



Ultraviolet light-induced spectral change in cubic nanocrystalline $\text{Y}_2\text{O}_3:\text{Eu}^{3+}$

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Abstract

Ultraviolet light-irradiation induced spectral change was studied in cubic nanocrystalline $\text{Y}_2\text{O}_3:\text{Eu}^{3+}$. Under the irradiation of the ultraviolet lights separated from xenon lamp, the excited charge transfer band of Eu^{3+} decreased after irradiation. The smaller the particle size and the shorter the wavelength, the larger the spectral change. It was attributed to the local structural change surrounding Eu^{3+} ions in/near the surface. Under the irradiation of the 266-nm pulsed laser, some Eu^{3+} in nanoparticles was reduced to Eu^{2+} .

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1. Introduction

Recently, considerable attention has been demonstrated to research for new materials to be used for optical storage [1–3]. The interest in photoluminescent materials showing photoinduced persistent spectral change has significantly grown, because a combination of such phenomenon and near-field optical microscopy is very promising when applied to high-density optical storage with nanometer resolution [1]. Luminescent materials in nanometer scale are attracting current interests due to their special electronic properties in comparison with the bulk materials and potential application in high-resolution dis-

play. The two main electronic features of nanometer particles are (1) the quantum size effect and (2) the increase of surface/volume ratio [4–6]. In many cases, the surface effects in nanometer particles cause the luminescent quantum efficiency to decrease, because the surface defects usually take as nonradiative transition channels [7]. The atoms in/near the surface of nanoparticles are generally unstable. They are easier to be optically rearranged, leading to spectral change. It is expected that this behavior may take a positive role in some applications such as optical storage, photoinduced charge transfer and so on. In this Letter, we report for the first time to our knowledge, the size-dependent photoinduced spectral change in nanometer yttria doped with trivalent europium ions, $\text{Y}_2\text{O}_3:\text{Eu}^{3+}$. The bulk $\text{Y}_2\text{O}_3:\text{Eu}^{3+}$ is the unsurpassed red emitting phosphor in fluorescence lamps and projection television tubes [8,9].

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2. Experiments

The nanocrystalline $\text{Y}_2\text{O}_3:\text{Eu}^{3+}$ powders 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% in 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. [10]. The bulk $\text{Y}_2\text{O}_3:\text{Eu}^{3+}$ powders were formed by annealing at 1200 °C. The bulk and nanocrystalline powders all exhibit cubic structure, which was confirmed by X-ray diffractometry. The average diameters of the nanoparticles used in the present study were determined to be 5 and 20 nm by transmission electron microscopy, while that of the bulk one was determined to be $\sim 3 \mu\text{m}$ 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 with a power density of 10–100 $\mu\text{W}/\text{cm}^2$ were used as irradiation source. A 266-nm pulsed laser came from a Nd: YAG laser combined with a fourth-harmonic generator was also used as irradiation (It is with a pulsed duration of 10 ns, repetition frequency of 10 Hz and power density of $\sim 1 \text{ W}/\text{cm}^2$.) or the excitation source. All the experiments were performed in air.

3. Results and discussion

Fig. 1 shows the emission spectra associated with the ${}^5\text{D}_0\text{--}{}^7\text{F}_J$ transitions of Eu^{3+} . The detail origins of the emissions were labeled in the figure. It was seen that the intensity ratio of ${}^5\text{D}_0\text{--}{}^7\text{F}_2$ to ${}^5\text{D}_0\text{--}{}^7\text{F}_1$ increased with decreasing particle size. The values of the ratio in the 5-nm, 20-nm and the 3- μm powders were determined to be 5.2, 4.2 and 3.8, respectively. As well known, ${}^5\text{D}_0\text{--}{}^7\text{F}_2$ is an electric dipole transition and ${}^5\text{D}_0\text{--}{}^7\text{F}_1$ is a magnetic dipole one. The intensity ratio of ${}^5\text{D}_0\text{--}{}^7\text{F}_2$ to

