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Potential of vibro-milling technique for preparation of electroceramic nanopowders

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Abstract

The potential of the vibro-milling technique as a simple method to obtain usable quantities of single-phase electroceramic powders with nanosized particles was examined. A detailed study considering the role of both milling time and firing condition on phase formation and particle size of the final product was performed. The calcination temperature for the formation of the desired phase was lower when longer milling times have been applied. More importantly, by employing an appropriate choice of the milling time and calcination condition, high purity electroceramic nanopowders have been successfully prepared with a simple solid-state reaction method.

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1. Introduction

Recently, it has been reported that many nanoparticles can be successfully synthesized by using several mechanical milling method [1–3]. From the point of view of energy efficiency, the vibro-mill (or vibratory mill or vibro-energy mill, which is a machine for vibrating vessel filled with grinding media at amplitudes up to a approximately 5 cm) seems to be more attractive than the ball mill [1]. Relative to ball-milling, vibro-milling produces finer particles and a narrower size distribution at a faster rate [1–3]. This implies that mills, especially, fine grinders such as the vibro-mill are recognized as a tool for producing nanopowders, and the milling time is a key operation for such materials processing, as well as for the nanopowder preparation. Moreover, the advantage of using a solid-state reaction method via mechanical milling for preparation of nanopowders lies in its ability to produce mass quantities of powder in the solid state, using simple equipment and low cost starting precursors. Although some research has been done into the preparation of electroceramic powders via a vibro-milling technique [1–3], to our knowledge a detailed study considering the role of both milling times and firing conditions on the preparation of electroceramic nanopowders has not yet been widely reported. In the present study, we have demonstrated the potential of a rapid vibro-milling technique in the production of several important electroceramic nanopowders such as $PbZrO_3$ or PZ, $PbTiO_3$ or PT and $BaTiO_3$ or BT.

2. Experimental procedure

The raw materials used were commercially available lead oxide, zirconium oxide, titanium oxide and barium carbonate (Fluka, >99% purity). These oxide powders exhibited an average particle size in the range of 3.0–5.0 μm. $PbZrO_3$, $PbTiO_3$ and $BaTiO_3$ powders were 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 powders [2]. The grinding vessel consists of a 125 ml capacity polypropylene jar fitted with a screw-capped, gasketless, polythene closure. The jar is packed with an ordered array of identical, cylindrical, grinding media of polycrystalline corundum. A total of 48 milling media cylindrical with a powder weight of 20 g was kept constant in each batch. The milling operation was carried out in isopropanol, inert to the polypropylene jar. Various milling times ranging from 0.5 to 35 h were selected in order to investigate the phase formation characteristics of all desired powders and to obtain the smallest particle size. After drying at

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120 °C for 2 h, various calcination conditions, i.e. temperatures ranging from 500 to 1200 °C, dwell times ranging from 1 to 6 h and heating/cooling rates ranging from 10 to 30 °C/min, were applied (the powders were calcined inside a closed alumina crucible) in order to investigate the formation of the desired phases.

All powders were examined by room temperature X-ray diffraction (XRD; Siemens-D500 diffractometer) using Ni-filtered CuK$_\alpha$ radiation, to identify the phases formed and the firing conditions for the production of single-phase powders. The average crystallite size is also estimated from XRD patterns [4]. The particle size distributions of the powders were determined by a laser diffraction technique (DIAS 1640 laser diffraction spectrometer) with the particle sizes and morphologies of the powders observed by scanning electron microscopy (JEOL JSM-840A SEM).

3. Results and discussion

XRD patterns of the calcined $PbZrO_3$ powders after different combination of milling time and calcination condition are given in Fig. 1. For the uncalcined powder subjected to 15 h of vibro-milling, only X-ray peaks of the precursors PbO (●) and ZrO_2 (○) are present, indicating that no reaction was yet triggered during the vibro-milling process. However, after calcination at 800 °C, for 1 h, it is seen that the perovskite $PbZrO_3$ becomes the predominant phase indicating that the reaction has occurred to a considerable extent. It should be noted that when the dwell time of the calcination at 800 °C was extended up to 2 h, then a single phase of perovskite PZ (yield of 100% within the limitations of the XRD technique) was obtained. This was apparently a consequence of the enhancement in crystallinity of the perovskite phase with increasing degree of mixing and dwell time, in good agreement with other works [2–3]. In general, the strongest reflections apparent in the majority of these XRD patterns indicate the formation of the lead zirconate, $PbZrO_3$ (JCPDS file number 35-0739) [5], consistent with other works [6,7]. For 15 h of milling, the optimum calcination condition for the formation of a high purity $PbZrO_3$ phase was found to be about 800 °C for 2 h with heating/cooling rates of 30 °C/min.

