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Sol–gel synthesis of $Bi_{3.25}La_{0.75}Ti_3O_{12}$ nanotubes

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ABSTRACT

Ferroelectric $Bi_{3.25}La_{0.75}Ti_3O_{12}$ (BLT) nanotubes were synthesized by sol–gel technique using nanochannel porous anodic aluminum oxide (AAO) templates, and were characterized by X-ray diffraction (XRD), field emission scanning electron microscopy (FE-SEM), transmission electron microscopy (TEM) and high resolution transmission electron microscopy (HRTEM). BLT nanotubes with diameter of around 240 nm and the wall thickness of about 25 nm exhibited a single orthorhombic perovskite structure and highly preferential crystal growth along the [1 1 7] orientation, which have smooth wall morphologies and well-defined diameters corresponding to the diameter of the applied template. The formation mechanism of BLT nanotubes was discussed.

1. Introduction

$Bi_4Ti_3O_{12}$ (BT) is one of the most important perovskite ferroelectric materials, which has been paid much attention owing to interesting properties such as high piezoelectric coefficient, high dielectric constant and low dielectric loss [1]. Rare earth substituted $Bi_4Ti_3O_{12}$, such as $Bi_{3.25}La_{0.75}Ti_3O_{12}$(BLT), $Bi_{4-x}Ce_xTi_3O_{12}$, $Bi_{4-x}Nd_xTi_3O_{12}$ and $Bi_{4-x}Sm_xTi_3O_{12}$, have been intensively studied in recent years for piezoelectric and ferroelectric devices due to their high fatigue endurance, low coercive fields, low operating voltage, high remanent polarization and piezoelectric coefficients [2,3]. The synthesis of nanotube materials has attracted great interest over the past few years because the nanotubes have distinctive physical properties and potential applications in the nanodevices [4–9]. The individual single-crystalline $BaTiO_3$ nanowire with the diameter of 10 nm was used to fabricate nonvolatile memory devices with an integration density of approaching 1 terabit/cm^2 [10]. Urban et al. reported that the $BaTiO_3$ ferroelectric phase transition temperature (Tc) was depressed with decreasing nanowire diameter [5]. The diameter was determined to be 3 nm when T_c dropped to below room temperature.

One-dimensional (1D) ferroelectrics have been successfully synthesized by various methods such as electrophoretic deposition technique [11], liquid source misted chemical deposition [8], sol–gel dipping template synthesis [12], hydrothermal method [13], and solution decomposition method [14]. Among these techniques, the sol–gel dipping template synthesis is a versatile and inexpensive technique for producing nanostructures, and particularly facilitates to synthesize complex oxide nanotubes or nanowires [15,16]. Compared with the synthesis of the general nanotubes such as carbon nanotubes with simple crystal structure, the synthesis of ferroelectric compound is difficult due to the multielement and complex crystal structures of these ferroelectrics. In this work, one-dimensional BLT nanotubes on anodic alumina (AAO) templates were synthesized by immersing a template membrane in sol without polymeric additive, and microstructures of BLT nanotubes were characterized.

2. Experimental

1D BT and BLT nanotubes are synthesized using sol–gel dipping template technique. Chemically homogeneous BLT ($[Bi^{3+}] = 0.2$ M) sol was synthesized using $Ti(OBut)_4$, $BiONO_3$ and $La(NO_3)_3{\cdot}6H_2O$) as starting materials, 2-methoxyethanol as a solvent and glacial acetic acid as a catalyst. Anodic membranes (Whatman Corporation) with a pore size of around 200 nm served as template sand were repeated dipped into the sol (5 min), dried at 100 °C for 4 h, and preprocess at 350 °C for 1 h, then calcined at 750 °C for 0.5 h in air, to both densify and crystallize the BLT nanotubes. After calcination, AAO templates were etched in a KOH solution (4 M) at room temperature to obtain 1D BLT nanotubes. The samples were rinsed carefully with deionized water to remove the residual contaminants on the 1D BLT (for SEM characterization) and then dispersed in alcohol (for TEM characterization).