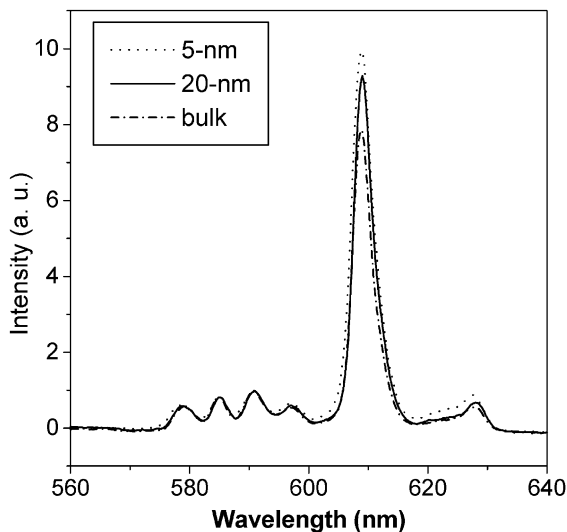


Fig. 1. Emissions for ${}^5\text{D}_0\text{--}{}^7\text{F}_J$ transitions of the Eu^{3+} ions in $\text{Y}_2\text{O}_3:\text{Eu}^{3+}$ powders (the intensity of ${}^5\text{D}_0\text{--}{}^7\text{F}_1$ was normalized).

${}^5\text{D}_0\text{--}{}^7\text{F}_1$ depends on the symmetry of the local environment of the Eu^{3+} activators [11]. The increased intensity ratio of ${}^5\text{D}_0\text{--}{}^7\text{F}_2$ to ${}^5\text{D}_0\text{--}{}^7\text{F}_1$ means the lower local symmetry surrounding Eu^{3+} . More atoms are located at the particle surface as the particle size decreases, and numerous surface defects exist. These defects may increase the degree of disorder and lower the local symmetry of Eu^{3+} ions located at the surface of the particles. As a consequence, the transition probability of ${}^5\text{D}_0\text{--}{}^7\text{F}_2$ increases [12].

Fig. 2 shows the excitation spectra for the emissions of ${}^5\text{D}_0\text{--}{}^7\text{F}_2$ before and after irradiation with a xenon-lamp. The band varied from 200 to 300 nm is associated with the charge transfer (CT) excitation [13,14], and the lines are associated with the direct ${}^7\text{F}_0\text{--}{}^5\text{D}$, ${}^5\text{G}$ or ${}^5\text{L}$ excitation of Eu^{3+} . The CT band is related closely to the covalency between O^{2-} and Eu^{3+} . The decrease in energy for electron transfer from O^{2-} to Eu^{3+} represents the increase in the covalency, i.e., the decrease in ionicity between oxygen and Eu^{3+} [14]. It can be observed that the intensity of the CT band decreased, while the direct excitation lines of Eu^{3+} had little change after irradiation. This means that after 254-nm light irradiation, the emission intensity of ${}^5\text{D}_0\text{--}{}^7\text{F}_2$ changed corresponding to the CT

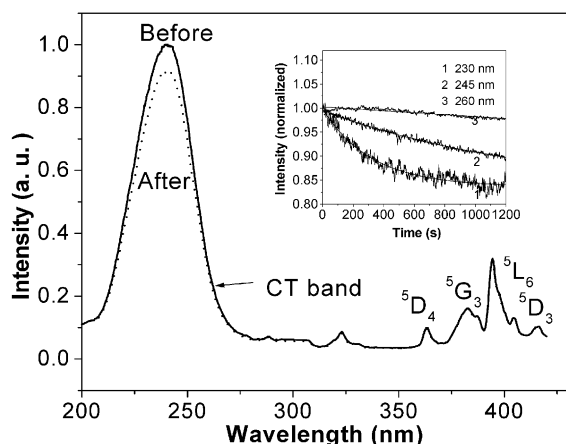


Fig. 2. Excitation spectra of the 5-nm $\text{Y}_2\text{O}_3:\text{Eu}^{3+}$ before and after the 245-nm light-irradiation for 30 min (the power density of irradiation light was $10\text{--}100 \mu\text{W}/\text{cm}^2$ and the time was 20 min). Inset: the normalized emission intensity at 611 nm as a function of irradiation time and wavelength.

