Synthesis of PbTiO₃ nanoplates by two-step hydrothermal method with pH-adjusting agent of ammonia solution

Guangyuan Yang, Zheming Li, Sanwen Peng, Jianglai Yue, Zhixiong Huang and Dongyun Guo

ABSTRACT
PbTiO₃ nanoparticles were synthesized by a two-step hydrothermal method, and ammonia solution was chosen as a pH-adjusting agent. The effect of ammonia concentration in the second-step precursors, Pb-Ti feedstock concentration, reaction temperature, and time on crystallization and morphologies of PbTiO₃ nanocrystals was investigated. The typical single-crystal PbTiO₃ nanoparticles with stair-like edge were formed, as the nominal ammonia concentration in the first-step precursors was 8.8 mol/L, the nominal ammonia concentration in the second-step precursors was 4.4 mol/L, the nominal Pb-Ti feedstock concentration was 0.05 mol/L, and they were synthesized at 200°C for 20 h. The thickness of the PbTiO₃ nanoparticles was about 45 nm, and the lateral size was about 400 nm. The ammonia solution played an important role in the formation of PbTiO₃ nanoparticles, and the growth mechanism of PbTiO₃ nanoparticles synthesized by the two-step hydrothermal method in ammonia solution was discussed.

1. Introduction

Lead titanate (PbTiO₃) is one of the typical perovskite oxides in ferroelectric families with a high Curie temperature of 490°C, which has been widely applied in electronic devices [1–3]. With the increasing demand for higher integration and miniaturization of electronic devices, PbTiO₃ nanocrystals with different morphologies have been synthesized by various techniques, such as solid-state reaction, co-precipitation, sol-gel and hydrothermal methods, etc [4–7]. Among these techniques, the hydrothermal method has been widely applied in synthesis of PbTiO₃ nanocrystals due to its low cost and low-temperature characteristics [7–15]. In the traditional hydrothermal process, NaOH or KOH was usually used as a pH-adjusting agent, which inevitably introduced the undesirable alkali impurities to PbTiO₃ nanocrystals, and the alkali ions caused the hardening of Pb-based perovskite oxides. As pointed by Cho et al [12], the choice of pH-adjusting agent was the most important in the hydrothermal process, and the choices of pH-adjusting agent should be made on the basis that undesirable impurities could not be incorporated in the crystal structure and they could have a favorable effect on the crystal growth. They synthesized PbTiO₃ particles by the hydrothermal method with an alkali-free pH-adjusting agent of tetramethylammonium hydroxide (TMAH) to avoid the contamination of alkalis, and the pH-adjusting agent of TMAH was a critical factor in forming PbTiO₃ particles.

Takada et al [13] also reported that Pb(Zr,Ti)O₃ cubes were synthesized by the hydrothermal method with TMAH. The Pb(Zr,Ti)O₃ cubes with single perovskite phase were synthesized at 180°C, and the size of Pb(Zr,Ti)O₃ cubes was estimated to about 1 μm. The piezoelectric properties were confirmed for single Pb(Zr,Ti)O₃ cubes using the piezoresponse force microscopy mode of a scanning probe microscope. However, TMAH is quite expensive with strong corrosive and toxic properties. It is necessary to find the eco-friendly alkali-free pH adjusting agent with low cost. In our previous study, the ammonia solution was used as the alkali-free pH-adjusting agent to take the place of TMAH, and the dendritic PbTiO₃ nanorods were formed by the hydrothermal method [14,15]. Due to the weak alkalinity of ammonia solution, only irregular dendritic PbTiO₃ nanorods were synthesized. To synthesize the PbTiO₃ nanocrystals with well crystallization, a two-step hydrothermal method was employed to synthesize PbTiO₃ nanocrystals [16].

