Optical properties of Eu^{3+}, Dy^{3+} co-doped ZnO nanocrystals*

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ZnO nanocrystals doped with trivalent europium ions (Eu^{3+}) and dysprosium ions (Dy^{3+}) were synthesized by the precipitation method. The structural and optical properties of the samples are investigated by the X-ray diffraction (XRD) and photoluminescence (PL). The results show that rare earth ions are incorporated into the lattice of ZnO, and the combination of blue, green and red emissions can be obtained. Specially, the emission can be obtained even under the nonresonant excitation of 320 nm, which is explained based on the energy transfer. The concentration quenching mechanism is also presented in this paper.

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In recent years, semiconductor luminescent materials have attracted much attention and a variety of strategies have been explored to optimize the luminescence properties[1-3]. Among these semiconductors, zinc oxide (ZnO) has become a suitable host material to dope different kinds of dopants[4-6]. Selective elements doping in semiconductors can offer an effective way to adjust their electrical, optical and magnetic properties, and rare earth is one of the promising materials due to the abundant energy levels and temperature-independent luminescence in the infrared/visible range[7,8]. In recent years, various methods have been used to prepare rare earth doped ZnO, for example, solid-phase reaction method, sol-gel method, hydrothermal method, electro-deposition and pulsed laser deposition[9-13]. Rare earth doped semiconductors have been widely used in the optoelectronic devices, such as field emission, photocatalysis, phosphor and flat panel display. The doping of rare earth in ZnO can not only enrich the color of light, but also has the important value on basic research in optoelectronic materials and devices.

In this work, Eu^{3+} and Dy^{3+} co-doped ZnO nanocrystals were synthesized by a simple precipitation method. The structure and luminescence properties of ZnO:Eu^{3+}, Dy^{3+} nanocrystals are observed. The energy transfer between the ZnO and Eu^{3+}, Dy^{3+}, and the concentration quenching mechanism are studied.

4.435 g $Zn(OOCCH_3)_2{\cdot}2H_2O$ was dissolved in the mixture solution (37.5 mL ethanol and 25 mL deionization water). 0.0705 g europium oxide was dissolved in nitric acid. The two solutions were mixed to form the mole ratios of Zn^{2+} to Eu^{3+} (or Dy^{3+}) at 1:0.005, 1:0.02, 1:0.04 and 1:0.06, respectively, and the mole ratio of Eu^{3+} to Dy^{3+} is 1:1. Then the solution was stirred for 20 min under 30 °C. The sodium acetate was gradually added to the above solution until pH of the solution is about 6, and then the 0.5 mL acetoxyacetone was added to act as surface active agent. With the addition of 1.715 g sodium hydroxide, the solution turned into a white suspension. The white precipitation was obtained by drying in oven at 90 °C. Finally, the precipitation was calcined in furnace at 150 °C for 1 h.

The structure of the samples is investigated by X-ray diffraction (XRD) using a D8 ADVANCE with CuKα at λ=0.15406 nm. The PL spectra are measured using the FLS920 fluorescent spectrometer made by Edinburgh Instruments with an Xe lamp as the excitation source. All of these measurements are carried out at room temperature.

The typical XRD patterns of the as-obtained ZnO:Eu^{3+}, Dy^{3+} nanocrystals with different doping concentrations are shown in Fig.1. The observed main diffraction peaks can be indexed to ZnO with hexagonal wurtzite structure (JCPDS No.36-1451). The diffraction peaks related to Eu_2O_3 and Dy_2O_3 cannot be observed. It indicates that the Eu^{3+} and Dy^{3+} have been incorporated into the lattice of ZnO. The average size of the nanocrystals calculated by the Scherrer formula ($d = k\lambda/\beta\cos\theta$) from XRD peaks is about 35 nm.

The photoluminescence excitation (PLE) spectra of ZnO: Eu^{3+}, Dy^{3+} with a doping concentration of 2% are shown in Fig.2. Fig.2(a) is the PLE spectrum of Dy^{3+}

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monitored at 575 nm. The excitation peaks of Dy^{3+} ions located at 425 nm, 450 nm and 468 nm are observed in the samples. The PLE spectrum of Eu^{3+} ions monitored at 611 nm is shown in Fig.2(b), and the excitation peaks are located at 394 nm, 464 nm and 537 nm, respectively.

