

## Low Temperature Preparation of SrTiO<sub>3</sub> Nanocrystalline by Hydrothermal Method

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A low temperature (90 °C) hydrothermal method was proposed for the synthesis of SrTiO<sub>3</sub> nanoparticles. The characterization results from X-ray diffraction reveals that the resultant products are phase-pure perovskite structure. The SrTiO<sub>3</sub> nanoparticles synthesized in ≥ 1.8 mol/L KOH solution and their crystallite size increases with increasing the reaction time and temperature. The infrared spectrum shows the characteristic absorption peaks of SrTiO<sub>3</sub> along with OH<sup>-</sup> groups. UV-VIS absorption spectra indicate the band gap of SrTiO<sub>3</sub> nanoparticles is high than that of bulk SrTiO<sub>3</sub> and it exhibits an increasing trend with decreasing particle size.

**Key Words:** Strontium titanate, Nanoparticles, Optical properties.

### INTRODUCTION

Strontium titanate (SrTiO<sub>3</sub>) with perovskite structure has been widely studied due to its functional dielectric and ferroelectric properties for potential applications in random access memory devices, oxygen sensors, actuators and electrooptical devices<sup>1,2</sup>. For the above applications, great effort has been devoted to the synthesis of SrTiO<sub>3</sub> nanoparticles, driven by the excitement of understand new science and the hope for better performances and novel applications.

Various synthesis techniques have been widely used to fabricate SrTiO<sub>3</sub> nanoparticles, such as sol-gel route<sup>3</sup>, solvothermal method<sup>4</sup>, solid phase grinding<sup>5</sup>, molten salts method<sup>6</sup>, hydrothermal route<sup>7</sup>, etc. However, all these methods except hydrothermal and solvothermal route need high calcining temperature. Hydrothermal method is of great interest because it is environmentally friendly synthesis performed at moderate temperature (around 200 °C) and size, morphology and composition of the particles are uniform and controllable<sup>8,9</sup>. Fuentes *et al.*, prepared the SrTiO<sub>3</sub> nanomaterial using the sol-gel-hydrothermal reaction of TiCl<sub>4</sub> and a SrCl<sub>2</sub> solution in an oxygen atmosphere at 180 °C<sup>7</sup>. Lee *et al.*<sup>10</sup> reported that SrTiO<sub>3</sub> nanostructures were synthesized using Sr(OH)<sub>2</sub>·8H<sub>2</sub>O and H<sub>2</sub>Ti<sub>3</sub>O<sub>7</sub> in an ethanol/water mixed solvent at 120 °C. However, this method is not cost-effective in mass production of SrTiO<sub>3</sub> nanoparticles. Therefore, for industrial applications, it is still desirable to develop an alternative cost-effective method for large-scale production of SrTiO<sub>3</sub> nanoparticles at a reaction temperature as low as possible.

In this study, we have synthesized SrTiO<sub>3</sub> nanoparticles at low temperature of 90 °C by hydrothermal method. The obtained products were characterized by X-Ray diffraction (XRD), Fourier transform infrared spectrometer (FT-IR) and ultraviolet (UV)-visible spectrometer.

### EXPERIMENTAL

All chemicals were purchased and used without further purification. A typical procedure for preparing 0.03 M SrTiO<sub>3</sub> nanoparticles was as follows: 6.573 g strontium acetate ((CH<sub>3</sub>COO)<sub>2</sub>Sr·0.5H<sub>2</sub>O) was accurately weighed and dissolved in 20 mL of deionized water and 10.419 g tetra-*n*-butyl titanate (C<sub>16</sub>H<sub>36</sub>O<sub>4</sub>Ti) was diluted with 6.068 g acetylacetone (C<sub>8</sub>H<sub>8</sub>O<sub>2</sub>) to form a yellowish solution. The above two solutions were mixed to form strontium titanium solution (the molar ratio of Sr to Ti is 1 in the reactants). With stirring, KOH solution was added to the strontium titanium solution to form 100 mL white colloidal strontium titanium slurry. The mixed solution was transferred into a 200 mL Teflon-lined stainless steel reactor, sealed and then heated at 90-180 °C for 6-48 h. At the end of the reaction, the autoclave was allowed to cool down room temperature. The as-synthesized powder was filtrated and washed with deionized water and ethanol to remove the remaining ions and dried at 100 °C for 6 h.