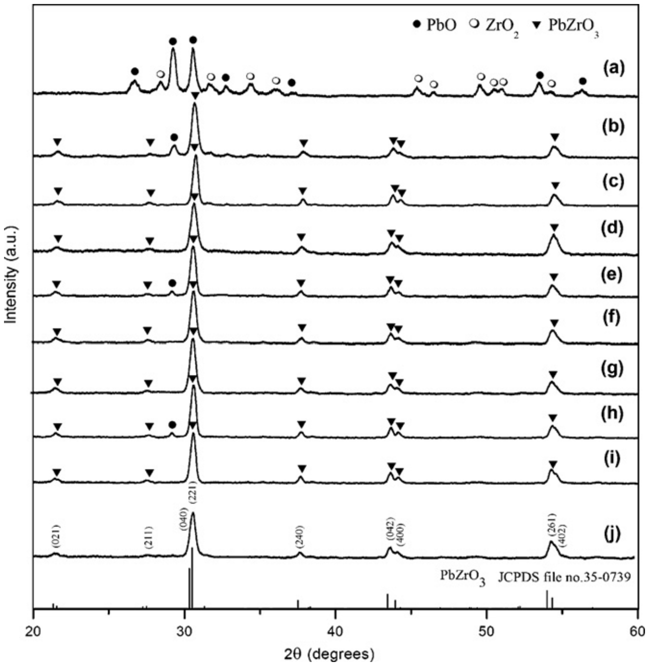

Fig. 1. XRD patterns of PZ powders milled for 15 h (a) uncalcined, and calcined at 800 °C for (b) 1 h and (c) 2 h with heating/cooling rates of 10 °C/min and (d) 30 °C/min; milled for 25 h and calcined at (e) 750 °C for 5 h (f) 800 °C for 1 h with heating/cooling rates of 10 °C/min and (g) 30 °C/min; and milled for 35 h and calcined at 750 °C for (h) 3 h and (i) 4 h with heating/cooling rates of 10 °C/min and (j) 30 °C/min.

To further study the phase development with increasing milling times, an attempt was also made to calcine mixed powders milled at 25 and 35 h under various conditions as shown in Fig. 1(e–j). In this connection, it is seen that by varying the calcination condition, the minimum firing temperature for the single-phase formation of each milling batch is gradually decreased with increasing milling time. The main reason for this behavior is that a complete solid-state reaction probably takes place more easily when the particle size is milled down by accelerating an atomic diffusion mechanism to meet the suitable level of homogeneity. It is thought that reducing the particle size significantly reduces the heat diffusion limitations. It is therefore believed that the solid-state reaction to form perovskite PZ phase occurs at lower temperatures on decreasing the particle size of the oxide powders.

In the work reported here, evidence for the presence of the minor phase of PbO which coexists with the parent phase of $PbZrO_3$ is found after calcination at temperature 750–800 °C, in agreement with literature [8]. This second phase has an orthorhombic structure with cell parameters $a = 589.3$ pm, $b = 549.0$ pm and $c = 475.2$ pm (JCPDS file number 77-1971) [9]. This observation could be attributed mainly to the poor reactivity of the lead and zirconium species [8] and also the limited mixing capability of the mechanical method [2,3]. A noticeable difference is noted when employing milling times longer than 15 h (Fig. 1(e–j)), since an essentially monophasic $PbZrO_3$ of the perovskite structure was obtained at 800 °C for 1 h (or 750 °C for 4 h) for the milling time of 25 h (or 35 h). This was apparently a consequence of enhancement in the crystallinity of the perovskite phase with increasing degree of mixing and dwell time, in good agreement with other work [2,3].