In this study, the PbTiO₃ nanocrystals were synthesized by the two-step hydrothermal method using the ammonia solution as the pH-adjusting agent, and the effect of ammonia concentration, Pb-Ti feedstock concentration, synthesis temperature, and time on crystallization and morphologies of PbTiO₃ nanocrystals was systematically investigated. The growth mechanism of PbTiO₃ nanocrystals in the ammonia solution was discussed.
2. Experimental details

The reagents were of analytical-grade purity and were used without further purification in this study. PbTiO₃ nanocrystals were synthesized from Pb(CH₃COO)₂·3H₂O (Macklin 99%), bis(ammonium lactate) titanium dihydroxide (C₆H₁₆N₂O₆Ti, TALH, Macklin 50 wt%) by the two-step hydrothermal method, and ammonia solution was used as the pH-adjusting agent. The desired amounts of Pb(CH₃COO)₂·3H₂O and ammonia were dissolved in deionized water with stirring to form transparent Pb-Ti solutions. Then, ammonia solution was slowly added in the transparent Pb-Ti solutions to form the first-step precursors (30 ml) with continuous stirring. In the first-step precursors, the nominal ammonia concentration was 8.8 mol/L, and the nominal concentration of Pb-Ti feedstock varied from 0.025 to 0.1 mol/L. When the suspended gels were formed, they were centrifuged and washed with deionized water. Then, the precipitates were dispersed in the deionized water to form the suspended second-step precursors (30 ml) with different nominal ammonia concentrations (0–13.2 mol/L). The 30 ml second-step precursors were added to Teflon-lined autoclaves of 50 ml capacity, and they were sealed tightly. The autoclaves were heated at different synthesis temperatures (140–260°C) for different time (1–72 h), and then naturally cooled to room temperature with continuous stirring. The precipitates were centrifuged and washed with deionized water and ethanol in sequence.

These samples were analyzed by an X-ray diffractometer (XRD, D/Max-RB) with CuKα radiation (40 kV, 30 mA). The scanning rate was 2°/min with a scanning step of 0.02°. The morphologies of these samples were characterized by a field emission scanning electron microscope (FESEM, JSM-7500 F) and a high-resolution transmission electron microscopy (HR-TEM, JEM-2100 F).

3. Results and discussion

3.1. Effect of ammonia concentration in the second-step precursors

In this hydrothermal process, ammonia solution is used as the pH-adjusting agent, which has an influence on crystallization and morphologies of PbTiO₃ nanocrystals. The nominal Pb-Ti feedstock concentration in the first-step precursors was 0.05 mol/L. In the second-step precursors, the nominal ammonia concentration varied from 0, 4.4, 8.8 to 13.2 mol/L, and the corresponding pH values were 10.98, 12.06, 12.62, and 13.16. The hydrothermal synthesis was reacted at 200°C for 20 h.

Figure 1 shows the XRD results of the samples synthesized with different nominal ammonia concentrations in the second-step precursors. These XRD patterns were indexed according to JCPDS No. 78-0298 (tetragonal PbTiO₃ phase with space group P4mm). All samples showed the clear and sharp diffraction peaks, which were well consistent with the diffraction peaks of tetragonal PbTiO₃ phase. These results indicated that the single-phase PbTiO₃ samples were obtained. As the nominal ammonia concentration increased from 0 to 4.4 mol/L, the intensity of diffraction peaks obviously increased. With the continuous increase of nominal ammonia concentration from 4.4 to 13.2 mol/L, the diffraction peak intensity of PbTiO₃ samples almost did not change.

Figure 2 displays the morphologies of PbTiO₃ samples synthesized with different nominal ammonia concentrations in the second-step precursors. When the PbTiO₃ sample was synthesized without ammonia, the irregular nanoparticles were observed. As the PbTiO₃ sample was synthesized with nominal ammonia concentration of 4.4 mol/L, it mainly consisted of nanoplats with about 45 nm thickness. One side of the PbTiO₃ nanoparticles was relatively smooth, and the other side of the nanoplats was rough. From the rough surface, it was observed that it was composed of nanoparticles. With increasing the nominal ammonia concentration to 8.8 and 13.2 mol/L, both surfaces of the PbTiO₃ nanoplats became rough, and the nanoparticles on the surface of nanoplats obviously grew up. According to the SEM images (Figure 2), only irregular PbTiO₃ nanoparticles were obtained without ammonia solution in the second-step precursor, and the diffraction peak intensity was weak. When there was ammonia solution in the second-step precursors, the large-size PbTiO₃ nanoparticles were synthesized, and the diffraction peak intensity was strong. These results were consistent with the XRD results (Figure 1). It indicated that the ammonia solution in the second-step precursors played an important role to form the
PbTiO₃ nanobelts. Based on these results, the nominal ammonia concentration in the second-step precursors was kept at 4.4 mol/L for the next research.

