TiO₂ powders with the mixing molar ratio of 1/1/2 were well ground with a planetary ball mill. The resulting mixture was sintered at 800°C for 2 h and fractured so that the precursor powders were obtained for the solid-phase preparation of BNT ceramics. For the evaluation of piezoelectric properties of BNT fine particles, BNT ceramics were prepared as follows. Hydrothermally and solid-phase prepared BNT powders were obtained using 4.0 and 8.0 mol dm⁻³ to 4.0 and 8.0 mol dm⁻³ concentrations. When the initial concentrations are adjusted to 4.0 and 8.0 mol dm⁻³, broad diffraction peaks, can be assigned as the formation of BNT phase with a rhombohedral crystal structure (JCPDS No. 01-070-9850), are observed as a major phase, and the crystallite sizes of the BNT particles obtained using 4.0 and 8.0 mol dm⁻³. NaOH were calculated to be 12.2 and 20.5 nm, respectively, from the XRD patterns with Scherrer’s equation. In spite of the formation of BNT phase, the anatase-type TiO₂ phase as a starting material is still observed. As the initial NaOH concentrations increased up to 10 mol dm⁻³, the formation of BNT phase becomes single phase but the anatase phase is negligible (Fig. 1(c)). The BNT peaks are sharpened by the further increase in the NaOH concentrations from 10 to 16 mol dm⁻³ as shown in Fig. 1(c)–(f). The crystallite sizes of the BNT fine particles obtained at the NaOH concentrations of 10, 12, 14.

3. Results and Discussion

3.1 Effect of NaOH concentration on formation of BNT particles

For metallic oxide particle synthesis in hydrothermal system, hydroxide ion concentration is a decisive factor to form BNT particles, because of TiO₂ solubility and the formation rate of oxide due to alkaline conditions.

Effect of initial NaOH concentrations has initially investigated on the formation rate of BNT fine particle. Aging temperature and period of mixed aqueous suspensions consist of anatase, Bi(OH)₃, and NaOH were fixed at 250°C and 3 h, respectively. Figure 1 shows X-ray diffraction (XRD) patterns of solid particles formed by different initial NaOH concentrations. When the initial concentrations are adjusted to 4.0 and 8.0 mol dm⁻³, broad diffraction peaks, can be assigned as the formation of BNT phase with a rhombohedral crystal structure (JCPDS No. 01-070-9850), are observed as a major phase, and the crystallite sizes of the BNT particles obtained using 4.0 and 8.0 mol dm⁻³ NaOH were calculated to be 12.2 and 20.5 nm, respectively, from the XRD patterns with Scherrer's equation. In spite of the formation of BNT phase, the anatase-type TiO₂ phase as a starting material is still observed. As the initial NaOH concentrations increased up to 10 mol dm⁻³, the formation of BNT phase becomes single phase but the anatase phase is negligible (Fig. 1(c)). The BNT peaks are sharpened by the further increase in the initial NaOH concentrations from 10 to 16 mol dm⁻³ as shown in Fig. 1(c)–(f). The crystallite sizes of the BNT fine particles obtained at the NaOH concentrations of 10, 12, 14,
and 16 mol dm$^{-3}$ were calculated as 21.6, 24.9, 34.0, and 72.8 nm, respectively, from a peak of 32.4° in 2θ of XRD pattern. FE-SEM images of as-prepared particles are shown in Fig. 2. Morphology and particle mean size of the resulting particles are drastically changed by the initial NaOH concentrations. Namely, nearly spherical BNT fine particles with rough surfaces are obtained in the NaOH concentrations range from 4 to 10 mol dm$^{-3}$. In contrast, basically cubic-shaped BNT fine particles with sharp edges are obtained at the higher NaOH concentrations (Figs. 1(d), (e), and (f)). The average particle sizes of the BNT fine particles were calculated by counting 100 particles taken by FE-SEM observation, and the mean sizes with a size distribution of BNT particles at different NaOH concentration were 287 ± 62 nm (4.0 mol dm$^{-3}$), 364 ± 78 nm (8.0 mol dm$^{-3}$), 334 ± 55 nm (10 mol dm$^{-3}$), 418 ± 91 nm (12 mol dm$^{-3}$), 2.56 ± 0.42 μm (14 mol dm$^{-3}$), and 10.4 ± 2.9 μm (16 mol dm$^{-3}$). Thus, the particle mean sizes are increased by the increasing initial NaOH concentrations. In any case, the particle mean size was much larger than the crystallite size calculated from XRD pattern so that as-prepared particles were polycrystalline. Since bismuth metal as by-product was not found in any case, the intended objective to prevent it could be achieved.

