

Communication

Microwave-assisted hydrothermal synthesis of lead zirconate fine powders

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Abstract: A rapid synthesis of lead zirconate fine powders by microwave-assisted hydrothermal technique is reported. The influences of type of lead precursor, concentration of potassium hydroxide mineraliser, applied microwave power and irradiation time are described. The synthesised powders were characterised by powder X-ray diffraction, field emission scanning electron microscopy, energy-dispersive X-ray spectroscopic microanalysis and light scattering technique. The merits of the microwave application in reducing reaction time and improving particle mono-dispersion and size uniformity as well as the drawbacks, viz. low purity of the desired phase and increasing demand of mineraliser, are discussed in relation to conventional heating method.

Keywords: lead zirconate, hydrothermal synthesis, microwave-assisted synthesis

INTRODUCTION

Lead zirconate (PbZrO_3 or PZ) is an important precursor in the preparation of a number of technologically important solid solutions, particularly those of the $\text{PbZr}_{1-x}\text{Ti}_x\text{O}_3$ series [1-2]. Recently, new studies have revealed novel applications of PZ as a phase-transformation-induced electro-mechanical actuator and a pyroelectric sensor [3-4]. The findings resulted in the reviving of interest in the synthesis of nano-sized PZ powders. Along this line, various synthetic techniques are available, e.g. hydrothermal, vibro-milling, sol-gel and precipitation, each of which exhibits characteristic drawbacks. The formation of aggregates, for instance, is an inherent problem for the hydrothermal technique [5-8]. The synthesis of fine PZ powders composing of mono-dispersed particles of uniform shape and size by this technique is therefore a challenge. According to our previous study, the fine powders of

orthorhombic PZ could be synthesised as a single phase under hydrothermal conditions at a temperature of at least 180°C for 24 hours [8]. The space group of the resulting PZ was the unusual *Pbma* with refined cell parameters $a=5.88(6)$ Å and $c=4.27(3)$ Å. The formation of aggregates was the major drawback. Nonetheless, the highly dispersed and well-defined cubic particles could be afforded when the reaction temperature and time were increased to 200°C and 72 hours respectively [8]. The attempt to use organic additives, e.g. polyvinyl alcohol, polyvinylpyrrolidone and cetyltrimethylammonium bromide, which are commonly employed in the synthesis of other oxide powders [9-11], may be an answer to this problem, although they need to be removed in the post-synthesis step.

Herein, the application of the microwave heating in the synthesis of PZ fine powders under hydrothermal conditions is reported. The primary objective of the synthesis is to promote the mono-dispersion of particles of the synthesised PZ powders without the assistance of organic additives. The influences of various synthetic parameters on the obtained powders and the advantages and shortcomings of the microwave heating are described and discussed.

MATERIALS AND METHODS

Equimolar mixtures of zirconyl nitrate hexahydrate [$\text{ZrO}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$, 27% Zr (gravimetric), Fluka, 0.0115 mole] and one of the following lead precursors, i.e. lead(II) nitrate (99.0%, Univar), lead(II) acetate (99.5%, Ajax Chemicals), lead(II) fluoride (99.0%, Univar), lead(II) chloride (99.0%, Riedel de Haën) and lead(II) iodide (99.0%, Aldrich), were prepared in 10.0 cm³ of deionised water. Pellets of potassium hydroxide (85%, Merck) was gradually added to each mixture with stirring to a concentration ranging from 6 to 14 moles dm⁻³. Each mixture was then transferred to an 18-cm³ Teflon reactor, which was sealed and placed in a 95(±5)°C water bath placed in a domestic microwave oven (Whirlpool XT-25ES/S, 900W, 2.45 GHz). The reaction was performed under autogenous pressure developed by the microwave heating (720W and 810W) for 3-5 hours. The resulting powder was recovered by filtration and washed with deionised water until the pH of the filtrate was approximately 7, followed a final washing with dilute acetic acid.

The synthesised powders were characterised for crystalline phases by powder X-ray diffraction (XRD) (using D8 Advance, Bruker, Cu $K\alpha$, Ni filter, $\lambda=1.540598$ Å, 40 kV, 30 mA). A field-emission scanning electron microscope equipped with energy-dispersive X-ray spectrometer (JSM-6335F, Jeol) was used in the examination of particle shape and size and elemental composition. In order to evaluate the aggregation, size distributions of the bulk powder samples were measured by light scattering technique (using Zetasizer Nano S, Malvern Instruments, 4mW He-Ne laser operated at 633 nm, particle size range 0.3nm-10µm).