The phase composition of products was investigated by XRD (Bruker D8 Advanced, Germany) with Cu K<sub>α</sub> radiation. The impurity in the products was analyzed over 4000-400 cm<sup>-1</sup> by using FT-IR spectrometer (Bruker Tensor27, Germany). The samples were ultrasonically dispersed in distilled water

and its optical properties were analyzed by using UV-VIS spectrometer (Unico UV-2102PC, America).

## RESULTS AND DISCUSSION

Change in XRD patterns of SrTiO<sub>3</sub> synthesized in different concentration of KOH solution at 180 °C for 24 h is shown in Fig. 1. When the concentration of KOH solution is low (pH = 12), diffraction pattern showing perovskite-type structure cubic SrTiO<sub>3</sub>, according to JCPDS cards No. 35-0734, is observed with impurity phases of TiO<sub>2</sub> and Ti<sub>3</sub>O<sub>5</sub>. As the concentration of KOH solution is increased up to 1.8 mol/L (the molar ratio of OH to Sr/Ti being 6), the obtained pH value is above 14. No other characteristic peaks except SrTiO<sub>3</sub> peaks are observable for any impurities in the products, revealing that the purity of the products is high. When the concentration of KOH solution is further increased from 1.8-3.6 mol/L, there are no new diffraction peaks present, which indicates that there is no new substance or crystal phase present.

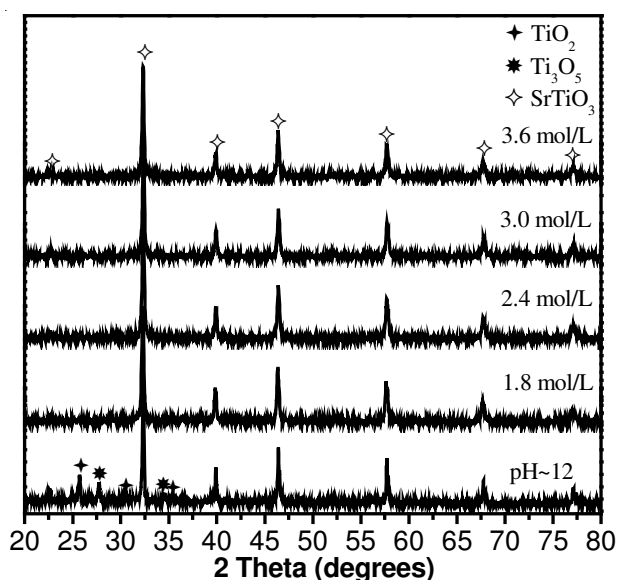


Fig. 1. XRD patterns of SrTiO<sub>3</sub> powder synthesized in different concentration of KOH solution at 180 °C for 24 h

In order to analyze the effect of the concentration of KOH solution on the crystal size of synthesized SrTiO<sub>3</sub> powders, the average crystal size of the products can be calculated by using Debye-Scherrer formula:  $D = 0.89\lambda/(\beta \cos \theta)$ , where  $\lambda$  is the wavelength of the incident X-ray beam and  $\beta$  is the full width at half maximum of the XRD peak. The calculated crystal sizes of SrTiO<sub>3</sub> powders synthesized in 1.8-3.0 mol/L KOH solution at 180 °C for 24 h are given in Table-1. It can be seen from Table-1 that there is no obvious change in crystal size of SrTiO<sub>3</sub> powders with increasing the concentration of KOH solution.

XRD patterns of SrTiO<sub>3</sub> powder synthesized in 3 mol/L KOH solution at 180 °C for different heating time are presented in Fig. 2. All the products, obtained at different reaction time, have almost the same XRD patterns. All the reflection peaks can be indexed to cubic perovskite phase SrTiO<sub>3</sub>. There is no obvious change in peak profile of diffraction lines with the increase of heating time. However, it can be

TABLE-1  
CRYSTAL SIZE OF SrTiO<sub>3</sub> NANOPARTICLES  
SYNTHESIZED BY HYDROTHERMAL METHOD AT  
DIFFERENT REACTION CONDITIONS

