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Synthesis of $PbTiO_3$ nanowires via a simple hydrothermal method

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$PbTiO_3$ nanowires with diameters of 20-30 nm and lengths of about 2-3 um have been synthesized by a simple surfactant-free hydrothermal method. The resulting products were characterized by X-ray powder diffraction (XRD), energy dispersive X-ray spectroscopy (EDX), and scanning electron microscopy (SEM). It was found that KOH concentration played an important role in the formation of large quantities of $PbTiO_3$ nanowires and a possible mechanism for the formation of nanowires is discussed.

Key words: Hydrothermal, $PbTiO_3$ nanowires.

Introduction

Nanoscale one-dimensional (1D) materials, such as nanotubes, nanorods, nanowires, and nanobelts, have become the focus of intensive research owing to their wide range of potential applications in nanodevices [1-4]. Differing from those of their bulk counterparts, the magnetic, optical and electric properties of these nanosturctured materials are very special due to their reduced size and large surface-to-volume ratios. Lead titanate ($PbTiO_3$) is an important ferroelectric and piezoelectric material, which exhibits a perovskite structure and a Curie temperature of 490 °C [5].

A sol-gel template and molten salt methods have been reported for the synthesis of $PbTiO_3$ (abbreviated to PTO) nanowires, nanotubes, and nanorods [6-12]. A hydrothermal method is a promising route to prepare nanomaterials at low temperature. Recently, PTO nanowires have been fabricated by a surfactant-free hydrothermal method [13], but the quantity of PTO nanowires also needs to be improved. A simple method to synthesize large scale one-dimensional materials at a low temperature has been a goal for many researchers in this field.

In this paper, we report a large scale synthesis of PTO nanowires by a simple surfactant-free hydrothermal method.

Experimental

All the chemicals were of analytical grade purity. Based on the nominal composition of $PbTiO_3$, a stoichiometric amount of $Ti(SO_4)_2$ was dissolved in a dilute HNO_3 solution to form a Ti^{4+} solution. Subsequently, the $Ti(CO_3)_2$ suspension was prepared by introducing the mixed solution into a K_2CO_3 solution under stirring. Next, equivalent amounts of $Pb(NO_3)_2$ solution was dropped into the suspension under constant magnetic stirring. Then, the suspension was filtered with distilled water to remove NO_3^-, CO_3^{2-}, and K^+ ions. Then, the precipitate obtained was poured into a stainless-steel autoclave with a KOH solution for the hydrothermal treatment. The autoclave was sealed, heated up to 200 °C and held for 24 h, and then cooled to room temperature naturally. The products were filtered, washed with distilled water and absolute ethanol several times, and then dried at 70 °C for 4 h for characterization.

X-ray diffraction was performed on a Rigaku X-ray diffractometer with high-intensity CuKα radiation. Scanning electron microscope (SEM) images were obtained from a SIRION field-emission scanning electron microscope with EDX equipment.

Results and Discussion

Fig. 1 shows XRD patterns of the samples prepared by the hydrothermal process at 200 °C for 24 h using KOH concentrations of 4, 6, 8, and 10M. All XRD

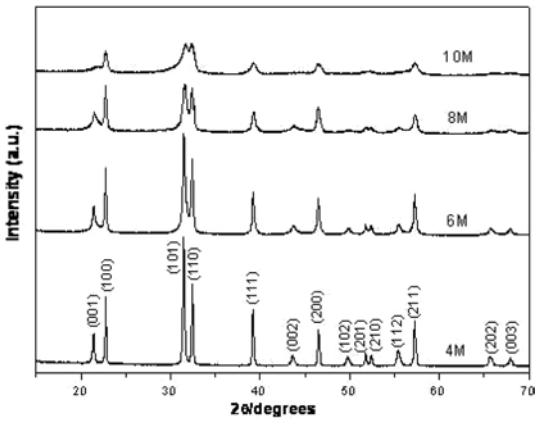

Fig. 1. XRD patterns of the as-prepared PTO samples synthesized by the hydrothermal process at 200 °C for 24 h using KOH concentrations of 4, 6, 8, and 10M, respectively.