X-ray diffraction (XRD) measurement was recorded at room temperature on Japan Rigaku D/MAX-2500/PC system with the Cu Kα radiation. Scanning electron microscopy (SEM) observation was performed using a CamScan MX-2600 field emission scanning electron microscope (FE-SEM). Transmission electron microscopy (TEM) and high-resolution TEM (HRTEM) were performed on a JEOL JEM-2100 electron microscope operating at 200 kV.

3. Results and discussion

Fig. 1(a)–(c) shows top view of the empty AAO template and BT nanotubes with AAO template. It can be seen in Fig. 1(b) that almost all pores are filled and the BLT nanotubes have distinct tubular walls

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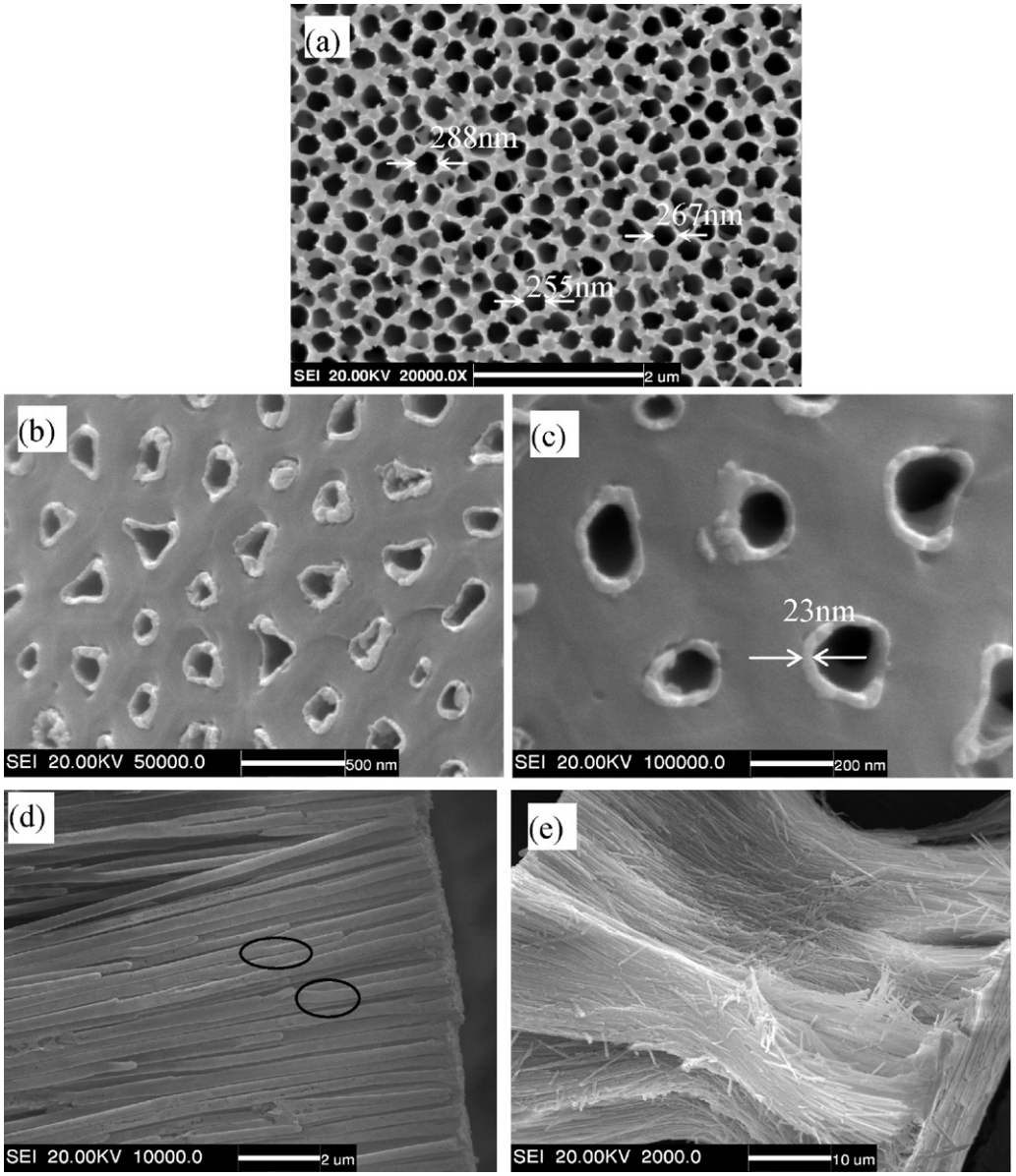

