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Surface and size effects and energy transfer phenomenon on the luminescence of nanocrystalline X_1–Y_2SiO_5:Eu^{3+}

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Abstract

Optical luminescence of nanocrystalline $Y_{2-x}Eu_xSiO_5$ arises from four distinct sites. We show that one previously uncharacterized sites is a Eu^{3+} ion near the surface of the nanocrystal. The energy transfer rate between the two main sites varies with temperature and Eu^{3+} concentration and the dynamics of this transfer is explained theoretically. Luminescent quenching occurs at a much higher concentration and stronger luminescent intensity than in bulk Y_2SiO_5:Eu^{3+}. This is due to the hindering effects of particle boundaries to energy transfer.

Keywords: Luminescence; Nanocrystal; Energy transfer

1. Introduction

The novel properties of nanosize materials have recently attracted considerable interest. Doped nanosize materials are expected to have different properties from bulk materials due to the influence of confinement effects and surface effects. In particular, the particle boundaries may reduce resonant energy transfer in doped nanostructures and it may be possible to produce higher concentration and higher brightness luminescent materials. Oxysilicates are good luminescent hosts due to their high stability and are widely used as cathodoluminescent phosphors [1,2]. We have previously measured the photoluminescence properties of nanocrystal and amorphous nanosize particles of Y_2SiO_5:Eu^{3+} [3]. We present here an analysis of the surface and size effects and related energy transfer phenomenon.

2. Sample preparation and measurements

Nanocrystalline Y_2SiO_5:Eu^{3+} were prepared with Y_2O_3, Eu_2O_3 (99.99% purity), and ethyl silicate by the sol–gel technique. Normal-sized powders were prepared by a high-sintering method at a temperature of 1500°C. The details of the preparation are presented in Ref. [4].

There are two types of Y_2SiO_5 crystal. The crystallographic groups are $P_{2_1/c}$ (X_1 type) [5] and B_2/b (X_2 type) [6], respectively. The crystal structures of the samples were analyzed by a D/max-rA X-ray diffraction apparatus. The samples produced by heating the gels above 900°C are X_1-type crystals. The diffraction results have no significant variations for samples with different Eu^{3+} concentrations heated at the same temperature, which suggests that dopant Eu^{3+} ions substitute directly for Y^{3+}. The morphology and particle size were studied using a Hitachi H-900 NAR high-resolution transmission electron microscope. Samples synthesized by the sol–gel technique and heated above 900°C form crystals with particle size less than 50 nm. Those heated below 900°C contain chain-like and mesh-like amorphous particles with sizes smaller than the former samples. The samples synthesized by the high-sintering method are composed of particles of 2 μm.

Emission spectra of nanocrystalline $Y_{2-x}Eu_xSiO_5$ ($x = 0.01$) were measured at both room temperature and 15 K under UV 254 nm cw excitation by a GDM-1000 double grating monochrometer. The spectra arise mainly from two different Eu^{3+} sites in the X_1-type crystals. Further study by selective excitation of a dye laser pumped by a YAG:Nd laser shows that there are actually four sites, as shown in Fig. 1. The excitation wavelengths are 579.7, 577.7, 578.7 and 580.9 nm for the four sites, respectively. The first two correspond to the luminescence of the two distinct sites in bulk Y_2SiO_5:Eu^{3+} [3] and the fourth to Eu^{3+} in bulk

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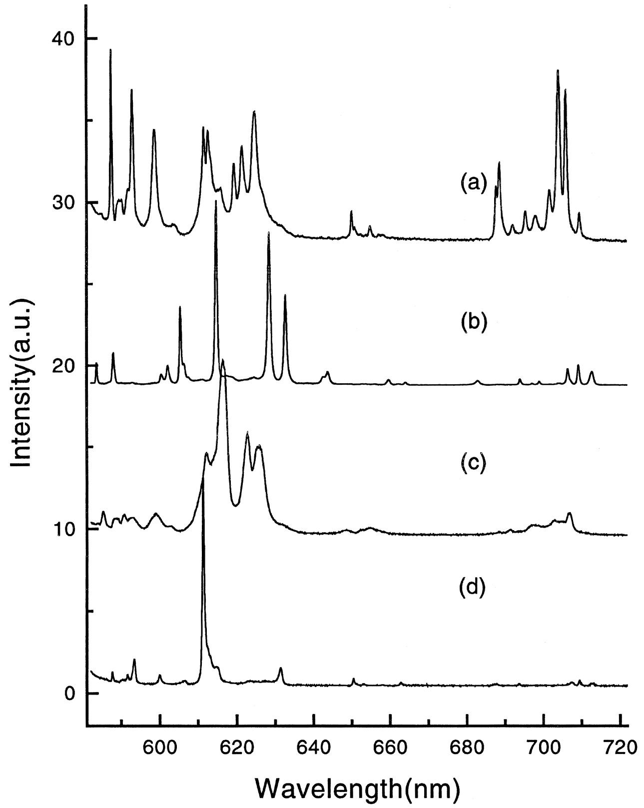

