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Structure and photoluminescence of β-Ga_2O_3:Eu^{3+} nanofibers prepared by electrospinning

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ABSTRACT

Eu^{3+}-doped β-Ga_2O_3 nanofibers were fabricated by electrospinning. The influence of Eu^{3+} concentration on the photoluminescence properties of the obtained nanofibers was investigated. The morphology and structure of β-Ga_2O_3:Eu^{3+} were characterized by field emission scanning electron microscopy (FE-SEM), X-ray diffraction (XRD) and Raman spectra. The diameter of the Eu^{3+}-doped β-Ga_2O_3 nanofibers was in the range of 180–300 nm. When the β-Ga_2O_3:Eu^{3+} nanofibers were excited by 325 nm wavelength, the main emission peak of the samples was 620 nm ($^5D_0 \rightarrow {}^7F_2$), which corresponded to a typical red emission ($^5D_0 \rightarrow {}^7F_j$ (j = 1, 2, 3, 4) intra-4f transitions of Eu^{3+} ions). In addition, the concentration quench effect and energy transfer mechanism in β-Ga_2O_3:Eu^{3+} were also discussed.

1. Introduction

One-dimensional nanomaterials, such as nanorods, nanowires, or nanofibers have attracted great attention due to their unique electronic, optoelectronic and mechanical properties [1–3]. These nanostructures may play different roles in light emitters, waveguides and light detectors [4–6]. There are several methods to synthesize nanostructures, such as hydrothermal [7], thermal evaporation [8], electrospinning [9], chemical vapor deposition (CVD) [10], and arc discharge [11]. Among these methods, the electrospinning technique is attractive for its convenience, simplicity and low cost, high surface area to volume ratio, tunable porosity, the ability to manipulate nanofiber composition in order to get desired properties and function and the ability to produce ultra-fine fibers ranging from nanometer to submicron in diameter. This technique is simple to adopt and utilizes the principle of applying electric potential between a syringe needle and grounded target. When an electrostatic force exceeds the surface tension of the droplet formed at the tip of the syringe needle, a charged fluid jet is ejected and the nanofibers are finally deposited onto a target substrate. In the continuous-feeding mode, numerous copies of fibers can be formed within a period of time as short as a few seconds.

In general, Ga_2O_3 exhibits different polymorphic phases such as rhombohedral α-, monoclinic β-, cubic γ- and δ-phases. Among monoclinic gallium oxide (β-Ga_2O_3) is a versatile oxide semiconductor material with the band gap (~4.9 eV), which exhibits particular conduction and luminescence properties [12,13]. Pure or doped β-Ga_2O_3 has wide applications in transparent conducting electrodes, gas sensors, dielectric gates, etc. [14–16]. Its wide band gap enables it to modify the luminescence properties by the incorporation of suitable ions in the Ga_2O_3 lattice. In particular, doping Ga_2O_3 with optically active ions, such as rare earth (RE) ions, allows the fabrication of devices based on this material which can emit light in different wavelengths spanning from the UV, all the way through the visible to the IR ranges.

To our knowledge, many methods have been mentioned in literature to prepare β-Ga_2O_3:Eu^{3+} nanomaterials [17–19], but the electrospinning preparation has not been reported. In this paper, we prepared the β-Ga_2O_3:Eu^{3+} nanofibers by electrospining method, and investigated the morphology, structure and photoluminescence properties of the obtained nanofibers.

2. Experimental

β-Ga_2O_3 nanofibers were prepared by electrospining using the sol containing $Ga(NO3)_3{\cdot}6H_2O$ (99.999%), $Eu(NO_3)_3{\cdot}6H_2O$ (99.9%), C_2H_5OH, H_2O, and poly(vinyl pyrrolidone) (PVP, Sigma–Aldrich, $M_w \approx 1{,}300{,}000$) and used without further treatment. In a typical procedure, PVP solution (5 wt.%) was prepared by dissolving PVP powder in the mixed of ethanol and distilled water and vigorous stirring for 3 h at room temperature. Then $Ga(NO_3)_3{\cdot}6H_2O$ (0.1 g) and $Eu(NO_3)_3{\cdot}6H_2O$ (0.5 mol%, 1 mol%, 2 mol%, 3 mol%, 5 mol%) were added to the solution of PVP used as the polymeric component of the composite because of its good solubility in ethanol and

