

Synthesis of BaTi₂O₅ nanobelts

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Abstract

BaTi₂O₅ nanobelts with 60–100 nm in thickness, 200–300 nm in width, and several micrometers in length have been successfully synthesized through a two-step hydrothermal reaction. Sodium titanate nanobelts are synthesized via the reaction of titania nanoparticles and NaOH aqueous solution at 180 °C for 24 h. After the reaction, resulting sodium titanate nanobelts are ion-exchanged with barium ions and then treated at 180 °C for 60 h under alkaline condition, BaTi₂O₅ nanobelts are formed. The morphologies and crystal structures of sodium titanate and BaTi₂O₅ nanobelts are characterized by field-emission scanning electron microscope (FE-SEM), transmission electron microscope (TEM) and X-ray powder diffractometer (XRD), respectively.

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1. Introduction

In recent years, one-dimensional (1D) nanostructures, such as nanorods, nanowires, nanotubes, and nanobelts, have received considerable attention due to their novel physical properties and potential applications in electronic devices and sensors, etc. [1–3]. Among them, the belt-like nanostructures are expected to represent important building blocks for nanodevices [4]. Alkaline earth titanates such as BaTiO₃ with a cubic perovskite structure are noteworthy for their exceptional dielectric, piezoelectric, and electro-optic properties [5–10]. Moreover, the superior properties of these applications are proposed to be achieved by using 1D nanostructures with a principal axis of the unit cell preferentially aligned along its length [9,11]. Recently, considerable efforts have been made on the controllable synthesis of 1D nanostructures of alkaline earth titanates. Park and co-workers [12] synthesized single-crystalline perovskite nanorods composed of barium titanate and strontium titanate by solution-phase decomposition of bimetallic alkoxide precursors in the presence of coordinating ligands. Fisher and co-workers [13] reported the sol–gel synthesis of barium titanate and lead titanate nanotubes using masked Whatman anodisc membranes as templates. Li and co-workers [14] fabricated sodium titanate and potassium titanate nanobelts by hydrothermal synthesis. Wong and co-workers [15] utilized a low-temperature hydrothermal reaction to generate crystalline barium titanate and strontium titanate nanotubes. The synthesis of the barium titanate nanobelts still remains a great challenge to materials scientists. In this letter, we report the synthesis of BaTi₂O₅ nanobelts at low temperature through a two-step hydrothermal process.

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2. Experimental

2.1. Materials

Titanium tetrabutoxide, *n*-butanol, absolute ethanol, sodium hydrate, barium hydroxide, and barium chloride were of analytical grade and were used without further purification. Distilled water was used in all reactions.

2.2. Preparation of sodium titanate nanobelts

Fifteen milliliters of tetrabutyl titanate was added into *n*-butanol–water solution (volume ratio, 1:1) with stirring. After the precipitate was filtered, dried at 75 °C in air for 3 h, and sintered at 500 °C for 2 h, TiO₂ nanoparticles were obtained. Then, 2 g of the obtained nanoparticles were placed into a teflon-lined autoclave of 50 mL capacity. The autoclave was filled with 10 M NaOH aqueous solution up to 80% of the total volume and then sealed. After being maintained at 180 °C for 24 h, the autoclave was naturally cooled to room temperature. Finally, the sodium titanate product was obtained by washing with distilled water and absolute ethanol until the pH value of the supernatant was about 7.

2.3. Preparation of barium titanate nanobelts

In a typical synthesis, 1.5 g of the obtained sodium titanate nanobelts were dispersed into 18 mL of 2 M BaCl₂ solution, and then an appropriate amount of NaOH aqueous solution was added dropwise to the mixture to adjust pH values in the range of 12–14. The slurry solution was placed in a 50 mL autoclave with a teflon liner after ultrasonic vibration for 2 min. The autoclave was maintained at 180 °C for 60 h and then air-cooled to room temperature. The white precipitate was collected and washed with hydrochloric acid, distilled water, and absolute ethanol several times, and then dried in vacuum at 60 °C for 10 h. The molar ratio of titanium to barium is 1:1 in the reaction.

2.4. Characterization

The crystal structures of sodium titanate and barium titanate were characterized on a D/MAX-500 X-ray powder diffractometer with Cu K α radiation ($\lambda = 1.5418 \text{ \AA}$). The morphologies and sizes of sodium titanate and barium titanate were characterized by transmission electron microscopy (TEM, JEM-2000EX) and field-emission scanning electron microscopy (FE-SEM, JEOL JSM-6700F). Before SEM imaging, the samples were sputtered with thin layers of platinum on Si wafer as substrate. X-ray analysis (EDXA) was measured by energy-dispersive X-ray microanalysis system (Oxford INCA).

