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# Effect of vibro-milling time on phase formation and particle size of barium titanate nanopowders

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## Abstract

Barium titanate (BT) nanopowder was synthesized by a solid state reaction via a rapid vibro-milling technique. The effect of milling time on phase formation and particle size of BT powder was investigated. Powder samples were characterized using XRD (X-ray diffraction) and SEM techniques. It was found that the resulting BT powders have a range of particle size depending on milling times. Production of a single-phase BT nanopowder can be successfully achieved by employing a combination of 30 h milling time and calcination conditions of 1200 °C for 2 h.

*Keywords:* A. Milling; Powders: solid state reaction; D. $BaTiO_3$

## 1. Introduction

Barium titanate ($BaTiO_3$ or BT), which exhibits a perovskite structure and a Curie temperature ~120 °C, is a classical ferroelectric material that has been extensively exploited both for academic and technological utilizations over the past decades [1,2]. Owing to its high dielectric constant, large mechanical-quality factor, large pyroelectric coefficient, non-toxic handling and low cost of manufacturing, compared to several lead-based perovskite ferroelectrics, BT-based ceramics have been a strong candidates for several electronic applications, including ultrasonic transducers, multilayer capacitors, pyroelectric detectors, semiconductors with positive temperature coefficient of resistance (PTCR) and electro-optic devices [3,4]. To fabricate them, a fine powder of perovskite phase with a minimal degree of particle agglomeration is needed as the starting material to achieve a dense and uniform microstructure at a given sintering temperature. In order to improve the sintering behavior of ceramics, a crucial focus of powder synthesis in recent years has been the formation of uniform-sized, single morphology particulates ranging in size from nanometer to micrometers.

The development of a method to produce nanopowders of precise stoichiometry and desired properties is complex, depending on a number of variables such as nature and purity of starting materials, processing history, temperature, etc. To obtain nanosized BT powders, many investigations have focused on several chemistry-based preparation routes, such as sol–gel [5], sol-precipitation [6], hydrothermal reaction [7], besides the more conventional solid state reaction of mixed oxides [8]. All these techniques are aimed at reducing the particle size and temperature of preparation of the compound even though they are more involved and complicated in approach than the solid state reaction. The advantage of using mechanical milling for preparation of nanosized powders lies in its ability to produce mass quantities of powders in the solid state using simple equipment and low cost starting precursors [9,10]. The ball-milling technique is a very popular solid state reaction because of easy and low cost technique, however the size of particle from this technique is still large (micrometer). Thus, the potentiality of vibro-milling technique will be then focused in order to achieve the nanosized powder. Although some research has been done in the preparation of BT nanopowders via a vibro-milling technique [11], to our knowledge a systematic study regarding the influence of milling time on the preparation of BT nanopowders has not yet been reported. Therefore, in this work, the effect of milling time on phase formation, and particle size of BT nanopowders was investigated in this connection. The potential of the vibro-

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milling technique as a simple and low-cost method to obtain usable quantities of single-phase BT powders at low temperature and with nanosized particles was also examined.

## 2. Experimental procedure

Commercially available powders of $BaCO_3$ and $TiO_2$ (anatase form), (Fluka, >99% purity) were used as starting materials. $BaTiO_3$ powder was synthesized by the solid state reaction of these raw materials. A vibratory laboratory mill (McCrone Micronizing Mill) powered by a 1/30 HP motor was employed for preparing the stoichiometric $BaTiO_3$ powder [9]. The mixed powder was vibro-milled for 0.5 h with corundum media in isopropyl alcohol (IPA). Drying was carried out for 2 h at 120 °C. Various calcination temperatures ranging from 700 to 1400 °C were selected to investigate the phase development of BT. Moreover, in order to investigate the effect of milling time on phase formation and particle size, the milling times were then ranged from 0.5 to 30 h. All powders were examined by room temperature X-ray diffraction (XRD; Siemens-D500 diffractometer) using Ni-filtered Cu Kα radiation, to identified the phase formed and the optimum firing temperature for the production of single-phase BT powders under various milling conditions. The crystallite size and tetragonality factor (*c*/*a*) were also estimated from these XRD patterns [12]. The morphologies of the powders observed by scanning electron microscopy (JEOL JSM-840 A SEM).

