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# Effect of attrition milling on the piezoelectric properties of $Bi_{0.5}Na_{0.5}TiO_3$-based ceramics

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**Abstract** Bismith sodium titanate (BNT)-based powders were prepared by conventionally mixed-oxide method using $Bi_2O_3$, $Na_2CO_3$ and $TiO_2$. The $La_2O_3$ was added as the modifier to the BNT composition for easily poling and reducing an abnormal dielectric loss at high temperatures. In this study, the investigated compositions were $Bi_{0.5}Na_{0.5}TiO_3$ and $Bi_{0.5}Na_{0.485}La_{0.005}TiO_3$. The powders were calcined at 900 °C for 2 h by slow heating rate at 100 °C/h. The calcined BNT-based powders were then attrition-milled for 3 h with a high speed at 350 rpm. After drying, the fine powders were uniaxially pressed and then cold-isostatically pressed (CIP) at 240 MPa for 10 min. All pressed pellets were sintered at 1000–1100 °C for 2 h in air atmosphere. The microstructure of sintered pellets was investigated by SEM. Results of dielectric and piezoelectric property measurement were also reported.

**Keywords** Lead-free piezoelectric · Bismuth sodium titanate · Attrition milling · Perovskite

## 1 Introduction

The perovskite-structure bismuth sodium titanate ($Bi_{0.5}Na_{0.5}TiO_3$, BNT) has been considered as the prominent lead-free candidate for the replacement of lead-based piezoelectric ceramics for last three decades. It was found that BNT composition presented a high coercive field of 73 kV/cm$^2$ and a Curie temperature at 320 °C [1–3]. To improve its electrical and piezoelectric properties, compositional modifications at A-site and B-site cations of the BNT system were performed. The results indicated that the 0.5 at.% La substitution in $Na^+$ site provided the great improvement in piezoelectric properties [1]. Samples of the BNT with La modification exhibited a dielectric permittivity of 515, electromechanical coupling factors $k_t$ of 45% and $k_p$ of 13%, a piezoelectric charge coefficient $d_{33}$ of 100 pC/N, and a hydrostatic piezoelectric coefficient $d_h$ of 120 pC/N.

Recently grain orientation has been used as one of the effective methods to enhance the piezoelectric properties of polycrystalline ceramics. The new approach allows the complex single-crystal shapes to be produced by seeding and recrystallizing ceramics under the influence of grain boundary curvature. One of the key requirements for successful method is a high surface free energy of the matrix which implies very fine grain sizes for the polycrystalline ceramics [4]. It is typically accepted that sol–gel process is the best route to obtain multicomponent ceramics at lower firing temperature [5]. However, the process is relatively expensive, difficult to scale up for mass production and requires a high sintering temperature. The comminution processes of milling are widely used in ceramic processing to reduce the average particle size of a material, to modify the particle size distribution and to modify the shape of particles [6]. One of the common mills used for grinding ceramic materials is an attrition mill used industrially for wet grinding to below 1 μm and for the dispersion of agglomerates of submicron particles. This comminution process can produce very fine particles in a shorter milling time compared with the common ball milling technique.

The purpose of this paper is to investigate the sintering and piezoelectric characteristics of the BNT and La-modified BNT systems from powder processing viewpoint.

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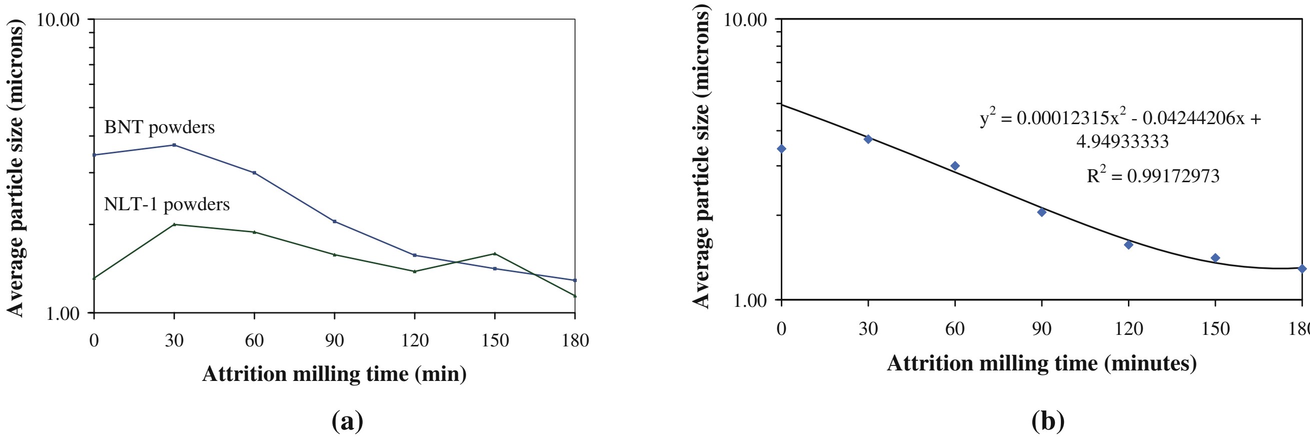


