

## Structure and composition-dependent optical properties of $(\text{Pb}_x\text{Sr}_{1-x})\text{TiO}_3$ ( $x=0.4, 0.6$ ) nanotube arrays

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**Abstract:** Lead strontium titanate  $(\text{Pb}_x\text{Sr}_{1-x})\text{TiO}_3$  ( $x=0.4, 0.6$ ) nanotubes were synthesized by sol-gel template method via spin coating. The structures and morphology of the as-prepared samples were characterized by X-ray diffractometry, scanning electron microscopy and transmission electron microscopy. X-ray photoelectron spectroscopy was used to determine the chemical composition of the sample and the valence state of elements. Raman spectroscopy of the as-prepared  $(\text{Pb}_x\text{Sr}_{1-x})\text{TiO}_3$  ( $x=0.4, 0.6$ ) nanotubes at room temperature was also investigated. The results indicate that as-prepared  $(\text{Pb}_x\text{Sr}_{1-x})\text{TiO}_3$  ( $x=0.4, 0.6$ ) nanotubes are perfectly crystallized and there is a trend of structure change from PST40 to PST60. A weak peak at  $508\text{ cm}^{-1}$  assigned to E(3TO) mode can be seen in the Raman spectrum of  $(\text{Pb}_{0.6}\text{Sr}_{0.4})\text{TiO}_3$  sample. Photoluminescence spectra of samples at room temperature reveal three intense emission bands centered at 356, 400 nm for  $(\text{Pb}_{0.4}\text{Sr}_{0.6})\text{TiO}_3$  and 413, 433, 451 nm for  $(\text{Pb}_{0.6}\text{Sr}_{0.4})\text{TiO}_3$  nanotubes, respectively. The peak positions of the emission band have a significant blue shift as Pb content increases.

**Key words:**  $(\text{Pb}_x\text{Sr}_{1-x})\text{TiO}_3$ ; nanotube; sol-gel; AAO template; Raman spectrum; photoluminescence

### 1 Introduction

Recently, increasing efforts have been made to synthesize and investigate the ferroelectric nano-materials and nanostructures because of their novel properties and potential applications in nano-scale piezoelectric transducers and actuators, nano-nonvolatility memory devices and nano-optics devices [1–5]. A good understanding of the ferroelectric size effect, i.e., ferroelectric properties vanish below a critical size, is of great interest and importance for future application of ferroelectric materials [6]. Theoretical prediction indicates that one-dimensional ferroelectric nanostructure can greatly increase the storage density of nonvolatile ferroelectric random access memories [7–9] and thus more effort has been made in fabrication and investigation of one-dimension ferroelectric nano-structures. Therefore, perovskite ferroelectric nanowires and nanotubes have been extensively developed. Some methods, such as hydrothermal, electro-spinning and

sol-gel template methods, have been widely used to prepare ferroelectric nanostructures. The template method has been accomplished using polycarbonate membranes, nano-channel alumina and anodized aluminum oxides (AAO). AAO templates possess regular and highly ordered porous structures and advantages, such as low-cost, high purity, homogeneous components and easy chemical doping of materials prepared. Moreover, the axis orientation of pore perpendicular to membrane surface and the controllable diameter of the pore facilitate synthesis and properties of one-dimensional nanostructured materials. LIMMER and NOURMOHAMMADI et al [10–11] had successfully prepared ferroelectric nanostructures by combining template-assisted synthesis and sol-gel processing via the direct filling of sol-gel solution and electrophoretic deposition, respectively.

Lead strontium titanate  $(\text{Pb}_x\text{Sr}_{1-x})\text{TiO}_3$  is typical ferroelectric materials with high spontaneous polarization, dielectric permittivity and tunability [12–14]. Nowadays, studies have mainly focused on the

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preparation and electrical properties of  $(\text{Pb}_x\text{Sr}_{1-x})\text{TiO}_3$  ceramics and thin films. It is known that lead titanate ( $\text{PbTiO}_3$ ) with 3.0 eV band gap and strontium titanate ( $\text{SrTiO}_3$ ) with 3.4 eV band gap are typical wide band gap semiconductors [15–16]. Impurities, surface states and defects in the samples play an important role in the PL properties of perovskite-type oxides. LUO et al [17] reported the photoluminescence of PST nanocrystalline thin films and considered that PST thin film can be a very promising material for flat panel display applications and integrated light emission devices. In this paper, we investigate the structure and optical properties of  $(\text{Pb}_x\text{Sr}_{1-x})\text{TiO}_3$  ( $x=0.4$  and  $0.6$ , abbreviated as PST40 and PST60, respectively) nanotubes, which are synthesized by a sol-gel process and a spin coating technique from AAO template.

