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Visible photoluminescence from amorphous barium titanate nanofibers

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ABSTRACT

Broad visible emission at the wavelength range of 400–800 nm was obtained at room temperature in amorphous barium titanate ($BaTiO_3$) nanofibers, which were prepared by electrospinning and calcined at low temperatures. Structure and morphology of the $BaTiO_3$ nanofibers were investigated by X-ray diffraction (XRD), transmission electron microscope (TEM), thermo-analysis and Raman spectroscopy. XRD data shows that the $BaTiO_3$ nanofibers calcined at temperatures below 650 °C are amorphous, in which intense photoluminescence (PL) emission bands at 600 nm have been detected. More importantly, PL performance of the $BaTiO_3$ nanofibers exhibited a strong dependence on the calcination temperature. Observable emission was only found in the low-temperature treated fibers. Mechanism of the observed photoluminescence has been discussed. The achievements shown herein may be help to find new light-emitting materials.

1. Introduction

Barium titanate ($BaTiO_3$), a lead-free ferroelectric and piezoelectric material with a perovskite structure, has been intensely studied for applications including multilayer capacitors, infrared detectors, memory cells and piezoelectric devices [1–4]. To ensure the reproducible properties, wet chemical routs such as hydrothermal [5], sol–gel [6], coprecipitation [7] and organic precursor methods [8] have been developed to replace the classical solid-state reaction for preparation of $BaTiO_3$. Driven by the importance of $BaTiO_3$ in the electronic industry, previous researches into $BaTiO_3$ have mainly been focused on its ferroelectric, thermoelectric, and piezoelectric properties [9–11].

Traditionally, $BaTiO_3$ ceramics have not been integrated in optoelectric devices due to its wide energy band gap at about 3.57 eV in crystalline state [12]. It is the recent study that visible photoluminescence was observed in amorphous ABO_3 (A and B are cations and O is oxygen) compounds that has boost the increasing interest in the synthesis of amorphous $BaTiO_3$ for its visible photoluminescence properties [13–15]. Even though photoluminescence in $BaTiO_3$ has so far been reported in several papers, the luminescence emission is very weak and may hinder the possibility of any practical applications [16,17]. Moreover, with the development of micro-optic and electronic technologies, a low-cost and industrially viable technique that can harvest nano light-emitting materials with visible luminescence in a more efficient fashion is urgently needed. In the near future, when cost is taken into consideration, the under-investigated disordered insulators are expected to replace single crystal semiconductors in many optoelectronic devices.

Nanoscale materials with particular structures such as nanorods, nanofibers, and nanotubes have been a hot area of research for years due to their unique properties and applications [18–20]. As a kind of one dimensional nanomaterial, nanofibers have attracted considerable attention due to their structure dependent characteristics. In recent years, electrospinning has been adopted to produce nanofibers with extreme lengths and high aspect ratios. Compared with other nanofiber fabrication methods, for example thermal evaporation method [21], electrochemical deposition [22], hydrothermal [23], vapor–liquid–solid epitaxy [24], chemical vapor deposition, etc., electrospinning has been recognized as a simple and scalable technique to obtain fine nanofibers with low-cost and high efficiency [25], and hence has been holding increasing interest for the fabrication of various one-dimensional nanostructures [26–29]. According to its remarkable simplicity and versatility, nanofibers with rich varieties of inorganic components have been successfully synthesized including TiO_2 [30], ZnO [31], NiO [32], ZnS [33], and GaN [34]. On the other hand, outstanding catalysis, electricity, optic and magnetic properties have been discovered in electrospun nanofibers. $BaTiO_3$ nanofibers have also been produced by electrospinning in several studies, and the curie temperature of $BaTiO_3$ nanofibers was found to be 220 °C, which is nearly 90 °C higher than that of normal $BaTiO_3$ ceramics. However, all of these studies about $BaTiO_3$ are based on the polycrystalline structure after high temperature calcination. Here, we have tried to prepare the amorphous $BaTiO_3$ nanofibers using a simple electrospinning process, and studied their visible photoluminescence properties.

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2. Experimental details

The precursor solution for electrospinning was prepared by dissolving 3 wt% polyvinylpyrrolidone (PVP, MW = 13,000,000) in a 2.0 g ethanol-acetic acid mixture (1:1, weight ratio). 0.3144 g tetrabutyl titanate ($Ti(oBu)_4$) and 0.2360 g barium acetate were successively added to the solution and stirred until all the components dissolved. The precursor solution was then delivered to a needle made of stainless steel within radius of 0.4 mm. The needle was connected to a high-voltage power supply. When a high voltage of 20 kV was applied on the needle, precursor nanofibers were collected on a grounded aluminum foil, accompanied with the solvent evaporation. The distance between needle tip and grounded aluminum foil was 20 cm. The obtained precursor nanofibers were then calcined in air for two hours at temperatures from 300 to 650 °C.

Crystal structure and morphology of electrospun nanofibers were investigated by X-ray diffraction (XRD, D/max-2550, Rigaku Co., Japan), transmission electron microscopy (TEM, JEM-2010, JEOL, Japan), and scanning electron microscope (SEM, LEO-1530, LEO, German). Reaction process of the formation of $BaTiO_3$ and PVP nanofibers was determined by Thermo-analysis (TG/DSC, STA 409, NETZSCH, German). Raman (HR 800, Jobin Yvon, France) was conducted with an excitation light wavelength of 633 nm. The photoluminescence (PL) (HR 800, Jobin Yvon, France) measurement of these nanofibers was carried out at room temperature with an excitation light wavelength of 325 nm. To eliminate hidden variables as much as possible, all the nanofibers were electrospun under the same parameters, and all the spectra were obtained in one session under identical excitation and collection conditions.