**Fig. 1** Average particle size of BNT and NLT-1 compositions after attrition milling from 30–180 min. (**a**) A comparison of average particle size between BNT and NLT-1 powders. (**b**) The relationship between the average particle sizes of BNT-powders and milling time

To reveal the influence of comminution, two series of ceramics with different comminution, i.e., ball milling and attrition milling, were prepared. It was found that difference in comminution altered the densification of the BNT-based ceramics and enhanced the piezoelectric properties.

## 2 Experimental procedure

Bismuth sodium titanate ($Bi_{0.5}Na_{0.5}TiO_3$, BNT) and 0.5 at.% lanthanum modified BNT ($Bi_{0.5}Na_{0.485}La_{0.005}TiO_3$, NLT-1) were prepared using the conventional mixed-oxide method. The starting raw materials were $Bi_2O_3$ (Fluka, purum >98.5%) and $Na_2CO_3$ (Fluka, Puriss >99%) and the rutile ($TiO_2$) of Alfa Aesar (purity >99.5%). For the NLT-1, $La_2O_3$ (Fluka, puriss >99%) was utilized. All compositions were ball milled for 24 h in polypropylene bottles. After drying, powders were calcined at 900 °C for 2 h. The calcined powders were then separated into two groups for ball milling and attrition milling. The milling times of ball mill (BM) and attrition mill (AM) were 24 and 3 h, respectively, with the solid loading at 50%. The speed of attrition mill was 350 rpm. Every 30 min of attrition time interval, the slurry was sampled for particle size determination using laser diffraction technique (Mastersizer S, Malvern). After drying, both BM and AM powders were uniaxially pressed to form pellets of 20 mm. in diameter and cold-isostatically pressed (CIP) at 240 MPa for 10 min, then, sintered in air atmosphere at 1000–1100 °C for 2 h. The pellets were polished to investigate microstructure using scanning electron microscopy (SEM: JEOL, JSM-5401). After polishing, the polished sections were thermally etched at 50 °C below the sintering temperature for 10 min to reveal grain boundary.

The phase development and X-ray densities of the sintered specimens were obtained by X-ray diffraction technique (XRD, JEOL, JDX-3530). The pellets were polished and, then, electroded with the silver paste. The relative permittivity ($\varepsilon_r$) at room temperature were measured at 1 kHz using 4194A Impedance Gain/Phase analyzer (Hewlett Packard). The piezoelectric charge coefficient ($d_{33}$) of the samples was measured using a piezo $d_{33}$-meter (Piezometer system PM25) at 100 Hz. The thickness ($k_t$) and planar coupling coefficient ($k_p$) were determined using the resonance method [7] and Onoe's formulas [8].

**Table 1** Comparison of physical properties of BNT and NLT-1 compositions.

| Compositions | Type of milling | Average particle size (μm) | Sintering conditions (°C for 2 h) | % theoretical density | Average grain size (μm) |
|---|---|---|---|---|---|
| BNT | BM for 24 h | 1.80 | 1100 | 91.94 | 3–5 |
| | AM for 3 h | 1.38 | 1080 | 95.74 | 1–2 |
| NLT-1 | BM for 24 h | 2.07 | 1100 | 94.47 | 2–3 |
| | AM for 3 h | 1.19 | 1080 | 95.18 | 1 |

*BNT* $Bi_{0.5}Na_{0.5}TiO_3$, *NLT-1* $Bi_{0.5}Na_{0.485}La_{0.005}TiO_3$, *BM* ball milling, *AM* attrition milling