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water and its compatibility with nitrates. The chemical reactions could be expressed as follows:

$$Ga^{3+}+3OH^{-} \leftrightarrow Ga(OH)_3$$

$$2Ga(OH)_3 \rightarrow Ga_2O_3+3H_2O$$

The solution was further stirred for 10 h to form a viscous solution. Then the prepared solution was loaded into a plastic syringe equipped with a stainless needle. The needle was connected to a high-voltage power supply that is capable of generating DC voltages up to 60 kV. A plate of aluminium foil as the collection screen was placed with a distance of 22.5 cm from the needle tip. Then the electric voltage of 23 kV was applied between the stainless needle and the collector. The electrospinning process was carried out in air and the deposition was conducted for 1 h so that dense mats were obtained. The as-prepared nanofibers were dried at 70 °C for 5 h. Then the nanofibers were annealed at 900 °C in air for 3 h to obtain the β-Ga_2O_3:Eu^{3+} polycrystalline fine nanofibers.

Field emission scanning electron microscopy (FE-SEM) images of the sample were recorded by Hitachi S-4800 scanning electron microscope. The crystal structure of β-Ga_2O_3:Eu^{3+} nanofibers were characterized by X-ray diffractometer (Philips, X'pert Pro) with a monochromatized source of Cu K alphal radiation at a wavelength of 0.15405 nm and Raman spectra using the 325 nm of He–Cd laser as an exciting source (JY-HR800). Room temperature PL emission spectra of β-Ga_2O_3:Eu^{3+} nanofibers were recorded using a 325 nm He–Cd laser as an excitation source.

3. Result and discussion

The morphologies of samples were investigated by the SEM observations. FE-SEM images of the β-Ga_2O_3:Eu^{3+} nanofibers with different Eu^{3+} concentration after being annealed at 900 °C are shown in Figs. 1 and 2. It can be seen that the nanofibers are uniform with a length of several tens to hundreds of micrometers. The surfaces of all the samples are not smooth due to the decomposition of the organic species and the formation of inorganic phase after being annealed at high temperature. The diameters of all the nanofibers range from 180 to 300 nm. No big particles are formed on the surface of the pure nanofibers as shown in Fig. 1. The morphology becomes coarse and some particles can be seen clearly on the surface of the fibers due to the increase of Eu^{3+} concentration as shown in Fig. 2. Besides, varying the doping concentration within this range had no obvious influence on the diameter of fibers.

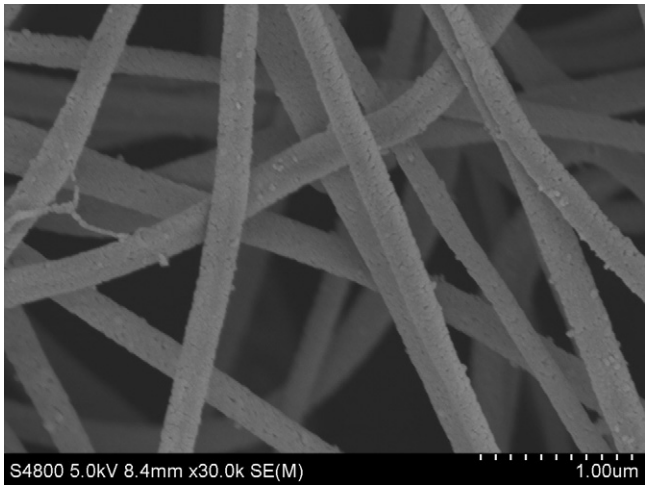

Fig. 1. SEM image of the pure β-Ga_2O_3 nanofibers annealed at 900 °C.

