

Hydrothermal synthesis of $\text{Pb}(\text{Zr}_{0.52}\text{Ti}_{0.48})\text{O}_3$ powders at low temperature and low alkaline concentration

ZHONG-CHENG QIU, JIAN-PING ZHOU*, GANGQIANG ZHU, PENG LIU and XIAO-BING BIAN

School of Physics and Information Technology, Shaanxi Normal University, Xi'an 710062, People's Republic of China

MS received 29 July 2008; revised 26 September 2008

Abstract. $\text{Pb}(\text{Zr}_{0.52}\text{Ti}_{0.48})\text{O}_3$ (PZT) powders were prepared by hydrothermal method. The effects of experimental parameters, including Pb/(Zr, Ti) ratio, alkaline concentration, reaction temperature and time on the product powders were studied in detail. Pure PZT powders were synthesized at suitable experimental conditions and Raman spectra confirmed the PZT with a perovskite-type structure. The homogeneous PZT powders with cubic-shaped morphology were formed at alkaline concentration of 1.2 M after reacting at 230°C for 2 h. The pure PZT powders obtained at low temperature and low alkaline concentration were attributed to precursors, TiCl_4 , with high activity and mineralizer NaOH with small cation radius.

Keywords. Crystal growth; perovskites; PZT; hydrothermal method.

1. Introduction

$\text{Pb}(\text{Zr}_{0.52}\text{Ti}_{0.48})\text{O}_3$ (PZT)-based ceramics with a perovskite-type structure are widely used in modern electric devices due to its high d_{33} and electromechanical coupling. The ceramic preparation generally involves two steps: synthesizing the ceramic powders and sintering the shaped structures. High temperatures (above 1200°C) are needed to obtain the high compact PZT ceramics by conventional solid state reaction. At this temperature, PbO volatility deteriorates the ceramic properties. Therefore, several methods have been developed to reduce the sintering temperature at which the ferroelectric PZT phase crystallizes, such as high energy ball-milling (Lee *et al* 2007), sol-gel method (Faheem and Shoaib 2006; Linardos *et al* 2006; Tahar *et al* 2007; Sangsubun *et al* 2008), hydrothermal method (Traianidis *et al* 2000; Deng *et al* 2003; Euphrasie *et al* 2003; Piticescua *et al* 2004; Wang *et al* 2004; Ahn *et al* 2006; Ko *et al* 2007; Yang *et al* 2007; Dunn 2008) and wet chemical method (Sahoo *et al* 2006). Hydrothermal synthesis is one of the most important tools for advanced material processing at low temperature (Byrappa and Adschiri 2007). It was used for preparing PZT powders (Deng *et al* 2003; Piticescua *et al* 2004; Wang *et al* 2004; Dunn 2008), films (Euphrasie *et al* 2003; Ahn *et al* 2006; Ko *et al* 2007) and even nanowhiskers (Yang *et al* 2007) from different precursor feedstocks. The desirable products can be synthesized by

controlling the experimental parameters such as alkalinity, reagent, mineralizer, hydrothermal treatment temperature and time.

In the open literature of PZT synthesis, the undesirable products such as $\text{Pb}_2\text{Ti}_2\text{O}_6$ (Wang *et al* 2004), PbO and TiO_2 (Deng *et al* 2003; Dunn 2008) accompanied in the powders. These would depress the PZT properties. In this paper, we prepare a series of PZT powders by the hydrothermal method and investigate the influence of the hydrothermal parameters on the phase of the product powders in detail.

2. Experimental

PZT powders were synthesized by using $\text{Pb}(\text{NO}_3)_2$, $\text{ZrOCl}_2 \cdot 8\text{H}_2\text{O}$ and TiCl_4 as the starting materials. $\text{Pb}(\text{NO}_3)_2$ and $\text{ZrOCl}_2 \cdot 8\text{H}_2\text{O}$ were dissolved in distilled water, and TiCl_4 in ethanol. The precursor was prepared by mixing these solutions with an appropriate amount of NaOH under mechanical stirring. The alkaline concentration was also controlled by suitable NaOH. Then, the mixture was transferred into a Teflon vessel filled at 3/4 of its volume. The vessel was put into an oven for reaction with different temperatures and times. After cooling down to room temperature with the oven, the resultant powders were washed several times and then oven dried at 90°C for 12 h.