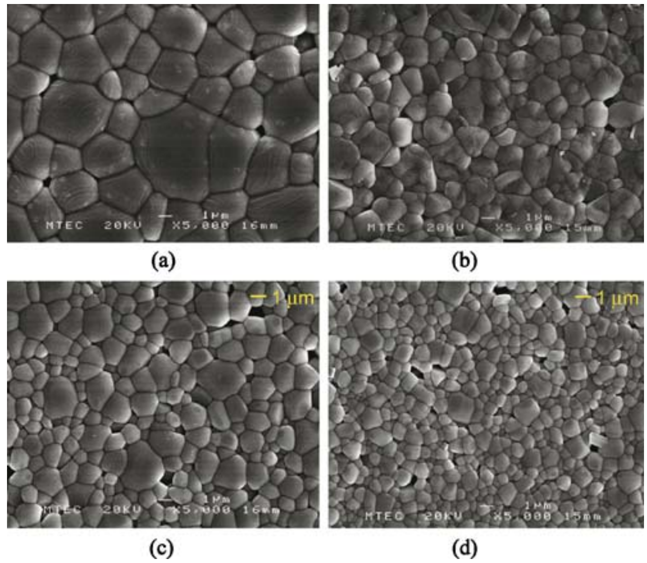


**Fig. 2** SEM micrographs of the modified BNT prepared via ball milling for 24 h and attrition milling for 3 h, sintered at 1100 and 1080 °C/2 h. BNT sintered at 1100 °C/2 h, ball milling (**a**), 1080°C/2 h, attrition milling (**b**). NLT-1 sintered at 1100 °C/2 h, ball milling (**c**), 1080°C/2 h, attrition milling (**d**). *BNT* $Bi_{0.5}Na_{0.5}TiO_3$, *NLT-1* $Bi_{0.5}Na_{0.485}La_{0.005}TiO_3$

## 3 Results and discussion

### 3.1 Effect of attrition milling on sintering conditions

Figure 1(a) shows the mean particle size of BNT and NLT-1 compositions after attrition milling. Every 30 min of milling time, the slurry was taken for particle size measurement. It should be noted that a finer starting particle size (e.g., 1.31 µm of NLT-1 powder) is more resistant to attrition, comparable to a coarser starting particle size (e.g., 3.45 µm of BNT powder). The reduction ratio of the BNT powders is quite high at the first milling time and becomes plateau after milling for 3 h [Fig. 1(b)]. As a result, the upper limit for size reduction with this technique is not smaller than 1 µm under the milling condition of 50% of solid loading and 300 rpm of milling. The upper size-reduction limit of the attrition milling is much higher than that of the ball milling for 24 h of which the particle size is approximately 2 µm (Table 1).

Table 1 shows the physical properties of BNT and NLT-1 compositions which are prepared via ball milling and attrition milling. The sintering temperatures could be reduced to 1.8% for BNT and NLT-1 compositions whereas densities of sintered BNT and NLT-1 pellet prepared by attrition milling were higher than 95% of theoretical densities.

It was found that the attrition milling altered the microstructure of sintered pellets. Figure 2 shows SEM micrographs of the sintered BNT and NLT-1 compositions both prepared by ball milling and attrition milling. It is seen that the specimens with compositions prepared by attrition milling have very fine grain sizes, which their values of grain sizes are summarized in Table 1. The average grain sizes of the attrition-milled powders become very fine at approximately 1 µm.

By introducing the attrition milling for powder preparation, the manufacturing cost for milling and firing could be reduced due to shorter milling time and lower sintering temperature. In addition, these small grain sizes and high

**Table 2** Comparison of dielectric and piezoelectric properties of BNT-based compositions.

| | Powder processing | Poling condition (kV/cm) | $\varepsilon_r$ (1 kHz) | Piezoelectric coef. | | Coupling factors | | Frequency const. | |
|---|---|---|---|---|---|---|---|---|---|
| | | | | $d_{33}$ (pC/N) | $g_{33}$ (mVm/N) | $k_t$ (%) | $k_p$ (%) | $N_t$ (Hz/m) | $N_p$ (Hz/m) |
| BNT | BM | 60 | 395 | 100 | 26 | 47 | 18 | 3,269 | 3,260 |
| | AM | 55 | 437 | 107 | 29 | 42 | 14 | 2,498 | 3,221 |
| NLT-1 | BM | 60 | 470 | 119 | 24 | 48 | 16 | 2,744 | 3,271 |
| | AM | 45 | 666 | 26 | 4 | 32 | 13 | 2,846 | 3,380 |
| $PbTiO_3$ [9] | – | – | 240 | 56 | 33 | 43 | 10 | 2,120 | 2,690 |

*BNT* $Bi_{0.5}Na_{0.5}TiO_3$, *NLT-1* $Bi_{0.5}Na_{0.485}La_{0.005}TiO_3$, *BM* ball milling, *AM* attrition milling

