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Effect of Impact Milling and Ball Milling on Microstructure of Lead Titanate Powders Synthesized by Solid-State Reaction

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Abstract: Single phase lead titanate ($PbTiO_3$) was prepared by solid-state route using lead (II) oxide (PbO) and titanium dioxide (TiO_2) as precursors. The effects of using impact mill (IM) and ball mill (BM) in solid state reaction have been observed. X-ray diffraction (XRD) pattern was recorded at room temperature and analyzed by employing Rietveld method. X-ray diffraction (XRD) pattern shows that the $PbTiO_3$ particles are tetragonal with tetragonality (c/a) ratio ranging from 1.058 to 1.063 and average crystallite size from 40.8 to 64.2 nm. It is found that the impact mill (IM) can be used to produce pure tetragonal perovskite with a lower tetragonality and average crystallite size.

Key words: Milling, crystallite size, X-ray methods.

1. Introduction

Lead Titanate ($PbTiO_3$) is a tetragonal perovskite with a tetragonality (c/a) ratio of 1.063 at room temperature, which is the largest known for lead-based perovskite compounds. It is a ferroelectric material that displays pyroelectric and piezoelectric properties and presents a Curie temperature of 490 °C and possesses high spontaneous polarization [1-8]. Considerable research attention has been given to increase quantity and quality in $PbTiO_3$ powder synthesis. There are many investigations that focused on several chemistry-based preparation routes to prepare $PbTiO_3$ powder, such as sol-gel [9], co-precipitation [10], hydrothermal reaction [11], and besides the more conventional solid state reaction of mixed oxides [12].

The advantage of solid-state route lies in its ability to produce mass quantities of powders using simple equipment and low cost starting precursors [13]. Ball mill (BM) has traditionally been preferred, but is restricted in its ability to induce phase transformation; thus normally a phase-forming calcination is required after the milling process. On the other hand, impact mill (IM) process can provide high amount of kinetic energy to promote solid state reaction, and hence able to produce $PbTiO_3$ without a phase-forming calcination [14]. At the same time, this high amount of kinetic energy is possible to reduce crystallite size of $PbTiO_3$, and thus tetragonality changes may be induced.

Low tetragonality of $PbTiO_3$ is more preferable for ceramics preparation. A large tetragonality (c/a = 1.064) of tetragonal phase $PbTiO_3$ resulting in a high stress within the lattice leads to a frangibility and brings difficulty to prepare corresponding ceramics. Therefore in this paper, we study the effects of ball mill (BM) and impact mill (IM) process on tetragonality and crystallite size in $PbTiO_3$ synthesis.

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2. Experiments

A solid state mixed oxide route was used to prepare $PbTiO_3$ powder. Stoichiometric ratio of lead *(*II*)* oxide (PbO) and titanium dioxide (TiO_2) with 99.0% purity were mixed thoroughly with the help of impact mill (IM) from Retsch (Mixer Mill 300) and ball mill (BM) from Fritsch (Planetary Ball Mill PULVERISETTE 6). Lead *(*II*)* oxide (PbO) was manufactured by R&M Chemicals (U.K.) and titanium dioxide (TiO_2) was by Fisher Scientific (USA). The vial and the balls are made up of hardened steel. The ball-to-powder ratio was 5:1. Ethanol was used as milling medium. Ball milling was done at 300 rpm while impact milling at 15 Hz. Range of milling durations used was 3 h, 6 h, 12 h and 24 h. Precursors were dried overnight and calcinated at 750 °C for 4 h. All the above sintering processes were carried out in air. XRD pattern at room temperature for the sample was recorded by using PANalytical X'Pert PRO diffractometer using monochromated CuKα radiation (λ = 1.54184 Å) and analyzed by employing Rietveld method. The average crystallite size was calculate using the Scherrer equation as shown below, which based on the half-width of (101) reflection of the observed X-ray data.

$$D = k\lambda/(B\cos\theta) \quad (1)$$

where D is the size of powder, λ is the X-ray wavelength, B is the FWHM of diffraction peak, θ is the diffraction angle and the constant, $k \approx 0.9$.

3. Results and Discussion

Lead (II) oxide (PbO) and titanium dioxide (TiO_2) powders were mixed for various milling durations using impact mill (IM) and ball mill (BM). Powder samples were characterized using X-ray diffractrometer (XRD). In all the samples analyzed, no significant $PbTiO_3$ peaks detected in precursor stage. The result appears to contradict a study carried by Xue et al. [14] which successfully prepared $PbTiO_3$ via a shaker-mill (impact mill) operated at 900 rpm for 5 to 20 h, which skips the phase-forming calcination that is always required for the solid state reaction.

