

Fine grained bismuth sodium titanate ceramics prepared via vibro-milling method

O. Khamman · A. Watcharapasorn · K. Pengpat · T. Tunkasiri

Received: 7 December 2005 / Accepted: 3 May 2006 / Published online: 13 July 2006
© Springer Science+Business Media, LLC 2006

In the past few decades, the production of piezoelectric and dielectric materials has considerably increased world-wide especially in the electronic ceramic industries. However, most of the important commercial ceramics, consist of lead-based compounds such as $\text{Pb}(\text{Zr,Ti})\text{O}_3$ (PZT), PbTiO_3 (PT) and $\text{Pb}(\text{Mg}_{1/3}\text{Nb}_{2/3})\text{O}_3$ (PMN) which normally require sintering temperature about 1200–1250 °C. At these temperatures, vaporization of lead tends to occur at unknown rate and is considered to be one of the most important environmental pollutants. Therefore, a number of researchers have attempted to find new lead-free or low-lead-content ferroelectrics having similar properties to those found in the lead based materials.

Bismuth sodium titanate ($\text{Bi}_{0.5}\text{Na}_{0.5}\text{TiO}_3$) or BNT is known to be one of the promising candidates for lead-free materials. It is ferroelectric at room temperature, having the perovskite structure with a formula ABO_3 where Bi and Na situate at A site [1]. It also has a rhombohedral crystal structure [2]. The BNT compound has an anomaly phase transformation of ferroelectric rhombohedral to antiferroelectric tetragonal at about 220 °C and to paraelectric tetragonal phase at $T_c = 320$ °C [3]. The tetragonal phase above 320 °C finally changes to cubic phase above 520 °C [4]. At 320 °C, the dielectric constant is highest and temperature dependence of the BNT ceramics shows a diffused behaviour with strong ferroelectricity similar to relaxor-type ferroelectrics [5, 6]. Therefore, BNT

seems to be a potentially good candidate as lead-free ceramics for many applications such as dielectric, piezoelectric and pyroelectric applications [7, 8].

The piezoelectric properties such as piezoelectric constant (d_{33}) and electromechanical coupling factors (k_{33} and k_{31}) of the BNT ceramic are still below those of the high-lead-content piezoelectrics especially commercial PZT. Hence, many attempts to improve the piezoelectric and dielectric properties of BNT have been carried out. Kuharungrong and Schulze [9] reported that Pb-doped BNT ceramics showed a uniform small grain structure with high density. Subsequently, they obtained high dielectric constant. However, the studies of optimum processing parameters for the fabrication of BNT ceramics having optimum dielectric properties have scarcely been done. Consequently, the possibility of improving such properties via optimization of processing parameters might be an easy and economical way. According to Kashcheev and Zemlyanoi [10], powder processing via vibro-milling could stimulate a higher grain activity [10] and the onset of sintering was observed to occur at lower temperature. Therefore, in this work, vibro-mill was employed to produce BNT powders. In addition the effects of sintering temperatures, density, phase formation as well as microstructural evolution of ceramics have been carefully studied in order to find the optimum processing conditions for forming highly dense BNT ceramics.

The BNT ($\text{Bi}_{0.5}\text{Na}_{0.5}\text{TiO}_3$) powder of stoichiometric composition was prepared using a vibro-milling technique. Bi_2O_3 (Fluka, ≥ 98.0 % purity), Na_2CO_3 (Aldrich, $\geq 99.5\%$ purity) and TiO_2 (Aldrich, $\geq 99.5\%$ purity) powders were used as starting materials. The oxide powders were milled via a McCrone vibro-mill

O. Khamman · A. Watcharapasorn · K. Pengpat (✉) · T. Tunkasiri
Department of Physics, Faculty of Science, Chiang Mai University, Chiang Mai 50200, Thailand
e-mail: kpengpat@gmail.com

using a common plastic container for 30 min and 1 h with zirconia balls in ethanol and dried at 120 °C for 12 h. The powder mixtures were calcined at temperatures between 500 and 1100 °C for 1 h with heating/cooling rate of 5 °C min⁻¹ in air. After that, all calcined powders were investigated by X-ray diffraction techniques in order to identify the crystalline phase existing in the calcined powder.