Reactions were carried out at a series of experimental conditions with Zr/Ti ratio near the morphotropic phase boundary (52/48), since the Zr/Ti ratio in the range of 20/80~70/30 had limited effects on the resultant PZT phase (Dunn 2008). X-ray diffraction (D/max 2550 V)

*Author for correspondence
(zhoujp@snnu.edu.cn; zhoujp@tsinghua.org.cn)

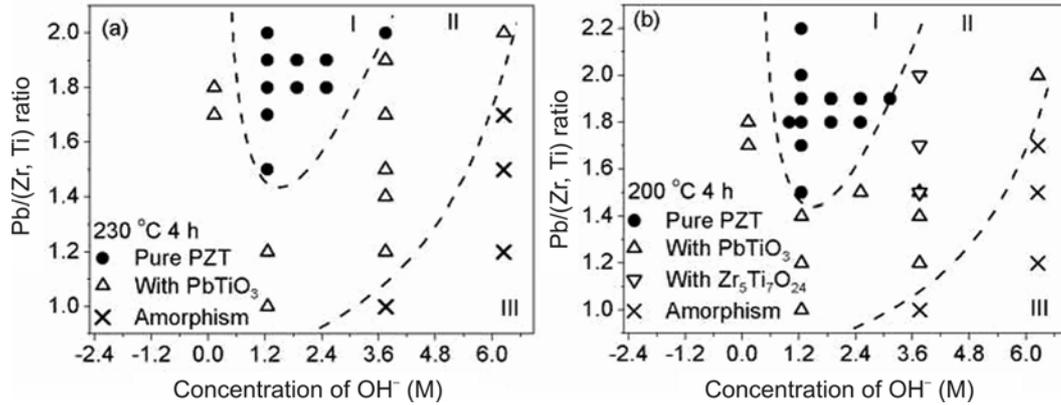


Figure 1. The product phases at different NaOH concentrations and Pb/(Zr, Ti) ratios after reacting for 4 h at (a) 230°C and (b) 200°C.

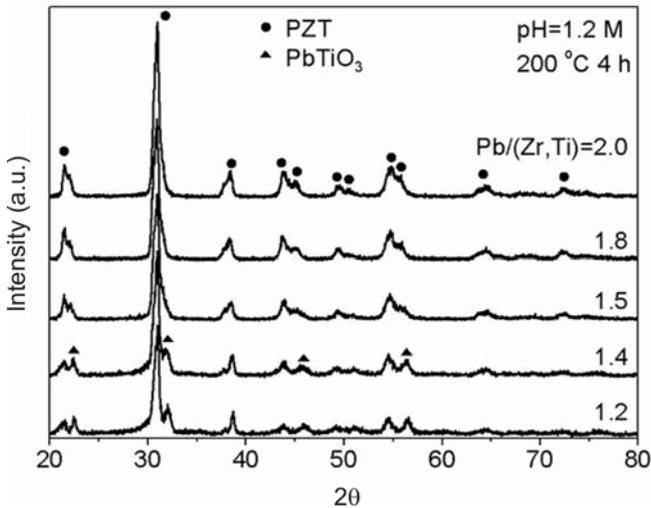


Figure 2. Typical XRD diffraction patterns for the powders reacted under the conditions of OH^- concentration, 1.2 M, 200°C and 4 h with various Pb/(Zr, Ti) ratios.

was used to determine the powder phases. The particle size and morphology of the products were investigated with a scanning electron microscopy (SEM Quanta 200). PZT structures were affirmed by Raman spectroscopy (ALMEGA-TM).