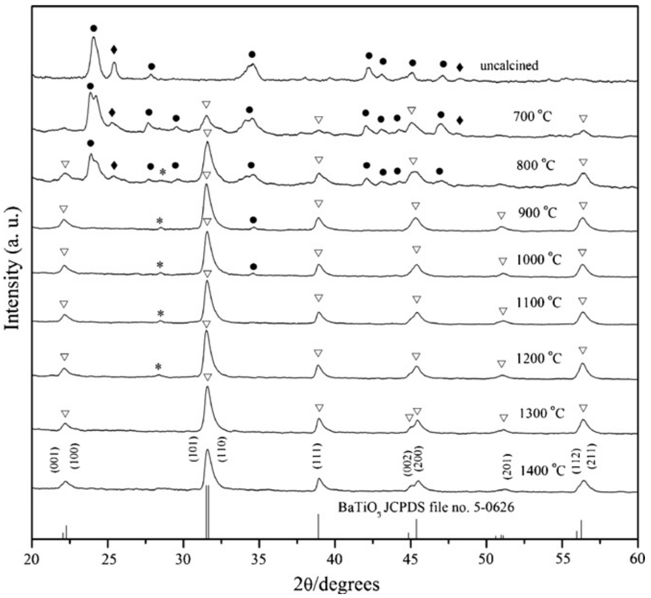

Fig. 1. XRD patterns of BT powders calcined at various temperatures for 2 h with heating/cooling rates of 10 °C/min (● = $BaCO_3$, ◆ = $TiO_2$, ▽ = $BaTiO_3$ and * = $Ba_2TiO_4$).

## 3. Results and discussion

From the TG-DTA data in previous work [13], the range of calcination temperatures between 700 and 1400 °C were designed for BT powder to investigate the phase formation. To study the phase development with increasing calcination temperature in BT powder prepared from vibro-milling technique for 0.5 h, it was calcined for 2 h in air at various temperatures, up to 1400 °C, followed by phase analysis using XRD. As shown in Fig. 1, for the uncalcined powder, only X-ray peaks of precursors, $BaCO_3$ (●) and $TiO_2$ (◆), which could be matched with JCPDS file numbers 5-0378 [14] and 21-1272 [15], respectively, are presented, indicating that no reaction had yet been triggered during the milling process. In this work, it is seen that the desired perovskite $BaTiO_3$ (▽) was already observed in the powder calcined at 700 °C, accompanying with unreacted $BaCO_3$ and $TiO_2$ precursors as separated phases, in good agreement with literature [16,17]. Moreover, the unknown phase (★) started to occur at $2\theta \sim 28.5°$, consistent with earlier work of Simon-Seveyrat et al. [18]. According to the literature [19,20], the reaction sequence of the phase formation in the BT mixture can be described as follow.

$$2BaCO_3 + TiO_2 \rightarrow Ba_2TiO_4 + 2CO_2 \quad (1)$$

$$Ba_2TiO_4 + TiO_2 \rightarrow 2BaTiO_3 \quad (2)$$

It was believed that this unknown phase corresponds to $Ba_2TiO_4$, which could be matched with JCPDS file numbers 72-0135 [21], always found in conventional mixed oxide processing [16,22]. As the temperature increased to 1000 °C, the intensity of the $BaTiO_3$ peaks was further enhanced. The starting materials completely disappeared after calcination at 1100 °C, however, the unwanted $Ba_2TiO_4$ phase still be detected. Upon calcination at 1300 °C, an essentially monophasic of $BaTiO_3$ phase was obtained. This observation agrees well with other workers [23,24]. This BT phase was indexable according to a tetragonal perovskite-type structure with lattice parameters $a = 3.994$ Å and $c = 4.038$ Å, space group *P*4*mm* (no. 99), consistent with JCPDS file number 5-0626 [25].

