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The spectral properties of different structural centers in nanocrystalline $Gd_2O_3:Eu^{3+}$

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Abstract

Monoclinic and cubic $Gd_2O_3:Eu^{3+}$ were prepared by combustion synthesis. The optical and structural properties have been investigated using photoluminescence (PL), photoluminescence excitation (PLE), site-selective excitation (SSE) spectra as well as fluorescence lifetime measurement. Three nonequivalent C_s centers in monoclinic phase and C_2 center in cubic phase are distinguished. The energy transfers between three different C_s centers in monoclinic phase of nano-material were observed. The lifetime of $^5D_0$ of Eu^{3+} in the nano-material is longer than that in bulk lattice, due to the effective refractive index decreasing.

Keywords: $Gd_2O_3:Eu^{3+}$ nanocrystallines; Monoclinic and cubic phases; Combustion method; Site-selective excitation

1. Introduction

Rare-earth sesquioxides have three different crystallographic structures: hexagonal, cubic and monoclinic phases. In cubic $Gd_2O_3:Eu^{3+}$, Eu^{3+} ions occupy two kinds of lattice sites (C_2 and S_6) after substituting the Gd^{3+} ions. In monoclinic Gd_2O_3 [1], the Eu^{3+} substitute three nonequivalent sites of C_s symmetry. The photoluminescence properties of bulk $Gd_2O_3:Eu^{3+}$ have been studied extensively until scarcity of papers are reported on optical properties of nano-structure $Gd_2O_3:Eu^{3+}$.

In this paper nano-sized cubic and monoclinic $Gd_2O_3:Eu^{3+}$ were prepared by combustion method. The spectral properties of Eu^{3+} with C_s symmetry in monoclinic phase and with C_2 symmetry in cubic phase were studied by PL, PLE, SSE and fluorescence decay curves etc.

2. Experiments

The samples were prepared by combustion synthesis [2]. Sample a is $Gd_{1.9}Eu_{0.1}O_3$ annealed at 600 °C for 1 h, sample b is $Gd_{1.8}Eu_{0.2}O_3$ annealed at 1000 °C for 1 h and sample c is $Gd_{1.8}Eu_{0.2}O_3$ annealed at 800 °C for 1 h.

PL measurements of $Gd_2O_3:Eu^{3+}$ were excited by the triple-frequency harmonic of YAG:Nd laser at 355 nm. SSE spectra were measured with Rh6G dye laser (from 570 nm to 610 nm) pumped by the second harmonic of YAG:Nd laser. The beam was split by the Spex-1403 monochromator with double gratings. A boxcar integrator provides electronically gated signal processing.

3. Results and discussion

The samples a and b are monoclinic-cubic phase and c is pure cubic from the XRD measurements. Figs. 1(a)–(c) are the PL spectra concerning the $^5D_0 \rightarrow {}^7F_J$ ($J = 0, 1, 2$) transition of the three $Gd_2O_3:Eu^{3+}$ materials, viz. samples a of 10 nm, b bulk material and c of 30 nm under 355 nm excitation at 10 and 77 K. In Fig. 1(a) for nano-monoclinic sample it is shown that there are three emission peaks assigned to $^5D_0 \rightarrow {}^7F_0(C_s)$ transition. It would indicate there exist at least three kinds of PL centers. In Fig. 1(c), three spectral peaks located at 16361, 16280 and 15862 cm^{-1} were observed. It can be confirmed that they all come from the Eu^{3+} ions occupying the C_2 sites.

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Fig. 2(a)–(i) presents the PLE spectra in the $^7F_0 \rightarrow {}^5D_0$ region of sample a by monitoring the different emissions of the $^5D_0 \rightarrow {}^7F_2$ transition. There are four spectral peaks in Figs. 2(a)–(h) for monoclinic nanomaterial (10 nm). This indicates that there are at least four kinds of emitting centers. Comparing with Ref. [1], three different emission centers noted as A, B and C with C_s symmetry can be identified. Monitoring the emission of 16361 cm^{-1}, the PLE peak is at 580.6 nm, as shown in Fig. 2(h). PLE spectra for cubic sample c ($Gd_{1.8}Eu_{0.2}O_3$) are shown in Fig. 2(i) monitoring the emission 16361^{-1} cm. The peak at 580.6 nm in Fig. 2(h) is located at the same position as that in Fig. 2(i). It indicates that the peak at 580.6 nm in Fig. 2(h) comes from the C_2 site of cubic phase. This confirmed the result of XRD pattern from which sample a has a mixture structure of both monoclinic and cubic phases.