3. Results and discussion

The effects of Pb/(Zr, Ti) ratio and alkaline concentration on the product phases were studied first. Figure 1 shows different product phases after reacting for 4 h at 230°C and 200°C. They share similar characteristics. The pure PZT powders can be synthesized in the Pb/(Zr, Ti) ratio range of 1.5~2.0 and alkaline concentration range of 1~3 M shown as region I in figures 1(a) and (b). Foreign phases appear in the powders in region II, and the products

are amorphism in region III. We choose part of samples in figure 1(b) prepared at OH^- concentration of 1.2 M for future understanding. Figure 2 shows the typical XRD diffraction patterns for the powders reacted under the conditions of pH = 1.2 M, 200°C and 4 h with various Pb/(Zr, Ti) ratios. The second phase, PbTiO_3 , appears at low Pb/(Zr, Ti) ratio and it disappears while Pb/(Zr, Ti) > 1.5. During the early stages of the hydrothermal reaction, Pb^{2+} ions play an important role in infiltrating and help to dissolve the coprecipitated Zr–Ti gel (Dunn 2008). As PZT crystals precipitate, the Pb^{2+} concentration in solution falls, hence reducing the rate of dissolution. Thus, the superfluous Pb^{2+} ions are necessary to aid the PZT crystallization (Dunn 2008).

The alkaline concentration is another important factor to affect the products. It was reported that the pure PZT phase could be formed at the KOH concentration of 1.6~2.1 M (Wang *et al* 2004). But pure PZT phase is obtained at NaOH concentration of 1.2 M, 200~230°C and Pb/(Zr, Ti) > 1.5 in the present study. When the alkaline concentration increases, the foreign phases appear. When OH^- is high enough, the product powders cannot crystallize and are characterized as amorphous materials.

The effects of reaction temperature and time on the product phases were investigated in the Pb/(Zr, Ti) = 2 condition and alkaline concentration of 1.2 M. Figure 3 shows the product phases at different reaction temperatures and times. At low reaction temperature, PbTiO_3 appears and it can be removed by prolonging the reaction time to obtain pure PZT powders. So prolonging reaction time at low temperature can make the precursors react fully, having the same effect with the condition of high temperature and short time. But when the reaction temperature is lower than 120°C, PbTiO_3 still exists even after 30 h of reaction. The results indicate that the lowest soaking temperature for the PZT formation is 130°C. This is consistent with the lowest reaction temperature of 135°C to form the pure PZT phase (Wang *et al* 2004).

Figure 4 shows the XRD patterns for the pure PZT powders produced at different temperatures and times. They do not show clear difference, indicating that prolonging the reaction time at low temperature can make the precursors react fully, which has the same effect with high temperature and short time.

Considering alkaline concentration, temperature, time and Pb/(Zr, Ti) ratio, the experimental equilibrium reactions occur in the complex system, Pb–Ti–Zr–H₂O. In high alkaline concentration, Pb²⁺, Ti⁴⁺ and Zr⁴⁺ completely transform to the correspondent hydrous oxide. The precursor TiO₂ needs high alkaline environment to dissolve (Traianidis *et al* 2000; Li *et al* 2007; Sangsubun *et al*

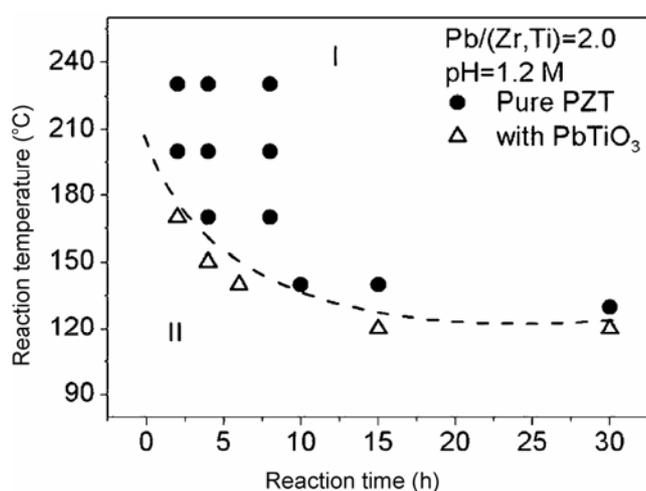


Figure 3. The product phases at Pb/(Zr, Ti) = 2.0 and alkaline concentration of 1.2 M with different reaction temperatures and times.

