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Rapid synthesis and luminescence of the Eu^{3+}, Er^{3+} codoped ZnO quantum-dot chain via chemical precipitation method

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ABSTRACT

ZnO quantum-dot chains codoped with Eu^{3+} and Er^{3+} were synthesized by the chemical precipitation method and the codoping effects on the structures, morphologies and optical properties of the powders were briefly investigated. The X-ray diffraction (XRD) and energy dispersive spectroscopy (EDS) results indicated the Eu^{3+} and Er^{3+} were incorporated into the crystal lattice of ZnO host. Transmission electron microscope (TEM) measurements showed the sizes of the ZnO quantum dots decreased with the increase of Eu^{3+} and Er^{3+} doping concentration, and the quantum-dot chains were formed by codoping with Eu^{3+} and Er^{3+}. The green emissions in the photoluminescence spectra were attributed to 4f–4f of Er^{3+} inner shell $^2H_{11/2} \rightarrow {}^4I_{15/2}$ and $^4S_{3/2} \rightarrow {}^4I_{15/2}$ transitions, and the characteristic red emissions of Eu^{3+} ions were attributed to the $^5D_0 \rightarrow {}^7F_1$ and $^5D_0 \rightarrow {}^7F_2$ transitions, respectively. Moreover, the red emission of the Eu^{3+} ions gradually decreased with the Er^{3+} ions doping concentration increased, which may be due to the different energy storage centers in the powders.

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1. Introduction

Recently, rare-earth (RE) ion doped semiconductors attract the investigation due to their unique optical properties and promising applications in optoelectronic devices [1–5]. Zinc oxide (ZnO) with a wide band-gap energy (3.37 eV) at room temperature turns out to be one of the potential candidates as the suitable host materials for doping transition metal ions, since it is optically and magnetically active [6–12]. RE-doped nanocrystals exhibit the highly efficient luminescence even at room temperature so that they have been widely applied into the integrated optoelectronic devices, such as visible (blue, green, and red) and infrared luminescent devices [2,13]. Normally, the optical properties of RE-doped nanocrystals are related with the RE^{3+} electronic structure, which mainly depends on the direct and indirect optical transitions between 4f intrashell energy levels. Among the RE^{3+} ions, Eu^{3+} ion is a representative dopant, and the red emission of Eu^{3+} ion is intensively studied and widely used in light-emitting devices [14–17]. The Er^{3+} ion is also an ideal candidate since its metastable levels $^4I_{9/2}$ and $^4I_{11/2}$ can be conveniently populated by the commercial low-cost near-infrared laser diodes [18]. Up to now, RE-doped ZnO nanostructures including nanowires, nanoparticles, nanobelts, nanoneedles and nanorods [19–23] have been prepared by different synthesis routes, such as vapor deposition method, thermal evaporation method, spray pyrolysis method and sol–gel method [3,24–26]. Most of RE-doped ZnO nanostructures exhibit a quite versatile mixed color emission.

In this paper, we explore a simple chemical precipitation method to prepare the Eu^{3+}, Er^{3+} codoped ZnO quantum-dot chains and control the crystallization of samples successfully. Moreover, the optical properties of the as-synthesized Eu^{3+}, Er^{3+} codoped ZnO quantum-dot chains are also investigated in detail.

2. Experimental

Pure ZnO and $Zn_{0.96-x}Eu_{0.04}Er_xO$ powders ($x = 0$, 0.01 and 0.02) were prepared by the chemical precipitation method. In the experiment, all chemicals were analytical reagent grade and used without further purification. The experiment process can be described

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briefly as follows. First, $Zn(NO_3)_2{\cdot}6H_2O$ and appropriated amounts of $Eu(NO_3)_3$ and $Er(NO_3)_3$ were dissolved in deionized water to form the mixture solution. Second, the solution of NH_4HCO_3 was added into the solution, and then the white precipitations formed gradually. After 4 h reaction, the filtered white precipitations in the solution were washed with alcohol for several times and then dried in the oven at 50–60 °C for several hours. Finally, the final product was annealed at 400 °C for 2 h in air atmosphere.

XRD (MAC Science, MXP16, Japan), TEM (JEM-2100HR, Japan), EDS (200 keV, JEM-2100HR, Japan) and PL (He–Cd Laser, 325 nm) were used to characterize the crystal structures, morphologies, chemical composition and optical properties of the Eu^{3+}, Er^{3+} codoped ZnO quantum-dot chains. EDS measurement has been carried out at a number of locations throughout the samples.