After establishing the optimum combination between vibro-milling time and calcination condition, a similar investigation was also undertaken on the preparation of $PbTiO_3$ and $BaTiO_3$ powders as shown in Figs. 3 and 4, respectively. It should be noted that no evidences for the introduction of impurities due to wear debris from the selected milling process was observed in all calcined powders, indicating the effectiveness of the vibro-milling technique for the production of high purity nanopowders. As expected, there is evidence that, even for a wide range of calcination conditions, the single phase of all the selected electroceramic powders cannot easily be produced, in agreement with literature [1–3]. This could be attributed mainly to

Table 1
Effect of milling time on the variation of particle size of perovskite powders calcined at their optimum conditions with heating/cooling rates of 30 °C/min and measured by different techniques

Powders	Milling time (h)	Calcination condition (°C/h)	XRD	SEM		Laser scattering	
			A (nm)	*D* (nm)	*P* (nm)	*D* (nm)	*P* (nm)
PZ	15	800/2	60.41	280	53–692	700	35–2000
	25	800/1	35.11	223	31–400	170	35–750
	35	750/4	27.50	121	31–228	1570	10–6000
PT	5	600/1	22.50	101	67–135	690	290–1140
	15	600/1	22.00	78	43–114	4640	1640–7790
	25	600/1	21.50	63	17–109	180	70–310
BT	0.5	1300/2	38.32	610	250–1400	1000	400–1500
	25	1200/2	31.60	390	250–700	400	60–700
	30	1200/2	31.56	250	100–400	600	120–1000

A: crystallite size; *D*: average particle size; *P*: particle size distribution or range.

the poor reactivity of starting species [2,3] and also to the limited mixing capability of the mechanical method [1–3].

The variation of calculated crystallite size of all the single-phase perovskite powders milled for different times and calcined at their optimum conditions is given in Table 1. In general, it is seen that the crystallite size of all powders decreases with increasing milling times. These observations indicate that the particle size affects the evolution of crystallinity of the phase formed by prolonged milling treatment. Moreover, it has been observed that with increasing milling time, all diffraction lines broaden, as shown in Figs. 2(a), 3(a) and 4(a), which is an indication of a continuous decrease in particle size and of the introduction of lattice strain [4].