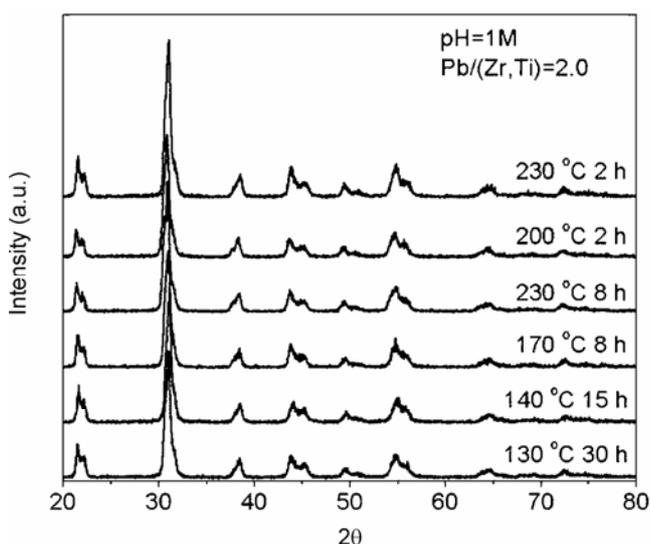


Figure 4. Typical XRD diffraction patterns for the powders reacted at different reaction temperatures and times.

2008). TiCl₄ is dissolved in ethanol and the Ti⁴⁺ ions transform to the hydrous titanium when mixing them with distilled water. On missing the TiO₂ solution process, hydrous oxides take part in reaction directly. Thus, PbTiO₃ phase is the first growing compound observed, different from the products PbO*TiO₂ and PbO*ZrO₂ that formed in the system (Piticescua *et al* 2004). In low alkaline environment, the products are the compounds of PZT and PbTiO₃, but not amorphous materials as reported before (Piticescua *et al* 2004). In hydrothermal mechanism, alkaline mineralizer can make the hydrous lead, zirconium and titanium reach favourable solution for reaction. Na⁺ ions with smaller radius in comparison with K⁺ ions (Traianidis *et al* 2000; Piticescua *et al* 2004; Wang *et al* 2004; Yang *et al* 2007; Sangsubun *et al* 2008) as mineralizer are easy to enter the Ti–O–Ti and Zr–O–Zr systems, breaking the gels and accelerating the crystallization. It was reported that the crystallization needed high alkaline concentration of 5 M (Deng *et al* 2003; Dunn 2008) and high reaction temperature of 180°C (Traianidis *et al* 2000) with the precursor TiO₂ and mineralizer KOH. But by using TiCl₄ and NaOH, the pure PZT powders can be produced at 1.2 M and 130°C.

Figure 5 shows typical SEM photographs of PZT powders synthesized at Pb/(Zr, Ti) = 2.0, alkaline concentration of 1.2 M and (a) 230°C, 2 h, (b) 200°C, 2 h, (c) 140°C, 15 h and (d) 130°C, 30 h. The powder images show well faceted and cubic-shaped particles, especially for the sample synthesized at 230°C for 2 h. The powders synthesized at 230°C exhibit small uniform particle sizes of 1–2 μm. During hydrothermal treatment, lead species are absorbed on the surface of the coprecipitated Zr–Ti particles, forming amorphous powders. Then, the diffusion of lead species into the coprecipitated network induces the formation of PZT solid solution through a dissolution–precipitation mechanism (Traianidis *et al* 2000; Wang *et al* 2004). The high reaction temperature enhances the ions activity, as a result, more crystal nucleations are formed at the beginning of dissolution-precipitation and grow to uniform particles. After 15 h of hydrothermal treatment at low temperature of 140°C, the pure PZT powders are also obtained, but the particles are inhomogeneous in size distribution, and small amount of slices appear. At low temperature and low alkaline concentration, the perovskite PZT grows more quickly in two dimensions than in the third dimension to form the slices (Li *et al* 2007). The slices grow layer by layer to form cubic shaped particles as shown in figures 5 (c) and (d).

Part of the samples was measured using Raman technique to show the PZT structure. The three samples share same vibration peaks as shown in figure 6. Obvious scattering peaks corresponding to different characteristic vibration modes of PZT can be seen in the spectra (Dobal and Katiyar 2002; Osada *et al* 2005). The Raman measurements give complementary evidence for the formation of perovskite-type PZT.