3.2 Time evolution of BNT particle formation

Figure 3 exhibits FE-SEM images of BNT fine particles obtained with aging time at 250°C with the different initial NaOH concentrations. In the case of the system using 8.0 mol dm$^{-3}$ NaOH, as the aging time was prolonged, formation of BNT fine particles, and the anatase phase was totally disappeared by XRD measurement. BNT fine particles with random in shape are still observed even if the aging period is changed to 24 h (Fig. 3(c)). Similar BNT fine particles are also seen in the system using 10 mol dm$^{-3}$ NaOH for 6 h aging as shown in Fig. 3(d). However, the further aging for 24 h at 250°C promotes the formation of cubic-shaped BNT fine particles as shown in Figs. 3(e) and

![Fig. 2 FE-SEM images of BNT fine particles formed by aging at 250°C for 3 h NaOH concentrations: (a) 4.0; (b) 8.0; (c) 10; (d) 12; (e) 14; (f) 16 mol dm$^{-3}$. The scale bar in (a) is common for images (b)–(e) but not for (f). The insets in (a)–(d) are expanded images for four times.](image1)

![Fig. 3 FE-SEM photographs of BNT fine particles formed by changing the NaOH concentrations at different aging time. The aging temperature was fixed at 250°C. (a)–(c): 8.0 mol dm$^{-3}$; (d)–(f): 10 mol dm$^{-3}$; (g)–(i): 12 mol dm$^{-3}$; (j)–(l): 14 mol dm$^{-3}$; (m)–(o): 16 mol dm$^{-3}$. The aging time is shown in the images. The scale bar in (a) is common for images (b)–(l). The insets in (a)–(i) are expanded images for four times.](image2)
3.3 Preparation of BKT particles: Effects of KOH concentration and aging period

This BNT synthesis system was applied to the formation of BKT fine particles, which is also a typical ferroelectric materials with a complex perovskite structure of tetragonal symmetry at room temperature, and has a relatively high Curie temperature of 380°C. Mixed aqueous suspensions consisting anatase-type TiO$_2$, Bi(OH)$_3$, and KOH were aged at 250°C and 3 h. Figures 4 and 5 show XRD patterns and FE-SEM images of solid particles obtained by changing initial KOH concentrations from 4.0 to 16 mol dm$^{-3}$. The scale bar in (a) is common for all images. The insets are 4 times magnified images of each photograph.

(f). Such morphological change might be derived by the dissolution and precipitation of BNT particles with random in shape and rough surfaces so as to form single-crystalline structures. At the higher NaOH concentrations of 14 and 16 mol dm$^{-3}$, once formed cubic morphology is kept if the aging periods are prolonged to 24 h. Particle growth such as Ostwald ripening is not observed during this aging period, possibly because of the low solubility of the BNT fine particles in this system. We have also investigated the effect of aging temperature on the BNT particle synthesis. If the aging temperature was changed to 200°C and aged for 3 to 24 h, BNT phase was obtained as a major product. However, unidentified needle-like particles were also found as a by-product.

BKT phase with a cubic crystal structure is obtained as a predominant one at the initial KOH concentration of 16 mol dm$^{-3}$, while the morphology is changed from cube to irregular-shapes with rough surfaces. Such morphological change might be due to coagulation process at the higher alkaline condition. The effect of the aging time with different KOH concentrations has been investigated. However, even if the time was changed from 3 to 24 h, any difference in size and morphology was not clearly observed.