Powders containing 3 % poly-vinyl alcohol (PVA) were pressed into discs of 10 mm in diameter and 2 mm in thickness. They were sintered at 1100, 1150 and 1175 °C for 2 h in an air atmosphere. The density of each sample was measured by the Archimedes method. The relative densities were calculated as a percentage of the theoretical densities. Microstructures of these samples and the calcined BNT powders were observed using a scanning electron microscope (JEOL, JSM-840A). An average grain size was obtained using a mean linear intercept method. Both surfaces of the sintered ceramic discs were polished and painted with silver-paste. The electrical measurements such as dielectric constant (ϵ_r) and loss tangent ($\tan\delta$) were measured at 1 kHz using an LCZ meter (HP 4276A). For comparison, BNT ceramics prepared from conventional ball-milled powders were also carried out. The calcining and sintering temperatures were 700 and 1100 °C, respectively. The microstructural evolution as well as other properties of these ceramics are also investigated.

The X-ray diffractograms of calcined BNT powders prepared via vibro-milling method are shown in Fig. 1. The single BNT phase started to show up at 700 °C and above. Every XRD peak could be attributed to rhombohedral perovskite-BNT phase, consistent with

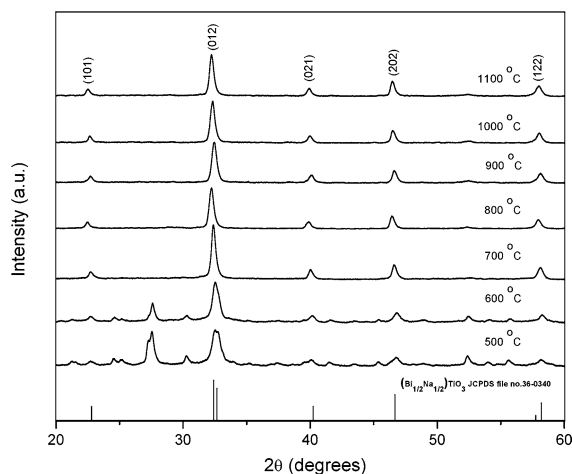


Fig. 1 XRD patterns of BNT powder milled via vibro-milling calcined at various temperatures for 1 h with heating/cooling rates of 10 °C/min

JCPDS file number 36–0340. This temperature was slightly higher than that reported by Hao et al. [11] who could obtain phase-pure BNT powder at 600 °C. This may be due to the differences in the synthesis method since Hao et al. [11] employed the stearic acid gel method to synthesize the $\text{Bi}_{0.5}\text{Na}_{0.5}\text{TiO}_3$ nano crystalline powders. The X-ray diffractogram of the calcined powders prepared using a conventional ball mill and the ceramics sintered at 1100 °C showed no significant difference to that shown in Fig. 1.

Scanning electron micrographs of BNT powders obtained via vibro-mill and conventional ball-mill techniques, calcined at 700 °C for 1 h are shown in Fig. 2. The average particle size of BNT powders estimated from both SEM micrographs were almost the same (0.2–0.4 μm). However, our results are comparable to that of Pookmanee et al. [12] despite the fact that they obtained the BNT powders through hydrothermal route.

