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Site selective excitation in La_2O_3:Eu^{3+} nanoparticles

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Abstract

Eu^{3+} is a favorite fluorescence probe for studying local structure in solids. In this report, Eu^{3+} ions in La_2O_3 nanoparticles were selectively excited; variation of the Eu emission spectra with the excitation wavelengths was observed.

It was found that emission spectrum of the Eu ions near the center of the nanocrystals was similar to that of the bulk, where the Eu ions locate at the C_{3v} symmetry site. By tuning the excitation wavelength, Eu ions in the vicinity of the particle surface may be selectively excited. A gradual variation in emission line positions was observed. Moreover, surface provided an additional non-radiative transition route for the rare-earth fluorescence, shortening the $^5D_0$ lifetime from 1.25 to 0.87 ms.

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1. Introduction

In recent years, luminescent nanomaterials have attracted great attentions. Due to quantum confinement effect and surface effect, nanosized materials may show electrical and optical properties different from the corresponding bulks. For rare-earth ions, however, where the average radius of the 4f wave function is about 0.1 nm, much smaller than the particle size, quantum confinement effect could not affect the energy levels and radiative transition rates significantly. Surface effect, instead, plays the most important role in determining its spectroscopic properties. The surface of the nanocrystals diversified the local environments of the dopant ions, leads to broadening the inhomogeneous linewidth, shifting the spectral lines and splitting some originally degenerate energy levels, and thus results in the spectrum different from bulk materials. On the other hand, rare-earth ions can be used as a probe for investigating the surface effect in nanocrystals. In this report, we employed site-selective excitation to probe the local environments of Eu^{3+} ions in La_2O_3 nanoparticles.

In bulk La_2O_3, doped Eu^{3+} ions substitute La^{3+} at C_{3V} symmetry site. Emission spectrum of the Eu^{3+} ions near the center of the nanocrystals is similar to that of the bulk. On the contrary, the emission spectrum of the Eu ions in the vicinity of the particle surface may be different from that of the bulk due to the degeneration of the local symmetry [1–3].

2. Experimental

La_2O_3:Eu^{3+} nanoparticles were prepared by combustion synthesis. The details of sample preparation were described in Ref. [4]. Concentration quenching of the $^5D_0$ fluorescence in La_2O_3:Eu nanocrystals was observed as the Eu molar concentration reaches above 5%. In this work, 3% concentration was chosen to avoid concentration quench. The particle size was distributed within the range of 9–22 nm, determined by transmission electronic microscopy (TEM) and X-ray diffraction (XRD). The spectra were measured with a spectrometer (Spex 1403), either the

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fourth harmonic of a YAG laser or an OPO was used as the excitation source.

3. Results and discussions

The excitation spectrum of La_2O_3:Eu^{3+} is composed of a charge transfer band peaked at 290 nm, and several $^7F_{0,1}\rightarrow{}^5D_J$ lines within 350–580 nm. In this work the charge transfer transition was used for nonselective excitation while the $^7F_{0,1}\rightarrow{}^5D_2$ at about 460 nm was used for selective excitation.

Emission spectra of Eu^{3+} under 266 and 466.5 nm excitations are shown in Fig. 1. The emission spectrum excited with 466.5 nm is the same as that of bulk sample. The $^5D_0$–$^7F_2$ transitions is with 3 lines peaked at 615, 620 and 627.6 nm. Except the spectral lines same as 466.5 nm excitation, new emission lines at 613.0 and 625.3 nm emerged in the emission spectrum excited with 266 nm.

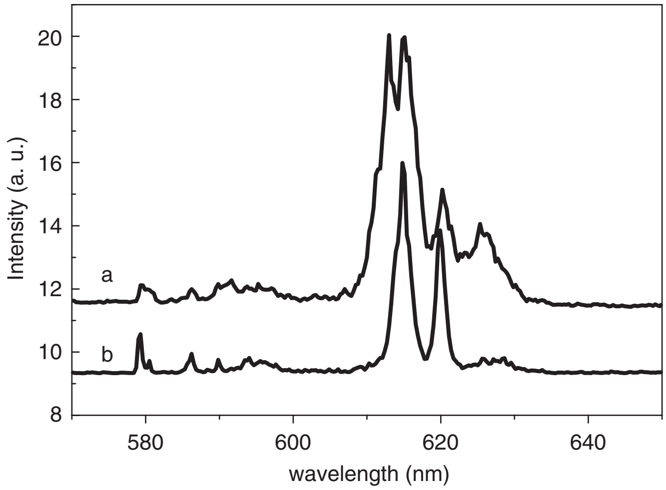

Fig. 1. Emission spectra of 11.2 nm La_2O_3:Eu^{3+} (3%) under (a) 266 nm and (b) 466.5 nm excitation.

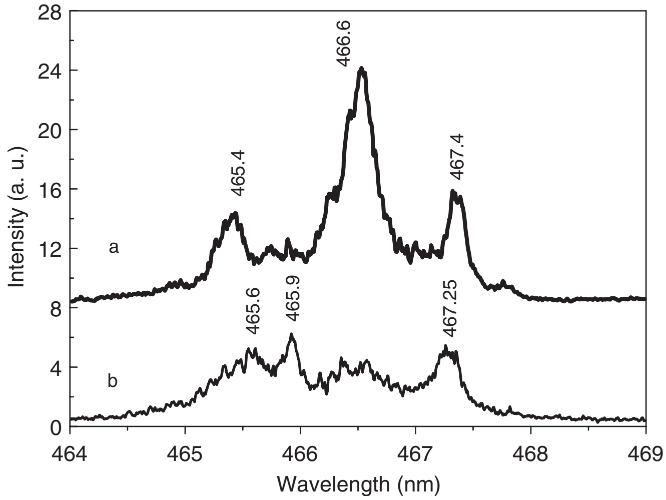

Fig. 2. Excitation spectra of La_2O_3:Eu^{3+} (3%) monitored at (a) 615 nm and (b) 613.5 nm.