3. Results and discussion

Micro-structure and morphology of the calcined nanofibers was characterized by TEM, as shown in Fig. 1. The nanofibers calcined at 400 °C show smooth surface (Fig. 1a), with highly disordered structure and no sign of crystallization (Fig. 1b). Amorphous nature of these $BaTiO_3$ nanofibers was further confirmed by electron diffraction image (Fig. 1c). As the calcination temperature increases to 650 °C, the surface of the nanofibers becomes much rougher (Fig. 1d). Shown in Fig. 1e, the d spacing estimated from the lattice fringe is 0.40 nm, which corresponds to the [010] crystal direction, indicating the nucleation and crystallization of the $BaTiO_3$ nanofibers. Seen from the selected area electron diffraction (SAED) (Fig. 1f), the diffraction rings (010, 110, 111, 020 and 120) marked in the SAED pattern correspond to perovskite $BaTiO_3$, indicating the polycrystalline structure of the electropun $BaTiO_3$ nanofibers calcined at 650 °C.

More detailed morphologies of the $BaTiO_3$ nanofibers calcined at different temperatures are displayed in SEM images (Fig. 2). In accordance with the above TEM results, nanofibers calcined at 300 °C, 450 °C, and 600 °C possess a smooth surface (Fig. 2a–c). However, the surface of those calcined at 650 °C is much rougher, which may be attributed to the grain growth.

Up to now, efforts have mainly been taken to investigate the ferroelectric and piezoelectric properties of $BaTiO_3$. In contrast, in this present research, we focus on the room temperature photoluminescence (PL) of the amorphous $BaTiO_3$ nanofibers. The PL emission spectra of the obtained $BaTiO_3$ nanofibers are shown in Fig. 3. The nanofibers calcined at 300 °C exhibit an intense PL emission at the wavelength range from 500 to 700 nm. With the calcination temperature increasing to 450 °C, the PL intensity is double than that at 300 °C. However, PL intensity sharply decreases as the

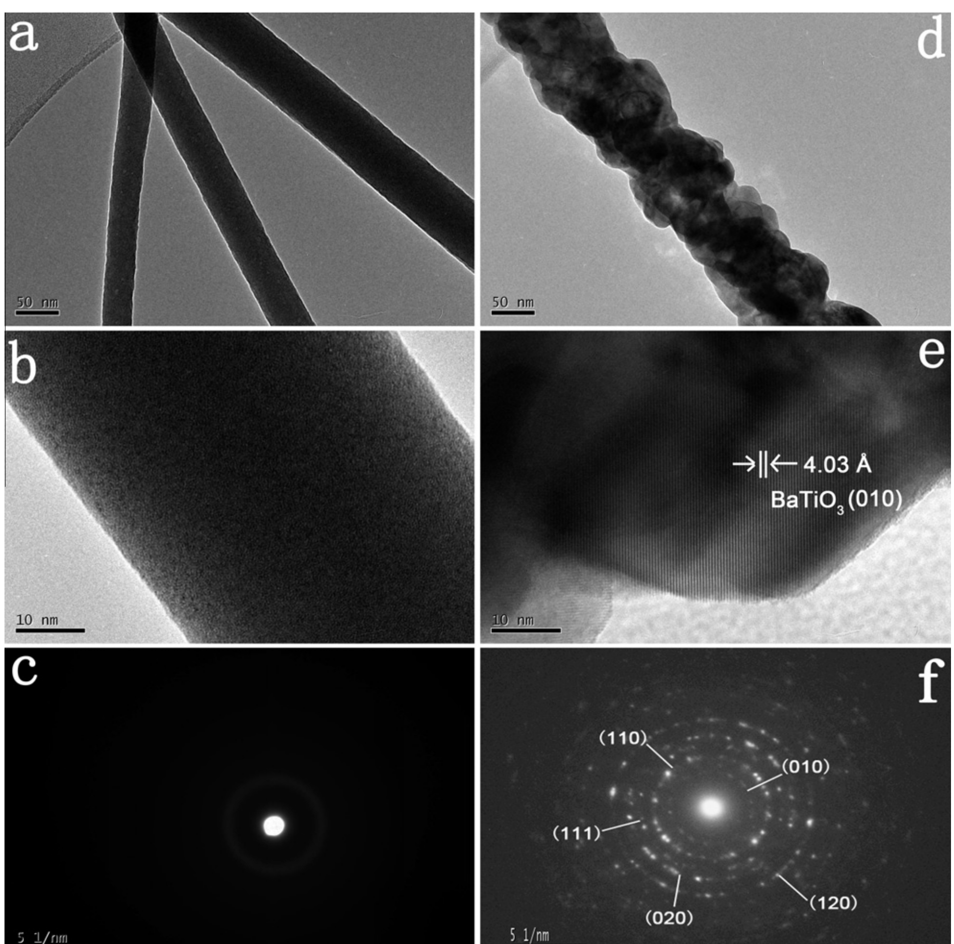

Fig. 1. TEM images of (a) and (b) $BaTiO_3$ nanofibers calcined at 450 °C for 2 h; (c) the corresponding electron diffraction pattern of part a; (d) and (e) $BaTiO_3$ nanofibers calcined at 650 °C for 2 h; (f) the corresponding electron diffraction pattern of part d.