RESULTS AND DISCUSSION

Although different lead precursors were used in the study, every reaction apparently provided the same off-white powders mixed with some red-block crystals, which were identified as lead oxide by XRD study. Although the contamination of lead oxide in the prepared powders seemed to be inevitable, they could be simply removed by washing with dilute acetic acid solution [12]. After the acid washing, it was found that only $\text{Pb}(\text{NO}_3)_2$ gave the well crystallised PZ while poorly crystallised powders were

obtained from the other lead precursors as depicted in Figure 1. This could be attributed to the low solubility of these lead precursors in aqueous solution compared to the readily dissolved $\text{Pb}(\text{NO}_3)_2$ [13]. The hardly dissolved lead precursors might bring about an insufficient nutrient in the solution and consequently the nucleation and crystal growth could not occur properly.

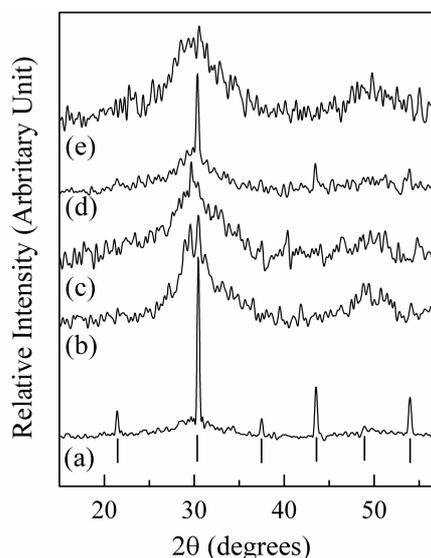


Figure 1. XRD patterns of the powders obtained from reactions between $\text{ZrO}(\text{NO}_3)_2 \cdot \text{H}_2\text{O}$ and different lead precursors in 14 moles dm^{-3} KOH solution for 3 hours: (a) $\text{Pb}(\text{NO}_3)_2$, (b) $\text{Pb}(\text{CH}_3\text{COO})_2$, (c) PbF_2 , (d) PbCl_2 and (e) PbI_2 . The vertical bars indicate diffraction characteristics of PZ (ICSD 077-0856).

For the $\text{Pb}(\text{NO}_3)_2$ case, according to the XRD patterns of the acid-treated powders as shown in Figure 2, a very high KOH concentration of 14 moles dm^{-3} was required for the success of the synthesis. Lower concentrations resulted in poorly crystallised powders. However, a development in intensity of the (200) diffraction peak with increasing KOH concentration was apparent, suggesting the evolvement of the desired PZ. Another observation was a substantial reduction of the effective reaction time from days to hours when compared with the conventional hydrothermal synthesis [8].

According to former studies on similar issues, the observed phenomena could be explained as follows. Under commonly used hydrothermal conditions, the formation of nanocrystalline ZrO_2 as the hydrolysis product of aqueous $\text{ZrO}(\text{NO}_3)_2$ [14] could also be accelerated by microwave heating. This caused the breaking of large water clusters in the hydration sphere and the formation of the smaller ones [15]. Such mechanism increased the mobility of the dissolved lead species as well as the number of reaction sites on the occurring ZrO_2 surfaces for the hydrated lead ion-water clusters to react. A rapid synthesis should therefore be expected. According to the same studies, the hydrolysis of the aqueous $\text{ZrO}(\text{NO}_3)_2$ also resulted in the generation of nitric acid, which could neutralise the hydroxide species in solution [14]. In addition, there was evidence for the reduced electrolytic reaction of the KOH solution by the microwave radiation [16]. These phenomena were probably responsible for the increase in the high KOH concentration required in this study. This assumption was supported by the

