

Synthesis of single-crystalline $\text{Pb}(\text{Zr}_{0.52}\text{Ti}_{0.48})\text{O}_3$ nanocrystals by hydrothermal method

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$\text{PbZr}_{0.52}\text{Ti}_{0.48}\text{O}_3$ nanocrystals were synthesized by a hydrothermal method. The effect of NaOH concentration, reaction temperature and time on nucleation and growth of $\text{PbZr}_{0.52}\text{Ti}_{0.48}\text{O}_3$ nanocrystals was investigated. As the 0.05 mol/L $\text{PbZr}_{0.52}\text{Ti}_{0.48}\text{O}_3$ precursors were heated at 200 °C for 21 h with NaOH concentration of 0.5 mol/L, the tetragonal $\text{PbZr}_{0.52}\text{Ti}_{0.48}\text{O}_3$ nanocrystals were formed, and the grain size was more than 20 nm. With increasing the NaOH concentration from 0.5 to 1.5 mol/L, the grain size of $\text{PbZr}_{0.52}\text{Ti}_{0.48}\text{O}_3$ nanocrystals decreased. When the precursors were heated at different temperatures (140 °C to 200 °C) for 21 h with 1.0 mol/L NaOH, single-phase $\text{PbZr}_{0.52}\text{Ti}_{0.48}\text{O}_3$ nanocrystals were obtained at 160 °C to 200 °C. With increasing the reaction temperature from 160 °C to 200 °C, the grains size of $\text{PbZr}_{0.52}\text{Ti}_{0.48}\text{O}_3$ nanocrystals increased from 5 nm to 9 nm. When the precursors were heated at 160 °C in different reaction times from 6 h to 21 h, the evolution from amorphous to crystalline $\text{PbZr}_{0.52}\text{Ti}_{0.48}\text{O}_3$ nanocrystals in correlation with the reaction time was observed. Single crystalline $\text{PbZr}_{0.52}\text{Ti}_{0.48}\text{O}_3$ nanocrystals with narrow size distribution (from 5 nm to 9 nm) were synthesized by controlling the NaOH concentration, reaction temperature and time. The obtained results can find potential application in preparing $\text{PbZr}_{0.52}\text{Ti}_{0.48}\text{O}_3$ thin films on flexible substrates.

Keywords: $\text{PbZr}_{0.52}\text{Ti}_{0.48}\text{O}_3$ nanocrystal; hydrothermal method; reaction temperature; reaction time; NaOH concentration

1. Introduction

Ferroelectric films have been widely applied in micro-actuators, capacitors, electro-optical devices and ferroelectric memories [1–3]. Perovskite-structured lead zirconate titanate ($\text{PbZr}_x\text{Ti}_{1-x}\text{O}_3$, PZT) is one of the most important members in the ferroelectric family [4–10]. $\text{PbZr}_{0.52}\text{Ti}_{0.48}\text{O}_3$ films in the vicinity of the so-called morphotropic phase boundary have been extensively researched due to their excellent ferroelectric, piezoelectric properties and coupling coefficients.

Many deposition methods have been employed to prepare $\text{PbZr}_{0.52}\text{Ti}_{0.48}\text{O}_3$ thin films, such as pulsed laser deposition [11], sputtering [12], chemical vapor deposition [13] and sol-gel method [14–16]. Among these methods, sol-gel method has been extensively used due to its low cost and possibility of fabrication homogeneous large-scale

films. However, the $\text{PbZr}_{0.52}\text{Ti}_{0.48}\text{O}_3$ films prepared by conventional sol-gel method, and then annealed at high temperature (more than 600 °C) to form good crystalline films, were not compatible with flexible substrates. Recently, a novel nanocrystal-based sol-gel method was developed to prepare high-crystalline Al-doped ZnO thin films at low temperature (400 °C) [17]. The well-crystalline Al-doped ZnO nanocrystals with the average size of 4 nm, 5 nm and 9 nm were dispersed in solvents, and the high-crystalline Al-doped ZnO thin films were prepared by spin-coating. This process has potential application in preparation of $\text{PbZr}_{0.52}\text{Ti}_{0.48}\text{O}_3$ thin films at low temperature (less than 400 °C) on flexible substrates. For this process, the most important step is the synthesis of $\text{PbZr}_{0.52}\text{Ti}_{0.48}\text{O}_3$ nanocrystals with narrow size distribution (ca. 10 nm).

Hydrothermal method enables one to obtain homogeneous and uniform nanosized particles with high purity and crystallinity, good

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stoichiometric control, and high yield at low-temperature treatment in supercritical state and/or subcritical state [18–20]. It is an aqueous-based precipitation method where the nucleation, growth and aging processes can be easily controlled in the aqueous solution. The hydrothermal method has been extensively applied in preparation of $\text{PbZr}_{0.52}\text{Ti}_{0.48}\text{O}_3$ nanocrystals. Kutty *et al.* [21] firstly prepared PZT powders by the hydrothermal method at 300 °C and almost neutral pH in 1984. However, the grain size of PZT powders was more than 300 nm. It is well known that the grain size and quality of PZT nanocrystals are affected by various process parameters, such as reaction temperature, time and mineralizer concentration in the hydrothermal process. Deng *et al.* [22] synthesized nanocrystalline PZT powders by hydrothermal method based on the reaction of TiO_2 , $\text{Pb}(\text{NO}_3)_2$, $\text{ZrOCl}_2 \cdot 8\text{H}_2\text{O}$ or $\text{Zr}(\text{NO}_3)_4 \cdot 5\text{H}_2\text{O}$ and KOH at 160 °C for 4 h. The PZT powder consisted of spherical grains with an average diameter ranging from 5 nm to 10 nm. However, the limited TEM characterization of these PZT nanocrystals has not revealed good crystalline features. Huang *et al.* [23] developed an effective way to produce PZT nanocrystals by controlling ramping and cooling rates of the hydrothermal process. The PZT nanocrystals with the size distribution ranging from 200 nm to 800 nm were obtained with good morphology and crystallinity. Recently, Takada *et al.* [24] synthesized the single-crystal PZT cubes at 180 °C by hydrothermal method, and the piezoelectric properties of the material were confirmed. The size of PZT cubes was estimated to be 1 μm . However, the grain size of PZT particles was too large to be suitable for application in the nanocrystal-based sol-gel process to prepare $\text{PbZr}_{0.52}\text{Ti}_{0.48}\text{O}_3$ thin films at low temperature (less than 400 °C).