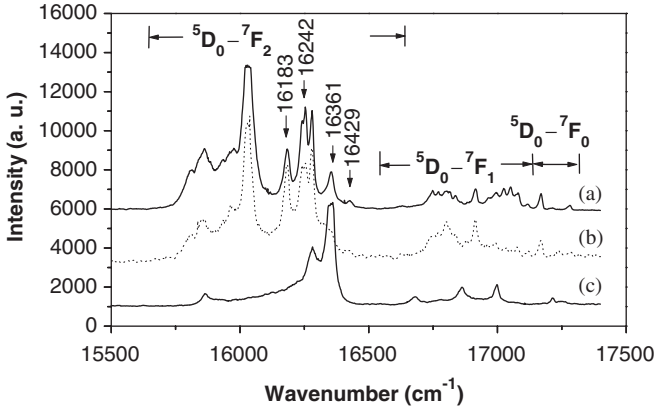

Fig. 1. PL spectra of Gd_2O_3:Eu^{3+} for $^5D_0 \rightarrow {}^7F_{0,1,2}$ excited by 355 nm: (a) monoclinic nano-material (10 nm) at 10 K; (b) monoclinic bulk material at 77 K; (c) cubic nano-material (30 nm) at 77 K. Arrows indicate the monitoring positions for lifetime measurement.

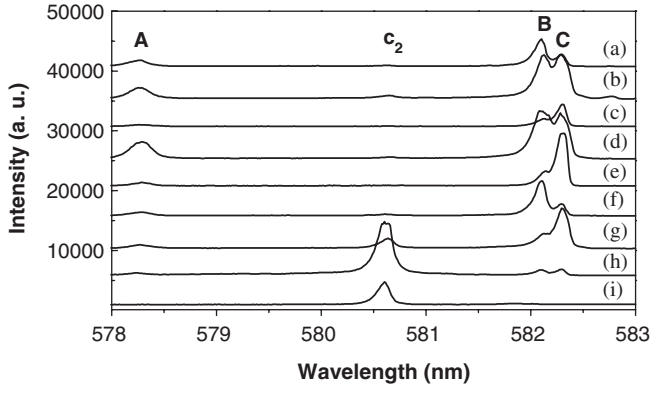

Fig. 2. The PLE spectra of monoclinic Gd_2O_3:Eu^{3+} nanocrystallines at 10 K, monitoring positions at 15 854 cm^{-1} (a), 16 013 cm^{-1} (b), 16 032 cm^{-1} (c), 16 047 cm^{-1} (d), 16 190 cm^{-1} (e), 16 242 cm^{-1} (f), 16 279 cm^{-1} (g), and 16 361 cm^{-1} (h). The PLE spectra of cubic Gd_2O_3:Eu^{3+} nanocryatalline at 77 K, monitoring position at 16 361 cm^{-1}(i).

In PLE spectra for cubic sample c there is only one peak at 580.6 nm of the $^7F_0 \rightarrow {}^5D_0$ transition for C_2 site. Another one located at lower energy 581.8 nm for the $^7F_0 \rightarrow {}^5D_0$ transition of S_6 site is not observed. There are 24 C_2 sites and eight S_6 sites in unit cell of cubic Gd_2O_3:Eu^{3+}. The occupation probabilities of Eu^{3+} ion of these two symmetric sites are the same [3].

According to the PLE spectra peaks in Fig. 2, we measured the SSE spectra under excitations of four different wavelengths for the monoclinic Gd_2O_3:Eu^{3+} (10 nm), shown in Fig. 3. The centers A, B and C of C_s symmetry and center of C_2 symmetry are selectively excited under 578.3, 582.1, 582.3 and 580.6 nm, respectively. The $^5D_0 \rightarrow {}^7F_J$ emissions from different emitting centers on C_s or C_2 sites can be distinguished by these SSE spectra. When the center A with high energy was excited, strong emissions from centers B and C can be seen in the SSE spectra. This indicates that there are effective energy transfers from A, to B and C centers.