Micrographs of BNT ceramics sintered at 1100, 1150 and 1175 °C prepared from vibro-milled powders are shown in Fig. 3(a–c). It can be seen that as the sintering temperature was increased, the grain size also increased remarkably. At 1175 °C, exaggerated grain growth occurred. A micrograph of ceramic sintered at 1100 °C using conventional ball-milled powders is shown in Fig. 3(d) for comparison. It can be seen that grain sizes of BNT ceramics obtained from vibro-milled powders are much smaller than that prepared from conventional ball-milled powders. SEM analysis confirmed that all BNT ceramics were sintered to a highly dense state. Some physical properties of BNT ceramics were summarized in Table 1, together with that of Kuharuangrong and Schulze [9], Pookmanee et al. [12] and Peng et al. [13]. It can be seen that the densities of ceramics sintered at 1100, 1150 and 1175 °C were almost the same, about 95% of the theoretical density (5.99 g/cm³), which was in the similar range of that found in Herabut and Safari [13] of between 93% and 95% and Nagata and Takenaka [14] of more than 90%. Furthermore, these density values were significantly higher than that obtained from the conventional ball-mill, i.e. ~85% in our result and 88% from Peng et al. case [15].

In Table 1, the dielectric constants at room temperature (ϵ_r) and at T_C ($\epsilon_{r\text{max}}$) of the BNT ceramics, prepared from vibro-milled powders, show a relatively higher value than that of Kuharuangrong and Schulze [9]. This may correspond to the effect of smaller grain size ceramics causing higher values of the dielectric constants as previously reported by Kinoshita and Yamaji [16]. Similar results were obtained in our experiment when the ceramics obtained by two techniques were compared at the same sintering

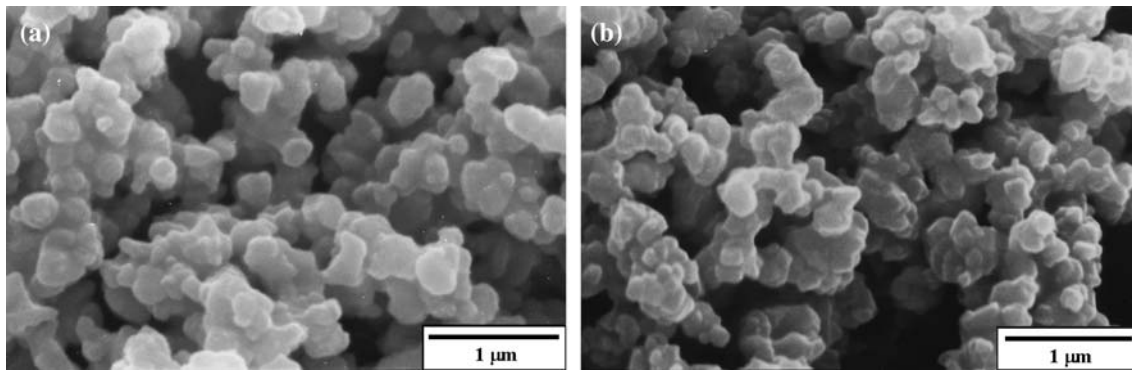


Fig. 2 SEM micrographs of BNT powder calcined at 700 °C for 1 h with vibro-milling technique prepared through (a) rapid vibro-mill and (b) conventional ball-mill