Sample	Reaction condition			Crystal size (nm)
	KOH conc. (mol/L)	Temperature (°C)	Time (h)	
1-1	1.8	180	24	48.0(5)
1-2	2.4	180	24	49.7(6)
1-3	3.0	180	24	52.3(6)
1-4	3.6	180	24	53.7(6)
2-1	3.0	180	6	45.6(5)
2-2	3.0	180	12	48.9(6)
2-3	3.0	180	24	52.3(6)
2-4	3.0	180	48	58.6(6)
3-1	3.0	90	24	35.7(4)
3-2	3.0	120	24	41.0(3)
3-3	3.0	150	24	48.0(9)
3-4	3.0	180	24	52.3(6)

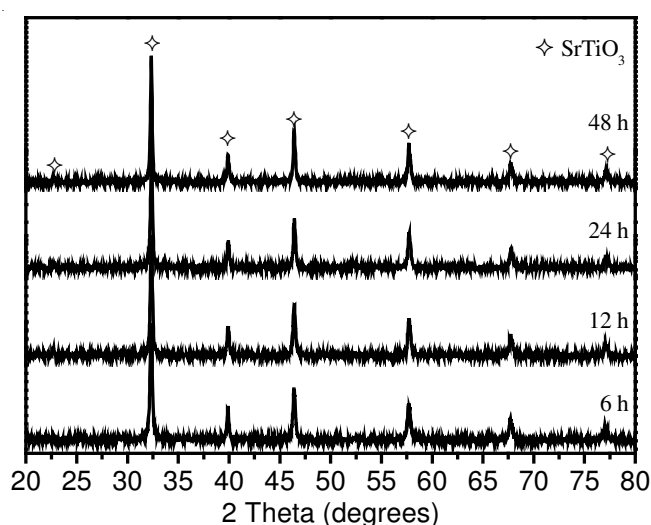


Fig. 2. XRD patterns of SrTiO<sub>3</sub> powder synthesized in 3 mol/L KOH solution at 180 °C for different heating time

seen from Table-1 that the calculated crystal sizes of SrTiO<sub>3</sub> powders increases with increasing the reaction time. This is because that the samples absorb more energy with the increase of the reaction time, which facilitates the growth of crystal grains.

XRD patterns of SrTiO<sub>3</sub> powder synthesized in 3 mol/L KOH solution at different temperature for 24 h are given in Fig. 3. It should be noticeable that only SrTiO<sub>3</sub> diffraction peaks are visible in the samples prepared at 90 °C. The synthesized temperature is much lower than those results reported previously<sup>7,10,11</sup>. As the reaction temperature is increased from 90-180 °C, there is no new diffraction peaks present and the intensity of the intensity of the diffraction peaks become higher, which indicates that there is no new substance or crystal phase present, but indicates that the products have higher crystallinity and larger crystallite size. As shown in Table-1, the higher the synthesized temperature is, the larger the crystallite size is.

Fig. 4 shows the FT-IR spectrum of the product synthesized in 3 mol/L KOH solution at 90 °C for 24 h. In the range of 1000-400 cm<sup>-1</sup>, it is found that the FT-IR spectrum have two strong absorption bands, located at *ca.* 434 and 610

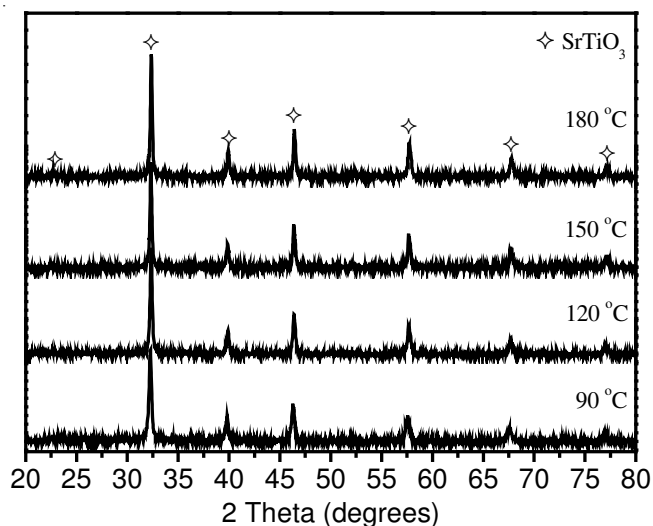


Fig. 3. XRD patterns of SrTiO<sub>3</sub> powder synthesized in 3 mol/L KOH solution at different temperature for 24 h

