

Characterisation of Nanocrystalline PZT Synthesised via a Hydrothermal Method

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ABSTRACT

This paper describes the progress made toward characterising lead zirconate titanate (PZT) synthesised via a novel hydrothermal method [1,2]. Low temperatures (≤ 200 °C) and high mineraliser (potassium hydroxide) concentrations were used to produce single-phase, perovskite PZT in a bomb-type reactor. Full phase purity was attained after just 30 minutes of processing at 160 °C. The particles had a wide size distribution, from nanoscale agglomerates with irregular morphology, up to micron-sized cubes. It is believed that the differences in morphology can be attributed to two distinct formation stages.

Keywords: hydrothermal, PZT, nanocrystalline

1 INTRODUCTION

Nanoscale lead zirconate titanate (PZT) has the potential to become a key component in a myriad of emerging future applications. Examples of such technologies include, but are not limited to, non-volatile ferroelectric random access memories and nanoelectronic mechanical systems (NEMS). A sound knowledge of the underlying physical and chemical processes involved in the formation and applications of these particles is clearly essential for successful device development.

The hydrothermal method involves using elevated temperatures and pressures to synthesise inorganic materials from aqueous or non-aqueous solutions. It has several key advantages over other methods when it comes to synthesising PZT. These include the ability to control particle morphology, size and agglomeration whilst retaining high product purity. From a processing point of view, the hydrothermal method is very simple and can also be cost effective [1,2]. In this paper the effects of processing temperature and time on the hydrothermal synthesis of PZT are investigated. Attempts are also made to control the stoichiometry of the resultant powders by altering the precursor ratios.

2 EXPERIMENTAL DETAILS

The precursors for the hydrothermal reaction were lead (II) nitrate ($\text{Pb}(\text{NO}_3)_2$), zirconyl chloride octahydrate ($\text{ZrOCl}_2 \cdot 8\text{H}_2\text{O}$) and titanium dioxide (TiO_2). All chemicals were reagent grade and obtained from Aldrich, UK or Fisher, UK. The quantities of zirconyl chloride and titanium dioxide were altered to produce the desired PZT stoichiometry ($\text{PbZr}_x\text{Ti}_{1-x}\text{O}_3$ where $x = 0.2 \rightarrow 0.7$). A 45 ml, Teflon lined autoclave (Parr Instruments, model no. 4744) was filled with the powder precursors and topped up with 25 ml of distilled water. After vigorous stirring, 7 g of potassium hydroxide (KOH) flakes were added slowly to give a 5 M mineraliser concentration. The autoclave was then placed into an oven and heated over a range of temperatures (130 – 200 °C) and times (0.5 – 6.0 hrs). After the hydrothermal treatment the PZT powders were filtered and washed with distilled water and ethanol and then dried at 60 °C for 24 hrs.

The phase composition of the powders was determined using a Siemens D5005 x-ray diffractometer. Qualitative comparisons were made between the resulting patterns and the powder diffraction file for tetragonal $\text{PbZr}_{0.52}\text{Ti}_{0.48}\text{O}_3$ (JCPDS #33-0784). The morphology and size distribution of the particles were analysed using a Sirion S-FEG SEM. Elemental analysis of samples was conducted using an EDAX detector attached to the SEM.

3 RESULTS AND DISCUSSION

3.1 The effects of processing time

The dependence on processing time was tested for 52:48 PZT at 160 °C. Fig. 1 shows XRD patterns of the unreacted precursor material and four PZT powders synthesised over a range of times. The precursor material is a mixture of tetragonal TiO_2 and an amorphous phase. No systematic change in peak intensity occurs after 0.5 hr processing time in the PZT patterns. This suggests that crystallisation is substantially complete within this time period. Any non-systematic variations in peak intensity can be explained by random preferential reflections due to the nature of the x-ray powder method.