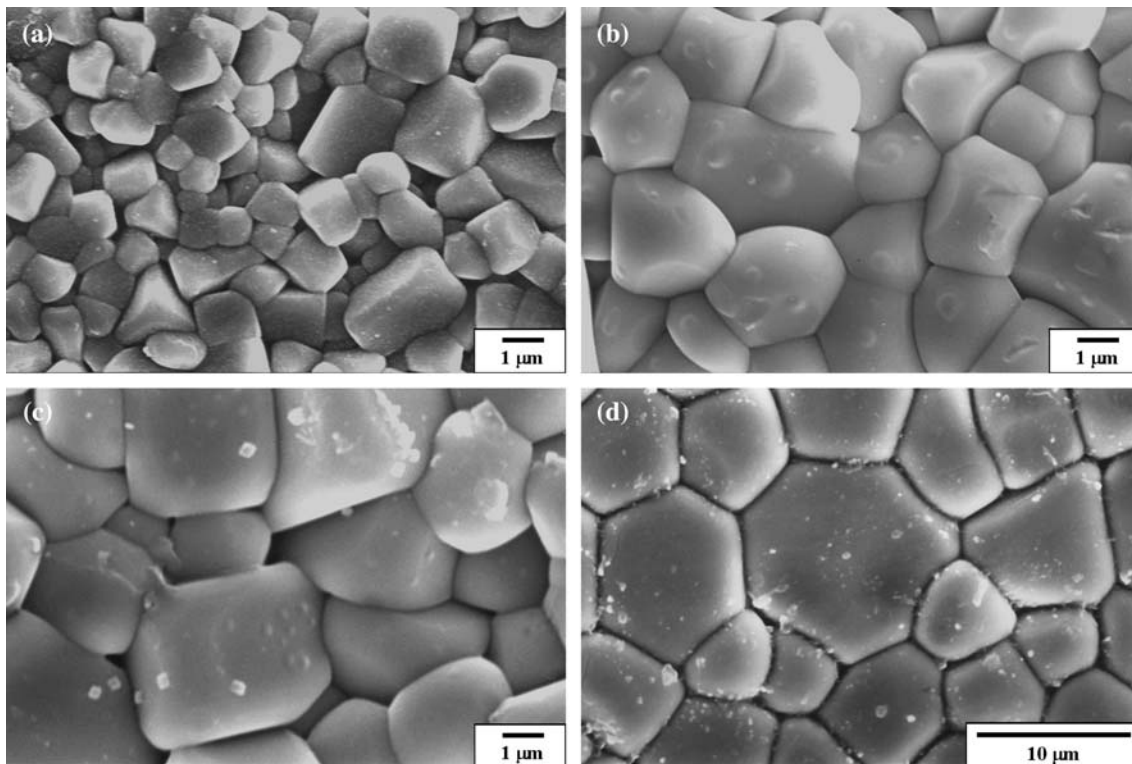


Fig. 3 SEM micrographs of BNT ceramics at different sintering temperatures (a) 1100 °C / 2 h (b) 1150 °C / 2 h and (c) 1175 °C / 2 h (via vibro-milling) and (d) 1100 °C / 2 h (via conventional ball-milling)

temperature. BNT ceramics from vibro-milled powders had an average grain size of 1.25 μm with ϵ_r of 773 while ceramics from ball-milled powders had a grain size of 5.22 μm with ϵ_r of 613. However, the ceramics (vibro-mill) sintered at different temperatures gave no trend for the dielectric constant at room temperature but the clearer trend was found for the $\epsilon_{r \text{ max}}$ at 1 kHz as the $\epsilon_{r \text{ max}}$ value increased with decreasing grain size. It seems that sintering temperatures affected both the grain size and dielectric properties simultaneously.

The plots of ϵ_r as a function of temperature for BNT ceramics prepared using various processing conditions

are shown in Fig 4. The maximum ϵ_r increases as the sintering temperature increases. The Curie temperature was slightly reduced when the grain size decreased. Similar trend was observed in BaTiO₃ ceramics [16]. Similar change of phase (antiferroelectric to paraelectric) which yields the maximum dielectric constant at T_C was also reported in lead based compound such as lead barium zirconate [17].

In conclusions, BNT compounds were successfully synthesized using powder mixture obtained via rapid vibro-milling method. Calcination was carried out at 500–1000 °C for vibro-milled powders and 700 °C for

Table 1 Relative density compared to the theoretical density, grain size, ϵ_r max and T_c of the BNT ceramics^a prepared in this work

Milling technique	Sintering temperature (°C)	Relative Density (%)	Grain Size (μm)	ϵ_r at room temp.	$\tan\delta$ (%) at room temp.	ϵ_r max at 1 kHz	T_c (°C)
Ball-milling ^a	1100	85	5.22	613	2.0	2200	320
Vibro-milling ^a	1100	95	1.25	773	1.5	3050	310
	1150	95	2.55	770	1.7	3400	310
	1175	94	2.85	736	2.0	4200	320
	1175	96	8.0	700	–	2700	320
Kuharuangrong and Schulze [9]	1175	96	–	–	–	–	–
Pookmanee [12]	1050	95	3.8	240	1.1	–	–
Herabut and Safari [13]	1200	>90	–	–	–	–	–
Nagata and Takenaka [14]	1180	88	–	~700	1.75	3700	320

