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# Light-induced change of charge transfer band in nanocrystalline $\text{Y}_2\text{O}_3:\text{Eu}^{3+}$

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In this letter, we report the observation of ultraviolet light-induced change of excited charge-transfer band in nanocrystalline  $\text{Y}_2\text{O}_3:\text{Eu}^{3+}$ , which is attributed to the rearrangements of local environments surrounding the  $\text{Eu}^{3+}$  ions in the near surface of nanoparticles. © 2002 American Institute of Physics. [DOI: 10.1063/1.1501441]

Yttria doped with trivalent europium ions,  $\text{Y}_2\text{O}_3:\text{Eu}^{3+}$  is the unsurpassed red emitting phosphor in fluorescence lamps and projection television tubes.<sup>1,2</sup> An optical quantum efficiency of almost 100% seems to make additional investigation of this material redundant.<sup>3</sup> The resolution of images is related closely to particle size of phosphors. Smaller particles are favorable for higher resolution. For this reason, the studies on luminescent properties of nanocrystalline  $\text{Y}_2\text{O}_3:\text{Eu}^{3+}$  has attracted extensive interests during the last few years.<sup>4-7</sup> Additionally, the advances made in the reduction of the size of electronic devices require the investigation of the physical properties of materials with particle sizes in nanometer regime.<sup>8,9</sup> The electronic properties of nanometer particles are twofold: (1) the quantum size effect and (2) the increase of surface/volume ratio.<sup>10-12</sup> Sometimes the interface effects can completely cover the expected quantum size effects.<sup>11,12</sup> In nanocrystalline  $\text{ZnS}:\text{Mn}$ , due to the effect of surface defects, the luminescent intensity of Mn was changed by the irradiation of UV light.<sup>13,14</sup> In  $\text{Y}_2\text{O}_3:\text{Eu}^{3+}$ , the electronic transition from  $2p$  orbital of  $\text{O}^{2-}$  to the  $4f$  orbital of  $\text{Eu}^{3+}$  produces excited charge transfer (CT) band.<sup>15,16</sup> In this study, we demonstrate the UV light-induced change of CT band in nanocrystalline  $\text{Y}_2\text{O}_3:\text{Eu}^{3+}$ . This study is important for the understanding of the interaction among surface states, host and rare earth ions in nanoparticles.

The  $\text{Y}_2\text{O}_3:\text{Eu}^{3+}$  nanocrystals were prepared by combustion. In the preparation,  $\text{Y}(\text{NO}_3)_3$ ,  $\text{Eu}(\text{NO}_3)_3$  and glycine were dissolved in distilled water and mixed to form the precursor solution. Then the solution was concentrated by heating until excess free water evaporated and spontaneous ignition occurred. The resultant  $\text{Y}_2\text{O}_3:\text{Eu}^{3+}$  (1 mol %) powders were formed after the combustion was finished. The particle size was controlled by the ratio of glycine to  $\text{Y}(\text{NO}_3)_3$ . A detailed description of the sample preparation was given by Tao *et al.*<sup>17</sup> The bulk  $\text{Y}_2\text{O}_3:\text{Eu}^{3+}$  crystal was formed by annealing at 1200 °C for 8 h. The bulk and nanocrystals exhibit cubic structure, which is confirmed by x-ray diffractometry. The average diameter of the nanocrystal used in the present study was determined to be 5 nm by transmission electron microscopy (TEM) (see Fig. 1), while that of the bulk one was determined to be 3  $\mu\text{m}$  by field-emission scanning electron microscopy. The excitation and emission spectra were

measured with a Hitachi F-4500 fluorescence spectrometer. The continuous lights separated from a xenon-lamp were used as irradiation, with a line width of 10 nm and a power density of 10–100  $\mu\text{W}/\text{cm}^2$ .

