Preparation of $SrTiO_3$ nanofibres by hydrothermal method

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Because of its high charge storage capacity, good insulating properties and chemical stability [1], strontium titanate is a very interesting material for application into microelectronics, such as high dielectric capacitors, positive temperature coefficient (PTC) resistors, transducers and ferroelectric memories [2], and a promising material for dynamic random-access memories in very large scale integrated devices [1]. In addition, it can also be applied as an insulating layer in thin film electroluminescent displays because of its excellent optical transparency in the visible region [3].

Perovskite materials of the ABO_3-type bulk ceramics and thin films have found wide applications in many electronic applications. Their ceramic fibers have a lot potential to reinforce ceramics and metal bodies. Fibrous materials have a number of specific properties, such as a highly crystal axis orientation of the grains, special morphologies of the functional ceramics will expand their utility in the microdevices such as sensors, transducers, and innovative optical modulating devices [4].

Some methods and techniques have been developed for the preparation of the special morphologies of Perovskite materials [4–6]. Gao [7] prepared strontium titanate thin films by liquid phase deposition method. Ding [8] fabricated $Ba_xSr_{1-x}TiO_3$ ceramic films using jet-printing technique. Yoshimura [9] synthesized single and double layers in the $BaTiO_3$–$SrTiO_3$ system under hydrothermal–electrochemical conditions using either closed autoclave or solution flow cell. Pasierb [10] deposited $Ba_xSr_{1-x}TiO_3$ thin films by the RF sputtering method and obtained good optical properties. Kao [11, 12] prepared strontium titanate ceramic powder from titanyl acylate precursor and from titanium alkoxide in strong alkaline solution. Zhang [13] synthesized $SrTiO_3$ powder from $TiO_2{\cdot}H_2O$ gel under moderate hydrothermal conditions. It showed that the crystallization of $TiO_2{\cdot}H_2O$ had an important influence on the product particle size and particle size distribution. $SrTiO_3$ single crystals 15–20 mm in diameter and 40–80 mm in length were prepared by a floating zone method with radiation heating [14]. Nanocrystalline $SrTiO_3$ powder was synthesized under moderate hydrothermal conditions derived from different precursors by hydrothermal method [15]. In this paper, we synthesized $SrTiO_3$ nanofibers using $Ti(OC_4H_9)_4$ and $SrCl_2$ as starting materials by hydrothermal method.

Tetraisopropyl titanate ($Ti(OC_4H_9)_4$, 1.0×10^{-3} mol) (density 0.955 g cm^{-3}, purity 97%, made in Beijing Chemical Factory) was dissolved in 20 ml ethanol. Enough distilled water was slowly dropped into $Ti(OC_4H_9)_4$–ethanol solution under stirring, until no sedimentation separated out. $TiO_2{\cdot}nH_2O$ was obtained by centrifugal sedimentation after the sedimentation was washed several times with distilled water and ethanol.

NaOH was dissolved in boiled water to get 100 ml, 0.03 mol dm^{-3} NaOH solution to which 1.0×10^{-3} mol $SrCl_2{\cdot}6H_2O$ was added (AR, made in Shanghai Chemical Factory). $Sr(OH)_2{\cdot}nH_2O$ was obtained by centrifugal sedimentation after washing with 0.03 mol dm^{-3} NaOH solution.

All the hydrothermal reactions were carried out in a self-made Teflon-lined closed stainless steel autoclave which had a volume of about 25 ml. The reactor was put into an oven which reached the necessary temperature before heating, and taken out to cool naturally at room temperature after the reaction.

After 2.5×10^{-4} mol amorphous $TiO_2{\cdot}nH_2O$ was added into 10 ml, 10 mol dm^{-3} NaOH solution and hydrothermally synthesized at 150±1 °C for 12 hr, crystalline $TiO_2{\cdot}nH_2O$ was obtained. Then the solution was mixed with 2.5×10^{-4} mol $Sr(OH)_2{\cdot}nH_2O$ and heated at

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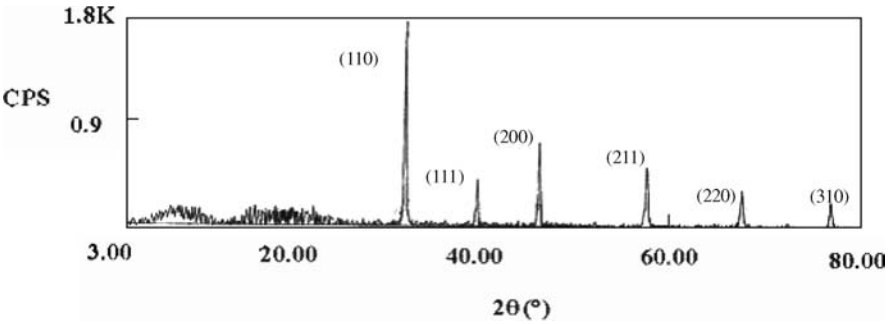

Figure 1 X-ray diffraction pattern of $SrTiO_3$ hydrothermally synthesized.

150±1 °C for 12 hr again. Suspension A was obtained. Suspension D was obtained by heating suspension A at 200±1 °C for 100 hr.

Amorphous $TiO_2{\cdot}nH_2O$ (5×10^{-4} mol) and $Sr(OH)_2{\cdot}nH_2O$ (2.5×10^{-4} mol) were added into 10 ml, 10 mol dm^{-3} NaOH solution. Then the solution was heated at 150±1 °C for 12 hr. Suspension B was obtained. Suspension C was obtained by heating suspension B at 200±1 °C for 100 hr.