The typical XRD patterns of the Eu^{3+}-doped β-Ga_2O_3 nanofibers with different doped concentration (1, 2, and 5 mol%) annealed at 900 °C are shown in Fig. 3. All the diffraction peaks in the pattern were indexed to β-Ga_2O_3 structure (JCPDS 41-1103). The increase of intensity and the decrease of full width at half minimum (FWHM) of the diffraction peak with decreasing of doped concentration indicate that the crystallinity of the nanofibers is improved after low doped concentration. The lattice constants derived from the peak positions were $a = 12.227$, $b = 3.308$, $c = 5.807$ Å, $\alpha = 90°$, $\beta = 103.7°$, and $\gamma = 90°$. This manifests that the precursor samples have crystallized at 900 °C. The diffraction peaks of β-Ga_2O_3:Eu^{3+} nanofibers are shifted a little to lower angles with respect to the position of the standard card of β-Ga_2O_3 (JCPDS: 41-1103) pattern. This is because the Eu^{3+} ion is bigger than the Ga^{3+} ion in the β-Ga_2O_3 host lattice [$R(Ga^{3+}) = 0.062$ nm and $R(Eu^{3+}) = 0.0950$ nm]. However, the shift is very small due to the low doping concentration of Eu^{3+} ions. With the Eu^{3+} ions concentration increasing, no additional phase was found and diffraction peaks related to Eu^{3+} compound could not be detected in our experiments, indicating that the Eu^{3+} ions have been effectively built into the β-Ga_2O_3 host lattice.

The Raman spectrum of different concentration Eu^{3+} ions doped β-Ga_2O_3 nanofibers (0.5, 1, 2, 3 and 5 mol%) annealed at 900 °C is shown in Fig. 4. β-Ga_2O_3 has a monoclinic structure and belongs to the C_{2h} space group. Its unit cell contains two formula units-GaO_6 (edge sharing) octahedra and GaO_4 (corner sharing) tetrahedral, 15 Raman active modes are expected in its vibrational spectrum. The Raman-active modes of β-Ga_2O_3 can be classified into three groups: high-frequency stretching and bending of GaO_4 tetrahedra (~770–500 cm^{-1}), midfrequency deformation of Ga_2O_6 octahedra (~480–310 cm^{-1}), and low-frequency libration and translation (below 200 cm^{-1}) of tetrahedra–octahedra chains. The peak position of all the peaks is the same as that another reported work for β-Ga_2O_3 [20].

Firstly, the peaks are very sharp and narrow, indicating good crystallinity of the samples. Secondly, the spectrum is in agreement with the reported one for β-Ga_2O_3 nanomaterial, all the peaks have a redshift of about 6 cm^{-1}. Defect-induced effects and quantum confinement effects could cause Raman frequency shift [21]. From Fig. 4 we can see that the intensity Raman peaks decreases with the increased Eu^{3+} concentration because Eu^{3+} concentration inhibits the crystalline of β-Ga_2O_3:Eu^{3+} nanofibers. It is shown that there is no change of global structure for samples doped with different concentration of Eu^{3+} ions annealed at 900 °C. This result is consistent with the XRD patterns.

Fig. 5 shows the emission spectra of different concentration Eu^{3+} ions doped β-Ga_2O_3 nanofibers (0.5, 1, 2, 3 and 5 mol%) annealed at 900 °C. The nanofibers are excited by 325 nm He–Cd laser. The red emission could be observed by naked eye. Four peaks at 598, 620, 665, and 704 nm are assigned to the intra-4*f* transition of $^5D_0 \rightarrow {}^7F_j$ ($j = 1, 2, 3, 4$) of Eu^{3+} ions, respectively. The integrated intensity of the $^5D_0 \rightarrow {}^7F_2$ transition as a function of Eu^{3+} ions doping concentrations is shown in Fig. 6. It can be found from Fig. 5 that the red emission (620 nm) intensity increases with the increasing Eu^{3+} concentration at first, It reaches a maximum value at 3 mol%, and then decreases with the increasing Eu^{3+} content due to the concentration quench effect [22]. At Eu^{3+} concentration of 3 mol%, the Eu–O–Ga bonds may be saturated, and with the increasing of Eu^{3+} content, the spatial separation between Eu^{3+} ions becomes smaller and the cross-relaxation rate gets higher. Therefore, the red emission intensity decreases at higher Eu^{3+} content.

In nanostructured β-Ga_2O_3:Eu^{3+}, the resonant energy transfer is hindered by numerous particle boundaries. Thus, luminescence quenching point and emission intensity of β-Ga_2O_3:Eu^{3+} nanofibers are enhanced in comparison with the bulk [23]. The β-Ga_2O_3 contains two kinds of Ga^{3+} ions in equal quantity, one