Optical properties of nanocrystalline Y$_2$O$_3$:Eu depending on its odd structure

Wei-Wei Zhang, Wei-Ping Zhang, Ping-Bo Xie, Min Yin, Hou-Tong Chen, Long Jing, Yun-Sheng Zhang, Li-Ren Lou, and Shang-Da Xia

Abstract

The structure of nanocrystalline Y$_2$O$_3$:Eu prepared by a combustion reaction was analyzed by XRD and high-resolution electron microscopy. Compared with a large-scale particles, 5-nm Y$_2$O$_3$:Eu particles presented as distorted crystallite and rough surfaces. Luminescent and absorption properties of nano-Y$_2$O$_3$:Eu showed remarkably particle size effects. At Y$_2$O$_3$:Eu particle sizes smaller than 10 nm some new results were observed: (a) a red shift of the charge-transfer-state absorption; (b) new emission bands of Eu$^{3+}$ in the $5D_0 \rightarrow 7F_2$ region; (c) luminescent decay of energy level $5D_0$ of Eu$^{3+}$ turning to a two-step exponential; and (d) a pronounced increase in quenching concentration and much lower phonon density compared with those of the bulk material. All these phenomena can be attributed to the effect of the softened lattice and surface state of the nanomaterial. The latter was confirmed by stronger excitation by the host absorption after the surface modification.

Keywords: Nanocrystalline; Electron microscopy; Luminescence; Surface modification

1. Introduction

In recent years, optical properties of nanocrystals of semiconductors, such as ZnS [1,2], CdS [3], and CdSe [4], have attracted much attention due to their surface effects and quantum confinement effects.

On the other hand, research on the luminescence of nanoscale insulating materials is less focused. It is well known that cubic Y$_2$O$_3$:Eu$^{3+}$ phosphors are widely used in low-pressure fluorescent lamps and cathode-ray tubes, as well as PDPs (plasma display panels) [5]. The luminescent properties of bulk Y$_2$O$_3$:Eu$^{3+}$ have been well investigated [6–10] and recently a small number of researches on nanoscale Y$_2$O$_3$:Eu have been conducted [11–18]. In addition, the optical properties of nanoscale monoclinic Y$_2$O$_3$:Eu have also been reported [19,20].

Early in 1997, our research group first reported the optical properties of combustion-synthesized nanoscale Y$_2$O$_3$:Eu [21]. However, later work on this material by other authors has not given an overall and detailed report on its luminescent properties yet. In this paper, we present the luminescent properties of nanoscale Y$_2$O$_3$:Eu with different particle sizes synthesized by the combustion synthesis (CS) method in detail.

2. Experimental

Bulk Y$_2$O$_3$:Eu with particle size 2–5 µm was prepared by conventional solid state reaction. Nanoscale Y$_2$O$_3$:Eu was synthesized by the combustion method. Combustion synthesis is of significant interest, mainly due to its simplicity and ease of controlling the particle size of the product [21,23,24]. The process is as follows: Rare-earth nitrate Y(NO$_3$)$_3$ and Eu(NO$_3$)$_3$ of 99.99% purity and analytical grade glycine (Gly) were dissolved in distilled water and mixed in an appropriate ratio. The mixture was stirred to form a uniform precursor solution. Then the solution was heated on a heating plate. When the water was almost dried out, the temperature rose quickly and the mixture was ig-
nited at about 250°C. The reaction was self-propagating and finished within 10 s with a resultant crispy snow-white ash of about 1 g $Y_2O_3$:Eu filling a 200-ml beaker. The reaction equation is

$$6R(NO_3)_3 + 10H_2NCH_2COOH + 18O_2 \rightarrow 3R_2O_3 + 20CO_2 + 5N_2 + 25H_2O + 18NO_2 + Q$$

where Gly serves as reductor, being oxidized by NO$_3^-$. All the samples emit red light under UV excitation without any additive heating treatment.