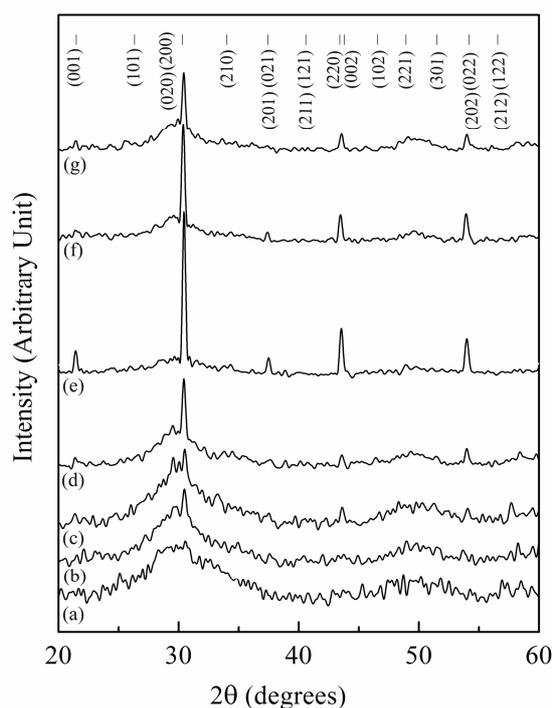


Figure 2. XRD patterns of the powders obtained from the reaction between $\text{ZrO}(\text{NO}_3)_2 \cdot \text{H}_2\text{O}$ and $\text{Pb}(\text{NO}_3)_2$ at 720 W for 3 hours in different concentrations of KOH solution: (a) 6 (b) 8 (c) 10 (d) 12 and (e) 14 moles dm^{-3} , compared to those obtained in 14 moles dm^{-3} KOH solution with different reaction times: (f) 4 hours and (g) 5 hours. The reference pattern is shown with vertical bars (ICSD 077-0856).

experiment in which a higher microwave power of 810 W was used. Rather than the desired PZ, mixtures of different oxides of lead and zirconium were obtained, which are the expected products of the hydrolysis reactions of the metal salts.

Based on the XRD patterns of the acid-treated powders, the synthesised PZ could be readily indexed as the orthorhombic *Pbma* phase with refined cell parameters $a=5.87(1)$ Å, $b=5.88(2)$ Å and $c=4.15(2)$ Å (ICSD 077-0856). These results were well consistent with the conventional hydrothermal case, although the refined c parameter was shorter than the conventional heating case, $c=4.27(3)$ Å [8], but closer to the standard, $c=4.134$ Å (ICSD 077-0856).

The field-emission scanning electron microscopic (FESEM) images, as typically illustrated in Figure 3(a), showed that the powders largely consisted of discrete cubic particles although some particles with irregular shape were also present. The energy-dispersive X-ray spectroscopic measurements on the surface of several cubic particles indicated stoichiometric Pb:Zr, whereas the irregular-shape particles were found to be Zr-rich. This could account for the noisy background observed for the XRD patterns [Figure 2(e)]. The sizes of the cubic particles measured from the FESEM images were distributed in a significantly narrow range of 0.4-1.2 μm with approximately 60% of the population having a size of about 1 μm [Figure 4(a)]. Light scattering experiment on the bulk powder samples showed slightly larger particle sizes distributed mostly between 1-2 μm [Figure 4(b)]. The difference in particle sizes obtained from the two techniques should be due to a potentially biased

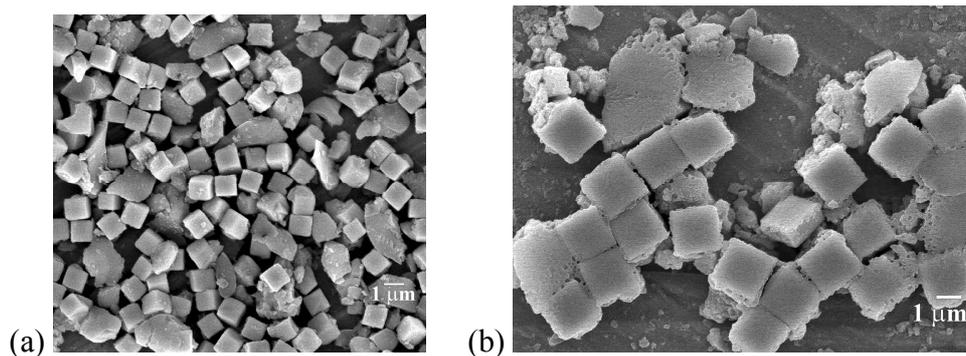


Figure 3. Typical FESEM photographs of PZ particles with corresponding XRD patterns shown in Figures 2(e) and 2(g) for crystals (a) and (b) respectively.