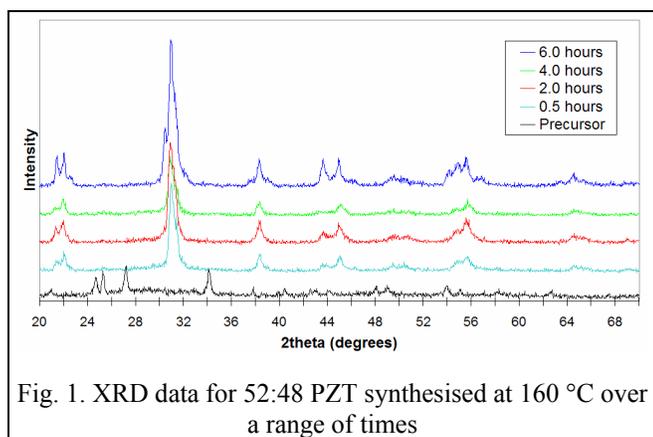


Fig. 1. XRD data for 52:48 PZT synthesised at 160 °C over a range of times

The 0.5 – 6.0 hrs patterns appear to contain a single phase that matches the powder diffraction file for tetragonal $\text{PbZr}_{0.52}\text{Ti}_{0.48}\text{O}_3$ (JCPDS #33-0784). Processing times less than 0.5 hr led to an incomplete reaction of the precursors.

The resultant particle morphology for each processing time is shown in Fig. 2, parts a) – d). The major particles are micron sized and cubic. Smaller, irregularly shaped agglomerates are also present, to varying degrees, in each sample (Fig. 3). Systematic changes in morphology do not appear to take place with increasing processing time – cubic particles, once formed, undergo little change.

Traianidis et al. [1] proposed a two-stage reaction mechanism to account for the existence of two types of particle morphology. In the first stage a Zr-Ti co-precipitate forms, into which lead ions diffuse. This leads to irregularly shaped agglomerates. As the reaction progresses these agglomerates are dissolved leading to the nucleation and growth of cubic PZT particles. A similar process seems to occur in this reaction. Further work is necessary to determine whether the PZT phase has been generated in the irregularly shaped agglomerates. Future experiments, planned to test the ferroelectric properties of nano-sized PZT particles, could verify this.

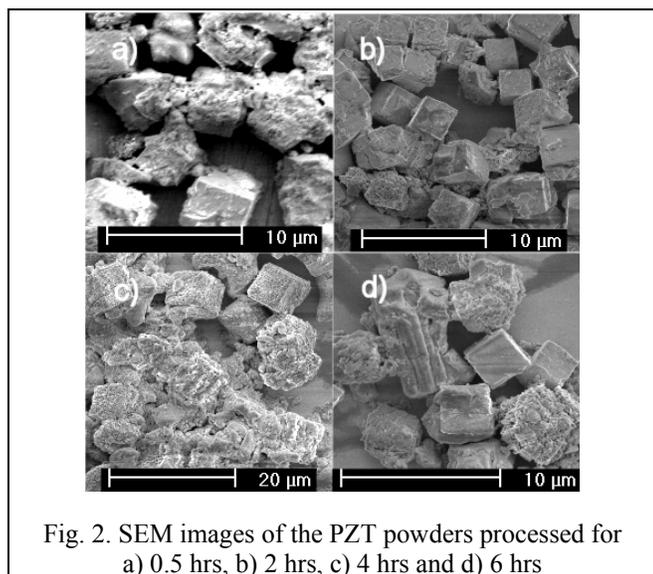


Fig. 2. SEM images of the PZT powders processed for a) 0.5 hrs, b) 2 hrs, c) 4 hrs and d) 6 hrs