X-ray powder diffraction (XRD) measurements were carried out on an MXP18AHF X-ray diffractometer (MAC Science Co. Ltd.). A JEOL-2010 high-resolution electron microscope (HREM) was used to observe the morphology and check the grain size. Excitation spectra in the UV region were measured by a 970 CRT fluorescence spectrophotometer. The emission spectra were recorded by a Jobin–Yvon HRD1 monochromator with a Hg lamp or a rhodamine 6G dye laser as excitation light source. The luminescent decay curve under the excitation of a frequency-tripled YAG:Nd laser was recorded by a LeCroy 9350M oscilloscope interfaced with a computer. Raman measurement was carried out on a Spex-1403 monochromator under the excitation of an Ar$^+$ laser, with a back-scattering configuration.

3. Results and discussion

3.1. Structure of the nanocrystal

Figure 1 shows the XRD patterns of our $Y_2O_3$:Eu samples, which are well consistent with JCPDS No. 25-1200 and confirm our samples as of a cubic structure. Particle sizes of nanocrystals can be estimated from the HWFM of the XRD peaks by the well-known Scherrer equation. The grain size of the resultant $Y_2O_3$:Eu depends on the flame temperature [23,24], which varied with the Gly-to-nitrate ratio ($\Phi = M_{Gly}/M_{NO_3}$, where $M$ = molar amount of the compound). In this work, $\Phi$ varies from 0.33 to 0.65 and the corresponding particle size is from 5 to 200 nm. The particle sizes of samples B, C, D, and E are 80, 40, 10, and 5 nm, respectively, while the bulk $Y_2O_3$:Eu phosphor (sample A) is larger than 3 µm. Furthermore, a slight red-shift of the XRD peaks of sample E was observed (the inset of Fig. 1). It indicates a softened lattice of the nanocrystal—the lattice constant of sample E is 0.47% larger than that of sample B. Such a shift was also found in $Y_2O_3$ nanoparticles prepared by other methods [18].
The HREM image of sample E is shown in Fig. 2a. Observed particles are spheroid and the average size is about 5 nm, in agreement with the results of XRD. This image shows that the 5-nm particle could be considered to consist of two structural components—a well-crystallized “core” and a very rough interface. We can also find great distortions and dislocations near the surface. For the samples with particle size larger than 10 nm, the lattice is more perfect (Fig. 2b). Such a characteristic structure of sample E may give a clue to the following experimental phenomena.

In the HREM experiment, there is also an interesting observation of fractal behavior. This result will be discussed later.

3.2. Photoluminescent spectra

Figure 3 presents the excitation spectra of nanoscale Y$_2$O$_3$:Eu (samples B and E) by monitoring the emission at 611 nm. The broadening of the excitation band with decreasing particle size can be seen (Fig. 3a) and related to the surface state. It has been widely reported and discussed. Furthermore, the different feature indicates a changed environment of Eu$^{3+}$, which leads to broken selection rules and different transition probabilities. Since the selection rules affect transitions in both excitation and emission, they will be discussed in detail later in the emission spectra.

Moreover, the CTS (charge transfer state absorption) peak position (Fig. 3b) shows a clear particle-size dependence. For samples with particle sizes of 80, 40, and 5 nm, the peaks are centered at 239, 243, and 250 nm, respectively (Table 1). Such a shift was also reported by Konrad et al. [17], who gave a 5-nm blue shift of the host’s absorption and an 11-nm red shift in the CTS band. However, the observed red shift of the excitation band of sample B to E is 11 nm. Such a huge red shift could not be explained by a conventional confinement effect in nanoscale materials. We then attribute this shift to the shift of the CTS band itself: the lattice constant of a nanocrystal is larger than that of a commercial bulk sample, or we can say that there is a larger Eu–O distance in a nanosample than in the normal one. Hoefdraad has summarized the CTS positions of Eu$^{3+}$ in oxides [22], which exhibited a shift toward lower energies in VIII and XII coordination with increasing bond length. Here we simply apply this principle in the situation of Y$_2$O$_3$:Eu, where the cation Y$^{3+}$ has VI coordination in a pure phase cubic Y$_2$O$_3$. However, such a qualitative analysis is still a bit ambiguous. A density function $\alpha$ is being used as a theoretic tool to clarify the problem.