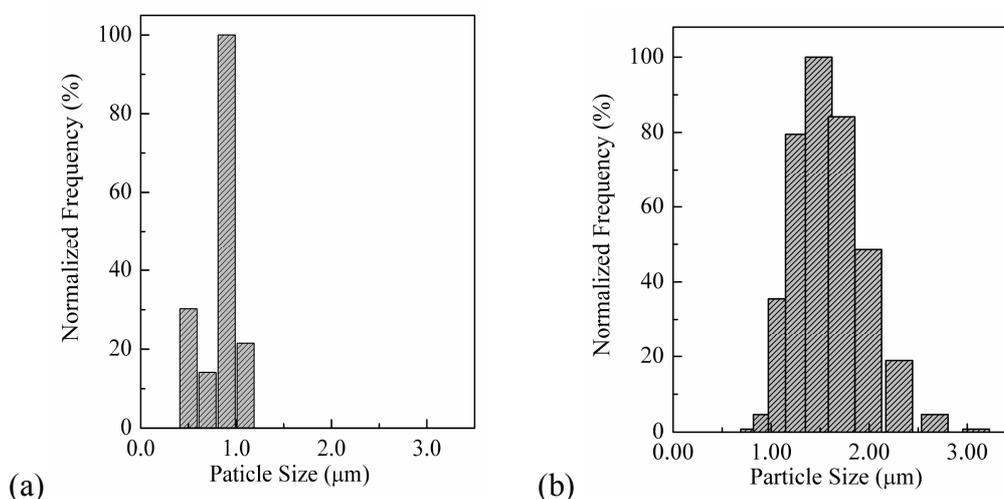


Figure 4. Particle size distribution of the cubic PZ particles measured from (a) FESEM images and (b) light scattering experiment (measured on the same powder sample)

analysis of the data. The non-spherical morphology of the particles normally introduces statistical errors to the laser light scattering data while a tendency of the particles to rest with preferred orientation on stub can induce bias in the data representation of the FESEM [17].

Thus, in comparison to the PZ powders derived from a conventional hydrothermal reaction where the particles were reportedly distributed in a 5-15 μm range with an average diameter of 7.5 μm [8], the pronouncedly narrower size distribution and the substantially smaller PZ particles have been achieved, although the negative effect on phase purity of the synthesised PZ and the contamination of some irregular Zr-rich particles were observed. A large number of nucleation induced by the localised microwave heating and the mechanism as described above, coupled with a poor crystal growth due to instantaneous and rapid ramping of such heating, could be the reasons for the approximate uniformity in the particle size [18-19]. Considering the PZ powders obtained from other chemical routes such as precipitation [20] and microemulsion [21], the apparent uniformity in particle shape and size may not be new. Both of these techniques can also give PZ powders composing of mono-dispersed spherical

particles typically 20 nm in diameter. However, calcination is required by both techniques, resulting in an unavoidable high temperature treatment and disadvantages incurred therein. As for the modified solid-state preparation of PZ powders, the problems with aggregation and particles with irregular shapes cannot be surmounted even though the vibro-milling is applied for over 25 hours [22].

The extension of the microwave heating time from 3 to 5 hours resulted in a reduction in intensity of the most intense (200) diffraction peak of the orthorhombic PZ and the appearing of a broad lump at the base of this peak as shown in Figure 2 (e-g). The FESEM images [Figure 3(b)] showed that the particles remained in the same cubic shape, although the bubbled surfaces and the necking between the adjacent particles could be observed. This indicated the boiling on the surfaces of these cubic PZ particles, which could be the result of a heat accumulation. The enlargement of the particles, which is a reflection of the particle growth process, and the disappearing of irregular particles with extended reaction time were also apparent.

CONCLUSIONS

In order to promote the mono-dispersion and the uniformity in shape and size of the hydrothermally derived PZ particles without the assistance of organic additives, microwave heating was attempted. The occurrence of lead oxide seemed to be inevitable and washing with dilute acetic acid was necessary. Among different variables studied, the type of lead precursor and the KOH concentration were most critical in the success of the synthesis. It was shown that the critical KOH concentration and the optimal microwave heating time were 14 moles dm^{-3} and 3 hours respectively. The highly dispersed cubic lead zirconate particles of approximately 1 μm in size could be synthesised in only 3 hour at 720 W of microwave heating. In comparison to conventional hydrothermal synthesis, the merits of the microwave method were clearly reflected by a shortening in hydrothermal reaction time, a reduction in particle size, an improved particle mono-dispersion, and a uniform particle size. However, the negative effects on the purity of synthesised powders, viz. the contamination of irregular particles, and the requirement for a very high concentration of potassium hydroxide mineraliser should be noted.

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