**Table 3** The XRF/WDS results of BNT and NLT-1 powders after attrition milling.

| Composition | Concentration by weight (%) | | | | |
|---|---|---|---|---|---|
| | $Bi_2O_3$ | $Na_2O$ | $TiO_2$ | $La_2O_3$ | $ZrO_2$ |
| $Bi_{0.5}Na_{0.5}TiO_3$, BNT | 56.09 | 7.29 | 36.09 | – | 0.54 |
| $Bi_{0.5}Na_{0.485}La_{0.005}TiO_3$, NLT-1 | 53.55 | 9.20 | 36.67 | <0.1 | 0.50 |

dense specimens affect the piezoelectric properties which will be discussed in the next section.

### 3.2 Piezoelectric properties BNT and NLT-1 compositions

The maximum poling conditions which could be applied without an electrical breakdown were investigated at an applied electric field of 50–70 kV/cm. Table 2 summarizes the dielectric and piezoelectric properties of all the modified BNT compositions. Samples of the NLT-1 with attrition milling could be poled, but only with great difficulty due to a breakdown during poling.

It was found that the suitable poling condition for the BNT prepared by attrition milling was 55 kV/cm, lower than the BNT prepared by ball milling. At the applied electric field of 55 kV/cm, the BNT samples prepared by attrition milling process exhibited a dielectric constant of 437, a $d_{33}$ value of 107 pC/N and a $k_t$ value of 42%. In contrary, it is seen a deterioration in piezoelectric properties of the NLT-1 prepared by attrition milling technique.

Since contamination due to wear of zirconia grinding balls was expected to occur, the chemical compositions of BNT and NLT-1 powders were then characterized using X-ray fluorescence/wavelength dispersive spectroscopy (XRF/WDS). The XRF/WDS results indicated that Zr contamination presented in both compositions (Table 3). The small amount of Zr content in the modified BNT compositions could influences the piezoelectric properties in many ways. The Zr contamination could reduce the applied electric field during poling for BNT specimens leading to an ease in poling; meanwhile, it could cause an abrupt change in the piezoelectric properties of NLT-1 specimens. Since the level of contamination generally increases with increasing the attrition milling time, then the optimum milling time for a given condition is of utmost important to achieve the desired properties. This issue is currently under investigation.

## 4 Conclusion

The effect of attrition milling on sintering, microstructure and piezoelectric properties of BNT-based ceramics was investigated. As the milling time increased, the particle size was reduced and became plateau after 3-h milling time. The upper limit of size reduction via the attrition milling was approximately 1 μm. The attrition milling technique was found to reduce the particle size, shorten the milling time drastically, lower the sintering temperature, decrease the grain size, and alter the piezoelectric properties of the BNT-based ceramics. The optimum attrition milling time is of importance to reduce the contamination from grinding balls. This technique would be more efficient and less expensive in matrix preparation for grain orientation technique, the recent method to enhance the piezoelectric properties of a polycrystalline ceramic.

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## References

1. A. Herabut, A. Safari, Proceedings of the Tenth IEEE International Symposium on Applications of Ferroelectrics, Vol. 2, E. Brunswick, New Jersey, USA, 775–778 (1996)
2. A. Herabut, A. Safari, J. Am. Ceram. Soc. **80**(11), 2954–2958 (1997)
3. A. Thanaboonsombut, P. Setasuwan, N. Vaneesorn, S. Kitaumnartsuk, S. Danwittayakul, NSTDA Annual Conference, S&T in Thailand: towards the Molecular Economy (NAC2005) (2005)
4. E.M. Sabolsky, A.R. James, S. Kwon, S. Trolier-McKinstry, G.L. Messing, Appl. Phys. Lett. **78**(17), 2551–2553 (2001)
5. P. Ravindranathan, S. Komareni, A.S. Bhalla, R. Roy, J. Am. Ceram. Soc. **74**(12) 2996–2999 (1991)
6. J.S. Reed, *Introduction to the Principles of Ceramic Processing* (Wiley Interscience, USA, 1988)
7. IRE standards on piezoelectric crystals: determination of the elastic, piezoelectric, and dielectric constants—the electromechanical coupling factor (Proceedings of the IRE, 1958)
8. M. Onoe, H. Jumonji, J. Acoust. Soc. Am. **41**(4), 974–980 (1967)
9. Yuhuan Xu, *Ferroelectic Materials and Their Applications* (Elsevier Science, New York, 1991)