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Piezoelectric/photoluminescence effect in one-dimensional lead-free nanofibers

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ABSTRACT

In present work, a multifunctional piezoelectric/photoluminescence effect, which originated from the combination of the piezoelectric properties and the photoluminescence effect, was realized in one-dimensional Er^{3+} doped lead-free $BaTiO_3$ nanofibers prepared by a sol-gel based electrospinning method. The X-ray diffraction (XRD), scanning electron microscopy (SEM), and high-resolution transmission electron microscopy (HRTEM) were utilized to characterize the morphologies and phase structures. The effect of the host crystallization and rare-earth concentration on the structure and photoluminescence properties was studied. In addition, temperature-dependent PL spectrum exhibited a piezoelectric/photoluminescence coupling effect, characterized by the enhanced photoluminescence intensity around the ferroelectric-paraelectric phase transition temperature of $BaTiO_3$.

Recently the development of multifunctional materials attracted much scientific and technological attention due to their outstanding coupling functions among the mechanical, electric, magnetic, and optical properties. Various two-parameter coupling effects have been reported in the scientific community such as electro-magnetic coupling, electro-mechanical interactions, magneto-optical, electro-optical interaction, and electro-caloric effects [1–5]. With the development of the functional material and device, it is attractive to design and explore new coupling effects and forms with multiple functions in single-phase materials [6–8]. Recently through the product of the piezoelectric effect and the electrochemical redox effect, a strong piezo-electro-chemical effect was realized in multiferroic $BiFeO_3$ micro-sheets [6]. In addition, a pyro-electro-catalysis coupling effect was realized from a combination of the pyroelectric effect and the electrochemical oxidation-reduction reaction in $BiFeO_3$ nanoparticles [7]. A multiple simultaneous electro-mechano-optical conversions was proposed in Pr^{3+} doped $BaTiO_3$–$CaTiO_3$ system, which effectively combined the piezoelectric effect of $BaTiO_3$ and the electroluminescent effect of Pr^{3+} doped $CaTiO_3$ [8]. However, multiple function coupling in a single-phase system was quite limited.

Piezoelectric and photoluminescence (PL) materials are two important smart effects which attracted extensive attentions during the past decades and were extensively utilized in sensors, transducers and luminescent devices [2,9]. Recently piezoelectric/photoluminescence multifunctional systems from the combination of the piezoelectric and photoluminescence effects were proposed which exhibited electro-mechano-optic effects in single-phase material [10–16]. On one hand, the introduction of the rare earth into the piezoelectric host could change the crystal lattice, leading to the enhanced piezoelectric and ferroelectric performance [11–12]. On the other hand, the piezoelectric or ferroelectric host could provide a suitable crystal field and the polarization could also improve the PL intensity output, which provided a new routine to modulate the PL performance [13–16]. Nevertheless, these previous works mainly focused on the bulk or the thin film form, one-dimensional single-phase nanostructure owning electro-mechano-optic effects was seldom studied. Furthermore, compared to the bulk and thin film form, the fiber form owns the advantage of high flexibility, large aspect ratio and high strain tolerance. It can effectively reduce the risk of potential fracture or damage of the piezoelectric materials and is also particularly attractive in flexible electromechanical devices such as sensors and energy harvesters [17]. Obtaining one-dimensional piezoelectric/photoluminescence nanofibers would be quite favorable for novel flexible multifunctional portable device applications. Furthermore, the fiber is easily accessible and the fabrication process is cost-effective. Therefore, in this work, we aim to report a one-dimensional upconversion PL Er^{3+}-doped $BaTiO_3$ nanofibers based on a sol-gel based electrospinning method. The effect of crystallization and rare-earth concentration on the structure and PL performance was studied. The X-ray diffraction (XRD), scanning electron microscopy (SEM), and high-resolution