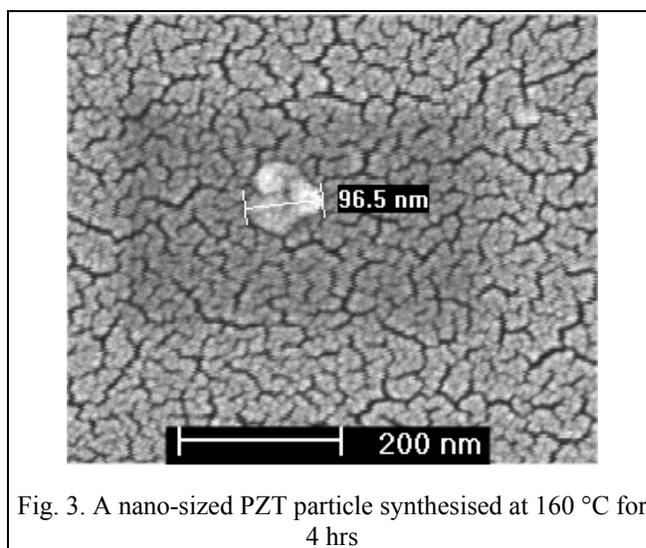


Fig. 3. A nano-sized PZT particle synthesised at 160 °C for 4 hrs

3.2 The effects of processing temperature

Having established that a minimum of 30 minutes processing time at 160 °C was necessary to produce phase-pure PZT, experiments were conducted to reduce processing temperature. Fig. 4 shows the evolution of the PZT phase from 140 – 160 °C. The indexed peaks refer to the accepted values for tetragonal $\text{PbZr}_{0.52}\text{Ti}_{0.48}\text{O}_3$. As the processing temperature increases the TiO_2 phase diminishes until phase purity is reached at 160 °C.

Further evidence for incomplete reaction was found when examining the morphology of the 140 °C powder. EDAX was used to confirm that the small round particles visible in the background of Fig. 5 consisted of unreacted TiO_2 ; a cubic PZT particle is shown in the foreground. Again, no systematic changes to morphology were evident in the PZT that was produced between 140 – 160 °C.

The breakdown of TiO_2 is a limiting factor for the reaction. In one experiment the mineraliser (KOH) concentration was reduced from 5 M to 0.5 M. After 18 hrs of processing at 200 °C no PZT phase was detectable in the XRD pattern. This indicates that the use of an oxide precursor imposes a minimum limit for processing temperature and mineraliser concentration.

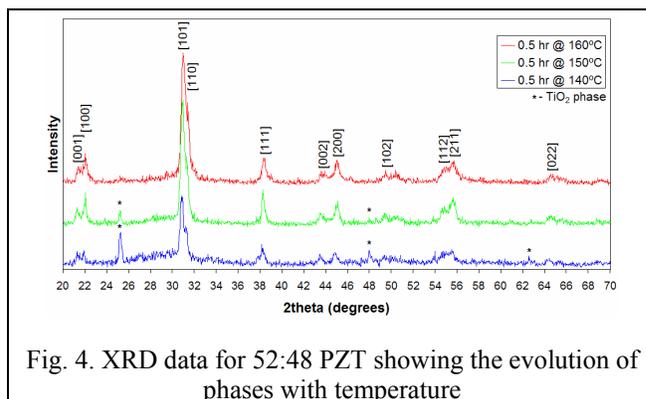


Fig. 4. XRD data for 52:48 PZT showing the evolution of phases with temperature

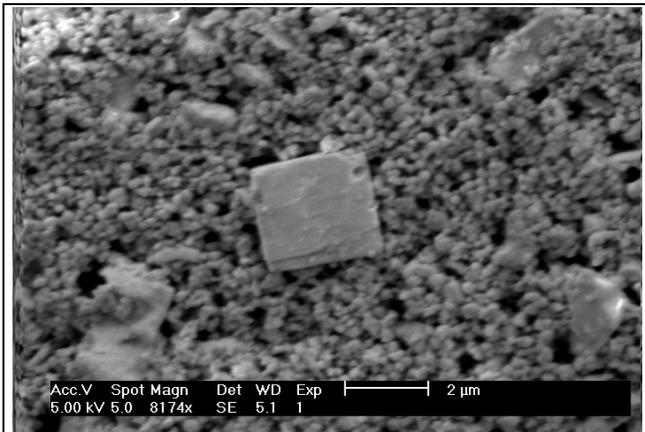


Fig. 5. SEM image of the PZT powder processed for 0.5 hr at 140 °C

3.3 Altering PZT stoichiometry

Attempts were made to synthesise different PZT stoichiometries by altering the Zr/Ti precursor ratio. Fig. 6 shows XRD data for powders produced using precursor ratios from 20:80 – 70:30. The PZT system has a morphotropic phase boundary (MPB) at approximately Zr/Ti = 52:48. Above this value the powders crystallise with a rhombohedral structure, while those below form a tetragonal structure.

If the synthesis of 70:30 PZT had been successful, we would expect to see a single (100) peak at 2theta ~ 22 degrees as opposed to the split (001) – (100) peaks, characteristic of the tetragonal PZT structure, which are visible in Fig. 6. The clear match of the 70:30 pattern with the peaks expected for 52:48 indicate that the latter has in fact been produced. This also appears to be the case with the attempt to synthesise 20:80 PZT. The presence of a TiO₂ phase in this pattern suggests that the extra titanium has failed to incorporate into the PZT lattice.