The fluorescence decay curves (corresponding to emissions pointed out by the arrows in Fig. 1) of $^5D_0 \rightarrow {}^7F_2$ for monoclinic nanosized and bulk material are shown in Fig. 4, and the results are tabulated in Table 1. The lifetime of the monoclinic nanomaterial is longer than that of the bulk material. Although the measurement of the bulk material is carried through at 77 K, correlating experiments showed that the lifetime change is very small in the range of 10–77 K. The lifetime of the electronic transitions of an ion embedded in a medium is described by [4]

$$\tau_R \sim \frac{1}{f(ED)} \frac{\lambda_0^2}{\left[\frac{1}{3}\left(n_{\text{eff}}^2+2\right)\right]^2 n_{\text{eff}}}. \quad (1)$$

The variation of lifetime with change of surrounding medium of center was attributed to decrease in the effective refractive index of the medium. Our results are similar to that for monoclinic nano-material Y_2O_3:Eu^{3+} reported by Meltzer.

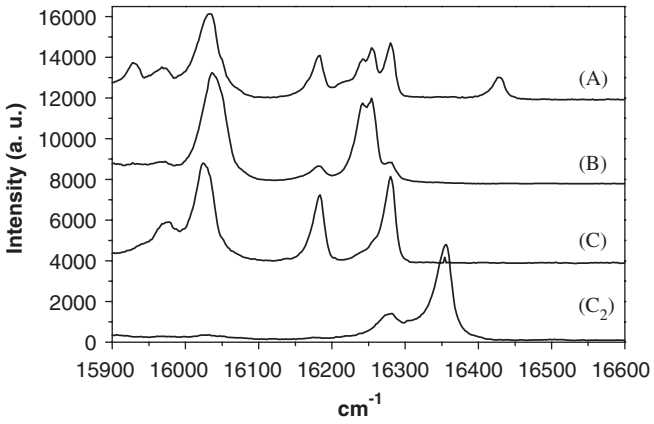

Fig. 3. Site-selective excitation spectra of monoclinic nanocrystalline at 10 K were excited at 578.3 nm(A); 582.1 nm(B); 582.3 nm (C); 580.6 nm (C_2).

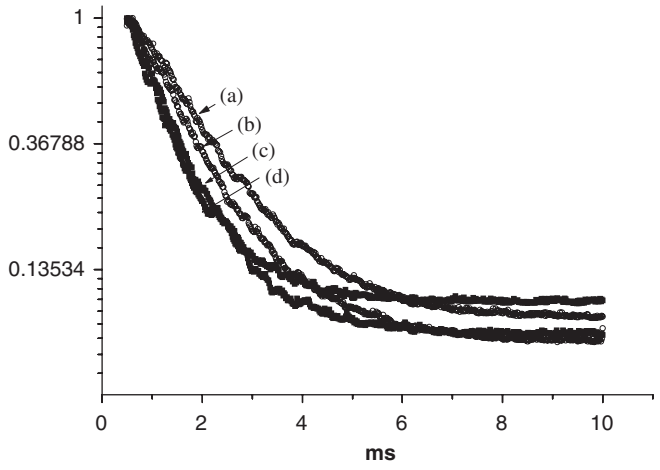

Fig. 4. Decay curves of monoclinic $Gd_2O_3:Eu^{3+}$ nanocrystalline, monitoring at 16 242 cm^{-1} (a), monoclinic $Gd_2O_3:Eu^{3+}$ nanocrystalline, monitoring at 16 183 cm^{-1} (b), bulk monoclinic $Gd_2O_3:Eu^{3+}$, monitoring at 16 254 cm^{-1} (c), bulk monoclinic $Gd_2O_3:Eu^{3+}$, monitoring at 16 280 cm^{-1} (d).

Table 1
The lifetimes of the fluorescence lines of $Gd_2O_3:Eu^{3+}$

	Monoclinic 10 nm (10 K)			Monoclinic Bulk (77 K)		
Monit. (cm^{-1})	16183	16242	16356	16429	16254	16280
Site	C	B	C_2	A	B	C
Lifet. (ms)	1.19	1.40	1.26	1.56	0.79	0.88

4. Conclusions

The PL spectra distributions for monoclinic nanosize $Gd_2O_3:Eu^{3+}$ are similar to that for bulk $Gd_2O_3:Eu^{3+}$. Energy transfer among three nonequivalent C_s centers in monoclinic nanosize $Gd_2O_3:Eu^{3+}$ is effective. The lifetimes of $Gd_2O_3:Eu^{3+}$ nanocrystalline are longer than that of the bulk. This may result from the decrease of effective refractive index of surrounding medium of luminescence center.

Acknowledgment

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