In this study, $\text{PbZr}_{0.52}\text{Ti}_{0.48}\text{O}_3$ nanocrystals were synthesized by the hydrothermal method, and NaOH solution was used as a mineralizer. The effect of reaction temperature, time and NaOH concentration on formation and morphology of $\text{PbZr}_{0.52}\text{Ti}_{0.48}\text{O}_3$ nanocrystals was investigated to control the growth of $\text{PbZr}_{0.52}\text{Ti}_{0.48}\text{O}_3$ nanocrystals.

2. Experimental

All the reagents were of analytical grade purity and were used without further purification. Lead acetate trihydrate ($(\text{Pb}(\text{CH}_3\text{COO})_2 \cdot 3\text{H}_2\text{O})$), zirconium nitrate pentahydrate ($\text{Zr}(\text{NO}_3)_4 \cdot 5\text{H}_2\text{O}$) and tetrabutyl titanate ($\text{Ti}(\text{C}_4\text{H}_9\text{O})_4$) were used as the starting materials, and NaOH solution was used as pH-adjusting agent. The desired amounts of $\text{Pb}(\text{CH}_3\text{COO})_2 \cdot 3\text{H}_2\text{O}$, $\text{Zr}(\text{NO}_3)_4 \cdot 5\text{H}_2\text{O}$ and $\text{Ti}(\text{C}_4\text{H}_9\text{O})_4$ were dissolved in deionized water under vigorous stirring at room temperature to form $\text{PbZr}_{0.52}\text{Ti}_{0.48}\text{O}_3$ precursors. Then, NaOH solution was added into the $\text{PbZr}_{0.52}\text{Ti}_{0.48}\text{O}_3$ precursors. The total volume of $\text{PbZr}_{0.52}\text{Ti}_{0.48}\text{O}_3$ precursors was 30 mL, and the concentration of $\text{PbZr}_{0.52}\text{Ti}_{0.48}\text{O}_3$ precursors was 0.05 mol/L. The NaOH concentration in the precursors was 0.5 mol/L, 1.0 mol/L to 1.5 mol/L. The obtained suspensions were added into Teflon-lined autoclaves of 50 mL capacity, and they were sealed tightly. The autoclaves were heated at different temperatures (140 °C, 160 °C, 180 °C and 200 °C) in different time periods (6 h, 12 h, 18 h and 21 h), and then naturally cooled to room temperature. The yellow precipitates were centrifuged, and washed with deionized water and ethanol in sequence.

The X-ray diffraction patterns of these samples were measured with an X-ray diffractometer (XRD, D8 Bruker Advance) with $\text{CuK}\alpha$ radiation (40 kV, 30 mA). The scanning rate was 2°/min with a scanning step of 0.02°. The morphologies of the samples were characterized by a field emission scanning electron microscope (FE-SEM, Zeiss Ultra Plus). The Raman spectra of the samples were obtained at room temperature between 150 cm^{-1} and 1000 cm^{-1} , using RENISHAW Raman microscope (InVia). The samples were characterized by a transmission electron microscope (TEM, JEM-2100UHR) at an acceleration voltage of 200 kV.

3. Results and discussion

3.1. Mineralizer concentration

For the hydrothermal process, the concentration of NaOH mineralizer plays an important role

in the formation and morphology of $\text{PbZr}_{0.52}\text{Ti}_{0.48}\text{O}_3$ nanocrystals. In this part, the effect of NaOH concentration on the formation of $\text{PbZr}_{0.52}\text{Ti}_{0.48}\text{O}_3$ nanocrystals is discussed. The NaOH concentration in $\text{PbZr}_{0.52}\text{Ti}_{0.48}\text{O}_3$ precursors was 0.5 mol/L, 1.0 mol/L to 1.5 mol/L, and the corresponding pH values of the $\text{PbZr}_{0.52}\text{Ti}_{0.48}\text{O}_3$ precursors were 13.13, 13.35 and 13.49, respectively. The reaction temperature was kept at 200 °C for 21 h. The precipitates were naturally dried at room temperature for XRD and SEM measurements.

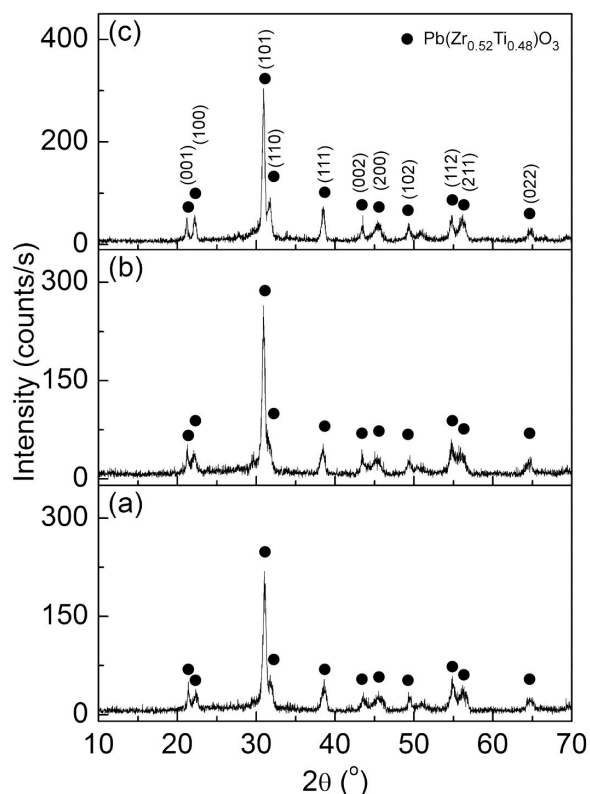
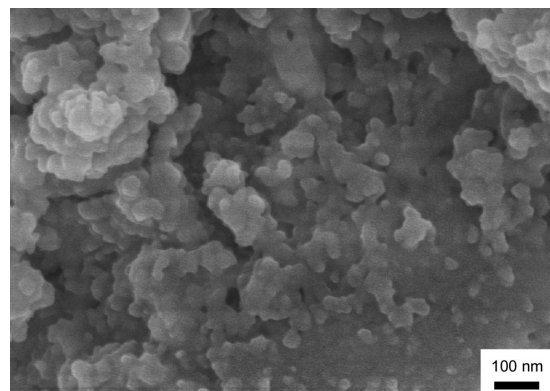
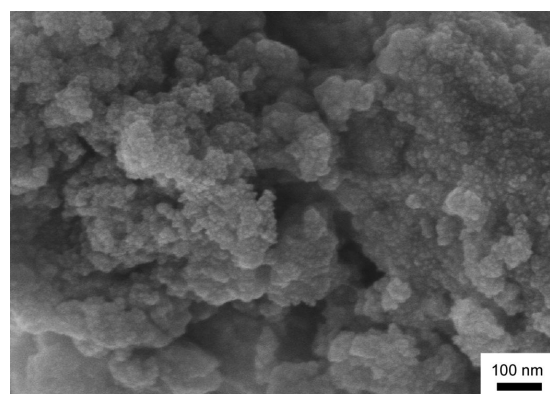