Phases such as Massicot (orthorhombic PbO), litharge (Tetragonal PbO) and anatase (TiO_2) were detected in all the powder samples milled by impact mill (IM) and ball mill (BM). Ball mill (BM) process has minimal effect on phase transformation compare to impact mill (IM) as indicated in Figs. 1 and 2. Fig. 2 also shows polonged milling duration in impact milling (IM) reduced massicot content in precursor drastically. Massicot can be transformed readily to litharge with a mechanical stimulation at room temperature; similar findings have been reported by Lin and Niedzwiedz [15].

The impact mill (IM) and ball mill (BM) mixed precursors were calcinated at 750 °C for 4 h. Sintering processes were carried out in air. All the precursor powders were successfully transformed to pure $PbTiO_3$ powders after calcination. No residual phases such as Massicot (orthorhombic PbO), litharge (Tetragonal

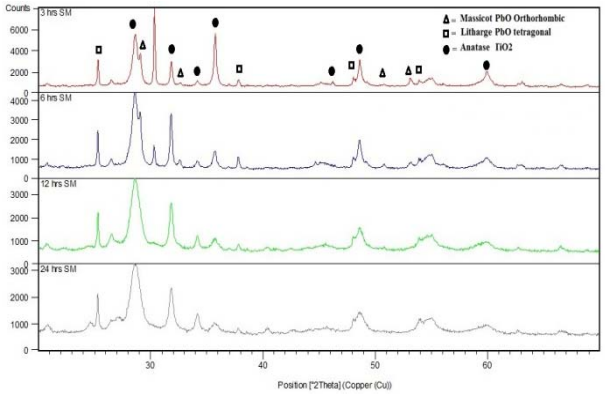

Fig. 1 XRD diffractogram of $PbTiO_3$ (ball mill) before calcinations.

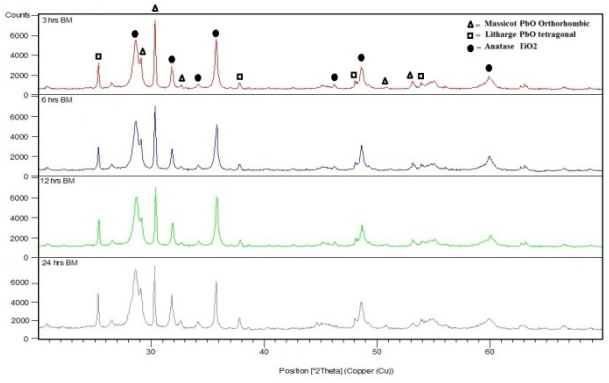

Fig. 2 XRD diffractogram of $PbTiO_3$ (impact mill) before calcinations.

PbO) and anatase (TiO_2) were detected in all the samples upon thermal reaction at 750 °C for 4 h as shown in Figs. 3 and 4.

For the calcinated impact mill (IM) mixed precursors, average crystallite size and tetragonality of the $PbTiO_3$ powders decreased with the increase of milling time.

Whereas there is not apparent trend of increasing or reducing in calcinated ball mill (BM) mixed precursors showed in Figs. 5 and 6. This could be a lower kinetic energy generated by the latter due to large amount of energy loss in the form of heat. Large amount of energy loss in ball milling process is resulted from oblique collisions and friction between balls and wall, while the lower temperature but higher intensity of the shaker mill (impact mill) is due to the larger proportion of frontal impacts [16]. The size of vial and balls could be another factor. It is apparent that ball mill (BM) and impact mill (IM) used in this study have different volume sizes, the ball mill (BM) vial volume is roughly eight times larger than of the impact mill (IM), thus providing a much lower degree of surface contact between the balls and the powder.

This makes the probability of powder not being evenly milled higher than of the impact mill (IM). Fig. 5 highlights the change in tetragonality or *c*/*a* ratio, for the impact milled (IM) $PbTiO_3$ powders. The reduced tetragonality, which reaches 1.057 from an initial state of 1.062 for milling duration of 24 h, is primarily due to an decrease in the *c*-lattice parameter, while the *a* parameter changes only slightly across the milling process. The ball milled (BM) $PbTiO_3$ powders produced are tetragonal perovskite with a c/a ratio ranging from 1.061 to 1.063. The crystallite size of the impact milled $PbTiO_3$ powders are ranging from 37.2 nm to 65.7 nm, and ball milled $PbTiO_3$ powders