3.2. Effect of Pb-Ti feedstock concentration

In this hydrothermal process, the Pb-Ti feedstock concentration in the first-step precursors varied from 0.025, 0.05, 0.075 to 0.1 mol/L. The nominal ammonia concentration in the second-step precursors was 4.4 mol/L, the hydrothermal synthesis was reacted at 200°C for 20 h.

In Figure 3, the XRD results of the samples synthesized with different Pb-Ti feedstock concentrations in the first-step precursors are shown. The single-phase PbTiO₃ samples with tetragonal structure were obtained. With the increase of Pb-Ti feedstock concentration from 0.025 to 0.1 mol/L, there was no obvious change of diffraction peak intensity of PbTiO₃ samples.

The morphologies of PbTiO₃ samples synthesized with different Pb-Ti feedstock concentrations in the first-step precursors can be observed in Figure 4. When the PbTiO₃ sample was synthesized with low Pb-Ti feedstock concentration (0.025 mol/L), it mainly consisted of nanobelts with about 30 nm thickness, and some nanobelts had holes. With increasing the Pb-Ti feedstock concentration to 0.05 mol/L, the PbTiO₃ nanobelts obviously became thicker, and the complete nanobelts were obtained. With the continuous increase of Pb-Ti feedstock concentration to 0.075 and 0.1 mol/L, the surfaces of PbTiO₃ nanobelts became rough, and the nanoparticles on the surface of nanobelts obviously grew up. Based on these results, the Pb-Ti feedstock concentration was kept at 0.05 mol/L for the next research.

3.3. Effect of synthesis temperature

In the hydrothermal process, the synthesis temperature plays a major role in formation of tetragonal perovskite PbTiO₃ structure. In this study, the Pb-Ti feedstock concentration was 0.05 mol/L in the first-step precursors, the nominal ammonia concentration in the second-step precursors was 4.4 mol/L, and the hydrothermal synthesis was reacted at different temperatures (140, 160, 180, 200, 220, 240 and 260°C) for 20 h.

Figure 5 shows the typical XRD results of the samples synthesized at different synthesis temperatures. As the sample was synthesized at 140°C, the intensity of the
synthesis of PbTiO$_3$ consisted of nanocrystals. When nanocrystals were synthesized in different concentrations, the diffraction peaks were weak, and there were two kinds of PbTiO$_3$ phases. One phase was indexed to tetragonal PbTiO$_3$ phase with space group P4mm (JCPDS No. 78–0298), and another phase was indexed to tetragonal PbTiO$_3$ phase with space group P4/4 (JCPDS No. 48–0105). At higher synthesis temperature (160–260°C), the single-phase PbTiO$_3$ (JCPDS No. 78–0298) was obtained. With increasing the synthesis temperature, the diffraction peak intensity of PbTiO$_3$ phase obviously increased.

Figure 6 displays the typical SEM images of PbTiO$_3$ nanocrystals synthesized at different temperatures. When the sample was synthesized at 140°C, the sample consisted of nanoparticles, fibers and nanoplates. At synthesis temperature of 160°C, the PbTiO$_3$ sample mainly consisted of nanoplates. With increasing the synthesis temperature from 160 to 260°C, the size of PbTiO$_3$ nanoplates gradually increased, and the grains on the surface of PbTiO$_3$ nanoplates also grew up.

3.4. Effect of synthesis time

In the hydrothermal process, the synthesis time is also important in the phase transformations from amorphous precipitate gels to perovskite PbTiO$_3$ phase. In this study, the Pb-Ti feedstock concentration was 0.05 mol/L in the first-step precursors, the nominal ammonia concentration in the second-step precursors was 4.4 mol/L, and the hydrothermal synthesis was reacted at 200°C for different time (1, 2, 4, 8, 14, 20, 48 and 72 h).