Samples A, B, C, D were obtained correspondingly after suspensions A, B, C, D were centrifugated respectively.

The X-ray diffraction analysis (XRD) was performed at room temperature to identify the crystalline phase of the powder with FeKα radiation on a D/MAX-IIIB X-ray diffractometer (Rigaku Ltd., Japan). The morphologies of the materials synthesized were studied by JEM-1200EX transmission electron microscopy (TEM) (JEOL Ltd., Japan).

The XRD pattern (Fig. 1) shows that all samples were crystalline $SrTiO_3$. The XRD patterns of samples A, B, C, D were very similar to one another. Crystalline $SrTiO_3$ was obtained by hydrothermal synthesis whether amorphous $TiO_2{\cdot}nH_2O$ from hydrolyzed $Ti(OC_4H_9)_4$ (samples B and C) or crystalline $TiO_2{\cdot}nH_2O$ pre-hydrothermally reacted (samples A and D) was used as a matrix. Fig. 2 shows that the morphologies of sample B were better than that of sample A, and sample C were better than sample D. The precursor $TiO_2{\cdot}nH_2O$ of samples A and D was pre-hydrothermally reacted while the precursor $TiO_2{\cdot}nH_2O$ of samples B and C was not. The precursor $TiO_2{\cdot}nH_2O$ had a little influence on the morphologies of $SrTiO_3$ and the reactivity of amorphous precursor $TiO_2{\cdot}nH_2O$ was higher than that of the precursor $TiO_2{\cdot}nH_2O$ pre-hydrothermally reacted. The hydrothermal reaction time and temperature were important for the morphologies of nanofibers of $SrTiO_3$. Fig. 2 shows that the nanofibers of sample C were longer, unwounder than that of sample B, and sample D was better than sample A.

All samples were fibrous $SrTiO_3$. Pinceloup [16] and Xu [17] proposed dissolution–precipitation mechanism. They thought that the formation of $SrTiO_3$ was a dissolution and recrystallization process. In strong alkaline solution**,** hydroxide ion reacted with $TiO_2{\cdot}nH_2O$ to form $[Ti(OH)_6]^{2-}$. Then $Sr(OH)_2{\cdot}nH_2O$ reacted with $[Ti(OH)_6]^{2-}$ at hydrothermal conditions to form seeds of $SrTiO_3$. Finally they formed one-dimensional nanostructure of perovskite. In this process, hydroxide ions played an important role. Our experiment gave evidence for this mechanism. Obvious difference was not found in the samples with a different matrix $TiO_2{\cdot}nH_2O$. According to dissolution–precipitation

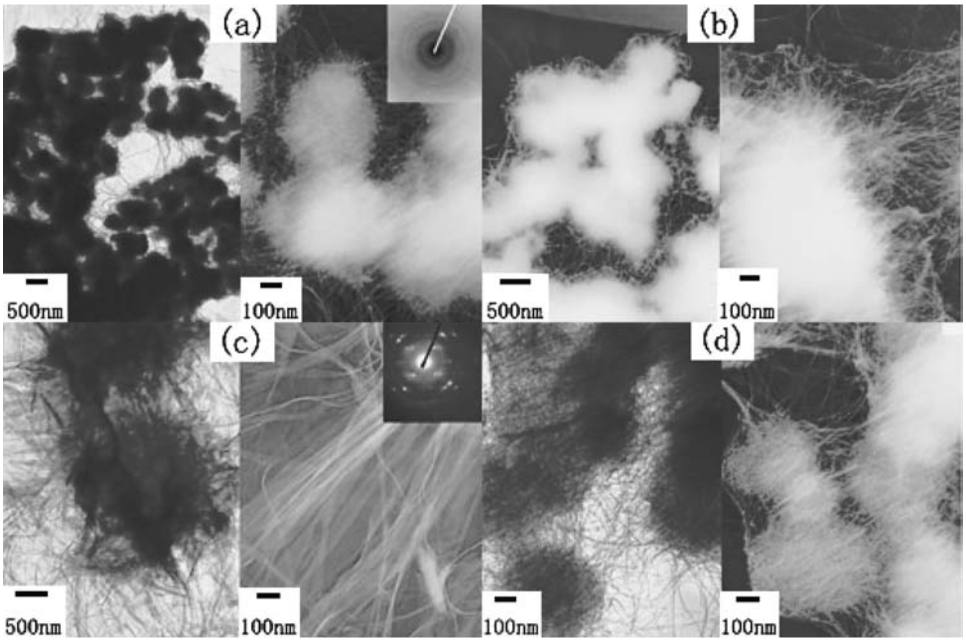

Figure 2 TEM of $SrTiO_3$ nanofibers: (a) sample A; (b) sample B; (c) sample C; (d) sample D.

mechanism, the rate-controlling process is the dissolution of precursory titania. Precursor of sample B and C was amorphous $TiO_2 \cdot nH_2O$ which was easier to react with OH^- and form nanofibers of $SrTiO_3$ than that of sample A and D. The morphologies of sample A was better than that of sample B, and sample C was better than sample D.

$SrTiO_3$ nanofibers were hydrothermally synthesized using $Ti(OC_4H_9)_4$ and $SrCl_2$ as starting materials for the first time. The crystallization of precursor $TiO_2 \cdot nH_2O$ had a little influence on the morphologies of nanofibers of $SrTiO_3$. In this hydrothermal process, hydroxide ions play an important role. For this reaction, (1) low concentration $TiO_2 \cdot nH_2O$, (2) high-reactivity $TiO_2 \cdot nH_2O$ and $Sr(OH)_2 \cdot nH_2O$, and (3) long reaction time were necessary.

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