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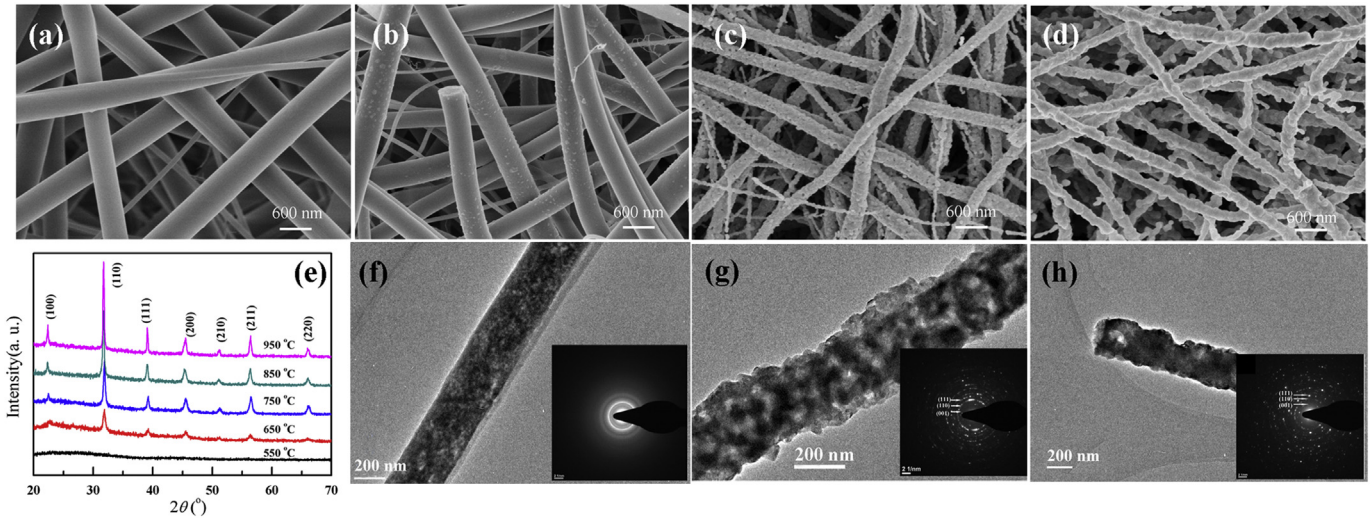

Fig. 1. (a)–(d) The typical surface morphologies for the (a) as-spun and annealed Er-0.02BTO nanofibers at (b) 550 °C, (c) 750 °C, and (d) 950 °C. (e) shows the corresponding XRD patterns for the Er-0.02BTO fibers annealed under different temperatures in the 2θ range of 20°–70°, and (f)–(h) HRTEM of the fiber annealed at 550 °C, 750 °C, and 950 °C, respectively.

transmission electron microscopy (HRTEM) were utilized to characterize the morphologies and phase structures. Composition-dependent photoluminescence spectra were characterized and the piezoelectric/photoluminescence coupling behavior was explored and discussed.

The Er-doped $BaTiO_3$ fibers were prepared using an electrospinning technique combined with a sol–gel process. Er ions were introduced into the *A*-site with the formula $Ba_{(1-3x)/2}Er_xTiO_3$ (Er-BTO, Er-*x*BTO) because of the superior PL intensity compared to the *B*-site substitution [15]. First, barium acetate was dissolved in acetic acid and stirred at 60 °C for 0.5 h. Titanium isopropoxide and erbium nitrate was dissolved in 2-methoxyethanol and acetylacetone was chosen as ligands. Then, the two solutions were mixed under continuous stirring conditions to form an Er-BTO precursor solution. The obtained solution was stirred for ~24 h with 1:1 volume ratio of ammonium hydroxide and monoethanolamine referred to as *A*. A second solution, referred to as *B*, was obtained by dissolving poly(vinyl pyrrolidone) (PVP, M_W = 630, 000) in ethanol. The solution was mechanically stirred for ~4 h. Solution *A* and *B* were then mixed under constant stirring conditions. The concentration of the final Er-BTO solution was controlled at ~0.2 M.