3. Results and discussion

Fig. 1 shows the XRD patterns of pure ZnO and $Zn_{0.96-x}Eu_{0.04}Er_xO$ powders ($x = 0$, 0.01 and 0.02). The diffraction peaks can be indexed to wurtzite-type ZnO structure for all the samples, and

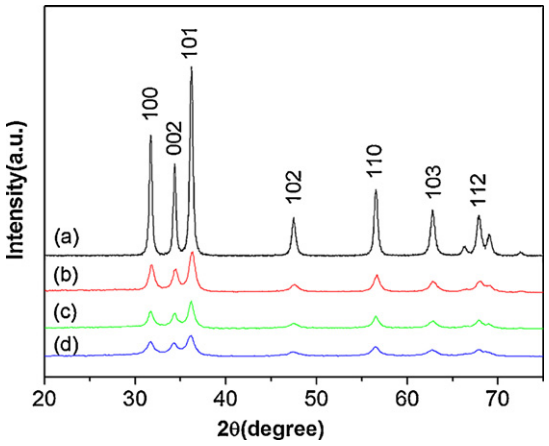

Fig. 1. XRD patterns of pure ZnO (a) and $ZnO_{0.96-x}Eu_{0.04}Er_x$ powders (b) $x = 0$, (c) $x = 0.01$, (d) $x = 0.02$.

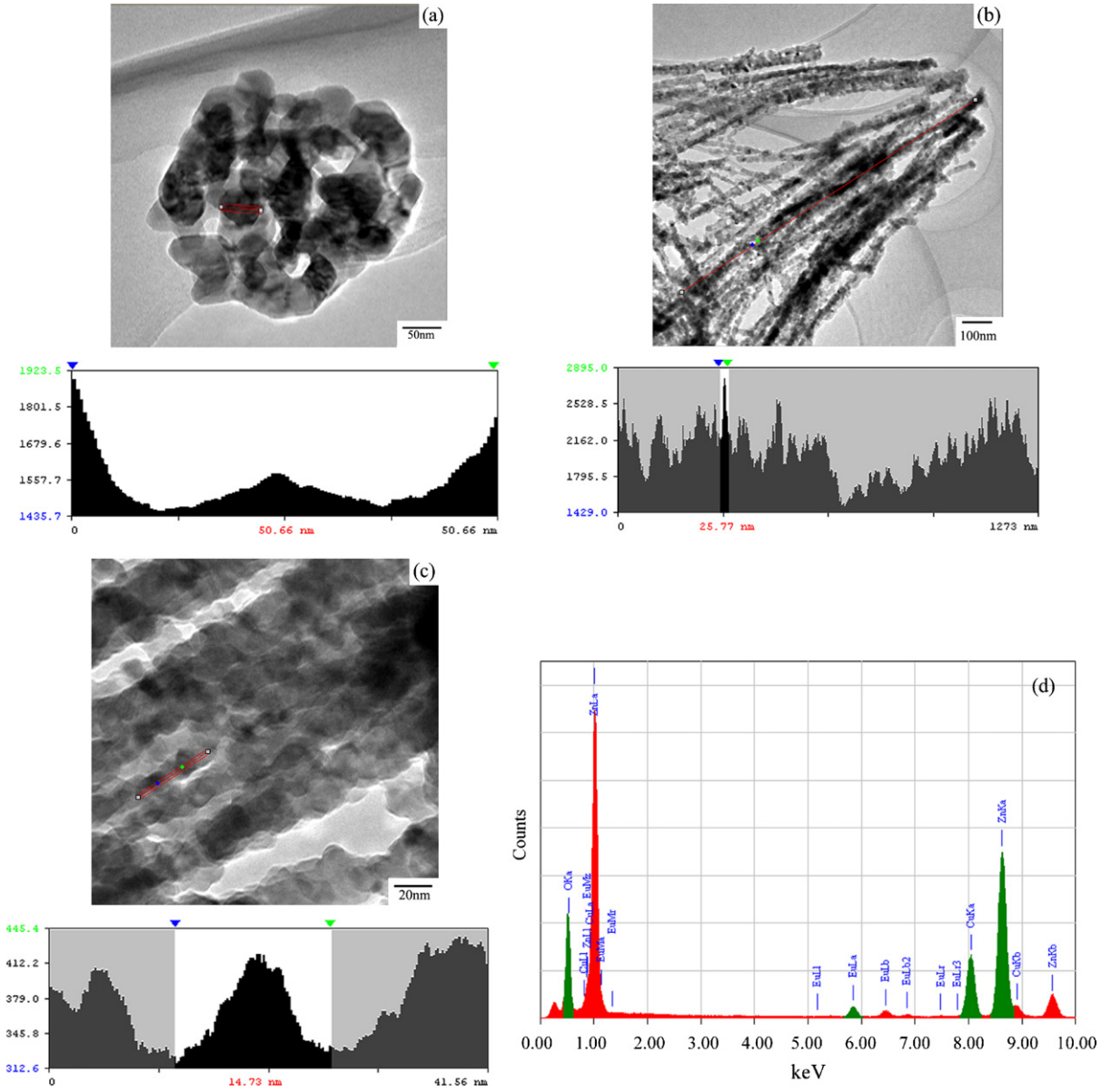

Fig. 2. TEM images of samples (a) ZnO, (b) $Zn_{0.96}Eu_{0.04}O$, (c) $Zn_{0.94}Eu_{0.04}Er_{0.02}O$, and (d) EDS of $Zn_{0.94}Eu_{0.04}Er_{0.02}O$.

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