Spectral difference between nanocrystalline and bulk Y_2O_3:Eu^{3+}

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Abstract

In this Letter spectral difference between nanocrystalline yttria doped with europium (Y_2O_3:Eu^{3+}) and the bulk ones was reported. Besides a 580.6-nm line similar to that in the bulk Y_2O_3:Eu^{3+}, a new broad excitation line at 579.9 nm was observed in the nanocrystals (NCs). The lifetime of the 579.9-nm line became slightly shorter than that of the 580.6-nm line. The 579.9-nm line was attributed to the Eu^{3+} ions near the surface of the NCs. Due to numerous surface defects, the crystal field on the surface degenerated, leading the energy levels of the electrons in 4f state to shift.
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1. Introduction

Over the last decade, luminescent nanomaterials doped with rare earth ions have attracted great interest. Among them, nanocrystalline Y_2O_3:Eu^{3+} is being given much attention, not only because of its tremendous potential applications, but also because of basic science research. The bulk Y_2O_3:Eu^{3+} is an unsurpassed red emitting phosphor in fluorescence lamps and projection television tubes. It is expected that higher resolution for display and higher luminescent quantum efficiency could be obtained in Y_2O_3:Eu^{3+} NCs. On the other hand, Eu^{3+} ion is an activator to study local environments in nanomaterials. In the past, much work

was either performed on the preparation of Y_2O_3:Eu^{3+} NCs [1–3], or carried on the luminescent properties of nanosized Y_2O_3:Eu^{3+} [4–7]. As is well known, the ratio of surface to volume remarkably increases as the particle size decreases to nanometer. The local structure of surface Eu^{3+} ions should differ from those in volume and may lead to spectral changes. It is natural to expect that Eu^{3+} ions near the surface can be spectrally distinguished from the interior ions. Eilers and Tissue [8] observed broad and shifted bands superimposed by sharp lines in monoclinic nanocrystalline Eu_2O_3. The sharp lines were assigned to the crystalline Eu_2O_3 particles, and the broad ones to the disordered small particles. Now it has been reached in agreement in the broadening of spectral line in nanocrystals (NCs) [2,6]. However, the shift of line still need further study to understand the surface ions in NCs. In this Letter, we report the spectral

difference in excitation spectra between the Eu^{3+} ions near the surface and the interior ones in Y_2O_3:Eu^{3+} NCs.

2. Experimental

The crystalline Y_2O_3:Eu^{3+} powders were prepared by combustion synthesis. The details of sample preparation were described in [9]. The bulk- and nanocrystalline-Y_2O_3:Eu^{3+} were both cubic in symmetry, as confirmed by X-ray diffraction (XRD). The average sizes of the two nanocrystalline Y_2O_3:Eu^{3+} powders used in the present study are determined to be 20 and 5 nm by transition electronic microscopy (TEM) and XRD. The particle sizes of the bulk powders are determined to be $\sim$3 µm by field-emission scanning electron microscopy. Fig. 1 shows the TEM micrographs of the 20-nm and 5-nm powders.

A Rodamine 6 G dye laser pumped by a pulsed Nd^{3+}:YAG laser (with a repetition frequency of

(a) 20 nm

(b) 5 nm

Fig. 1. TEM micrograph of Y_2O_3:Eu^{3+} NCs: (a) 20 nm; (b) 5 nm.

10 Hz and a duration of 10 ns) was used as resonant excitation source. The powder samples were put onto the cold finger of a close cycled crystal, where the temperature can be varied from 10 to 300 K. The emission spectra and fluorescent decay dynamics were measured by a spectrometer (Spex 1403), a photomultiplier, a boxcar averager and processed by a computer.