The obtained solution was then loaded into a plastic syringe equipped with a needle. The electrospinning was performed at 20 kV, 15 cm spacing between the needle tip and the collector under a feeding rate of 0.1 mm/min. The Er-BTO fibers were collected on an aluminum foil. The as-spun fibers were then dried at 90 °C for 4 h followed by thermal annealing between 550 °C and 950 °C for 2 h in air.

The crystal structures of the annealed fibers were determined from X-ray diffraction (XRD) patterns recorded with an X-ray diffractometry (D8 Focus, Bruker, Karlsruhe, Germany). A field emission scanning electron microscope (S-4800, Hitachi, Tokyo, Japan) was used to characterize the fiber morphologies. Annealed samples were also studied using high-resolution transmission electron microscopy (HRTEM, JEM 2100F, Japan) at an accelerating voltage of 200 kV. The composition and temperature PL spectra were recorded using a fluorescence spectrophotometer (Fluorolog-3-P, Jobin Yvon Inc., France).

Fig. 1(a)–(d) shows the typical surface morphologies for the as-spun (Fig. 1(a)) and annealed Er-0.02BTO nanofibers between 550 °C and 950 °C (here the nanofiber annealed at 550 °C, 750 °C, and 950 °C is shown in Fig. (b)–(d) and other data is given in the Fig. S1 of the supplementary data). The as-spun fibers were smooth, long, and continuous with the diameters around 600 nm. During the electrospinning process, it was found that the diameter of the fiber depended strongly on the applied voltage and the concentration of the precursor solution. Higher voltage and lower concentration both decreased the fiber diameter. After annealing, the fiber kept the long and continuous structure and the fiber diameter decreased due to the evaporation of the organic polymer. With the annealing temperature increasing from 550 °C to 950 °C, the

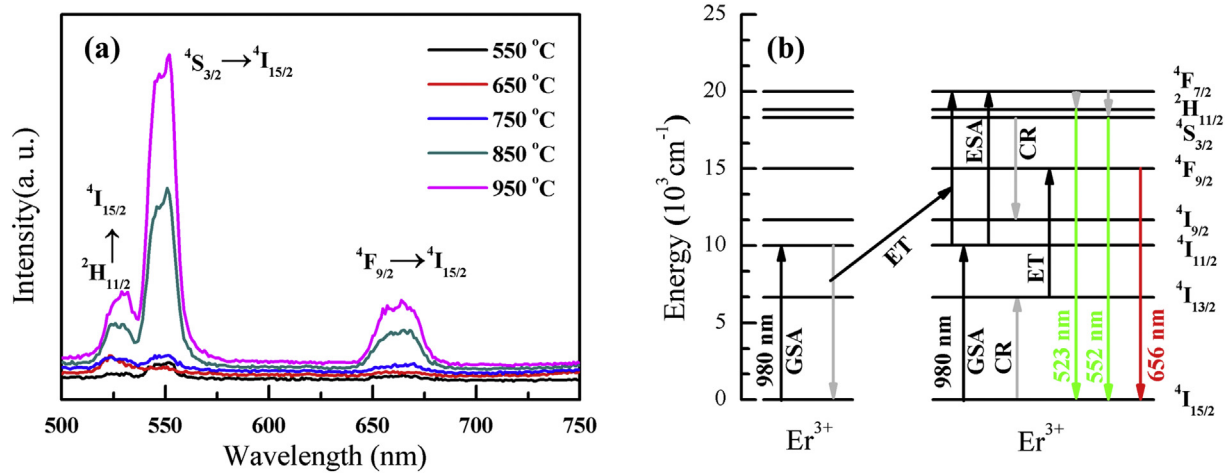

Fig. 2. (a) The upconversion PL spectra of the Er-0.02BTO nanofibers annealed at different temperatures and (b) the energy level diagram of Er^{3+} ion for illustrating the upconversion process.