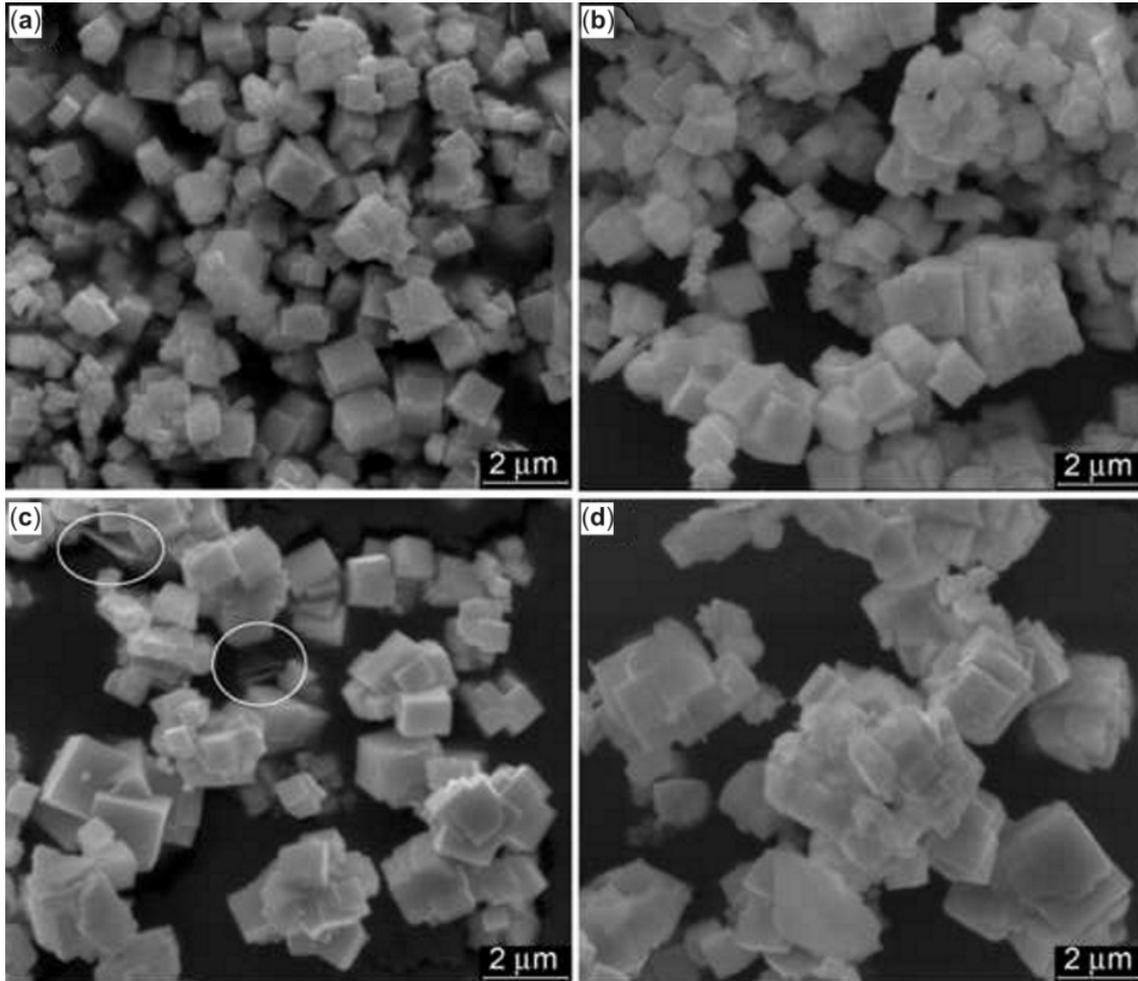


Figure 5. Powder morphologies of part samples synthesized at alkaline concentration of 1.2 M, Pb/(Zr, Ti)=2.0 and (a) 230°C, 2 h, (b) 200°C, 2 h, (c) 140°C, 15 h and (d) 130°C, 30 h. The circles indicate the slice PZT.

