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# The doping site analysis and control of $Eu^{3+}$ in ZnO:Eu crystal lattice

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ABSTRACT

A new effective and convenient method is put forward to accurately analyze and control the doping sites of $Eu^{3+}$ in ZnO:Eu nanocrystal. By analyzing the drift of XRD peaks, the splits of laser-stimulated fluorescence peak, intensity variation of $E_2$ Raman scattering peaks and lattice distortion from HRTEM, the position that $Eu^{3+}$ ions occupy in host lattice is accurately analyzed. There generally exists the symmetry broken regularity for disordered doped system such as ZnO:Eu — it is that $Eu^{3+}$ is inclined to occupy the position with low symmetry for equilibrium growth crystal. At high annealing temperature, the crystallographic symmetry of $Eu^{3+}$ is reduced from $C_{3v}$ to $C_2$, which fully evidences that $Eu^{3+}$ ions are separated out of host lattice. In the same time, the doping position of the Eu can be completely controlled by controlling annealing temperature. In the low symmetrical crystal field, 612 nm fluorescence peak splits to 4 splits, and the peak width of the strongest one is only about 4 nm. This nanomaterial with extremely narrow luminescence will have intensively potential applications in the fields of high quality light source with high contrast control and high signal to noise ratio such as fluorescence probe in high resolution bioimaging.

## 1. Introduction

For a long time, there are some basic problems lacking of convenient site analysis and characterization techniques, such as whether rare earth (RE) ions enter into the host lattice, and where RE ions occupy [1]. It is urgent to put forward a new effective method to accurately analyze the position of RE ions. In 2013, it was confirmed through the low temperature high resolution fluorescence spectrum [2] that $Eu^{3+}$ spectroscopic symmetry was reduced from $O_h$ crystallographic position to $C_s$ (or $C_2$) in the cubic phase of $NaYF_4$. While in the hexagonal phases of $NaYF_4$, it was reduced from $C_{3h}$ to $C_s$. Similarly, in 2017, by corrected spectral sensitivity system and detector, it is found that for $La_2Hf_2O_7$:Eu and $Gd_2Hf_2O_7$:Eu nanoparticles, the symmetry of crystallographic position of $Eu^{3+}$ ions occupied reduces as lattice deforms resulting from the difference in ion radius [3]. Nevertheless, these position analysis methods need either low temperature detection or very sophisticated equipment. Until now, it is still lacking of convenient and effective methods to analyze the position that RE occupied [4].

A new effective and convenient method is put forward to accurately analyze the position that RE ions incorporated in for $Eu^{3+}$ doped ZnO nanocrystal in this article. By analyzing the drift of XRD peaks, the splits of laser-stimulated fluorescence peak, intensity variation of $E_2$ Raman scattering peaks and lattice distortion from HRTEM, the position that $Eu^{3+}$ ions occupy in ZnO lattice is accurately analyzed. These room temperature characterization methods greatly promote the development of analysis technique of doping position. On the other hand, by compare our results and other literatures [2,3], the generally existent symmetry broken regularity is found for disordered doped system. For equilibrium growth of doped ZnO, $Eu^{3+}$ is inclined to occupy the position with low symmetry [5]. In this article, at high annealing temperature, the crystallographic symmetry that $Eu^{3+}$ occupied is reduced from $C_{3v}$ to $C_2$, which fully evidences that $Eu^{3+}$ ions are separated out of host lattice. Thus, the doping position of Eu in host lattice can be completely controlled. The break of the local symmetry around $Eu^{3+}$ ion could facilitate intra-4 f shell transitions, which can obviously improve the emission intensity of $Eu^{3+}$ doped ZnO [6]. On the other hand, in the $C_2$ symmetrical crystal field, 612 nm fluorescence peak of $Eu^{3+}$ splits to 4 splits, and the peak width of the strongest one is only about 4 nm. Combined with optical filtering technique, this extremely narrow luminescence provide high contrast control and high signal to noise ratio high quality light source, which will have intensively potential applications in the fields of fluorescence probe in high resolution bioimaging [7–9].