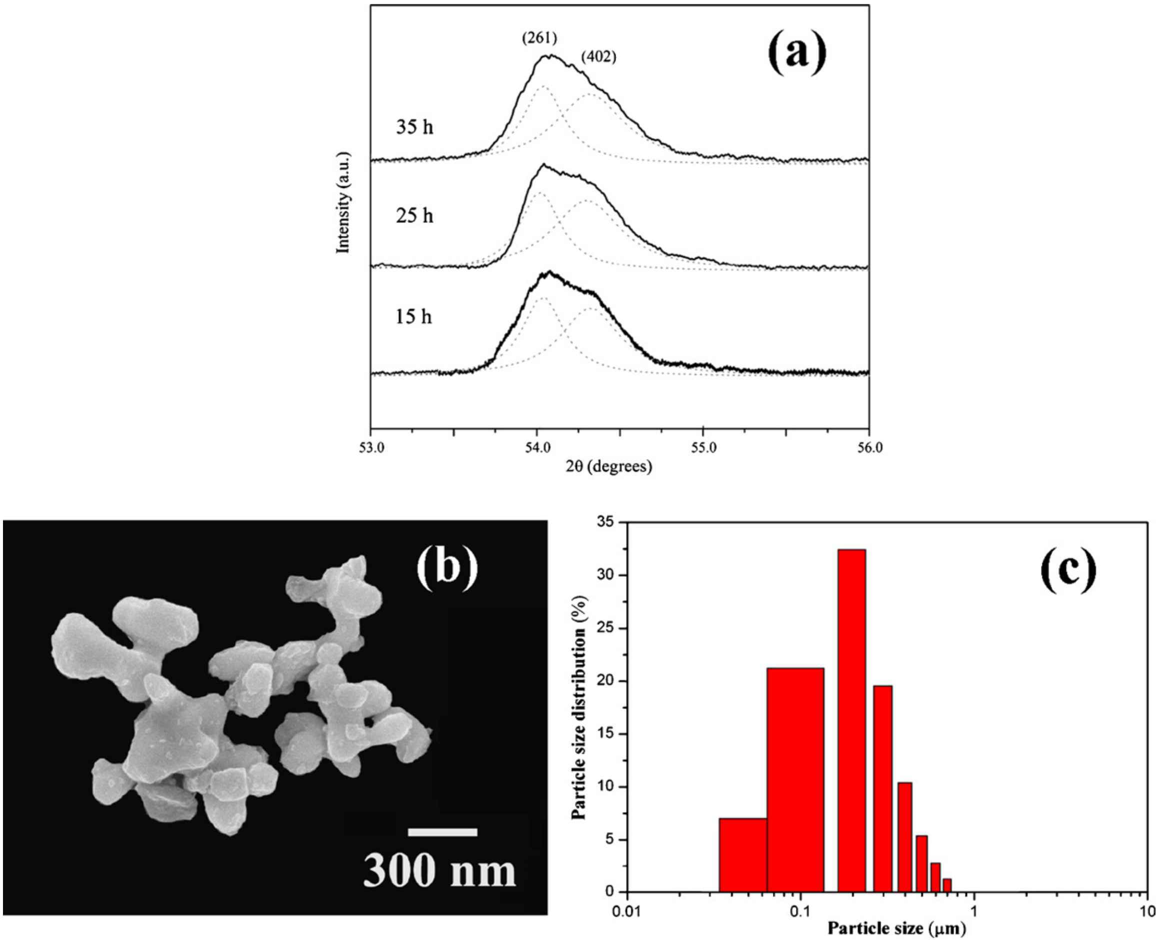

Fig. 2. (a) Enlarged zone of XRD patterns showing peaks broadening as a function of milling times of PZ powders, (b) SEM micrograph and (c) particle size distribution of PZ powders milled for 25 h and calcined at 800 °C for 1 h with heating/cooling rates of 30 °C/min.

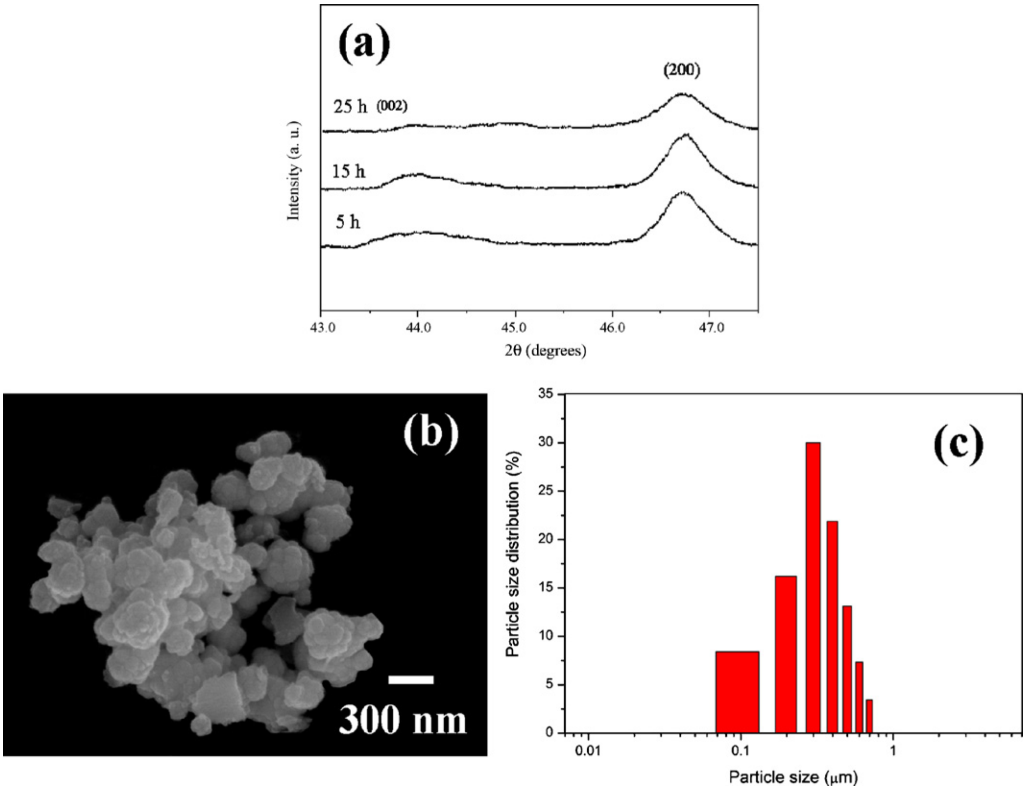

Fig. 3. (a) Enlarged zone of XRD patterns showing peaks broadening as a function of milling times of PT powders, (b) SEM micrograph and (c) particle size distribution of PT powders milled for 25 h and calcined at 600 °C for 1 h with heating/cooling rates of 30 °C/min.