Fig. 1. XRD patterns of $\text{PbZr}_{0.52}\text{Ti}_{0.48}\text{O}_3$ nanocrystals prepared with different NaOH concentrations: (a) 0.5 mol/L, (b) 1.0 mol/L and (c) 1.5 mol/L.

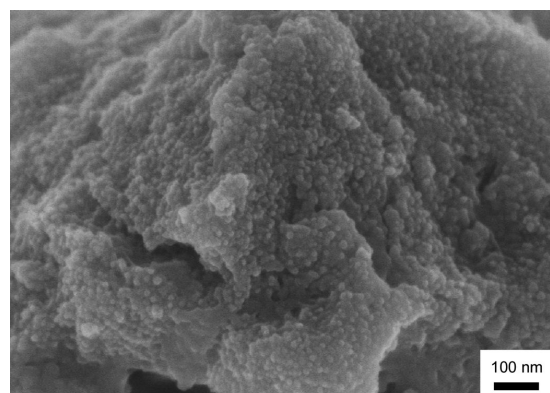
Fig. 1 shows the XRD results for the precipitates prepared with different NaOH concentrations. The XRD patterns were indexed to the tetragonal $\text{PbZr}_{0.52}\text{Ti}_{0.48}\text{O}_3$ phase (JCPDS Card No. 33-0784). The sample prepared with NaOH concentration of 0.5 mol/L was assigned to the tetragonal $\text{PbZr}_{0.52}\text{Ti}_{0.48}\text{O}_3$ phase. Increasing the NaOH concentration from 0.5 mol/L to 1.5 mol/L did not



(a)



(b)



(c)

Fig. 2. SEM images of $\text{PbZr}_{0.52}\text{Ti}_{0.48}\text{O}_3$ nanocrystals prepared with different NaOH concentration: (a) 0.5 mol/L, (b) 1.0 mol/L and (c) 1.5 mol/L.

cause any significant change in diffraction peaks for all the samples. Fig. 2 displays the morphologies of $\text{PbZr}_{0.52}\text{Ti}_{0.48}\text{O}_3$ nanocrystals prepared with different NaOH concentrations. As the NaOH

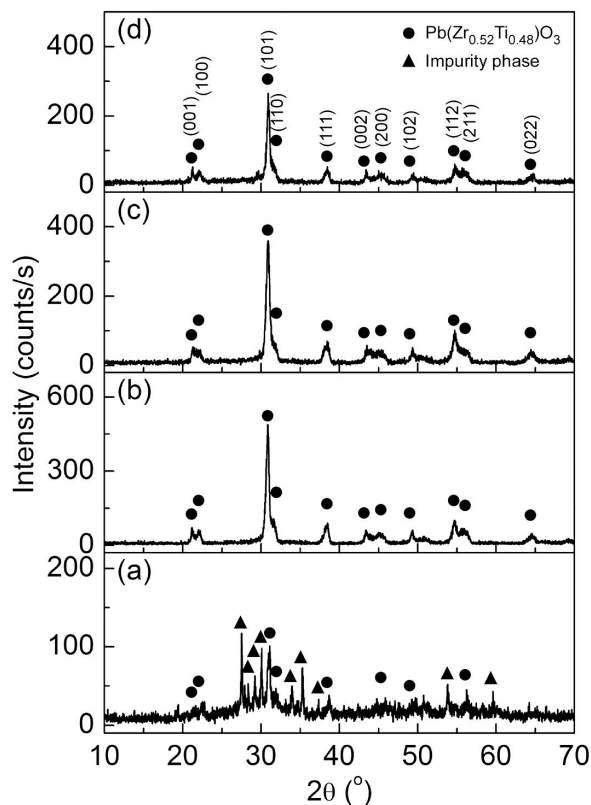


Fig. 3. XRD patterns of the samples prepared at different temperatures: (a) 140 °C, (b) 160 °C, (c) 180 °C and (d) 200 °C.

concentration was 0.5 mol/L, the sample was not uniform and the grain size of $\text{PbZr}_{0.52}\text{Ti}_{0.48}\text{O}_3$ nanocrystals was larger than 20 nm. With increasing the NaOH concentration to 1.0 mol/L and 1.5 mol/L, the grain size of $\text{PbZr}_{0.52}\text{Ti}_{0.48}\text{O}_3$ nanocrystals decreased, and the samples became uniform.