3. Results and discussion

The emission and excitation spectra of crystalline Y_2O_3 : Eu^{3+} are drawn as Fig. 2a,b, respectively. In Fig. 2, the bulk, 20-nm and 5-nm crystalline Y_2O_3:Eu^{3+} are in turn labeled as sample A, B and C. The 611-nm peaks in Fig. 2a are the dominant $^5D_0 \rightarrow {}^7F_2$ emissions of Eu^{3+}. There seems to be no obvious difference between the nanocrystalline and bulk powders except the broadened line width of Eu^{3+} in NCs. In Fig. 2b, the excitation spectra were measured by monitoring the emission at 609 nm, the wing of the 611-nm peak. Besides the same narrower excitation peak as the bulk at 580.6 nm, corresponding to the $^7F_0 \rightarrow {}^5D_0$ transition, Y_2O_3:Eu^{3+} NCs have another broader excitation peak at 579.9 nm. As the particle size decreases from 20 to 5 nm, the relative intensity of the 579.9-nm excitation peak
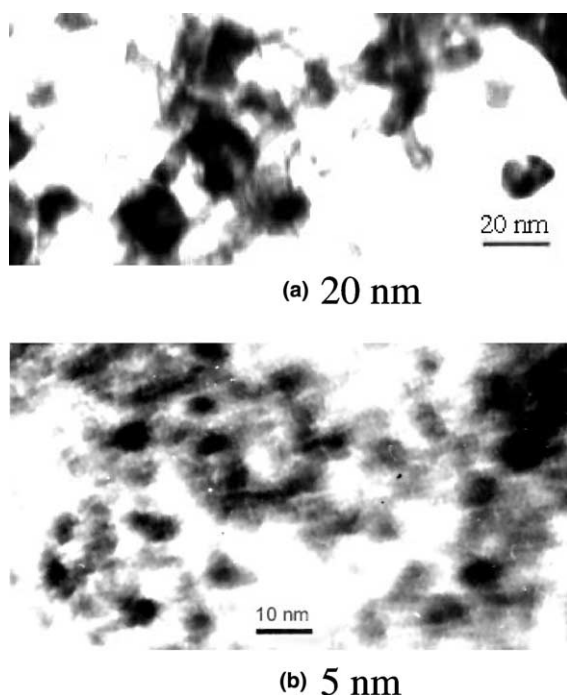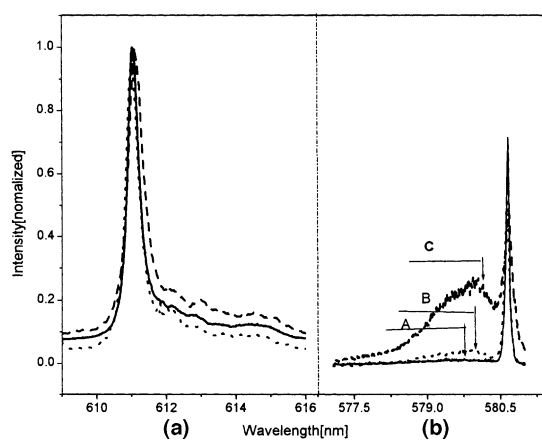

Fig. 2. Emission (a) and excitation spectra (b) of different Y_2O_3:Eu^{3+} powders at 10 K. The intensity was normalized. The spectra of samples A, B and C were drawn as solid, dot and dash lines, respectively.
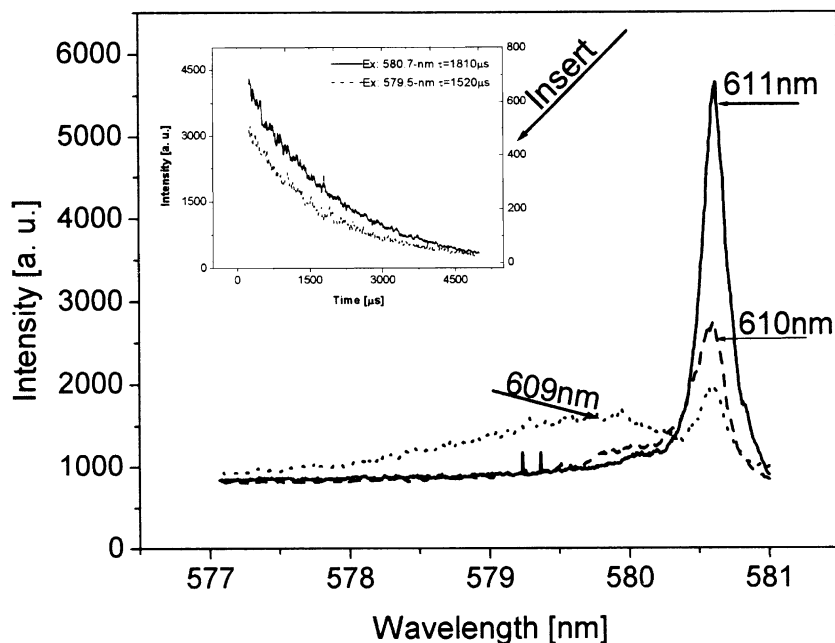
Fig. 3. Excitation spectra of the 5-nm Y_2O_3:Eu^{3+} NCs monitoring various sites at 10 K. The monitored wavelengths are shown as the arrows. The insert is the fluorescence decay curves of the emission at 611 nm under different excitation lights. The left y-axis corresponds to the decay curve under the 580.7-nm excitation, and the right y-axis to the 579.5-nm one.

becomes stronger in comparison with the 580.6-nm one.

The excitation spectra of the 5-nm Y_2O_3:Eu^{3+} NCs by monitoring different wavelengths are drawn as Fig. 3. It is obvious that as the monitored sites shift from peak to wing, the 579.9-nm excitation peak appears and its relative intensity becomes stronger. The insert shows the decay curves of the emission at 611 nm under the 580.7 and 579.5-nm excitation, respectively. It is clearly to see that the emission of Eu^{3+} under the 579.5-nm excitation decays faster than that under the 580.7-nm excitation. The corresponding lifetimes were determined by exponential fitting as 1520 and 1810 μs, respectively.