excitation, but did not change corresponding to the direct excitations of Eu^{3+} . This was also confirmed by comparing the emission spectra of $^5\text{D}_0\text{--}^7\text{F}_J$ between before and after irradiation. The results above definitely reveal that only the local environments surrounding Eu^{3+} ions changed by the irradiation of UV lights separated from xenon-lamp, the density of Eu^{3+} ions did not change [15]. The inset shows the normalized emission intensity at 611 nm as a function of irradiation time and wavelength. It is apparent that the emission intensity decreased with increasing irradiation time. The shorter the wavelength was, the larger the intensity change was. The dynamics were well fitted by exponential functions.

The irradiation was also performed in the other samples. Fig. 3 shows the normalized intensity change versus wavelength of the irradiation light and the particle size. It is apparent that the smaller the particle size and the shorter the wavelength, the larger the intensity variation. This result suggests that the decrease of CT is related to surface effects. Owing to the existent of numerous surface defects, the atoms in/near the surface are unstable. The local environments for the Eu^{3+} ions in/near the surface are easily rearranged by UV irradiation, leading to the change of the CT band. It should be noted that in a previous paper, we

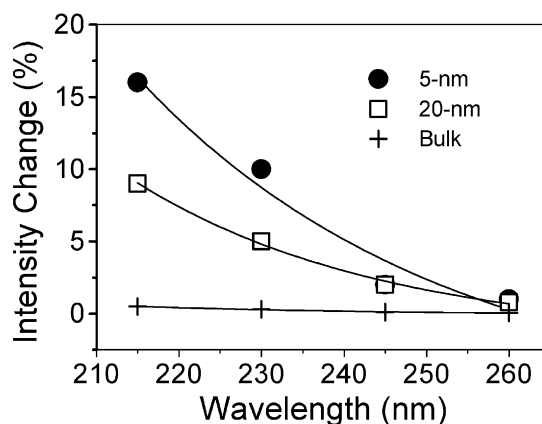


Fig. 3. Normalized intensity change versus the wavelength of the irradiation light and the particle size.

studied the light-induced change of CT band in one europium doped aluminosilicate glass. It was observed that in the glass the central location of the spectral change in CT band varied strongly depending on wavelength of the irradiation light [15]. In the nanocrystalline $\text{Y}_2\text{O}_3:\text{Eu}$, the central location of the spectral change was at ~ 245 nm all the time. It did not vary depending on wavelength of the irradiation light.

The intensity of the CT band decreased after irradiation, then increased again and tended to restore its original state as the irradiation light was shut off. Fig. 4 shows the relative change as a function of recovery time in the dark. In Fig. 4, the

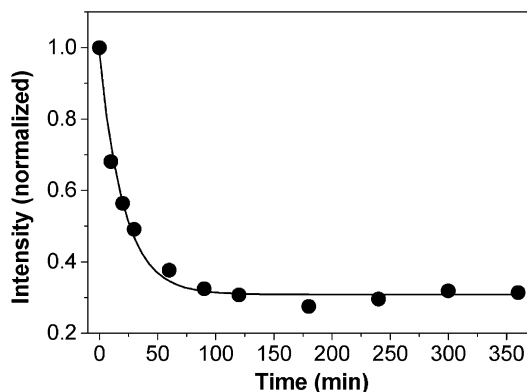


Fig. 4. Dependence of relative change of CT band as a function of recovery time in the dark.

relative intensity change was determined by the equation of $[I_a(0) - I_b]/[I_a(t) - I_b]$, where I_b is the intensity measured before irradiation, $I_a(0)$ is the intensity measured immediately after the irradiation light was shut off, $I_a(t)$ is the intensity measured after the irradiation light was shut off t hours. The experimental dots in the inset were fitted by a function of $\alpha_1 e^{-t/\tau} + (1 - \alpha_1)$. By fitting, α_1 and τ_1 were determined to be 0.7 and 20 min, respectively. This means that at least two recovery time constants exist. One is 20 min and the other is much longer. The component with the shorter recovery time constant is 70 % and the other component is 30%. The dark recovery time constant is dominated by the thermal activation rate between the changed and unchanged CT states. The appearance of two recovery time constants suggests that there exist two thermal activation rates between the changed and unchanged states, which may correspond to two kinds of structural changes.