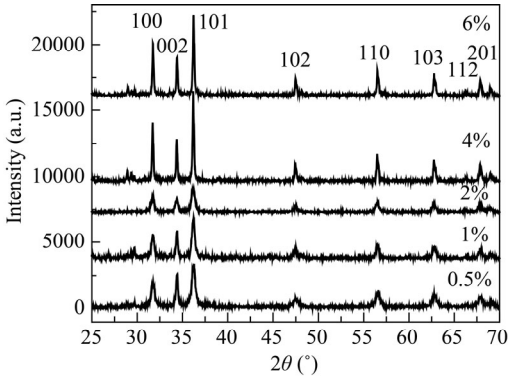

Fig.1 XRD patterns of ZnO:Eu^{3+}, Dy^{3+} nanocrystals with different doping concentrations

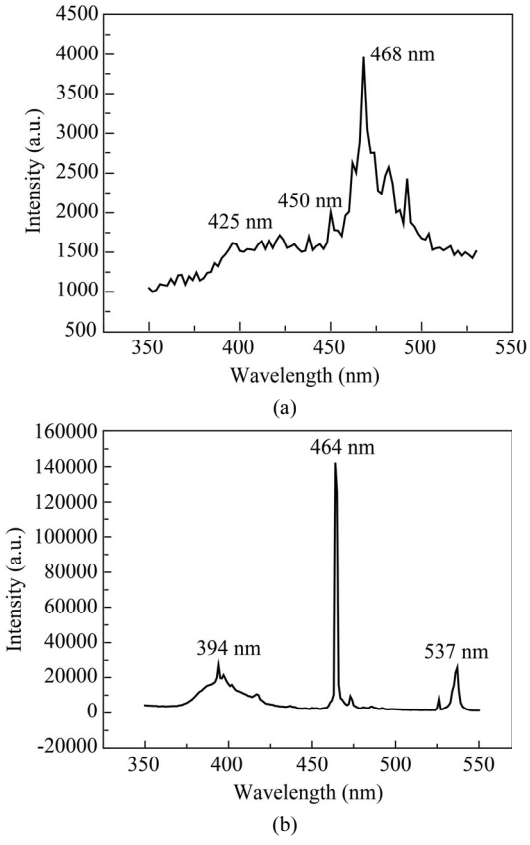

Fig.2 PLE spectra of ZnO: Eu^{3+}, Dy^{3+} nanocrystals with a doping concentration of 2% monitored at (a) 575 nm and (b) 611 nm

The PL spectra of ZnO: Eu^{3+}, Dy^{3+} nanocrystals with the excitation wavelengths of 394 nm, 464 nm and 425 nm are shown in Fig.3. The 394 nm and 464 nm, which are the excitation peaks of Eu^{3+}, can directly excite Eu^{3+} in ZnO: Eu^{3+}, Dy^{3+} (shown in Fig.3(a) and Fig.3(b), respectively). The emission peak 611 nm is a characteristic peak of the Eu^{3+} red emission, which is from Eu^{3+} transitions from the lowest excited state $^5D_0$ to the ground state $^7F_2$. Moreover, the weak emission 593 nm of Eu^{3+}, which is from $^5D_0$ to $^7F_1$, is detected too. The emission 483 nm of Dy^{3+} is also observed under the excitation of 425 nm which is the excitation peak of Dy^{3+} (shown in Fig.3(c)). The peak at 483 nm corresponds to $^4F_{9/2}$-$^6H_{15/2}$ transition of the Dy^{3+} ion.

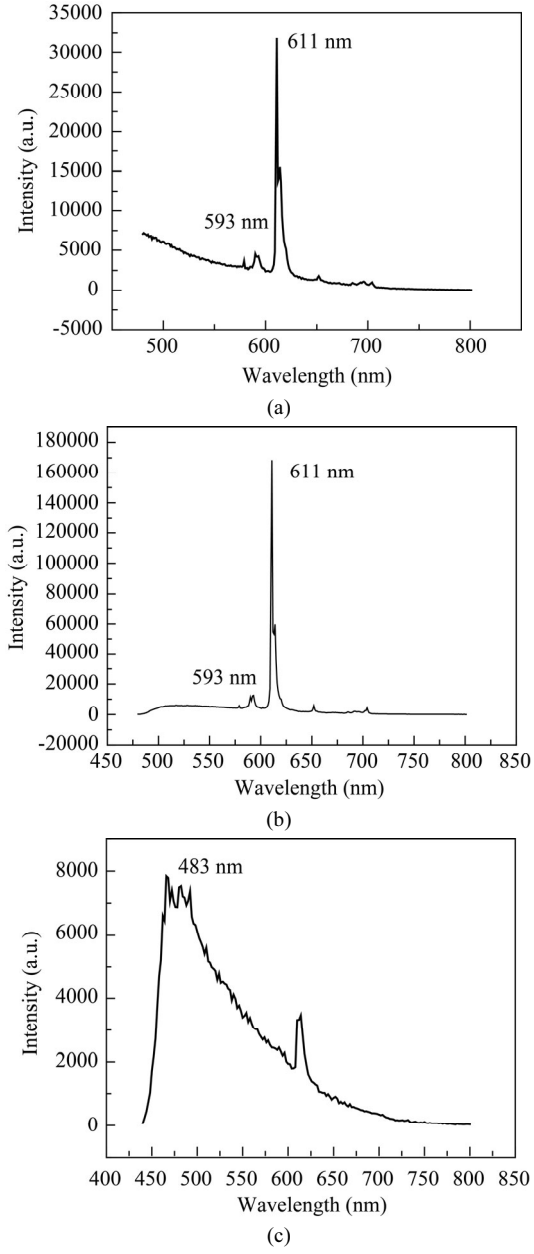

Fig.3 PL spectra for ZnO: Eu^{3+}, Dy^{3+} nanocrystals with excitation wavelengths of (a) 394 nm, (b) 464 nm and (c) 425 nm