The typical XRD results of the samples synthesized at 200°C for different time are shown in Figure 7. As the sample was synthesized at 200°C for 1 h, only several peaks with very weak intensity were observed. They were identified as TiO$_2$, Pb$_3$O$_2$(OH)$_2$, and Pb$_2$Ti$_2$O$_6$ phases, and no PbTiO$_3$ phase was detectable. The similar results were also reported by Bao et al [17]. When the sample was synthesized at 200°C for 2 h, the intensity of these peaks slightly increased, and the PbTiO$_3$ phase with weak diffraction peaks was detected. The phase transformation from amorphous precipitate gels to perovskite PbTiO$_3$ phase was completed at a synthesis time of 4 h. With increasing the synthesis time from 4 to 72 h, there was no obvious change of the diffraction peak intensity of PbTiO$_3$ samples.

The typical morphologies of the PbTiO$_3$ samples synthesized at 200°C for different time (4–72 h) can be observed in Figure 8. All PbTiO$_3$ samples consisted of nanoplates. With increasing the synthesis time from 4 to 72 h, more and more nanoparticles on the
nanoplate surface gradually grew up. At synthesis time of 72 h, it was found that these nanoparticles on the nanoplate surface grew up to form nanoplates.

To identify the crystallization of PbTiO₃ nanoplates, they were characterized by the TEM technique. Figure 9 presents the typical TEM images and selected area electron diffraction (SAED) patterns of the PbTiO₃ nanoplates synthesized at 200°C for different time. When the PbTiO₃ sample was synthesized at 200°C for 4 h, the nanoplates with large-scale area were obtained as shown in Figure 9(a). The nanoplates had stair-like edges, which was reported by Takada et al [18]. The black stripe-like nanocrystals corresponded to the side of nanoplates, which indicated that the thickness of the nanoplates was about 40 nm. According to the high-resolution TEM image (the inset of Figure 9(a)), the edge of nanoplates was rough. With increasing the synthesis time, the nanoplate thickness slightly increased, and the edges of nanoplates became smooth. The high-resolution TEM images (the insets of Figures 9(a, c, e, g) and SAED patterns (Figures 9(b, d, f, h) confirmed that the single-crystal PbTiO₃ nanoplates were obtained at 200°C for 4–72 h, and their normal axis corresponded to the c-axis.

3.5. Growth mechanism of PbTiO₃ nanoplates synthesized by two-step hydrothermal method

In this study, there are two steps to synthesize the PbTiO₃ nanoplates. In the first step, the suspended gels were formed in the first-step precursors as chemical reaction formulas (1) and (2). After the precipitates were dispersed in the ammonia aqueous solution to form the second-step precursors, nucleation and growth were two important aspects of PbTiO₃ nanocrystal growth in the hydrothermal precursors. At the early stage of hydrothermal reaction, the intermediate nuclei of Pb₃Ti₂O₆ pyrochlore phase (chemical reaction formula (3)) were formed as shown in Figure 7(a). Then, the phase transformation of intermediate pyrochlore nuclei to perovskite nuclei immediately occurred as chemical reaction formula (4) according to Figure 7(b). Finally, the intermediate phase was completely transformed into perovskite PbTiO₃ phase as shown in Figure 7(c).

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Pb^{2+} + 2OH^- \rightarrow Pb(OH)_2 \]  
(1)
As the PbTiO$_3$ nanocrystals were synthesized without ammonia solution in the second-step precursor, only irregular PbTiO$_3$ nanoparticles were observed as shown in Figure 2(a), which indicated that ammonia solution played an important role to form PbTiO$_3$ nanoplates. Xu et al. [11] synthesized perovskite PbTiO$_3$ nanoplates by the hydrothermal method. When NaNO$_3$ was used as an additive in the hydrothermal system for synthesis of PbTiO$_3$ crystals, Na$^+$ ions were effectively bound to the (001) surfaces by the enhanced covalent bonding. As a consequence, growth of PbTiO$_3$ species along the [001] direction was suppressed by the fastened Na$^+$ ions. The preferential deposition of PbTiO$_3$ species on the (100) and (010) surfaces resulted in single-crystal PbTiO$_3$ nanoplates with dominant (001) facets. In the current study, NH$_4^+$ ions had the same effect as Na$^+$ ions for formation of PbTiO$_3$ nanoplates in the hydrothermal process.
Based the above results, a mechanism for formation of PbTiO$_3$ nanocrystals was believed to involve dissolution and recrystallization of intermediate phase into nanoplates.