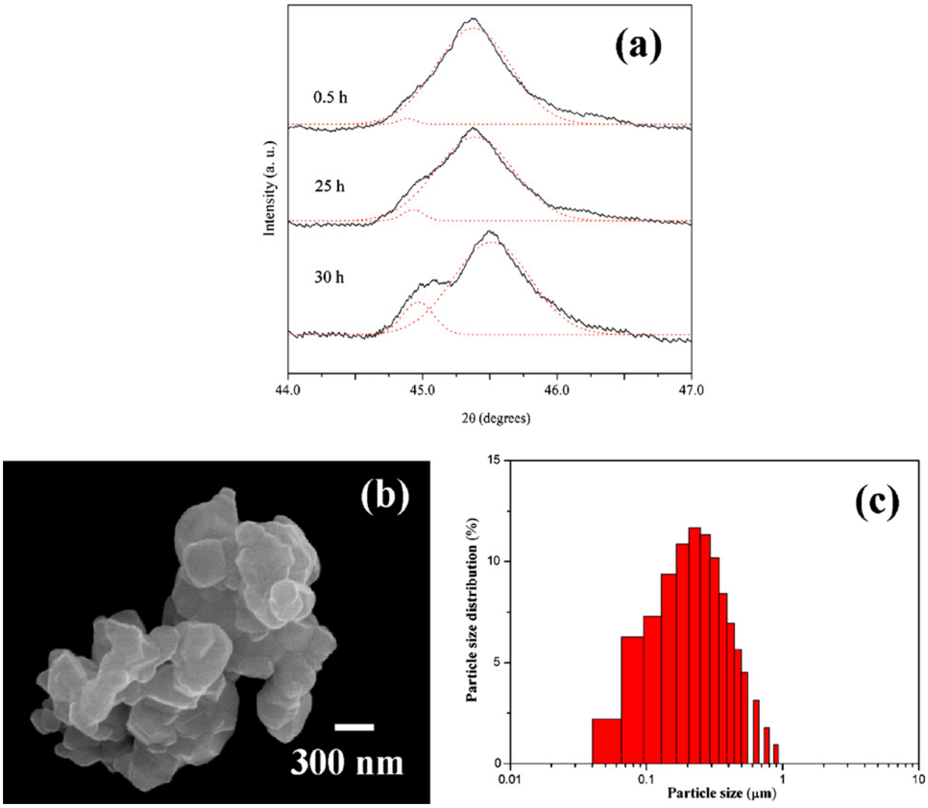

Fig. 4. (a) Enlarged zone of XRD patterns showing peaks broadening as a function of milling times of BT powders, (b) SEM micrograph and (c) particle size distribution of BT powders milled for 25 h and calcined at 1200 °C for 2 h with heating/cooling rates of 30 °C/min.

A combination of SEM and laser diffraction techniques was also employed for the morphology and particle size distribution measurement, as some examples shown in Figs. 2(b and c), 3(b and c) and 4(b and c). In general, all powders are agglomerated and basically irregular in shape, with a substantial variation in particle size, particularly in powders subjected to high firing temperatures (Fig. 4(b)). The powders consist of primary particles in the nanometers size range. It is also of interest to point out that degree of agglomeration tends to increase with milling time and calcination temperatures (Fig. 4(b and c)), in good agreement with other works [1–3]. This observation may be attributed to the occurrence of hard agglomeration with strong inter-particle bond within each aggregates resulting from firing process. The experimental work carried out here suggests that mass production of single-phase PZ, PT and BT nanopowders with the smallest particle size ~31 nm, 17 nm and 100 nm, respectively (estimated from SEM micrographs), can be achieved by employing a combination of suitable vibro-milling time and calcination condition. Moreover, the employed heating/cooling rates for all selected powders observed in this work are faster than for those reported earlier [10–12].

4. Conclusions

Using commercially available oxide powders as the starting materials, it has been demonstrated that a rapid vibro-milling technique has considerable potential for the low cost, large-scale production of several high purity electroceramic nanopowders.

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