## 2 Experimental

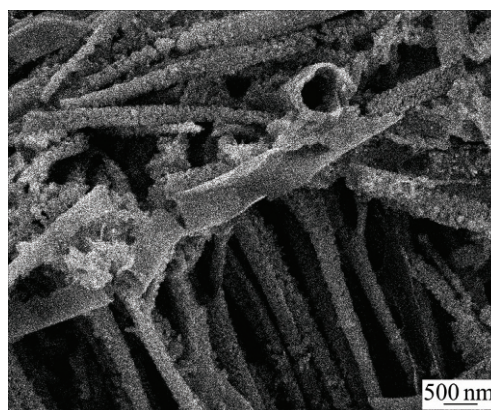
The precursor sols were synthesized from lead acetate tri-hydrate  $\text{Pb}(\text{CH}_3\text{COO})_2 \cdot 3\text{H}_2\text{O}$ , strontium acetate  $\text{Sr}(\text{CH}_3\text{COO})_2 \cdot 1/2\text{H}_2\text{O}$  and tetrabutyl titanate  $\text{Ti}(\text{OC}_4\text{H}_9)_4$  [18]. The stoichiometric amount of  $\text{Pb}(\text{CH}_3\text{COO})_2 \cdot 3\text{H}_2\text{O}$  with 10% excess in order to compensate for lead volatility was firstly dissolved in 10 mL glacial acetic acid and stirring for 30 min at  $70^\circ\text{C}$ .  $\text{Sr}(\text{CH}_3\text{COO})_2 \cdot 1/2\text{H}_2\text{O}$  was separately dissolved in warm acetic acid and addition of ethylene glycol was found to be effective for complete dissolution of strontium acetate in acetic acid. The required quantity of  $\text{Ti}(\text{OC}_4\text{H}_9)_4$  is initially dissolved in 2-methoxyethanol  $\text{C}_3\text{H}_8\text{O}_2$  and then mixed. Next, the mixed solution was stirred for several hours to obtain clear sol, without reflux or high temperature distillation to remove water. The concentration of the final solution can be adjusted to 0.2 mol/L and pH value to 2–4 by adding 2-methoxyethanol and acetic acid  $\text{CH}_3\text{COOH}$ . The whole process of preparing precursor solution is performed in an ambient atmosphere. Before spin-coating on the commercially available AAO template with nominal pore diameter of 200 nm and thickness of 60  $\mu\text{m}$ , the solution is filtered with filter paper to avoid particulate contamination. The coating solution of PST40 and PST60 was doped onto AAO template by spin coating at 3 000 r/min for 60 s so that the sol solution can penetrate into pore channels of the AAO template. After the spin coating process, the AAO template infiltrated with sol was dried at  $150^\circ\text{C}$  in air for 150 min and thereafter calcined at  $700^\circ\text{C}$  for 2 h in atmosphere at a rate of  $1^\circ\text{C}/\text{min}$  from room temperature.

The structural features and morphology of the as-prepared PST40 and PST60 nanotubes were analyzed by a X-ray diffractometry (XRD, D/Max 2200 Vpc, Rigaku, Japan), scanning electron microscopy (SEM,

JEOL, JSM-6060), and transmission electron microscopy (TEM, JEOL, JEM-2100). The AAO template was dissolved partially for SEM observations and dissolved entirely for TEM and high-resolution TEM (HRTEM) observations in 3 mol/L NaOH solution through controlling reaction time and temperature. For TEM observations, PST40 and PST60 nanotubes were dispersed by ultrasonic vibration and then dropped onto carbon films on copper grids. X-ray photoelectron spectroscopy (XPS) was carried out with the ESCALAB 250 (Thermo Electron Corporation) spectrometer by using  $\text{Al K}_\alpha$  (1 487 eV) radiation. Raman scattering investigation was carried out at room temperature with a wavelength of 514.5 nm He-Ne laser as excitation source. The photoluminescence (PL) properties of as-prepared PST40 and PST60 samples were recorded by a Hitachi F-7000 fluorescence spectrophotometer.

## 3 Results and discussion

Figure 1 shows typical SEM image of as-prepared nanotubes after partial removal of AAO template. It is seen that as-prepared samples have a hollow nanotube structure. The average outer diameter and wall thickness of nanotubes are about 200 and 40 nm, respectively. The outer diameter of nanotubes is consistent with the pore diameter of AAO template. The particles at tubes from the image may be due to incomplete removal of sol from template surface and some bended and even frangible nanotubes result from the sample preparation process, such as ultrasonic vibration.



**Fig. 1** Typical SEM image of as-prepared nanotube arrays after partial removal of AAO template

The XRD patterns of as-prepared PST40 and PST60 nanotubes embedded in AAO template are presented in Fig. 2. These XRD patterns can be well indexed according to available data (PDF, #521119) for bulk PST materials. The orientations and intensity ratios of PST40 and PST60 nanotubes match well with that of bulk PST materials. The precise peaks near  $2\theta$  of  $44^\circ$  and  $48^\circ$  for

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