Figure 2 shows the excitation spectra of  $\text{Eu}^{3+}$  for the emission of  $^5\text{D}_0-^7\text{F}_2$  in  $\text{Y}_2\text{O}_3:\text{Eu}^{3+}$ . A band extended from 200 to 300 nm was observed in both the nanocrystal and the bulk one, which was ascribed to the transition by CT. Igarashi *et al.* reported that the CT band in nanocrystalline  $\text{Y}_2\text{O}_3:\text{Eu}$  blue-shifted as the particle size decreased, while Tao *et al.* reported that it red-shifted. Here, we did not observe the shift of CT band, which indicated that the covalency between  $\text{O}^{2-}$  and  $\text{Eu}^{3+}$  did not change. In Fig. 2, the sharp lines are associated with the  $f-f$  transition of  $\text{Eu}^{3+}$ .

Figure 3 shows the excited CT band in the nanocrystalline  $\text{Y}_2\text{O}_3:\text{Eu}^{3+}$  before and after UV irradiation. It is clear that the intensity of CT band decreased as a whole as the crystal was irradiated with 230 nm and 245 nm lights. As the crystal was irradiated with a 260 nm light, the intensity at the irradiated site did not change, while the intensity for short-wavelength side increased. Only as the excitation is corresponding to the energy of CT band, the emission intensity of  $\text{Eu}^{3+}$  changes. The intensity of sharp excitation lines for  $f-f$  transition of  $\text{Eu}^{3+}$  does not change by irradiation, which indicates that the population of  $\text{Eu}^{3+}$  does not change. Figure 4 shows the dependence of emission intensity at 610 nm on irradiation time. It is obvious that the shorter the wavelength, the larger the intensity change at the irradiated sites. The dynamics were well fitted by exponential functions. The inset shows the relative change at the irradiated sites as a function of wavelength, which is proportional to  $\exp(-\lambda/\lambda_0)$ , where  $\lambda$  presents wavelength and  $\lambda_0$  is a constant. It should

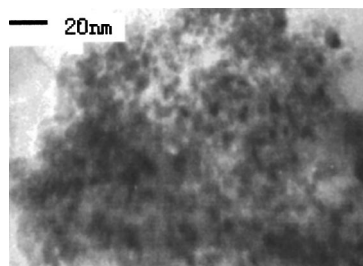


FIG. 1. TEM image of the  $\text{Y}_2\text{O}_3:\text{Eu}^{3+}$  nanoparticles.

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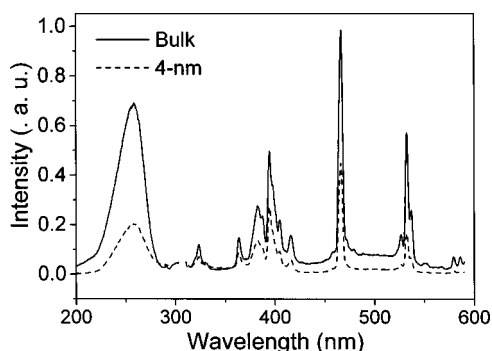


FIG. 2. Excitation spectra of  $\text{Eu}^{3+}$  in  $\text{Y}_2\text{O}_3:\text{Eu}^{3+}$  nanocrystal and bulk one for the emission at 610 nm.

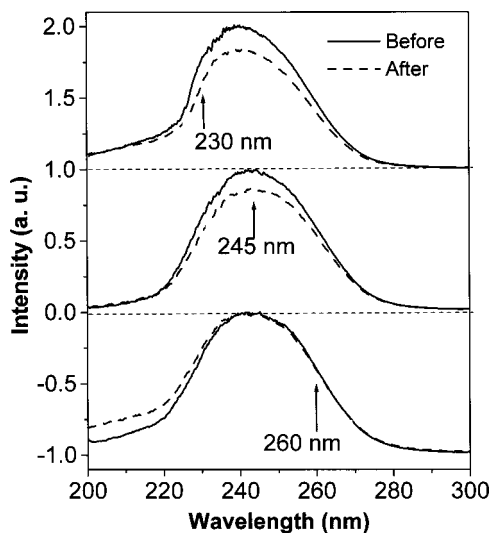


FIG. 3. Excited CT bands of nanocrystalline  $\text{Y}_2\text{O}_3:\text{Eu}^{3+}$ , measured before and after irradiation with various lights.