Fig. 1. FE-SEM images of (a) empty AAO template; (b and c) AAO template filled with $Bi_{3.25}La_{0.75}Ti_3O_{12}$ nanotubes; (d and e) cross-section of $Bi_{3.25}La_{0.75}Ti_3O_{12}$ nanotubes etched in a KOH solution for 60 min.

with a hollow center. Fig. 1(d) and (e) presents cross-sections of nanotubes at high and low magnification, respectively. The orderly aligned nanotubes have a uniform diameter throughout entire length of the template, and a smooth surface over all the length. The average diameter and length of BLT nanotubes is about 200 nm and 56 μm, respectively, corresponding well to the pore sizes of the AAO templates, which unambiguously demonstrates that the BLT nanotubes are grown under the control of the nanopores of the AAO template. The sol–gel process is so uniform that the inside of the pores are completely covered. Since the nanotubes imitated the pores of the AAO template, the branches presented in the templates are responsible for the growth of the Y-junctions nanotubes in the BLT (Fig. 1(d)). So it is reasonable to conclude that the porous AAO template has a complex channel structure and BLT nanotubes perfectly copy this three-dimensional structure of the template. Nanochannel porous AAO templates are obtained by anodization of aluminum plates at relatively high voltages (about 60 V), which results in the formation of branched nanochannels in porous AAO template [15].

The XRD patterns of BLT powders and nanotubes array with AAO template are shown in Fig. 2. From the XRD profiles, all the diffraction peaks can be indexed with the orthorhombic perovskite structure belonging to the *Fmmm* space group using JCPDS file no. 12-0213. The sharp and narrow XRD peaks indicate that BLT nanotubes are highly crystalline and consist of only a single compositional phase. The diffraction peak at about $2\theta = 30.19^\circ$ is very strong as compared with other peaks, which demonstrates that BLT nanotubes have a highly preferential crystal growth along the [1 1 7] orientation.

Typical TEM, HRTEM images and electron diffraction patterns of the isolated BLT and BT nanotubes are presented in Fig. 3. It can be clearly seen that nanotubes with diameter of around 240 nm and the wall thickness of about 25 nm are composed of small polycrystalline grains in the range of 10 nm. The Y-junctions are also observed in BT nanotubes. Fig. 3(b) shows a high resolution TEM micrograph of BT nanotubes. The distance between the parallel fringes is about 2.97 Å, which corresponds to the well recognized lattice spacing of {1 1 7} atomic planes. It agrees