3.4 Piezoelectric property of hydrothermally prepared BNT and BKT fine particles

As a result, the piezoelectric properties of BNT-based ceramics have been evaluated, where the sample was prepared with BNT fine particles obtained in the present study. For the investigation of the effect of particle size of the BNT on piezoelectric properties, two types of cubic-shaped BNT fine particles with different in size as shown in Fig. 3(e) and (k) were tested, where the average particle mean size with the size distribution was 250 ± 47 nm and 2.2 μm ± 0.4 μm, respectively. BNT ceramics were prepared from the cubic-shaped BNT fine particles (Figs. 3(e) and (k)), and the obtained ceramics were abbreviated as BNT1 and BNT2 (Figs. 6(a) and (b)). BNT3, prepared by solid phase synthesis method, the conventional one, was used as a comparison (Fig. 6(c)). The optimized sintered temperatures of the BNT ceramics BNT1, BNT2, and BNT3 are 1010, 1010, and 1150°C, respectively. The resulting grain diameters of the BNT ceramics BNT1, BNT2, and BNT3 are 8.6, 14.7, and 2.6 μm, respectively. BNT1 and BNT2 originally prepared by this method have great advantage in the grain size, compared with the conventional one. This result suggested that the hydrothermally prepared BNT has low-temperature sintering property. We have also tried to prepare BKT-based ceramics, however, low sintering property of BKT prevented to obtain pellet samples. Table 1 summarized piezoelectric properties of BNT ceramics sintered by different temperatures. Density ($\rho$) of the BNT ceramics was increased with the increase in the sintering temperature. The theoretical
density of BNT is 5.992 g cm\(^{-3}\), closely-packed BNT ceramics are obtained in the case of BNT1 because the maximum value was reached at 5.68 g cm\(^{-3}\) at 1110°C. However, the density of BNT2 was remarkably low so that BNT2 was so brittle as to polarize the resulting ceramics even at the sintering temperature of 1110°C. Hence, the further characterization of piezoelectric properties was not evaluated. On the other hand, in the case of BNT3, it is essential to sinter at higher temperature than the case of BNT1 to obtain the ceramics with high density. As a result of the comparison of piezoelectric properties such as loss tangent (\(\tan \delta\)), dielectric constant (\(\varepsilon_{33} / \varepsilon_0\)), coupling factor (\(k_p\)), and piezoelectric constant (\(d_{33}\)) of BNT1 and BNT3, BNT1 shows excellently comparable characteristic features even at the lower sintering temperature to BNT3. Such low-temperature sintering property of hydrothermally prepared submicron-sized BNT fine particles has large advantage for energy saving. Relatively lower \(d_{33}\) value of BNT1 than BNT3 might be due to the grain size of the resulting BNT ceramics. Further trial to optimize sintering conditions to obtain BNT ceramics with small grain sizes may lead to enhancement of the piezoelectric properties. Detailed investigations on effect of particle morphology etc. are now in progress for the development of lead-free piezoelectric materials with highest performance.

4. Conclusions

We have prepared BNT and BKT fine particles with cubic-shape controlling with size by a hydrothermal method starting from anatase-type TiO\(_2\) nanoparticles. Main concluding remarks obtained this work are as follows:

1. Cubic-shaped BNT fine particles were fabricated in a single phase starting from anatase-type TiO\(_2\), NaOH, and Bi(OH)\(_3\) by a highly condensed hydrothermal method. The particle mean sizes were readily controlled by the changing of the initial NaOH concentrations, the particle sizes were increased by the increasing NaOH concentrations.

2. BKT fine particles with cubic morphology were also prepared by the aging of mixed suspension consist of anatase-type TiO\(_2\), KOH, and Bi(OH)\(_3\). The crystal structure of the BKT fine particles was changed from tetragonal to cubic by the increasing of the KOH concentration up to 16 mol dm\(^{-3}\).

3. BNT ceramics obtained by sintering of hydrothermally prepared BNT fine particles showed lower sintering property than the corresponding BNT powders prepared by way of solid phase synthesis.

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REFERENCES