3. Results and discussion

Fig. 1a shows the XRD pattern of the products simply prepared by titania nanoparticles treated with 10 M NaOH aqueous solution at 180 °C for 24 h under hydrothermal condition, which is similar to that of sodium titanate reported by Li and co-workers [14]. When the sodium titanate was treated with BaCl₂ solution, the product is almost BaTi₂O₅ as shown in Fig. 1b. Most of the diffraction peaks in this pattern can be indexed to monoclinic crystalline phase BaTi₂O₅ with calculated lattice contents $a = 9.41 \text{ \AA}$, $b = 3.94 \text{ \AA}$, $c = 16.89 \text{ \AA}$, which is consistent with the literature values (JCPDS 08-0368), indicating that sodium titanate can react with BaCl₂ under the alkaline condition. However, when the sodium titanate was treated with Ba(OH)₂, the XRD pattern in Fig. 1c shows that the main product is crystalline BaTiO₃ (JCPDS 89-2475), which has a cubic perovskite structure with the unit cell parameter 4.017 \AA . In addition, small traces of BaCO₃ byproducts exist in BaTiO₃ products due to the atmospheric CO₂ [16].

Fig. 2a shows a typical SEM image of the as-prepared sodium titanate nanobelts. It is found that the product consists of a large quantity of uniform belt-like nanostructures. The width, thickness, and length of the sodium titanate are 200–300 nm, 60–100 nm, and several micrometers, respectively. Interestingly, some sodium titanate nanobelts can self-assemble into bundle-like structures. A typical TEM image of the as-prepared sodium titanate product (Fig. 2b) also reveals the belt-like nanostructures. The width and length of sodium titanate nanobelts are well consistent with that in SEM image (Fig. 2a). The ripple-like strain contrast can also be observed clearly in sodium titanate nanobelts. EDXA

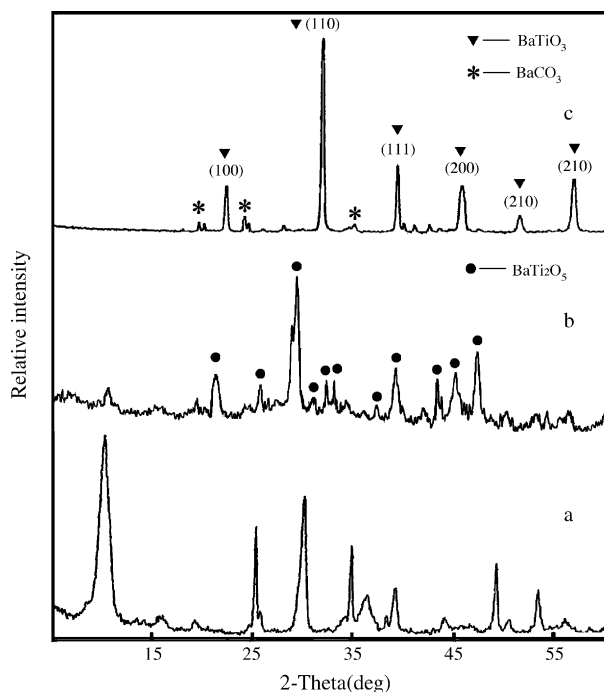


Fig. 1. The X-ray diffraction patterns of the titanate: (a) the sodium titanate precursor; (b) BaTi_2O_5 ; and (c) BaTiO_3 .

spectrum of the as-prepared sodium titanate nanobelts indicates that the product is made up of Na, Ti, and O, and the average atomic ratio of Na/Ti/O is about 1:3:5.5.

The choice of barium source is important for the formation of barium titanate nanostructures. Two kinds of barium titanates in different morphologies were obtained, when the sodium titanate nanobelts were treated with BaCl_2 and Ba(OH)_2 , respectively. The SEM image of BaTi_2O_5 nanobelts synthesized with BaCl_2 as barium source is presented in Fig. 3a. As is observed, belt-like BaTi_2O_5 nanostructures are obtained due to the ion-exchange interaction between sodium titanate nanobelts and BaCl_2 . These nanobelts have width of 200–300 nm, thickness of 60–100 nm, and length up to several micrometers respectively, which are similar to those of the precursor. EDXA spectrum (Fig. 3b) of the BaTi_2O_5 nanobelts shows that the atomic ratio of barium to titanium is about 1:2.1. In addition to Ba, Ti, and O, there are no other elements (such as Na, Cl) observed. The peaks of Si and Pt belong to the Si wafer and the thin layers of platinum, which were sputtered on the surface of samples.

As shown in Fig. 4a, BaTiO_3 nanoparticles coexist with rod-like structures in the products, when BaCl_2 was replaced with Ba(OH)_2 before hydrothermal treatment. EDXA spectrum (Fig. 4b) of the products indicates that the average atomic ratio of barium to titanium is about 1:1. It is indicated that sodium titanate nanobelts were destroyed and then converted to BaTiO_3 nanoparticles during the reaction with Ba(OH)_2 .