3.2. Reaction temperature

During this investigation, the NaOH concentration in $\text{PbZr}_{0.52}\text{Ti}_{0.48}\text{O}_3$ precursors was fixed at 1.0 mol/L, and the $\text{PbZr}_{0.52}\text{Ti}_{0.48}\text{O}_3$ precursors were heated at different temperatures (140 °C, 160 °C, 180 °C and 200 °C) for 21 h. The precipitates were naturally dried at room temperature for XRD and SEM measurements.

Fig. 3 shows the XRD results for the samples prepared at different reaction temperatures. As the sample was prepared at 140 °C, the tetragonal

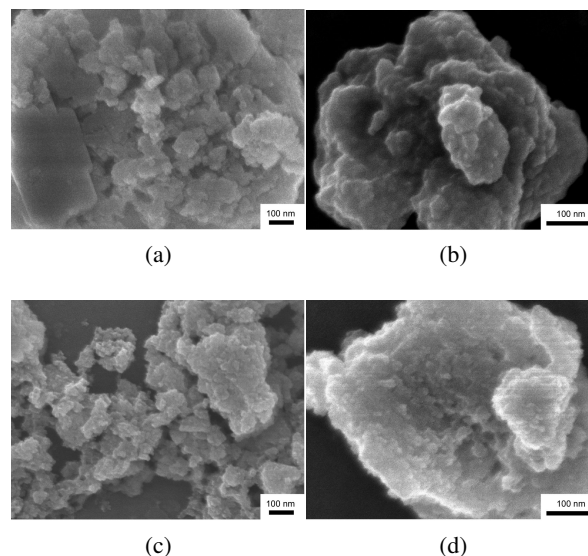


Fig. 4. SEM images of the samples prepared at different temperatures: (a) 140 °C, (b) 160 °C, (c) 180 °C and (d) 200 °C.

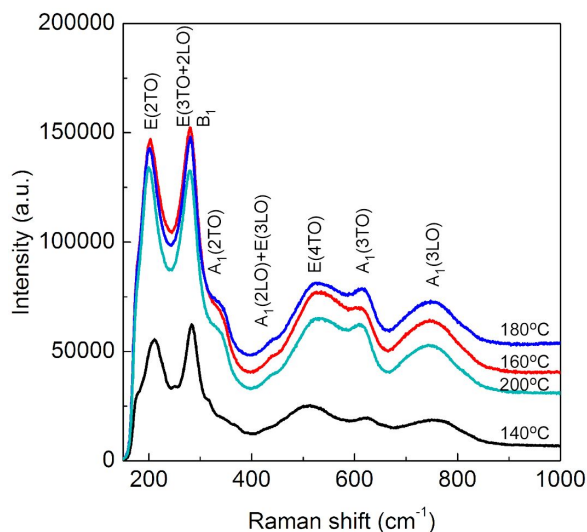


Fig. 5. Room temperature Raman spectra of $\text{PbZr}_{0.52}\text{Ti}_{0.48}\text{O}_3$ nanocrystals prepared at different temperatures.

$\text{PbZr}_{0.52}\text{Ti}_{0.48}\text{O}_3$ phase containing impurity phase was formed. With increasing the reaction temperature to 160 °C, the single-phase $\text{PbZr}_{0.52}\text{Ti}_{0.48}\text{O}_3$ grains were obtained. At higher reaction temperature (160 °C to 200 °C), all the products consisted of the single-phase $\text{PbZr}_{0.52}\text{Ti}_{0.48}\text{O}_3$ grains. Their morphologies are shown in Fig. 4. As the sample