Table 1
Effect of milling time on the optimum calcination temperature and the variation of particle size of BT powders measured by different techniques

| Milling time (h) | Perovskite phase (%) | Calcination temperature (°C) | XRD | | SEM | |
|---|---|---|---|---|---|---|
| | | | *A* (nm) | *c*/*a* | *D* (nm) | *P* (nm) |
| 0.5 | 100 | 1300 | 38.32 | 1.0090 | 610 | 250–1400 |
| 10 | 100 | 1250 | 32.09 | 1.0059 | 260 | 100–500 |
| 15 | 100 | 1250 | 32.38 | 1.0036 | 490 | 100–1000 |
| 20 | 100 | 1250 | 31.95 | 1.0058 | 590 | 250–700 |
| 25 | 100 | 1200 | 31.60 | 1.0065 | 390 | 250–700 |
| 30 | 100 | 1200 | 31.56 | 1.0056 | 250 | 100–400 |

*A* = crystallite size, *c*/*a* = tetragonality factor, *D* = average particle size, *P* = particle size range.

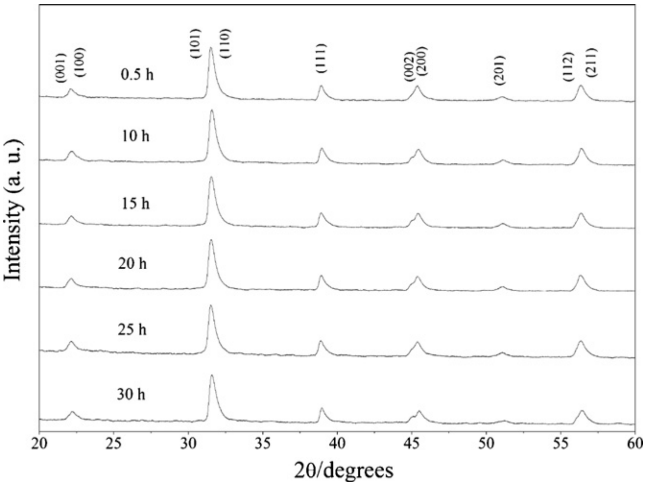

Fig. 2. XRD patterns of BT powders milled at different times.

Having established the optimum calcination temperature of BT powder vibro-milled for 0.5 h, an attempt was also made to calcine the BT powder under various milling times. The optimum calcination temperature of each powder was reported in Table 1 and the XRD patterns of all BT powders are shown in Fig. 2. It has been observed that with increasing milling time, all diffraction lines broaden, e.g., (0 0 2) and (2 0 0) peaks, an indication of a continuous decrease in particle size and of the introduction of lattice strain. These values indicate that the prolonged milling treatment affects the particle size and evolution of crystallinity of the phase formed. For BT powders, the longer the milling time, the lower the required (optimum) firing temperature. Additionally, the crystallite size and tetragonality factor (*c*/*a*) were estimated from these XRD patterns as also given in Table 1. The calculated crystalline size value was also found to decrease with increasing milling time. Though, the relative intensities of the Bragg peaks and the calculated tetragonality factor (*c*/*a*) for the powders exhibit independent of milling time, it is well documented that, as Scherer's analysis provides only a measurement of the extension of the coherently diffracting domains, the crystallite sizes determined by this method can be significantly under estimation [26]. In addition to strain, factors such as dislocations, stacking faults, heterogeneities in composition and instrumental broadening can attribute to peak broadening, making it almost impossible to extract a reliable particle size solely from XRD [27].