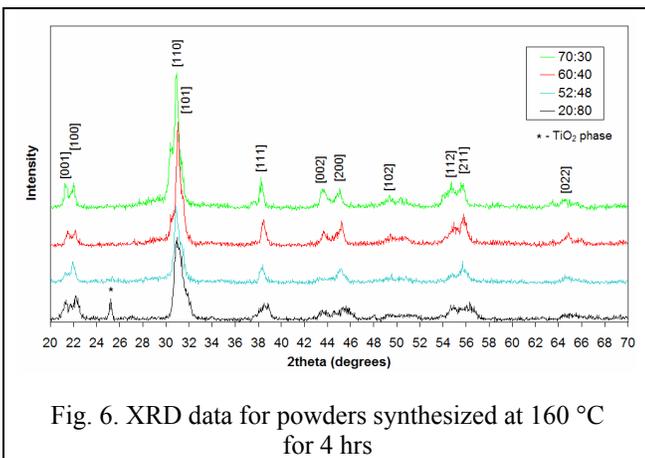


Fig. 6. XRD data for powders synthesized at 160 °C for 4 hrs

Kutty and Balachandran [3] found that the reaction temperature necessary to synthesise PZT was proportional to the Zr/Ti ratio. In other words, the rhombohedral phase required far more energy (340 °C) to form than the tetragonal phase. Attempts to synthesise lead titanate (the tetragonal end member of the PZT system) using this method have been successful, whereas similar attempts to produce lead zirconate have failed, giving credence to the applicability of this theory. However, an alternative explanation may be equally valid. Chen et al. [4] investigated the hydrothermal synthesis of Zr_xTi_{1-x}O₄ for x = 0.35 → 0.65. They found that the phases produced were dependent on the pH of the reaction medium. In highly basic solutions (pH = 13), TiO₂ was the only detectable phase when the precursor ratio Zr/Ti < 50:50 whilst ZrTiO₄ plus a tetragonal zirconia phase were produced when Zr/Ti > 50:50.

A similar pattern is seen when the results in this paper are compared. Although the zirconium-titanium compound, which forms when the precursors are first mixed, is not ZrTiO₄, it seems plausible that its behaviour could be similar, under the same hydrothermal conditions. To begin with, the reaction takes place in a highly basic medium. PbZr_{0.52}Ti_{0.48}O₃ plus an excess TiO₂ phase form when the precursor ratio Zr/Ti < 52:48. PbZr_{0.52}Ti_{0.48}O₃ forms when the precursor ratio Zr/Ti ≥ 52:48. The lack of a detectable zirconium phase may be due to the differences in the precursors. EDAX analysis has confirmed that a soluble zirconium compound forms when the precursor ratio Zr/Ti > 52:48. This compound gets washed away when the powders are filtered after the hydrothermal process.

4 CONCLUSIONS

Lead zirconate titanate (PZT) powders have been synthesised under a variety of hydrothermal conditions using high mineraliser concentrations, in aqueous solutions. The minimum requirements for phase-pure, PbZr_{0.52}Ti_{0.48}O₃ were 0.5 hrs of processing time at 160 °C.

The powders produced in this paper had a wide size distribution and consisted either of nano-scale, irregularly shaped agglomerates or micron-sized cubes. It was thought that particles with the former morphology transformed into the latter through a dissolution-precipitation mechanism.

The reactivity of the TiO₂ precursor was found to limit the formation of PZT. At lower temperatures, below 160 °C, insufficient energy was available to fully breakdown the TiO₂ and as such large quantities remained in the reaction product. These were detected both visually, using a SEM, and as a contaminant phase in the relevant XRD patterns.

Altering the ratio of precursor materials did not lead to changes in the resultant PZT stoichiometry. Two reasons were proposed for this anomaly. The first one relied on the fact that PZT stoichiometries, above the MPB, form at much higher temperatures – double those used in the current work. The second made a comparison with related

work regarding the dependence on pH for the hydrothermal synthesis of $Zr_xTi_{1-x}O_4$. It was suggested that the behaviour of the reaction intermediaries in the current work could be similar, under comparable hydrothermal conditions.

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