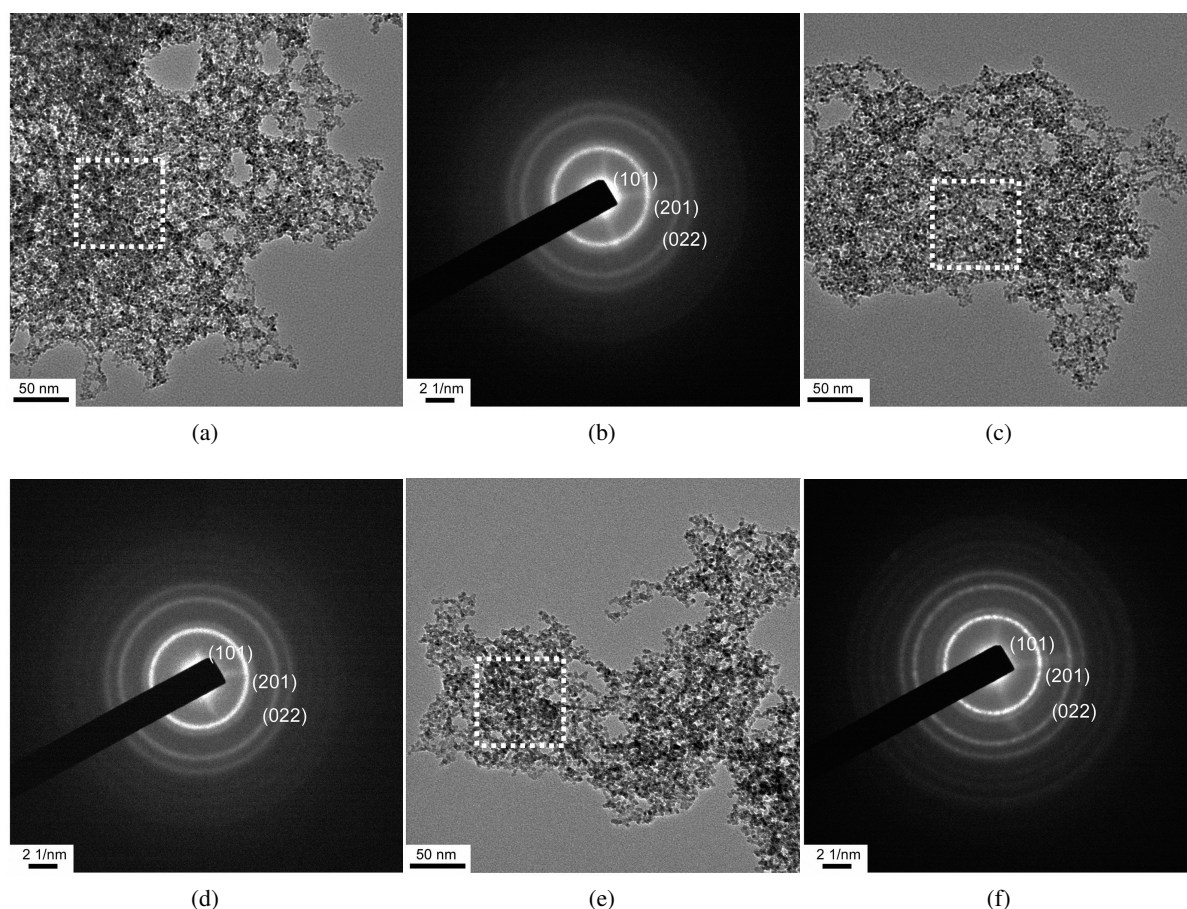


Fig. 6. TEM images and the corresponding selected area electron diffraction (SAED) patterns of $\text{PbZr}_{0.52}\text{Ti}_{0.48}\text{O}_3$ nanocrystals prepared at different temperatures: (a) and (b) 160 °C, (c) and (d) 180 °C, (e) and (f) 200 °C.

was prepared at 140 °C, it consisted of not uniform mud-like grains. The samples prepared at higher temperatures (160 °C to 200 °C), consisted of fine grains, and the grains were uniform. Fig. 5 depicts the Raman spectra of the samples prepared at different temperatures. All samples reveal the peaks at 182 cm^{-1} , 224 cm^{-1} , 293 cm^{-1} , 446 cm^{-1} , 511 cm^{-1} , 643 cm^{-1} and 741 cm^{-1} , which is in good agreement with the reported results [25]. It indicates that the obtained samples consist of tetragonal $\text{PbZr}_{0.52}\text{Ti}_{0.48}\text{O}_3$ phases.

The TEM images and the corresponding selected area electron diffraction (SAED) patterns of $\text{PbZr}_{0.52}\text{Ti}_{0.48}\text{O}_3$ nanocrystals prepared at different temperatures are shown in Fig. 6. The individual nanocrystals have a spherical shape

with a narrow size distribution. The grains sizes of $\text{PbZr}_{0.52}\text{Ti}_{0.48}\text{O}_3$ nanocrystals prepared at 160 °C, 180 °C and 200 °C were about 5 nm, 6 nm and 9 nm, respectively. With increasing the reaction temperature, the grain size of $\text{PbZr}_{0.52}\text{Ti}_{0.48}\text{O}_3$ nanocrystals increased, which indicates that the increasing of reaction temperature enhanced the growth rate of $\text{PbZr}_{0.52}\text{Ti}_{0.48}\text{O}_3$ nanocrystals. The SAED patterns of the $\text{PbZr}_{0.52}\text{Ti}_{0.48}\text{O}_3$ nanocrystals confirm the crystallinity and the perovskite structure of the samples. The high-resolution TEM image of $\text{PbZr}_{0.52}\text{Ti}_{0.48}\text{O}_3$ nanocrystal prepared by the hydrothermal reaction at 160 °C for 21 h is shown in Fig. 7. The lattice fringes are clearly observed in the $\text{PbZr}_{0.52}\text{Ti}_{0.48}\text{O}_3$ nanocrystal. The interplanar spacing was measured to be 0.2884 nm,

which corresponds to the (1 0 1) lattice spacing of tetragonal $\text{PbZr}_{0.52}\text{Ti}_{0.48}\text{O}_3$. The results indicate that single-crystalline $\text{PbZr}_{0.52}\text{Ti}_{0.48}\text{O}_3$ nanocrystals were formed.

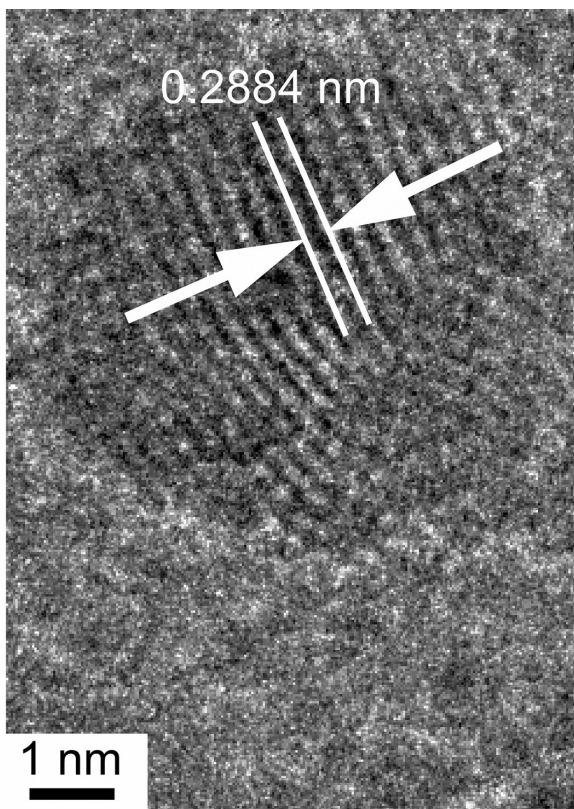


Fig. 7. HRTEM image of $\text{PbZr}_{0.52}\text{Ti}_{0.48}\text{O}_3$ nanocrystal prepared at 160 °C for 21 h.

3.3. Reaction time

In this investigation, NaOH concentration in $\text{PbZr}_{0.52}\text{Ti}_{0.48}\text{O}_3$ precursor was fixed at 1.0 mol/L, and the $\text{PbZr}_{0.52}\text{Ti}_{0.48}\text{O}_3$ precursors were heated at 160 °C for different reaction times (6 h, 12 h, 18 h and 21 h). Fig. 8 displays the XRD results for the samples prepared at 160 °C for different reaction times. As the sample was prepared for 6 h, no diffraction peaks were observed as shown in Fig. 8a, which indicated that this sample was amorphous. With increasing the reaction time to 12 h, 18 h and 21 h, the tetragonal $\text{PbZr}_{0.52}\text{Ti}_{0.48}\text{O}_3$ phase was observed. Fig. 9 shows the morphologies of the studied samples. For the sample prepared at 160 °C for only 6 h, the sample consists of tiny

grains. As the sample was prepared at 160 °C for 12 h, fine $\text{PbZr}_{0.52}\text{Ti}_{0.48}\text{O}_3$ nanocrystals are observed. With further increasing the reaction time to 18 h and 21 h, no obvious change in the appearance of $\text{PbZr}_{0.52}\text{Ti}_{0.48}\text{O}_3$ nanocrystals has been noticed.