However, in this study, according to the rough surface of PbTiO$_3$ nanoplates shown in the SEM images, the single-crystal nanoplate was composed of nanoparticles. How did these nanoparticles combine with each other to form the single-crystal PbTiO$_3$ nanoplate? Banfield et al. [19,20] demonstrated an important growth mechanism of oriented attachment. Oriented attachment involved spontaneous self-organization of adjacent nanoparticles so that they shared a common crystallographic orientation, followed by joining of these nanoparticles at a planar interface to reduce overall energy by removing surface energy. This growth mechanism is relevant in cases where nanoparticles are free to move in solution. During the growth of PbTiO$_3$ nanoplates in the hydrothermal process, the evidences of oriented attachment growth were also found. The single-crystal PbTiO$_3$ nanoplate sample was synthesized at 200°C for 8 h, as the nominal ammonia concentration in the second-step precursor was 4.4 mol/L, and the Pb-Ti feedstock concentration was 0.05 mol/L. Figure 10 displays the TEM images of the PbTiO$_3$ nanoplate sample. In Figure 10(a), the typical stair-like PbTiO$_3$ nanoplate was observed. A high-resolution TEM image of two attached nanoplates with very similar orientations is shown in Figure 10(b) corresponding to area b in Figure 10(a). Lattice fringe details indicated that the dislocation at the imperfect oriented attachment interface was formed. Figures 10(c) and (d) show the high-resolution TEM images of nanoparticles attached on PbTiO$_3$ nanoplate corresponding to areas c and d in Figure 10(a), respectively. Lattice fringe details indicated that the perfect oriented attachment was formed between the nanoparticles and nanoplate.

In the hydrothermal process, when the nominal ammonia concentration, Pb-Ti feedstock concentration, synthesis temperature and time increased, the supersaturation of PbTiO$_3$ nuclei increased. As the supersaturation of PbTiO$_3$ nuclei in the second-step precursors was low, the PbTiO$_3$ nuclei grew up due to the oriented attachment along the [100] and [010] directions. At the same time, the smooth surface was formed due to the Ostwald ripening. When the supersaturation of PbTiO$_3$ nuclei in the second-step precursors increased, the PbTiO$_3$ nuclei tended to be adsorbed and grow up on the surface of PbTiO$_3$ nanoplates due to oriented attachment.

Based on the above analysis, a schematic illustration of growth mechanism and formation process of single-crystal perovskite PbTiO$_3$ nanoplates under hydrothermal conditions using ammonia solution as the pH-adjusting agent is proposed as Figure 11.

![Figure 10](image-url)

**Figure 10.** TEM image (a) of PbTiO$_3$ nanoplates synthesized at 200°C for 8 h, high-resolution TEM images (b, c and d) corresponding to the selected areas (b, c and d) in (a), respectively.
4. Conclusions

The PbTiO$_3$ nanoplates were synthesized by the two-step hydrothermal method, and the ammonia solution was very important for formation of PbTiO$_3$ nanoplates. The typical single-crystal PbTiO$_3$ nanoplates with stair-like edges were formed, as the nominal ammonia concentration in the first-step precursors was 8.8 mol/L, the nominal ammonia concentration in the second-step precursors was 4.4 mol/L, the nominal Pb-Ti feedstock concentration was 0.05 mol/L, and they were reacted at 200°C for 20 h. In the two-step hydrothermal process, the intermediate nuclei of Pb$_2$Ti$_4$O$_9$ pyrochlore phase were formed at the early stage of hydrothermal reaction, then the phase transformation of intermediate pyrochlore nuclei to perovskite nuclei immediately occurred, finally, the intermediate phase was completely transformed into perovskite PbTiO$_3$ phase. The large-scale stair-like PbTiO$_3$ nanoplates were formed mainly due to oriented attachment.

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Disclosure statement

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