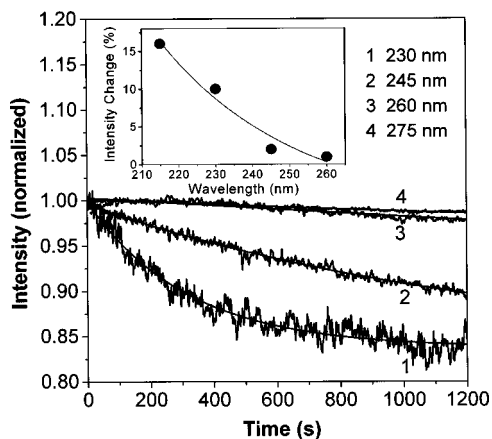


FIG. 4. Dependence of normalized intensity at 610 nm on irradiation time for various UV lights. Inset: the change at the irradiated sites as a function of wavelength.

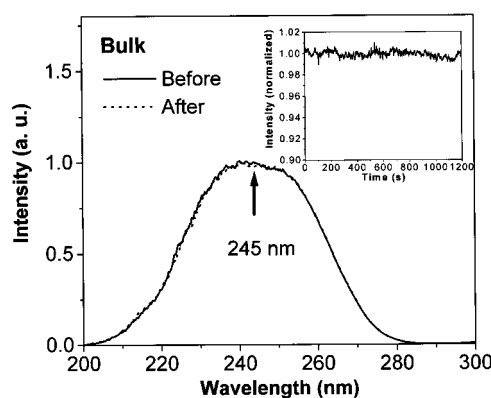


FIG. 5. Excited CT bands measured before and after the sample was irradiated with a 245 nm light in the bulk  $\text{Y}_2\text{O}_3:\text{Eu}^{3+}$ . Inset: The emission intensity at 610 nm as a function of irradiation time.

be noted that the light-induced change of CT band could preserve at least several hours at room temperature.

In comparison, we also measured UV light-induced change of CT band in the bulk  $\text{Y}_2\text{O}_3:\text{Eu}^{3+}$ . Figure 5 shows the CT band before and after irradiation with a 245 nm light. It is obvious that the CT band does not change after irradiation. The inset also indicates that the intensity of CT band at the irradiated site preserves a constant during irradiation. The CT band in the bulk crystal either does not change after it is irradiated at the other wavelengths.

The proportion of surface atoms in the  $\text{Y}_2\text{O}_3:\text{Eu}^{3+}$  nanocrystal (5 nm) is about 80%, while that in the bulk one (3  $\mu\text{m}$ ) is less than 1%. The increase in the proportion of surface atoms enhances the proportion of local displacement. The near surface of nanosized particle is particular unstable. Therefore, the local environments for the  $\text{Eu}^{3+}$  ions in the near surface are easily rearranged by UV irradiation, leading to the change of CT band of  $\text{Eu}^{3+}$ . The UV irradiation-induced structural change was also observed in the other materials.<sup>18</sup> A special case is that the energy states of surface defects are close to  $2p$  excited bands of  $\text{O}^{2-}$ . The electrons on the  $2p$  excited states are captured by the nearby surface defects through tunneling, leading the CT states to decrease after UV irradiation. The essence of this process is still the optical rearrangements of local environments surrounding  $\text{Eu}^{3+}$  ions.

In conclusion, the CT band in  $\text{Y}_2\text{O}_3:\text{Eu}^{3+}$  is changed by the irradiation of UV lights. This change is dependent of the particle size and the wavelength. It is attributed to the optical activated rearrangements of local environments surrounding the  $\text{Eu}^{3+}$  ions in the near surface of nanoparticles.

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