Figure 4 shows the emission spectra of samples with different sizes. The main region (600–640 nm) is in the red, which belongs to the $^5D_0 \rightarrow ^7F_2$ transition of Eu$^{3+}$ at the C$_2$ site [9,10]. As expected, the emission peaks of nanoscale

\begin{table}[h]
\centering
\caption{Properties of Y$_2$O$_3$:Eu with different particle sizes (a surface layer of 1 nm is assumed)}
\begin{tabular}{|c|c|c|c|c|c|}
\hline
Sample & A & B & C & D & E \\
\hline
Particle size (nm) & 3 & 80 & 40 & 10 & 5 \\
Surf.-to-vol. ratio & $<0.01$ & 0.07 & 0.14 & 0.49 & 0.78 \\
CTS position (nm) & 239 & 239 & 243 & 243 & 250 \\
HWFM of P$_0$ (10 K) (nm) & 0.8 & 0.9 & 1.1 & 1.3 & – \\
Lifetime of Eu$^{3+}$ (RT) (ms) & 1.7 & 1.39 & 1.28 & 1.08 & 1.04 \\
Quenching concentration (mol%) & $\sim 6$ & 12–14 & – & – & – \\
\hline
\end{tabular}
\end{table}

shape of the CTS peak in samples with large particle size is asymmetrical, because it consists of the CTS excitation band and the absorption of the host. As shown in Fig. 3b-E, absorption of the host’s gap is at 220 nm ($\sim 5.64$ eV, while for a bulk one, $E_g = 5.6$ eV) besides the CTS band. However, the observed red shift of the excitation band of sample B to E is 11 nm. Such a huge red shift could not be explained by a conventional confinement effect in nanoscale materials. We then attribute this shift to the shift of the CTS band itself: the lattice constant of a nanocrystal is larger than that of a commercial bulk sample, or we can say that there is a larger Eu–O distance in a nanosample than in the normal one. Hoefdraad has summarized the CTS positions of Eu$^{3+}$ in oxides [22], which exhibited a shift toward lower energies in VIII and XII coordination with increasing bond length. Here we simply apply this principle in the situation of Y$_2$O$_3$:Eu, where the cation Y$^{3+}$ has VI coordination in a pure phase cubic Y$_2$O$_3$. However, such a qualitative analysis is still a bit ambiguous. A density function $\alpha$ is being used as a theoretic tool to clarify the problem.

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samples broaden (as shown in Table 1), which is consistent with the excitation spectra.

Moreover, when the particle size is less than 10 nm, the spectrum changes greatly. The red emission now mainly consists of a sharp peak at 611 nm (P0) and two wide bands in the region 612–630 nm. Peak P0 is the same as that of samples with larger particle size. One of the two bands at 613 nm (P1) is a shoulder of the former spectra, and another one at 622 nm (P2) can be fitted by two peaks that disappear in larger samples. The relative intensities of the wide bands increase with decreasing particle size. It seems that band P2 can be linked with the luminescence of Eu$^{3+}$ in a surface state. The 4$f$ energy levels of Eu$^{3+}$ are hardly affected by the crystal field because of the shielding of the 5$s^2$5$p^6$ electrons. That is why there are no notable shifts in the emission peaks of Eu$^{3+}$. However, the selection rules and transition probabilities between states strongly depend on the crystal field. Relaxed selection rules of Eu$^{3+}$ in the surface state suggest a different emission. The peak P0 is supposed to be an emission from Eu$^{3+}$ in inner lattice. The detailed peak positions of the $^5D_0 \rightarrow ^7F_2$ transition of Eu$^{3+}$ in Y$_2$O$_3$ are summarized in Table 2. In our experiment, a different excitation light source, such as 254-nm UV light from an Hg lamp or dye laser, produces the same emission spectra. This can be owing to the fact that the transition peaks are greatly broadened and selective excitation is not effective any more.

The great changes of photoluminescence occur only when the particle size is less than 10 nm.

### 3.3. Fluorescent lifetime

The decay time of Eu$^{3+}$ fluorescence also changes with the particle size. The smaller the size, the shorter the lifetime. Figure 5 shows the results measured at room temperature. For the samples with particle size larger than 10 nm, the decay is one exponential process, with lifetime values of 1.7, 1.39, 1.28, and 1.08 ms for samples A, B, C, and D, respectively. Such differences can be attributed to the fact that a smaller particle has relatively more defects in it, as revealed in the image of HREM. The combustion synthesis reaction is a rapid process. When the system temperature dropped from higher than 1000°C to room temperature in several tenths of seconds, many defects which acted as quenching centers were “frozen” in the crystal. The lifetime $\tau$ is described by the equation

$$\tau = (\gamma_r + \gamma_{nr})^{-1},$$

where $\gamma_r$ is the radiative rate and $\gamma_{nr}$ is the nonradiative rate. With an increased nonradiative rate, the lifetime turns shorter accordingly.