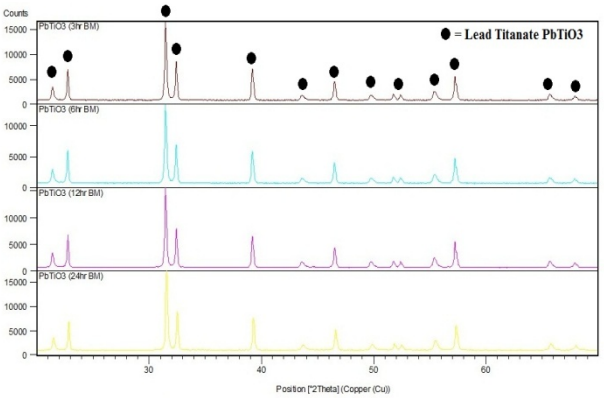

Fig. 3 XRD diffractogram of $PbTiO_3$ (ball mill) after calcination at 750 °C.

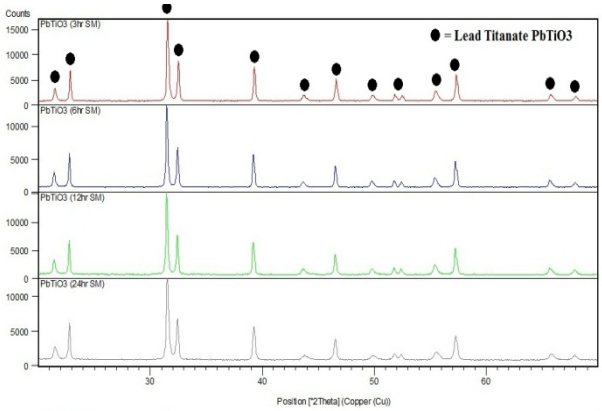

Fig. 4 XRD diffractogram of $PbTiO_3$ (impact mill) after calcination at 750 °C.

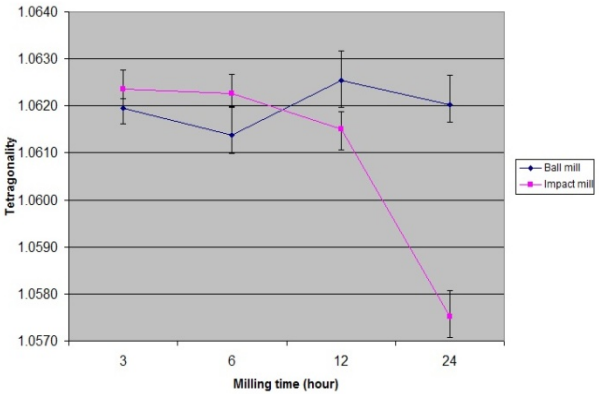

Fig. 5 Tetragonality vs milling time for $PbTiO_3$ milled using different technique.

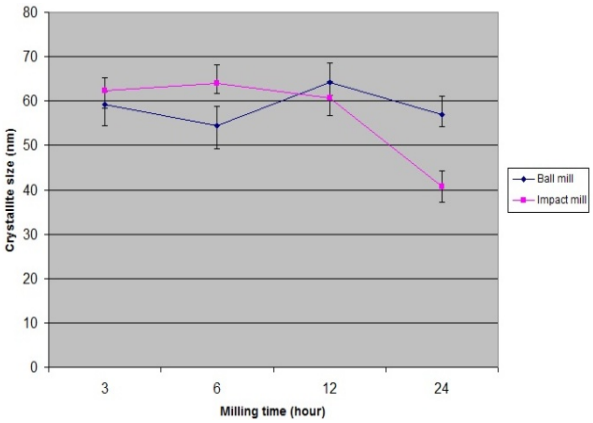

Fig. 6 Average crystallite size vs milling time for $PbTiO_3$ milled using different technique.

ranging to 49.2 nm to 68.6 nm shown in Fig. 6.

4. Conclusions

The ball mill (BM) and impact mill (IM) processes produce different amount of kinetic energy thus producing different crystallite size of $PbTiO_3$. In 24 h of milling duration, the average crystallite size of the impact mill (IM) $PbTiO_3$ is 40.8 nm, which is smaller compare to 57.0 nm in ball mill (BM). At the same milling duration, ball mill (BM) produces $PbTiO_3$ with a tetragonality value of 1.062 at room temperature whereas impact mill (IM) is capable to produce $PbTiO_3$ with a lower tetragonality value of 1.057. This results show tetragonality diminishes with a decrease in crystallite size. Impact mill (IM) which is capable to produce pure tetragonal perovskite with a lower tetragonality and average crystallite size compared to ball mill (BM) as shown in this study could be a suitable process for ceramics preparation.

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