Fig. 4 shows the excitation spectra of Eu^{3+} in the 5-nm Y_2O_3:Eu^{3+} at various temperatures. We can see that the intensity of the 579.9-nm peak relative to the 580.6-nm one decreases a little as temperature increases, indicating that the 579.9-nm peak is not a phonon satellite. Otherwise, the relative intensity of 579.9-nm peak should become stronger as temperature increases.
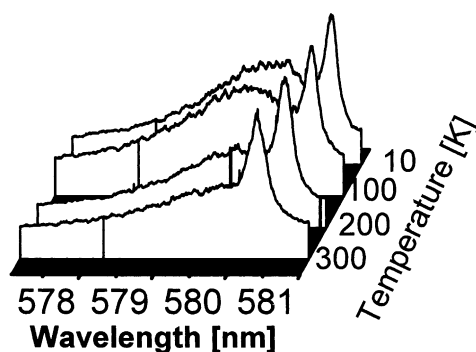

Fig. 4. Excitation spectra of the 5-nm Y_2O_3 : Eu^{3+} powders at various temperatures (monitored site: 609 nm). The intensity of the 580.6-nm peak is normalized.

Fig. 5 shows the excitation spectra before and after irradiation with different lights monitoring 609-nm light. It is clear to see that the increase of the relative intensity of the 579.9-nm line is prominent after irradiation with a 579.5-nm light, whereas the increase after irradiation with a 580.6-nm light is slight.
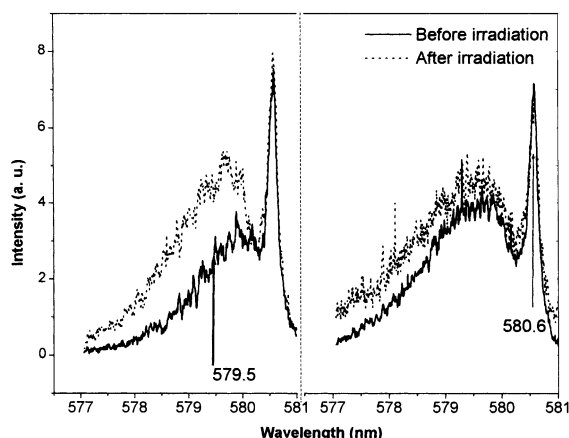
Fig. 5. Excitation spectra of the 5-nm Y_2O_3:Eu^{3+} NCs before and after irradiation. The sample is exposed to the lights for 15 min. The intensity of the 580.6-nm lines is normalized.

Different from Eilers and Tissue's hypothesis [8], we suggest that in our experiment the both two peaks originate from the same Y_2O_3:Eu^{3+} particle, that is, the broader 579.9-nm excitation peak from the luminescence of Eu^{3+} ions near the surface, and the 580.6-nm one from the interior Eu^{3+} ions. The surface to volume ratio is quite small (1%) in the micrometer particles, whereas it increases significantly as the particle size decreases to several nanometers. This will lead the surface effects to be effective. Igarashi et al. [10] reported that the lattice distortion of the NCs was seven times larger than that of the micrometer particles. Lattice distortion may lead to the decrease of the site symmetry and the degeneration of the crystal field. As well known, the energies of electrons in 4f states of rare earth ions are affected by the crystal field. In nanocrystalline, rare earth ions near the particle surface are at the sites microscopically inequivalent with those close to the center. Their energy levels may shift, and the degenerated spectral lines in the bulk sample may split. Though no additional splitting could be expected with Eu^{3+} occupying C_2 symmetry in Y_2O_3, the shift and broadening of the spectral lines do reflect this effect. Due to the appearance of numerous surface defects the crystal field in the surface of nanoparticles degenerates and the emission of $^5D_0-^7F_J$ shifts. It

should be noted that in the emission spectra, the Eu^{3+} ions near the surface were not distinguished from the interior Eu^{3+} ions. Despite this, we can know that the central emission under the 579.9-nm excitation is in the higher energy side of the 611-nm peak. Because the local environments surrounding Eu^{3+} ions near the surface are more disordered and surface defects may act as non-radiative transition channels, the width of the 579.9-nm line is broader and the lifetime becomes shorter.

The near surface region of NCs is quite unstable [9], therefore, the relative intensity of the 579.9-nm line is more liable to change with the corresponding irradiation than the 580.6-nm one.

4. Conclusion

In nanocrystalline Y_2O_3:Eu^{3+}, a new broad excitation line at 579.9 nm was observed. The relative intensity of 579.9-nm peak to the 580.6-nm one became weaker as temperature increased. The relative intensity increased a lot after irradiation with the 579.5-nm light, while it increased slightly with the 580.6-nm light. The lifetime of the 579.9-nm line became slightly shorter. According to these facts, the 579.9-nm line was attributed to the luminescence of Eu^{3+} ions near the surface of the NCs. The surface ions are unstable and symmetry in the near surface becomes lower due to numerous surface defects. This work indicates that laser spectroscopy is a useful technique to study surface physics.

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