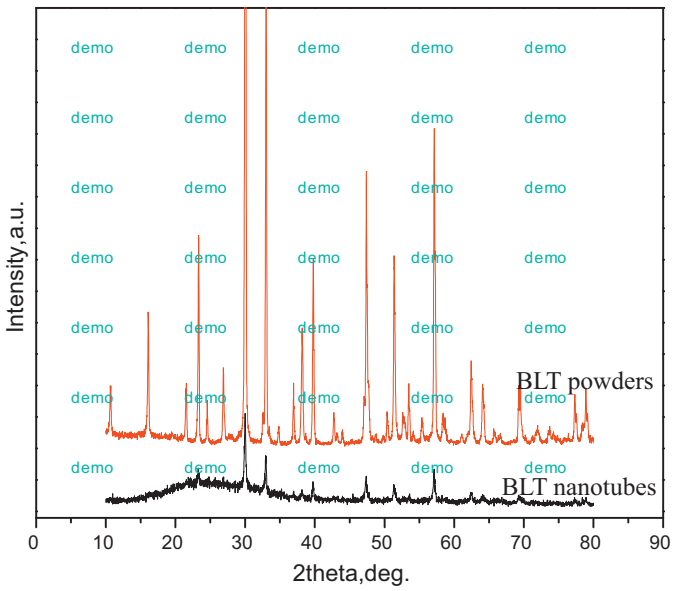

Fig. 2. XRD patterns of $Bi_{3.25}La_{0.75}Ti_3O_{12}$ powder and nanotube arrays with AAO template.

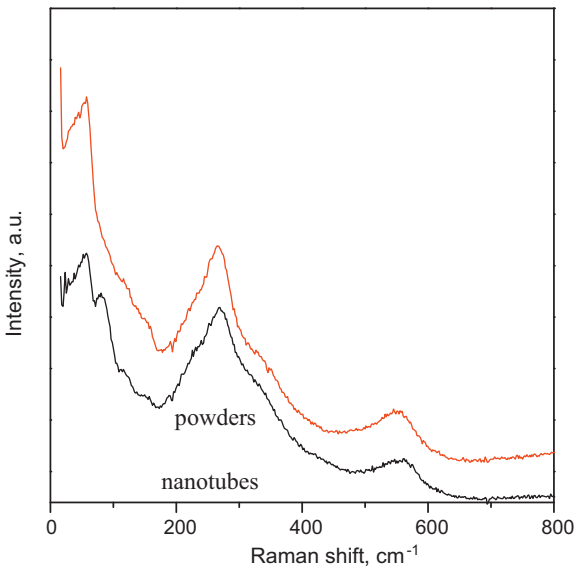

Fig. 4. $Bi_{3.25}La_{0.75}Ti_3O_{12}$ Raman scattering spectra.

well with the values from the XRD results, and confirms that the walls consist of nanoparticles with preferred (1 1 7) orientations.

Fig. 4 shows the Raman scattering spectra of BLT nanotube arrays and BLT powder, which were obtained at room temperature. The Raman peaks of the BLT nanotubes locates at around 57 cm^{-1}, 267.7 cm^{-1} and 553 cm^{-1} match well with the typical Raman peaks of perovskite BLT. The prominently intense, low-frequency peak at 267.7 cm^{-1} corresponds to the $B_{3g} + B_{2g}$ (O–Ti–O) modes. The peaks at 57 cm^{-1} and 553 cm^{-1} correspond to a Bi-layered rigid mode and A_{1g} (TiO_6) mode, respectively [17,18].

The formation process of BLT nanotubes is shown in Fig. 5. Sol is dipped in the templates and extends along the wall of the pores in driving force of capillary action, then changes into gel film undergoing the hydrolysis and condensation reaction, thus amorphous nanotubes first form in the wall of the pores. The packing of solids in the pores is very low, therefore it is necessary to repeat dipping a template membrane. Subsequently, the template was taken out from bake oven and then sintered in a furnace. During the sinter-