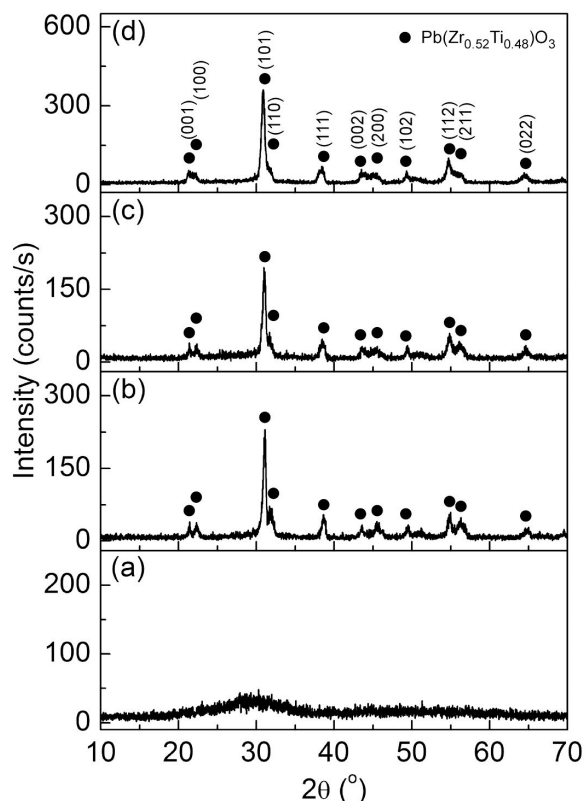
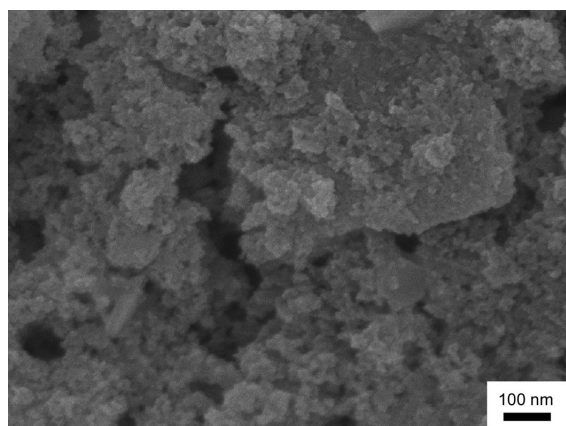


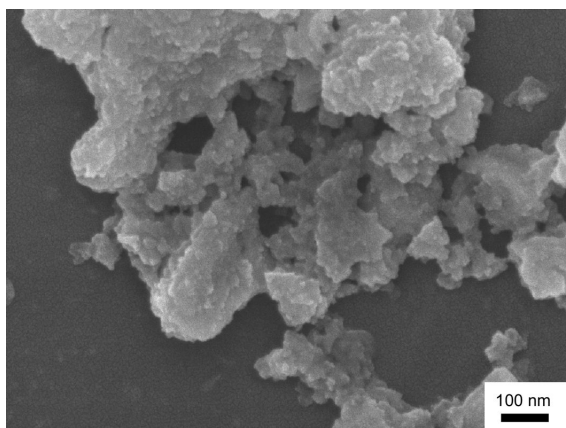
Fig. 8. XRD patterns of the samples prepared at 160 °C for different time periods: (a) 6 h, (b) 12 h, (c) 18 h and (d) 21 h.

Fig. 10 depicts the Raman spectra of the samples prepared at 160 °C for different reaction times. The sample prepared at 160 °C for 6 h shows no obvious peaks, which confirms that the sample is amorphous. The other samples prepared at 160 °C for 12 h, 18 h and 21 h, with the peaks at 182 cm^{-1} , 224 cm^{-1} , 293 cm^{-1} , 446 cm^{-1} , 511 cm^{-1} , 643 cm^{-1} and 741 cm^{-1} , are in good agreement with the reported results [25]. The Raman results give the evidence for the formation of well-crystalline tetragonal $\text{PbZr}_{0.52}\text{Ti}_{0.48}\text{O}_3$ nanocrystals.

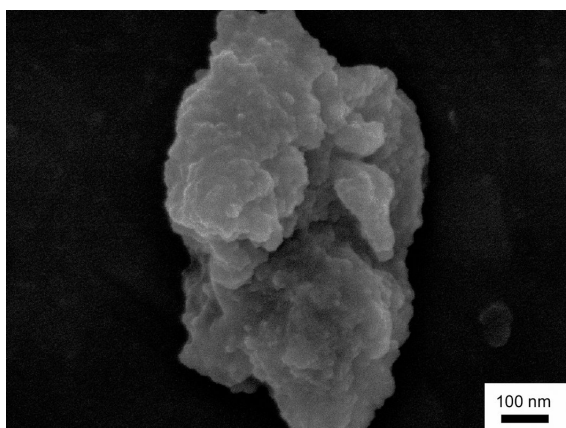
Fig. 11 depicts the TEM image and its corresponding SAED pattern of $\text{PbZr}_{0.52}\text{Ti}_{0.48}\text{O}_3$



(a)



(b)



(c)

Fig. 9. SEM images of the samples prepared at 160 °C for different time periods: (a) 6 h, (b) 12 h and (c) 18 h.

nanocrystals prepared at 160 °C for 12 h. The individual nanocrystals with a narrow size distribution are observed, and the grains size