However, the luminescent decay of sample E has a special feature. It decays very fast and its decay curve could only be fitted by a two-step exponential, with $\tau_1 = 1.04$ ms and $\tau_2 = 0.35$ ms. Taking into account the peculiar emission spectrum of this sample, it is reasonable to suppose that $\tau_2$ is the lifetime of Eu$^{3+}$ in the $^5D_0$ state on the surface. The lifetime of $\tau_1$ is the decay of a conventional emission, which obeys the rule of decreasing as sample A, B, C, and D suggested. At low temperatures, the phenomenon is almost the same except that all measured lifetimes are a bit longer.

### 3.4. Luminescent intensity and concentration quenching

High-concentration defects and dislocations could greatly quench the total luminescent intensity. However, light emission from such a rough crystal as sample E has an integrated intensity much higher than expected. The emission intensity of sample E can be about 80% of that of sample B. Such a result might be attributed to decreasing phonon density of...
sample E (Fig. 6) due to the enlargement of the lattice constant. In general, nonradiative relaxation is always assisted by phonons. Lower phonon density will reduce the probability of nonradiative processes and repress the effect of the quenching centers.

The nanoscale sample has a higher quenching concentration. Compared with the quenching concentration ($C_q$) of 12–14 mol% [21] for other CS samples, a value of about 18 mol% was obtained for 5-nm $Y_2O_3$:Eu, while for bulk material, $C_q$ is about 6 mol% [11,25]. Here a qualitative analysis is given: Resonant energy transfer (RET) exists among the Eu$^{3+}$ ions. This transfer greatly relies on the matching of emission energy and absorption energy. In sample E, as we saw in the emission spectra, the surface state works. The distortion of the surface circumstance leads to slight shifts of the energy levels. Multi-phonon-assisted RET instead of simple RET will dominate the process in this system. Multi-phonon-assisted RET is a high-ranking process and has a lower probability than low-ranking processes, such as simple RET and one-phonon-assisted RET. Moreover, as we addressed in the former paragraph, the density of phonons of the nanosamples is much lower than that of normal crystal. All these result in a decreased probability of energy transfer among Eu$^{3+}$ ions. Then higher concentration is needed to quench the luminescence.

### 3.5. Effect of surface modification

It is well known that surface modification can improve the luminescence of a nanosized phosphor. Sharma has done a lot of work on it [11,12]. Here a surfactant Tween-40 was used to modify sample E. Some elementary effects of the modification were investigated.

With the help of the HREM system, one can take a direct view of the surface-modified particles. It can be seen that the surfactant distributes uniformly on the surface of sample E (Fig. 7a). The layer of surfactant can repair the defects of the particle surface and thus improve the effective host absorption. The CTS absorption is a kind of host absorption. As shown in Fig. 8 the relative intensity of CTS to $4f^6$ transition increases after surface modification.

Compare the two image of Figs. 7a and 7b, one could easily find their similarity except for the surfactant layer, though they are taken in different scale. (One is about $130 \times 180$ nm, the other is about $1650 \times 2300$ nm.) Such a character indicates a fractal process of forming the nanocrystals. We give a more direct observation here, while F. Giuliani and co-workers have calculated the fractal dimension by small-angle X-ray scattering [26].

### 4. Conclusion

We synthesized a series of nanocrystalline $Y_{2(1-x)}$O$_3$: Eu$_x$ by combustion synthesis and analyzed their structural and optical properties. Some new interesting characters were found for the sample with particle size 5 nm. It seems that such effects happen only when the particle size is less than 10 nm. Conventional discussion based on size effect and confinement effect, which works successfully in most of semiconductors, does not work here. To explain the experimental results, discussions based on the effects of softened lattice and surface state were provided. The discussion and the phenomena are consistent. The explanation also agrees with other published results, no matter what kind of technique was used to prepare the nanocrystalline $Y_2O_3$:Eu.

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### References