## 2. Experimental

### 2.1. Sample preparations

To study doped nanocrystals with high crystal quality, ZnO:Eu

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nanoparticles were synthesized by a standard solvothermal method. Typically, zinc acetate (25 mmol), oxalic acid (25 mmol), europium nitrate (0.25 mmol) and alcohol (40 ml) were added into a beaker. After 10 min stirring, the mixture was poured into a stainless steel, Teflon-lined autoclave. The stainless-steel autoclave was sealed and then kept at 80 °C for 2 h. After the solvothermal reactions were completed, the white precipitates were taken out; washed repeatedly and dried at 60 °C for 1 h. Finally, white powders were put into a muffle furnace. The furnace temperature was increased to 450 °C and then kept for 2 h. The annealing temperature can be adjusted to 550 °C and 700 °C, respectively.

### 2.2. Characterizations

The as-grown sample was examined by X-ray powder diffraction (XRD) measurements on Bruker D8 Advance diffractometer (Cu Kα). The morphology, size, chemical composition and crystal structure were characterized by low-resolution transmission electron microscopy (TEM), scanning transmission electron microscopic-energy dispersive spectrometry (STEM-XEDS) and high-resolution TEM (HRTEM) on Tecnai G2 F20 S-TWIN with the operation voltage at 200 kV. The Reduced Fast Fourier Transform (RFFT) was obtained by use of the Gatan Microscopy Suite (GMS) software. The software was also employed to measure the interplanar spacing on HRTEM images and RFFT patterns. Both the laser-stimulated site-analysis luminescence spectra and Raman spectra were recorded on the VERTEX Senterra Raman Microscope under room temperature with excitation wavelength of 532 ± 1 nm. But the excitation power is different: incident laser power of 0.2 mW was employed for luminescence spectra while 5 mW was adopted for Raman spectra.

## 3. Results and discussion

### 3.1. Characterization of composition and morphology of ZnO:Eu nanoparticles

Fig. 1(a) show a typical TEM image of $ZnO:Eu_{0.03}$ nanocrystal

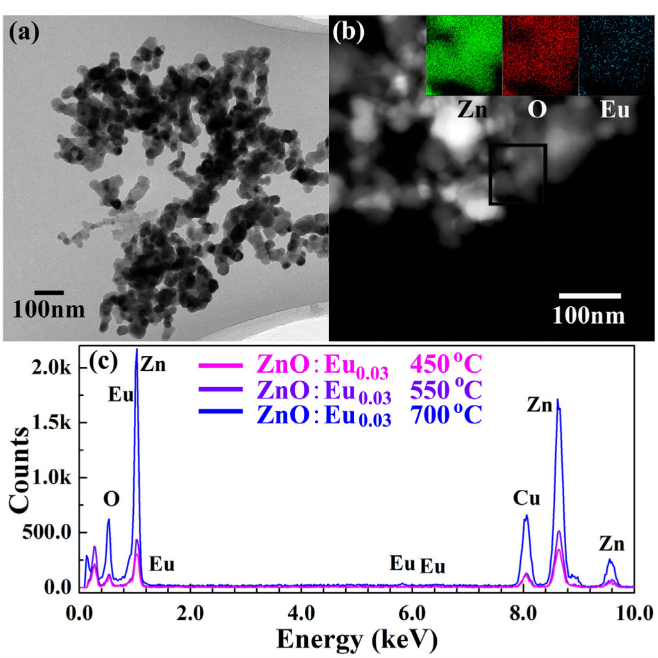


**Fig. 1.** The typical TEM (a) and STEM-HAADF (b) of as-prepared $ZnO:Eu_{0.03}$ annealed at the temperature of 550 °C. (c) The XEDS spectra of $ZnO:Eu_{0.03}$ annealed at different temperature. The insert of Fig. 1(b) is the 2D element mapping from the area in black frame.

annealed at 550 °C. Irregularly spherical nanoparticles with relatively uniform size are observed with the diameter of 24–70 nm. The typical scanning transmission electron microscopy (STEM) image shown in Fig. 1(b) further confirms the diameter of ZnO:Eu is smaller than 100 nm. The respective two-dimensional (2D) element mapping in the insert of Fig. 2(b) indicates that three elements of Zn, Eu, and O are uniformly distributed in nanoparticle. No isolated $Eu_2O_3$ particles are found along with ZnO:Eu nanocrystals.