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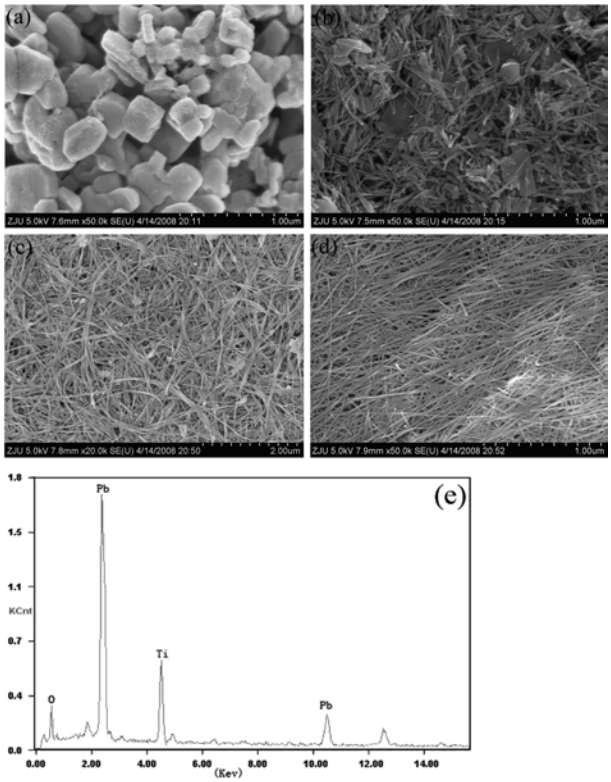

Fig. 2. SEM images of the as-prepared PTO samples synthesized by the hydrothermal process at 200 °C for 24 h with KOH concentrations of (a) 4M, (b) 6M, (c) 8M, and (d) 10M. (e) The EDX spectroscopy pattern for the as-prepared PTO nanowires.

patterns can be indexed to a pure tetragonal structure of PTO, consistent with the reported data (JCPDS:77-2002). However, when the KOH concentration increases from 4M to 10M, the intensities of diffraction peaks become weaker and broader. Furthermore, the (110) diffraction peaks becomes stronger compared with the (101) peaks. This implies that the KOH concentration has a great effect on the crystallization and evolution of PTO particles and may favor the growth orientation of the particles.

Fig. 2 displays SEM images of the PTO samples prepared by the hydrothermal process at 200 °C for 24 h with KOH concentrations of 4M, 6M, 8M, and 10M. It is worth pointing out that the morphology of the as-prepared PTO particles varied obviously with the KOH concentration. The PTO sample prepared with a 4M KOH concentration exhibits irregular particles with an average size of ca. 200 nm [Fig. 2(a)]. Interestingly, a small quantity of nanorods with diameters of 30-40 nm and lengths of about 200-400 nm began to appear on increasing the KOH concentration to 6M [Fig. 2(b)], and PTO nanowires instead of PTO nanorods was formed at 8M KOH [Fig. 2(c)]. As shown in Fig. 2(d), as the KOH concentration was further increased to 10M, PTO particles consist of uniform nanowires with diameters of 20-30 nm and lengths of about 2-3 um. The ratio of Pb, Ti and O, determined by EDS (Fig. 2e) taken on the nanowires obtained, is about 1:1:3, further demonstrating that

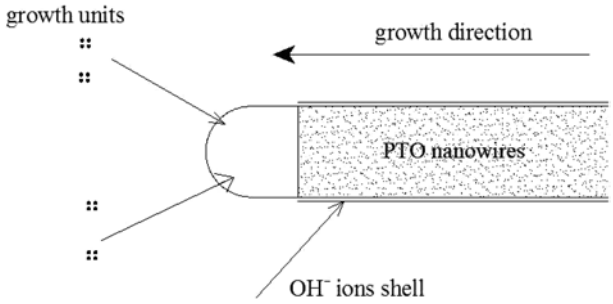

Fig. 3. The proposed model of the growth of PTO nanowires.

PTO nanowires have been synthesized successfully. Obviously, in the present study, the KOH concentration played a key role in promoting the growth orientation of the PTO nanowires.

The growth of the nanorods should be essentially attributed to the high concentration of OH^- ions and their adsorption on PTO particles. It is believed that KOH behaves not only as a mineralizer but also as a surfactant in the hydrothermal process [14]. The OH^- ions as a surfactant form "shells" surrounding the PTO particles, promoting the fabrication of the 1D nanostructures, as shown in Fig. 3. In addition, the formation of PTO nanowires also depends on the type of the precursor. PTO nanowires could not be obtained when $Ti(OH)_4$ and $Pb(OH)_2$ were used as precursors instead of $Ti(CO_3)_2$ and $PbCO_3$, which may be attributed to the difference in solubility between the carbonate and hydroxide. As the reaction mechanism and hydrothermal conditions are complicated, the exact reason for the PTO nanowires being synthesized in the present method needs to be further investigated.

Conclusions

PTO nanowires with diameters of 20-30 nm and lengths of about 2-3 um have been successfully prepared by a simple hydrothermal method without any surfactants. It was found that the KOH concentration played a key role in controlling the formation of PTO nanowires. A large quantity of PTO nanowires could be synthesized when the KOH concentration was increased to 8 M. It is rational to expect that $PbZr_{0.52}Ti_{0.48}O_3$ and $PbZrO_3$ nanowires may be synthesized by this surfactant-free hydrothermal method, and this work is in progress.

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