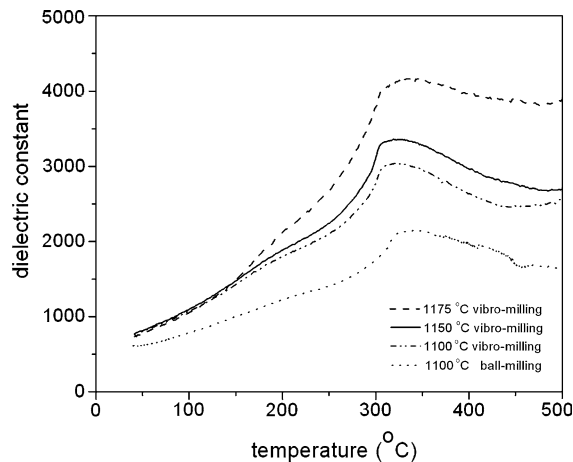


Fig. 4 Dielectric constants for various sintering temperatures of BNT ceramics

ball-milled powder. The average particle sizes of BNT powders obtained from both milling methods, calcined at 700 °C showed no significant difference and were in the range of 0.2–0.4 μm . The average densities of ceramics obtained from vibro-milled powders were about 95% of the theoretical density and were higher than that obtained from ceramics prepared from ball-milled powder (i.e. ~85%). The dielectric properties of the former were also higher than the latter. The results in this investigation suggest that vibro-milling technique is an efficient way to produce high quality BNT powders and ceramics.

Acknowledgements The authors would like to express their sincere thanks to the Thailand Research Fund and Graduate school and Faculty of Science, Chiang Mai University, THAILAND.

References

- Smolenskii A, Ispov VA, Agranovskaya AI, Krainik NN (1961) *Sov Phys Solid State* 2:2651
- Ivanova VV, Kapyshev AG, Venetsey YN, Zhdanov GS (1962) *Acad Sci USSR Bull Phys Ser* 26[3]:358
- Sakata K, Masuda Y (1974) *Ferroelectric* 7:347
- Zvirgzes JA, Kapostins PP, Zvirgzde JV, Kruzina TV (1982) *Ferroelectrics* 40:75
- Hagiyev MS, Ismailzade IH, Abiyev AK (1984) *Ferroelectrics*, 56:215
- Takenaka T, Maruyama K, Sakata K (1991) *Jpn J Appl Phys* 30[9B]:2236
- Takenaka T, Sakata K (1989) *Ferroelectrics* 95:153
- Hagiyev MS, Ismailzade IH, Abiyev AK (1984) *Ferroelectrics* 56:215
- Kuharuangrong S, Schulze W (1996) *J Am Cer Soc* 79 [5]:1273
- Kashcheev ID, Zemlyanoi KG (2005) *Refraction and Industrial Ceramics* 46[1]
- Hao J, Wang X, Chen R, Li L (2005) *Mater Chem Phys* 90:282
- Pookmanee P, Rujijanagul G, Ananta S, Heimann RB, Phanichphant S (2004) *J Eur Ceram Soc* 24:517
- Herabut A, Safari A (1997) *J Am Ceram Soc* 80:2954
- Nagata H, Takenaka T (2001) *J Euro Ceram Soc* 21:1299
- Peng C, Li JF, Gong W (2005) *Mat Lett* 59:1576
- Kinoshita K, Yamaji A (1976) *J Appl Phys* 47:371
- Bongkarn T, Rujijanagul G, Milne SJ (2005) *Mat Lett* 59:1200