In this connection, SEM was also employed for particle size measurement (Table 1). The morphological evolution of the powders as a function of milling time was also revealed, as illustrated in the SEM micrographs (Fig. 3). At first sight, the morphological characteristic of BT powders with various milling times is similar for all cases. In general, the particles are agglomerated and basically irregular shape, with a substantial variation in particle sizes. The powders consist of primary particles with nanometers in size. Increasing milling time over the range 0.5–30 h, the powders exhibit spatial fluctuation in their particle sizes. The extent of the fluctuation depends on the milling time as well as on the calcination temperature applied. In this study, it is seen that the optimum milling time for the production of the smallest nanosized BT powder with low firing temperature was found to be at 30 h. The finding of this

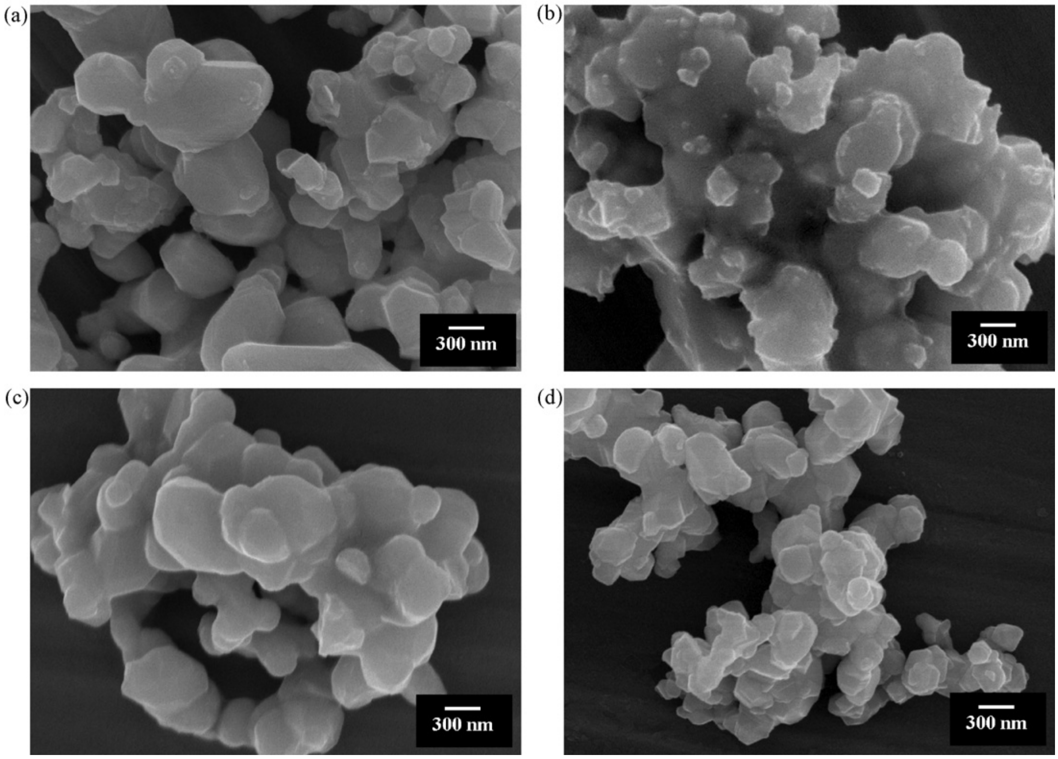

Fig. 3. SEM micrographs of BT powders after milling times of (a) 0.5, (b) 15, (c) 25 and (d) 30 h (calcined at their optimized conditions).

investigation indicates a strong relationship between the vibro-milling process and the yield of BT nanopowders.

## 4. Conclusions

The synthesis of perovskite BT nanopowder by a solid state reaction and the influence of milling time on its formation were studied. It was established that the milling time influences not only the development of the solid state reaction of BT phase but also particle size and morphology. It was shown that the increase of vibro-milling time significantly decreases the calcination temperature and particle size. A single phase of BT nanopowder can be successfully produced by employing a combination of 30 h milling time and calcination condition of 1200 °C for 2 h.

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