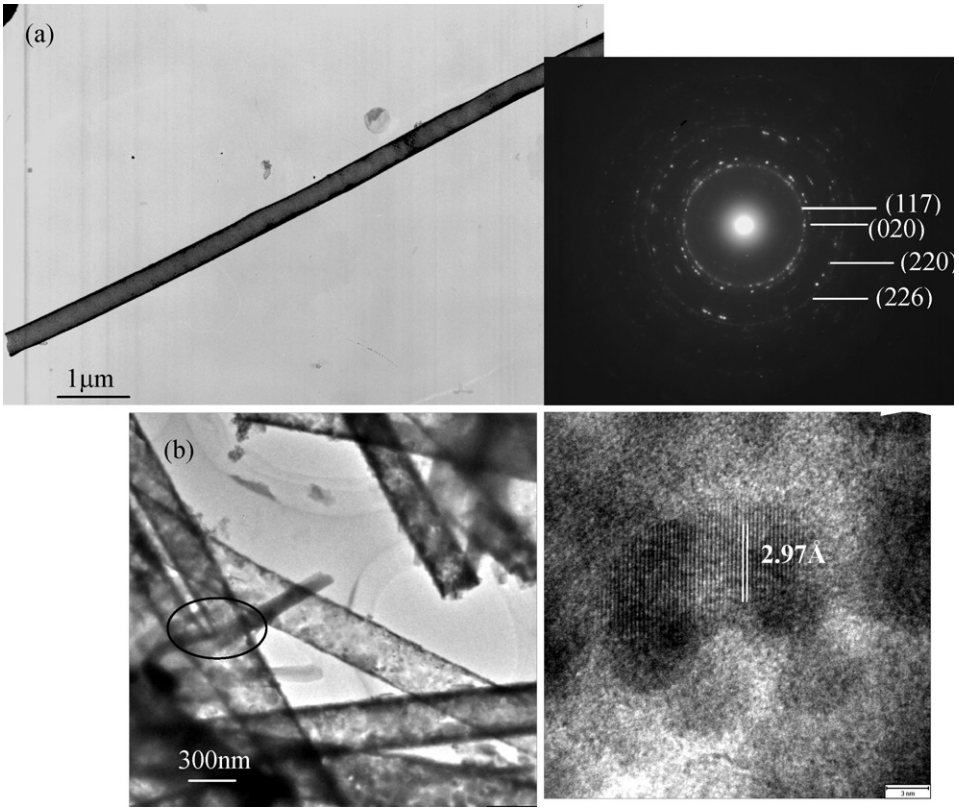

Fig. 3. TEM images of (a) $Bi_{3.25}La_{0.75}Ti_3O_{12}$ nanotubes and (b) $Bi_4Ti_3O_{12}$ nanotubes.

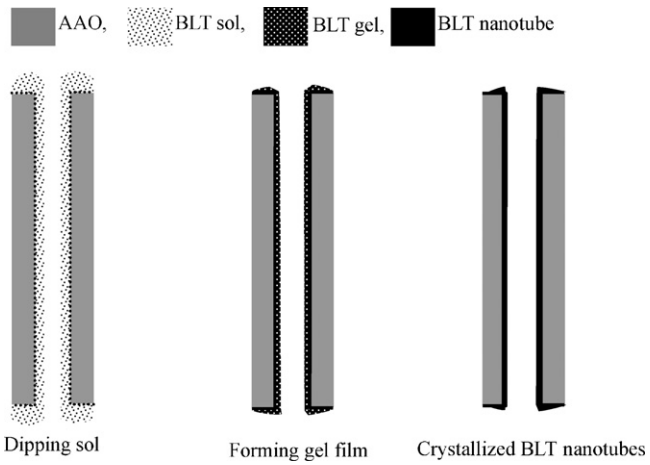

Fig. 5. The formation process of BLT nanotubes.

ing process, the gel film within the AAO's nanochannels would be turned to crystallized BLT nanotubes.

4. Conclusions

In summary, highly ordered BLT nanotubes were synthesized by the sol–gel method in the porous nanochannel alumina templates, and they have a single orthorhombic structure. The advantages on synthesis of nanostructures through template are (i) the structure of nanoarray is controlled by the structure of the template, and the material of interest which is inside the pores are confined by channels of the template, and (ii) a large amount nanotubes with the same structure can be synthesized. Sol–gel dipping template synthesis is very useful for large-scale preparation one-dimensional nanostructure, which is the basic building block of nanodevice.

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