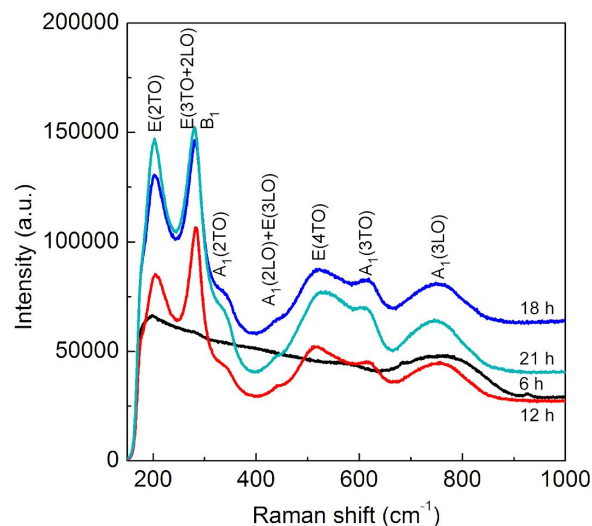
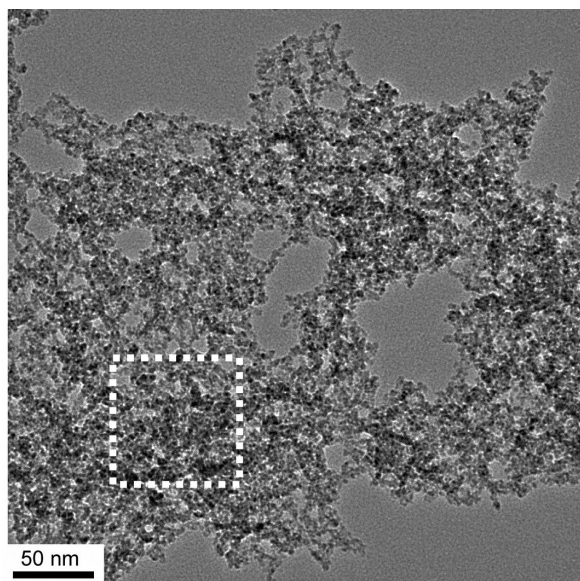


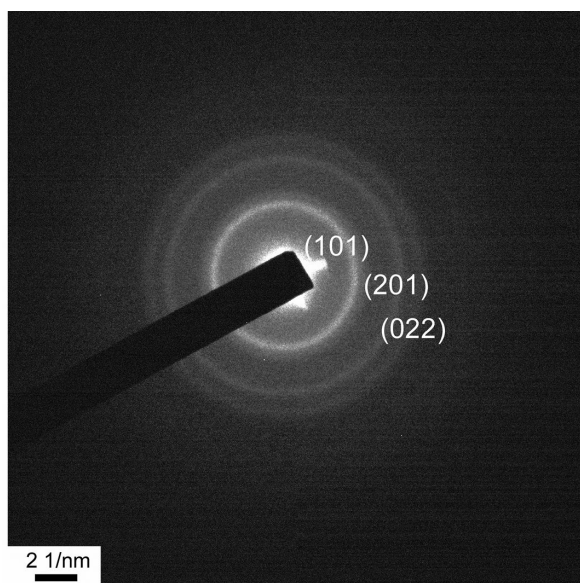
Fig. 10. Room temperature Raman spectra of the samples prepared at 160 °C for different time periods.

of $\text{PbZr}_{0.52}\text{Ti}_{0.48}\text{O}_3$ nanocrystals is about 4 nm. The SAED pattern of $\text{PbZr}_{0.52}\text{Ti}_{0.48}\text{O}_3$ nanocrystals confirms the crystallinity and the perovskite structure of the sample.

In this study, the effect of NaOH concentration, reaction temperature and time on the formation and growth of $\text{PbZr}_{0.52}\text{Ti}_{0.48}\text{O}_3$ nanocrystals was investigated. The NaOH concentration and reaction temperature play an important role in nucleation and growth of $\text{PbZr}_{0.52}\text{Ti}_{0.48}\text{O}_3$ nanocrystals. With increasing the NaOH concentration from 0.5 mol/L to 1.5 mol/L, the grain size of $\text{PbZr}_{0.52}\text{Ti}_{0.48}\text{O}_3$ nanocrystals decreased. As the sample was prepared at 140 °C, the $\text{PbZr}_{0.52}\text{Ti}_{0.48}\text{O}_3$ nanocrystals with impurity phase were formed. At high reaction temperature (160 °C to 200 °C), single-phase $\text{PbZr}_{0.52}\text{Ti}_{0.48}\text{O}_3$ nanocrystals were obtained. With increasing the reaction temperature, the grain size of $\text{PbZr}_{0.52}\text{Ti}_{0.48}\text{O}_3$ nanocrystals increased. When the precursors were heated at 160 °C from 6 h to 21 h, the evolution from amorphous to crystalline phase in correlation with the reaction time was observed. As the precursor was heated at 160 °C, the following steps were involved: (1) the tiny sized $\text{PbZr}_{0.52}\text{Ti}_{0.48}\text{O}_3$ nuclei were formed; (2) the nuclei grew to form $\text{PbZr}_{0.52}\text{Ti}_{0.48}\text{O}_3$ nanocrystals, and the nucleation rate declined as the reaction



(a)



(b)

Fig. 11. (a) TEM image of $\text{PbZr}_{0.52}\text{Ti}_{0.48}\text{O}_3$ nanocrystals prepared at 160 °C for 12 h, and (b) its corresponding selected area electron diffraction (SAED) pattern.

proceeded. The nanocrystal growth in solution has been widely studied, and two theories are generally accepted as the path of nanocrystal growth [26, 27]. According to the classic theory of crystal growth, nanoparticles are formed when individual atoms stick to high-energy crystal faces. The second

theory postulates that small nanoparticles are initially formed, approach one another, align their crystal faces, and finally attach to create larger nanoparticles, which is called oriented attachment. According to the SEM and TEM results, the nucleation and growth of $\text{PbZr}_{0.52}\text{Ti}_{0.48}\text{O}_3$ nanocrystals are consistent with the classical theory of crystal growth.