Fig. 5 shows the emission spectra after the 266-nm pulsed laser light-irradiation in the 5-nm sample. A broad band in the range of 450–550 nm and two sharp lines were observed. The two sharp

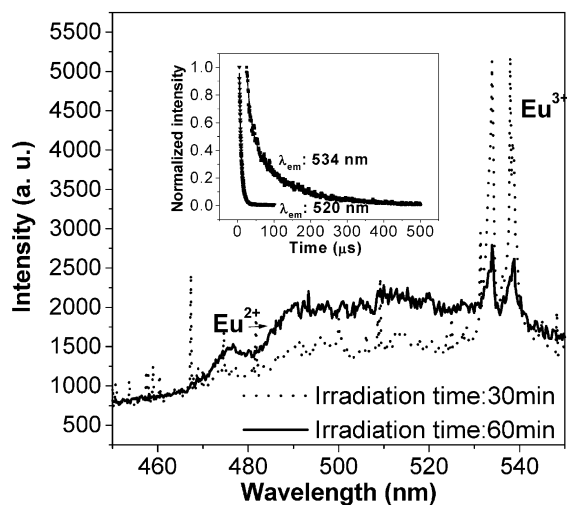


Fig. 5. Emission spectra of the 5-nm sample of $Y_2O_3:Eu^{3+}$ after irradiated with the 266-nm pulsed laser for different time (the power density of the irradiation light is $\sim 1 \text{ W/cm}^2$). Inset: fluorescence decay curves measured at different wavelengths, 520 and 534 nm.

lines at 534 and 538 nm are associated with the ${}^5D_1-{}^7F_1$ transitions of Eu^{3+} . It was seen that the emission intensity of Eu^{3+} decreased after the laser irradiation, while the intensity of the broad band increased. At the irradiated region, green phosphor-luminescence with lasting time of several 10 s was observed after the excitation light was shut off. The insert shows the fluorescence decays measured at different wavelengths. The fluorescence at 534 nm was mainly contributed by the ${}^5D_1-{}^7F_1$ transitions and the fluorescence at 520 nm was associated with the broad band. By fitting, the lifetime of ${}^5D_1-{}^7F_1$ was determined to be 108 μs , while that of the broad band to be 5.4 μs . The lifetime of the emission band was in consistent with of Eu^{2+} . According to the color, the appearance of phosphor-luminescence and the fluorescent decay time, the broad emission band was attributed to Eu^{2+} . The result above suggests that some Eu^{3+} ions were reduced into Eu^{2+} ions by the irradiation of the 266-nm pulsed laser. The UV-light induced photoreduction in $Y_2O_3:Eu$ strongly depended on the particle size. In the 3- μm sample, we did not observe that Eu^{3+} was reduced into Eu^{2+} under the same experimental conditions, suggesting that the photoreduction was related to the surface effects. It was suggested that the Eu^{3+} ions in the surface acted as electron-trapping centers, while the surface defects acted as electron donors. After the irradiation light was shut off 14 h, the emission spectra at the irradiated region were measured again under the excitation of the 266-nm light. The broad emission band caused by Eu^{2+} was still observed. This means that that Eu^{2+} caused by photoreduction can exist at RT for more than 10 h.

4. Conclusions

The light-induced spectral change was studied in nanocrystalline $Y_2O_3:Eu^{3+}$. Under the irradiation of the UV lights separated from xenon lamp, only the intensity of CT band decreased, but the direct excitation lines of Eu^{3+} did not change. The spectral change strongly depended on the particle size and thus was attributed to the local structural change surrounding the Eu^{3+} ions in/near the surface. Under the irradiation of the 266-nm laser

light, some Eu^{3+} was reduced into Eu^{2+} . We suggest that the Eu^{3+} ions in/near the surface act as electron-trapping centers, while the surface defects act as electron donors.

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