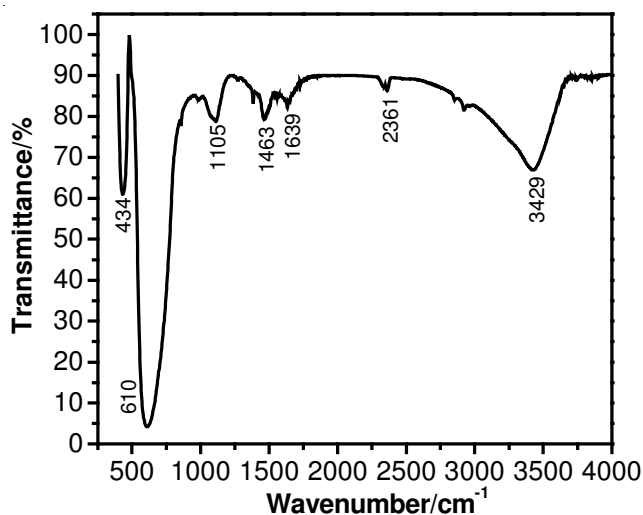


Fig. 4. FT-IR spectrum of SrTiO<sub>3</sub> nanoparticles synthesized in 3 mol/L KOH solution at 90 °C for 24 h

cm<sup>-1</sup>, which are attributed to TiO<sub>6</sub> octahedron bending and stretching vibration, respectively<sup>12</sup>. In the range of 4000-1000 cm<sup>-1</sup>, the two weak absorption bands at ca. 1463 and 1105 cm<sup>-1</sup> of indicate its low content in the product<sup>5</sup>. The weak absorption band centered at about 1639 cm<sup>-1</sup> can be assigned to the bending vibrations of OH<sup>-</sup> groups of absorbed water in the product and the broad absorption band at ca. 3429 cm<sup>-1</sup> can be attributed mainly to the stretching vibrations of OH<sup>-</sup> groups of absorbed water in the product.

The UV-VIS absorption spectra of SrTiO<sub>3</sub> nanoparticles synthesized in 3 mol/L KOH solution at 90 and 180 °C for 24 h are shown in Fig. 5. As can be seen, the product synthesized at 90 °C displays a narrow absorption peak centered at about 322 nm (3.8 eV), whereas the product synthesized at 180 °C exhibits a wide absorption peak centered at about 353 nm (3.5 eV), which is slightly blue-shifted compared with the band gap of bulk SrTiO<sub>3</sub> (3.4 eV)<sup>13</sup>. In addition, based on the results of XRD analysis, it implies that the product with small crystallite size has a high band gap energy. It is commonly observed that the band gap energy of nano-sized semiconductors exhibits an increasing trend with decreasing particle size<sup>14</sup>.

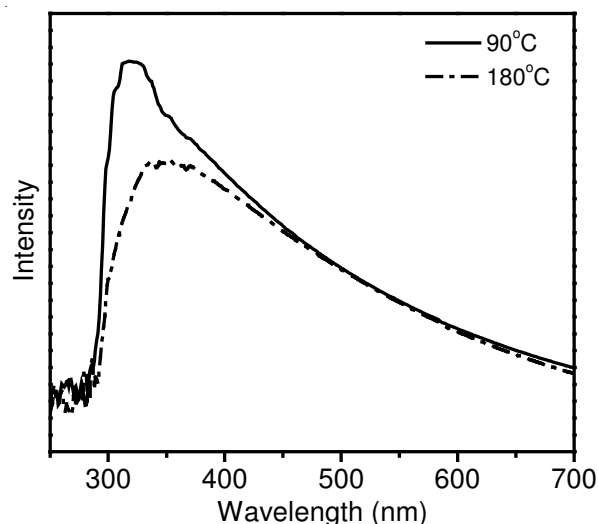


Fig. 5. UV-VIS absorption spectra of SrTiO<sub>3</sub> nanoparticles synthesized in 3.0 mol/L KOH solution at 90 and 180 °C for 24 h

## Conclusion

Phase-pure perovskite structure SrTiO<sub>3</sub> nanocrystals were synthesized by using hydrothermal method in ≥1.8 mol/L KOH solution at 90 °C. With increasing the reaction time and temperature, the crystallite size of SrTiO<sub>3</sub> nanoparticles increases and their crystallinity becomes higher. The infrared spectrum confirms the crystal water contained in the resultant product. The band gap of synthesized SrTiO<sub>3</sub> nanoparticles is high than that of bulk SrTiO<sub>3</sub> and it exhibits an increasing trend with decreasing particle size.

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