The X-ray energy dispersive spectra (XEDS) in Fig. 1(c) further indicates that nanoparticles are mainly composed of Zn, Eu, and O three elements. The TEM, STEM, element mapping and XEDS fully conform that ZnO:Eu nanoparticles are synthesized.

XRD patterns of $ZnO:Eu_x$ (where x = 0, 0.01, 0.02, 0.03) with different annealing temperature are shown in Fig. 2(a). Eight strong peaks appearing at about 31.7°, 34.4°, 36.9°, 47.5°, 56.6°, 62.9°, 68.0°, 69.0° for all samples confirm that the dominant component is ZnO. Strong XRD diffraction peaks show that the crystallinity of all the doped and undoped samples is not obviously decrease. Enlarged XRD patterns of all samples are shown in Fig. 2(b). For Eu doped ZnO annealing at 550 °C and 700 °C, there is one diffraction peak appearing at about 28.4°, which cannot be described as any diffraction peak of ZnO. It is consistent well with the (222) diffraction peak of $Eu_2O_3$. It indicates that annealing at higher temperature promote separation of $Eu^{3+}$ ions out of ZnO lattice. The intensity ratio of $Eu_2O_3$ (222) to the strongest peak of ZnO is shown in Fig. 2(c). When annealing at 450 °C, the very low intensity ratio indicate that the majority of $Eu^{3+}$ should enter into ZnO lattice. This low intensity ratio can be attributed to noise. After annealing at 550 °C or 700 °C, intensity ratio increases greatly. It indicates that many $Eu^{3+}$ ions should separate out of ZnO lattice. According to Bragg formula, $2d\sin\theta = \lambda$, we can get:

$$2\Delta d\sin\theta + 2d\cos\theta\Delta\theta = 0$$

by differential equations. Then

$$\Delta d/d = -\cot\theta\Delta\theta$$

can be obtained.

Thus, relative lattice distortion rate can be obtained by position and shift of diffraction peaks, which is shown in Fig. 2(c). The calculation process of lattice distortion rate is shown in Table S1 in supplementary material. For the doped samples annealing at 450 °C, the relative lattice distortion rates are relative big. It indicates that after bigger $Eu^{3+}$ ions (The radius of $Eu^{3+}$ is 0.094 nm and the radius of $Zn^{2+}$ is 0.074 nm) enter into ZnO lattice, they lead to lattice expansion [4]. Similarly, for the doped samples annealing at 700 °C, the relative lattice distortion rate is still bigger than zero, but decreases. The decrease of lattice expansion implies that part of the $Eu^{3+}$ ions separate out of ZnO lattice. But for the doped samples annealing at 550 °C, the lattice expansion is much small and even lattice contraction is found. It reflects that the separation of $Eu^{3+}$ is a very complicated process.

### 3.2. The splits of laser stimulated fluorescence peaks

The laser stimulated fluorescence spectra with excitation wavelength of 532 ± 1 nm are used to analyze the position of $Eu^{3+}$ in ZnO:Eu lattice, which is shown in Fig. 3. According to Russell-Saunders coupling theory, the more emission peak splits, the lower symmetrical positions the luminescent center occupy. After doped samples were annealed under 450 °C, only two splits of $^5D_0 \rightarrow {}^7F_1$ transition [5] and three splits of $^5D_0 \rightarrow {}^7F_2$ transition [10] are observed. Small number of splits indicates that $Eu^{3+}$ ions occupy high symmetrical positions. Further study indicates that when $Eu^{3+}$ occupy $C_{3v}$ site, the number of splits of both $^5D_0 \rightarrow {}^7F_1$ and $^5D_0 \rightarrow {}^7F_2$ transitions is well agree with the observation [4–13]. It confirms that at 450 °C annealing temperature, the majority of $Eu^{3+}$ enters into ZnO lattice and substitute $Zn^{2+}$. Atomic configurations of $C_{3v}$, $C_2$ and $S_6$ sites are on the bottom of the Fig. 3. For the doped samples annealing at 700 °C, more splitting peaks