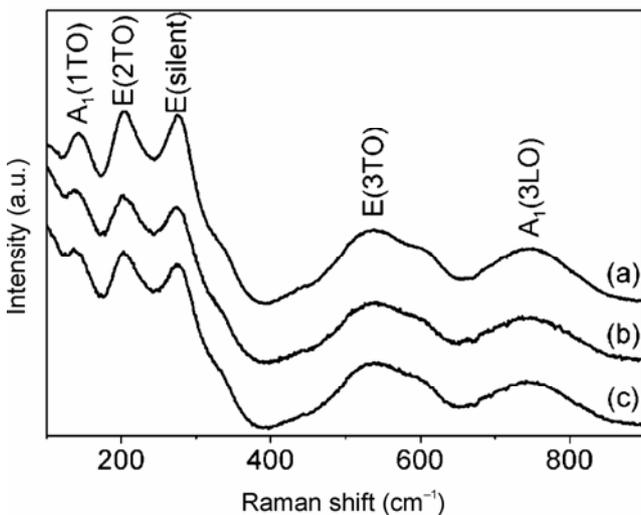


Figure 6. Raman spectra for part samples prepared at alkaline concentration of 1.2 M, Pb/(Zr, Ti)=2.0 and (a) 230°C, 4 h, (b) 170°C, 4 h and (c) 130°C, 30 h.

4. Conclusions

In summary, influence of Pb/(Zr, Ti) ratios, NaOH concentration, reaction temperature and time on the product powders was studied in detail. The pure PZT powders were synthesized at low temperature and low alkaline concentration because of the high active precursors and mineralizer NaOH with small cation radius. The PZT slices were formed and then grew to PZT particles at low temperature and alkaline concentration. The single phase PZT powder with homogeneous cubic-shaped morphology was obtained at Pb/(Zr, Ti)=2.0, NaOH concentration of 1.2 M, reacting at 230°C for 2 h.

Acknowledgements

This work was supported by the National Natural Science Foundation of China (Grant No. 50772065) and Innovation Funds of Graduate Programs, Shaanxi Normal University (Grant No. 2008CXS035).

References

- Ahn W S, Jung W W and Choi S K 2006 *J. Appl. Phys.* **99** 014103
- Byrappa K and Adschiri T 2007 *Prog. Cryst. Growth Ch. Mater.* **53** 117
- Deng Y, Liu L, Cheng Y, Nan C -W and Zhao S -J 2003 *Mater. Lett.* **57** 1675
- Dobal P S and Katiyar R S 2002 *J. Raman Spectrosc.* **33** 405
- Dunn H S S 2008 *J. Electroceram.* **20** 65
- Euphrasie S, Daviero-Minaud S and Pernod P 2003 *Mater. Sci. Eng.* **B104** 180
- Faheem Y and Shoaib M 2006 *J. Am. Ceram. Soc.* **89** 2034
- Ko F -H, Hsu Y -C, Wang M -T and Huang G S 2007 *Microelectron. Eng.* **84** 1300
- Lee J S, Choi M S, Hung N V, Kim Y S, Kim I W, Park E C, Jeong S J and Song J S 2007 *Ceram. Int.* **33** 1283
- Li T, Peng T and Yang S 2007 *Piezoelectrics & Acoustooptics* **29** 196
- Linardos S, Zhang Q and Alcock J R 2006 *J. Eur. Ceram. Soc.* **26** 117
- Osada M, Nishida K, Wada S, Okamoto S, Ueno R, Funakubo H and Katoda T 2005 *Appl. Phys. Lett.* **87** 232902
- Piticescua R M, Moisinb A M, Taloic D, Badilitaa V and Soare I 2004 *J. Eur. Ceram. Soc.* **24** 931
- Sahoo B, Jaleel V A and Panda P K 2006 *Mater. Sci. Eng.* **B126** 80
- Sangsubun C, Watcharapasorn A and Jiansirisomboon S 2008 *Curr. Appl. Phys.* **8** 61
- Tahar R B H, Tahar N B H and Salah A B 2007 *J. Cryst. Growth* **307** 40
- Traianidis M, Courtois C and Leriche A 2000 *J. Eur. Ceram. Soc.* **20** 2713
- Wang S F, Wang Y R, Mahalingam T, Chu J P and Lin K U 2004 *Mater. Chem. Phys.* **87** 53
- Yang X, Zhao Y, Yang Y and Dong Z 2007 *Mater. Lett.* **61** 3462