The excitation spectrum monitored at 615 nm (Fig. 2a) consists of three peaks at 465.4, 466.5, 467.4 nm. Since the excitation to these peaks results in emission spectrum similar to bulk materials, we attribute the excitation spectrum of Fig. 2a and the emission spectrum of Fig. 1b to the Eu^{3+} ions located at the sites close to the center of the nanoparticles. Fig. 2b is the excitation spectrum monitored at 613.5 nm. We also noticed that there are additional lines peaked at 465.6, 465.9 and 467.25 nm.

The spectrum monitored at 615 nm origins from the Eu^{3+} ions at the interior sites with C_{3V} site symmetry, while the appearance of the additional lines was resulted from the changes of the local environment, which may be relevant to the Eu^{3+} sites in the vicinity of the surface of nanocrystals.

If this is true, as the monitoring wavelength in the excitation spectrum or the excitation wavelength in the emission spectrum changes, the spectrum would change accordingly. With the site occupied by Eu^{3+} ion varies from the center toward the surface of the nanocrystals, the micro-environment of the Eu^{3+} ion changed gradually. Continuous evolutions of the emission spectra would be observed. On the other hand, if the rare-earth ion can occupy different

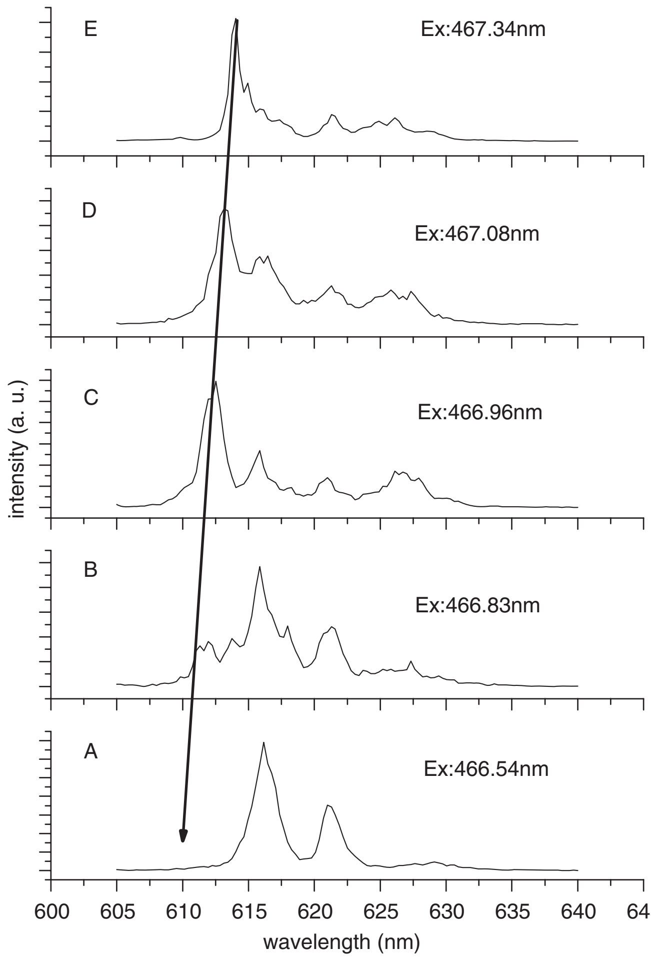

Fig. 3. $^5D_0\rightarrow{}^7F_0$ emission spectra excited by (A) 466.54 nm, (B) 466.83 nm, (C) 466.96 nm, (D) 467.08 nm and (E) 467.34 nm.

sites in the unit cell of the crystal or the sample is with multiphase, an abrupt variation should be observed. To clarify this question, we measured the emission spectra choosing five excitation wavelengths within 466.5–467.5 nm.

$^5D_0 \rightarrow {}^7F_2$ emission spectra excited by 466.54 (A), 466.83 (B), 466.96 (C), 467.08 (D) and 467.34 nm (E) are shown in Fig. 3. The spectrum A is similar to that of the bulk, which indicates that the luminescence centers located at C_{3V} symmetry site dominate the emission. As the laser turned from 466.54 to 467.34 nm, we did observe a gradual variation of the emission spectra.

Decay curves monitored at 613 and 615 nm were measured and the lifetimes derived from single exponential fitting were 865 and 1248 μs. The lifetime of Eu^{3+} ions at the particle surface would be shorter than that of the interior ions, because of dangling bonds, unsaturated bonds and defects increased the numbers of quenching centers at surface, thus shortening the lifetime [3,5,6]. Comparing two lifetimes further persuaded us that the 613 nm emission was related to the site closer to the surface.

4. Conclusion

We studied the luminescence spectra of nanocrystalline La_2O_3:Eu^{3+}. By tuning the excitation wavelength, Eu^{3+} ions located at the sites close to the center and near the surface of the nanocrystals can be selectively excited. A gradual variation in emission line positions with excitation wavelength can be observed. The $^5D_0$ lifetime decreased from 1.25 ms 0.87 ms for Eu^{3+} ions at the center to for that near the surface.

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