According to the results of the experiments, the basic reaction may be expressed as follows:

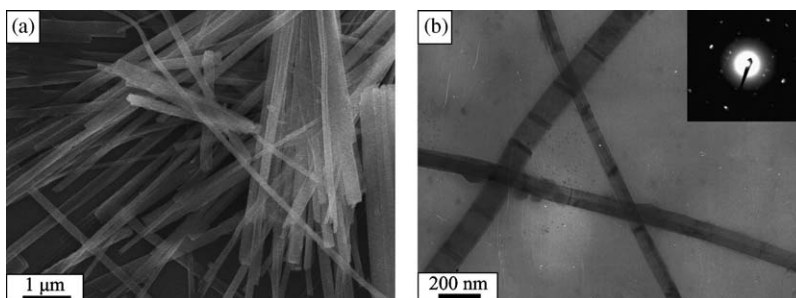
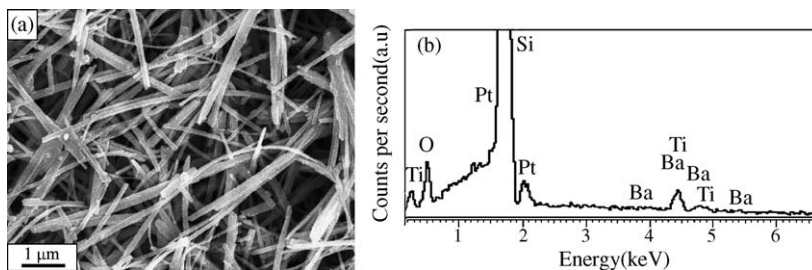
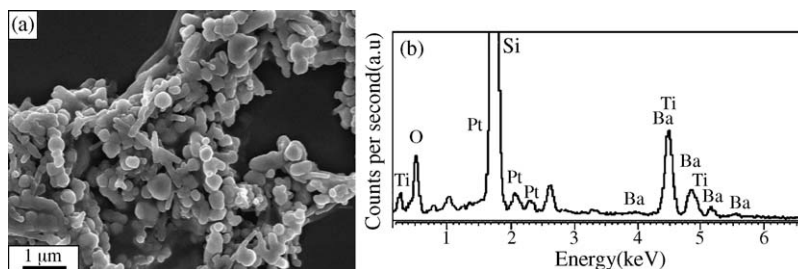
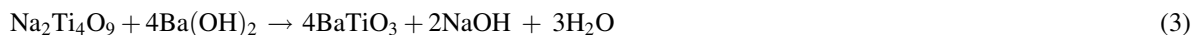
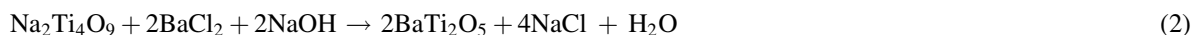
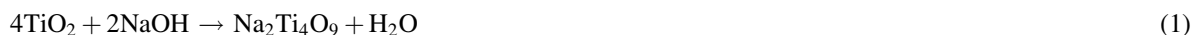


Fig. 2. SEM and TEM images of sodium titanate nanobelts.

Fig. 3. SEM image and the EDXA spectrum of BaTi₂O₅ nanobelts.Fig. 4. SEM image and the EDXA spectrum of BaTiO₃ nanobelts.

In the first step (Eq. (1)), the sodium ion is active and provides a possibility for ion-exchange between Na⁺ and other metal cations [17]. The selection of barium source plays an important role in the formation of BaTi₂O₅ nanobelts. When the sodium titanate nanobelts are treated with BaCl₂ before hydrothermal process, the ion-exchange reaction between Na⁺ and Ba²⁺ occurred, which does not change the morphologies of the nanostructures. This in situ reaction (Eq. (2)) is carried out under hydrothermal conditions, and crystalline BaTi₂O₅ nanobelts are finally synthesized. However, when BaCl₂ is replaced by Ba(OH)₂ before hydrothermal process, the ion-exchange between Na⁺ and Ba²⁺ is very weak due to the poor solubility of Ba(OH)₂. Consequently, the reaction (Eq. (3)) takes place and the belt-like structure of sodium titanate is destroyed, and then the BaTiO₃ particles and short rods are formed. The formation mechanism of the BaTi₂O₅ nanobelts needs further investigation.

4. Conclusion

In summary, we report a two-step process to the synthesis of BaTi₂O₅ nanobelts. The width, thickness, and length of BaTi₂O₅ nanobelts are about 200–300 nm, 60–100 nm, and up to several micrometers, respectively. The influence of barium sources on the morphologies and crystal structures has been investigated.

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