The PL spectrum of ZnO: Eu^{3+}, Dy^{3+} nanocrystals with an excitation wavelength of 320 nm is measured, as shown in Fig.4. It can be seen that the 483 nm and 575 nm, which are from the transitions of $^4F_{9/2}$-$^6H_{15/2}$ and $^4F_{9/2}$-$^6H_{13/2}$ of Dy^{3+}, respectively, are observed. Besides, the emissions of 394 nm, 458 nm, 593 nm and 611 nm of Eu^{3+} are obtained. The 320 nm is not in resonance with

any transition of Eu^{3+} and Dy^{3+}. So the effective energy transfer from ZnO to Eu^{3+} and Dy^{3+} occurs in the samples.

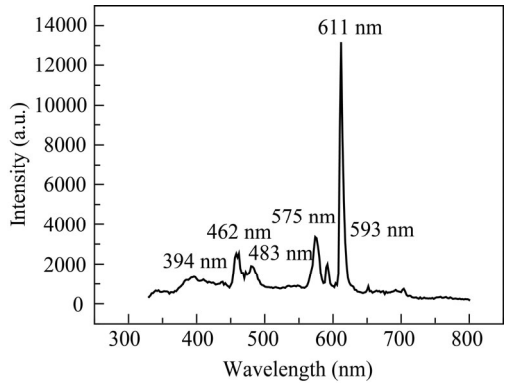

Fig.4 PL spectrum for ZnO: Eu^{3+}, Dy^{3+} nanocrystals with excitation wavelength of 320 nm

The mechanism of energy transfer behavior in the ZnO: Eu^{3+}, Dy^{3+} nanocrystals is shown in Fig.5. ZnO is excited by incident light and electron-hole pairs are generated. The generated electrons are then trapped by the defect states. As the matching of ZnO defect state energy levels and Eu^{3+}, Dy^{3+} energy levels, the Förster energy transfer occurs between the ZnO and the nearby Eu^{3+}, Dy^{3+} ions, which cause the characteristic emissions of Eu^{3+}, Dy^{3+} ions.

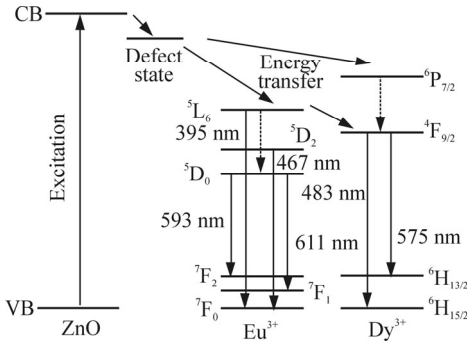

Fig.5 Schematic diagram of energy transfer process between ZnO nanoparticles and Eu^{3+}, Dy^{3+} ions

The PL spectra for ZnO: Eu^{3+}, Dy^{3+} with different concentrations are shown in Fig.6. It is found that the PL intensity of Eu^{3+} increases following the increased Eu^{3+} concentration, and then the intensity decreases at the concentration of 2%. In the range of increasing section, the increased luminescent centers make the emission intensity increased. The decreased intensity with increased concentration is ascribed to the concentration quenching. The concentration quenching of Eu^{3+} can be understood by the reduction of the energy transfer due to the nonradiation processes in ZnO and back-transfer from the excited rare earth to the host ZnO[14,15]. The increased Dy^{3+} emission from concentration 0.5% to 2% results from the energy transfer from Eu^{3+} to Dy^{3+}.

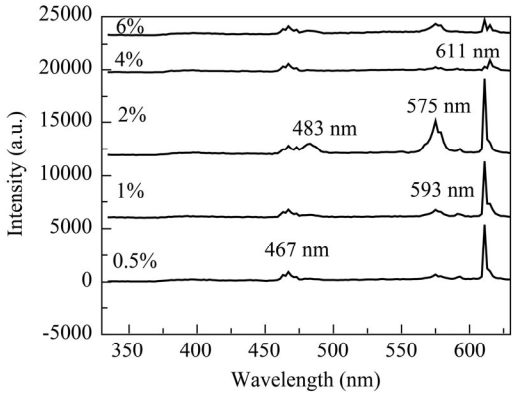

Fig.6 PL spectra for ZnO: Eu^{3+}, Dy^{3+} nanocrystals doped with different concentrations with excitation wavelength of 320 nm

In this paper, the ZnO: Eu^{3+}, Dy^{3+} nanocrystals have been successfully synthesized. A combination of blue, green and red emissions is obtained under nonresonant excitation of 320 nm, and the effective energy transfer occurs in the sample. Under the excitation of 320 nm, the decreased intensity can be explained by both the nonradiation processes and the energy back-transfer.

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