4. Conclusions

The $\text{PbZr}_{0.52}\text{Ti}_{0.48}\text{O}_3$ nanocrystals were synthesized by the hydrothermal method. As the precursors were heated at 200 °C for 21 h with NaOH concentration of 0.5 mol/L, tetragonal $\text{PbZr}_{0.52}\text{Ti}_{0.48}\text{O}_3$ nanocrystals were obtained, and the grain size was larger than 20 nm. With increasing the NaOH concentration from 0.5 mol/L to 1.5 mol/L, the grain size of $\text{PbZr}_{0.52}\text{Ti}_{0.48}\text{O}_3$ nanocrystals decreased. When the precursors were heated at different temperatures for 21 h with NaOH concentration of 1.0 mol/L, single-phase $\text{PbZr}_{0.52}\text{Ti}_{0.48}\text{O}_3$ nanocrystals were formed at 160 °C to 200 °C. With increasing the reaction temperature, the grains size of $\text{PbZr}_{0.52}\text{Ti}_{0.48}\text{O}_3$ nanocrystals increased from 5 nm to 9 nm. When the precursors were heated at 160 °C for different reaction times (from 6 h to 21 h), the evolution from amorphous to crystalline $\text{PbZr}_{0.52}\text{Ti}_{0.48}\text{O}_3$ nanocrystals in correlation with the reaction time was observed. By controlling the NaOH concentration, reaction temperature and time, single crystalline $\text{PbZr}_{0.52}\text{Ti}_{0.48}\text{O}_3$ nanocrystals were synthesized with narrow size distribution (from 5 nm to 9 nm), which have potential application in preparing $\text{PbZr}_{0.52}\text{Ti}_{0.48}\text{O}_3$ thin films on flexible substrates.

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References

- [1] SCOTT J. F., PAZ DE ARAUJO C. A., *Science*, 246 (1989), 1400.
- [2] PAZ DE ARAUJO C.A., CUCHIARO J.D., McMILLAN L.D., SCOTT M.C., SCOTT J.F., *Nature*, 374 (1995), 627.

- [3] WEBBER K.G., VOEGLER M., KHANSUR N.H., KAESWURM B., DANIELS J.E., SCHADER F.H., *Smart Mater. Struct.*, 26 (2017), 063001.
- [4] PARK K., SON J.H., HWANG G.T., JEONG C.K., RYU J., KOO M., CHOI J., LEE S.H., BYUN M., WANG Z.L., LEE K.J., *Adv. Mater.*, 26 (2014), 2514.
- [5] NUFFER J., LUPASCU D.C., RODEL J., *Acta. Mater.*, 48 (2000), 3783.
- [6] KANNO I., KOTERA H., WASA K., *Sens. Actuat. A*, 107 (2003), 68.
- [7] GLASS C., AHMED W., VAN RUITENBEEK J., *Mater. Lett.*, 125 (2014), 71.
- [8] KOMANDIN G.A., PORODINKOV O.E., SPEKTOR I.E., VOLKOV A.A., VOROTILOV K.A., SEREGIN D.S., SIGOV A.S., *Phys. Solid State*, 60 (2018), 1226.
- [9] DUFAY T., GUIFFARD B., SEVENO R., TOMAS J., *Energy Technol.*, 6 (2018), 917.
- [10] WAN Q., GU Q., XING J., CHEN J., *Mater. Lett.*, 92 (2013), 52.
- [11] RATH M., VARADARAJAN E., NATARAJAN V., RAO R., *Ceram. Int.*, 44 (2018), 8749.
- [12] WANG Z.D., LAI Z.Q., HU Z.G., *J. Alloy. Compd.*, 583 (2014), 452.
- [13] ZHAO J.S., PARK D.Y., SEO M. J., HWANG C.S., HAN Y.K., YANG C.H., OH K.Y., *J. Electrochem. Soc.*, 151 (2004), c283.
- [14] GUO D., MAO W., QIN Y., HUANG Z., WANG C., SHEN Q., ZHANG L., *J. Mater. Sci.-Mater. El.*, 23 (2012), 940.
- [15] GUO D., MAO W., QIN Y., HUANG Z., WANG C., SHEN Q., ZHANG L., *Bull. Mater. Sci.*, 35 (2012), 353.
- [16] FU C., MAO W., QIN Y., HUANG Z., GUO D., *J. Mater. Sci.-Mater. El.*, 22 (2011), 911.
- [17] GUO D., SATO K., HIBINO S., TAKEUCHI T., BESSHO H., KATO K., *J. Mater. Sci.*, 49 (2014), 4722.
- [18] ZHANG Z., LI X., HUANG Z., ZHANG L., HAN J., ZHOU X., GUO D., JU Y., *J. Mater. Sci.-Mater. El.*, 29 (2018), 7453.
- [19] DANG F., KATO K., IMAI H., WADA S., HANEDA H., KUWABARA M., *Cryst. Growth Des.*, 11 (2011), 4129.
- [20] LI X., HUANG Z., ZHANG L., GUO D., *Electron. Mater. Lett.*, 14 (2018), 610.
- [21] KUTTY T., BALACHANDRAN R., *Mater. Res. Bull.*, 19 (1984), 1479.
- [22] DENG Y., LIU L., CHENG Y., NAN C., ZHAO S., *Mater. Lett.*, 57 (2003), 1675.
- [23] HUANG H., CAO G. Z., SHEN I. Y., *Sens. Actuat. A*, 214 (2014), 111.
- [24] TAKADA Y., MIMURA K., KATO K., *Jpn. J. Ceram. Soc.*, 126 (2018), 326.
- [25] MENG Q., ZHU K., PANG X., QIU J., SHAO B., JI H., *Adv. Powder Technol.*, 24 (2013), 212.
- [26] LI D., NIELSEN M.H., LEE J., FRANDSEN C., BANFIELD J.F., DE YOREO J., *Science*, 336 (2012), 1014.
- [27] LIAO H., CUI L., WHITELAM S., ZHENG H., *Science*, 336 (2012), 1011.

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