Fig. 1. Photoluminescent spectra from four sites in nanocrystalline $X_1 - Y_2SiO_5:Eu^{3+}$ under selective excitation of the $^7F_0 \rightarrow {}^5D_0$ transition at 15 K. Excitation wavelengths are (a) 579.7 nm; (b) 577.7 nm; (c) 578.7 nm; and (d) 580.9 nm, correspondingly. The luminescence transitions are $^5D_0 \rightarrow {}^7F_1$ (<603 nm), $^5D_0 \rightarrow {}^7F_2$ (603–640 nm), $^5D_0 \rightarrow {}^7F_3$ (640–670 nm) and $^5D_0 \rightarrow {}^7F_4$ (670–715 nm) for all four sites.

$Y_2O_3:Eu^{3+}$ [7]. The third site has not been previously identified. The lifetimes of the four sites were measured using pulsed site-selective excitation as 3.0, 2.2, 1.2 and 1.3 ms.

It is possible that the third site is in the amorphous phase, because the samples heated below 850°C are amorphous. However, the spectra of amorphous nanosize $Y_2SiO_5:Eu^{3+}$ are different. Another possibility is that it is due to pairs of Eu^{3+} ions. However, the closest that a Eu^{3+} pair could be is third-nearest neighbors, and it seems unlikely that the spectra would be affected so strongly in that case.

In order to identify the third site, we measured the luminescent properties of $Y_2SiO_5:Eu^{3+}$ with various Eu^{3+} concentrations at both room temperature and low temperature (15 K) under different excitation wavelengths. The spectrum at room temperature under 254 nm UV excitation changed very little as the concentration of Eu^{3+} varied from $x = 0.01$, when most Eu^{3+} has no Eu^{3+} nearby, to $x = 0.7$, when most Eu^{3+} have at least one Eu^{3+} nearby. If the third site was composed of Eu^{3+} pairs we would expect the spectrum to show a large variation as x changes from 0.01 to 0.7. At low temperature, $T = 15$ K, and high concentration, either UV or selective excitation of sites 2 or 1 at high concentration gives luminescence that is mainly from site 1. We interpret this as evidence for energy transfer from site 2 to site 1 (back transfer is negligible because there are no appropriate phonons to be absorbed at low temperature). Under selective excitation of site 4, luminescence characteristic of $Y_2O_3:Eu^{3+}$ is observed irrespective of the concentration of Eu^{3+} and the temperature. This indicates that $Y_2O_3:Eu^{3+}$ is a separate phase mixed with $Y_2SiO_5:Eu^{3+}$. At high concentrations at 15 K selective excitation of site 3 gives a spectrum that comes mainly from the luminescence of site 1 but even at $x = 0.7$ significant luminescence from site 3 is still observed. This indicates that energy transfer from the site 3 to site 1 is weaker than that of from site 2 to site 1. In summary, the luminescence from site 3 is somewhat like luminescence of amorphous Eu^{3+}, but is not in a separate phase because there is energy transfer from site 3 to site 1. Therefore we deduce that site 3 is a center near the surface of $Y_2SiO_5:Eu^{3+}$.

The relative luminescence intensities from sites 1 and 2 change as a function of Eu^{3+} concentration and of temperature. At 15 K, under either 254 nm excitation or selective excitation of site 2, the ratio of luminescence intensity from site 2 to luminescence intensity from site 1 decreases as the concentration increases. On the other hand, at 300 K, under either 254 nm UV excitation or selective excitation of sites 1 or 2, the intensity ratio varies only slowly as x increases from 0.2 to 0.7. If the concentration is held constant the intensity ratio of site 2 to site 1 decreases as temperature increases. The luminescence spectrum of the sample with $x = 0.4$ at different temperatures under UV excitation are shown in Fig. 2.

3. Energy transfer dynamics

In order to understand the dynamics of the energy transfer between sites 1 and 2, we consider a simple model. The rate of change of the probability that ith site of type α (1 or 2) is in the excited $^5D_0$ state is

$$\begin{aligned}\frac{\mathrm{d}P_{\alpha i}}{\mathrm{d}t} = {} & g_\alpha - \gamma_\alpha P_{\alpha i} \\ & + \sum_j D_{ji} P_{\alpha j} - \sum_j D_{ij} P_{\alpha i} \\ & + \sum_j X_{ji}(\bar{\alpha} \rightarrow \alpha) P_{\bar{\alpha} j} - \sum_j X_{ij}(\alpha \rightarrow \bar{\alpha}) P_{\alpha i}.\end{aligned} \tag{1}$$

In this expression g_α is the pumping rate, γ_α the decay rate for isolated ions on sites of type α, D_{ij} the transfer rate between equivalent sites, and X_{ij} the transfer rate between ions on inequivalent sites (if α is 1 then $\bar{\alpha}$ is 2 and vice versa).

We find that γ_α varies only slowly with temperature and it is assumed constant in the following. Energy transfer

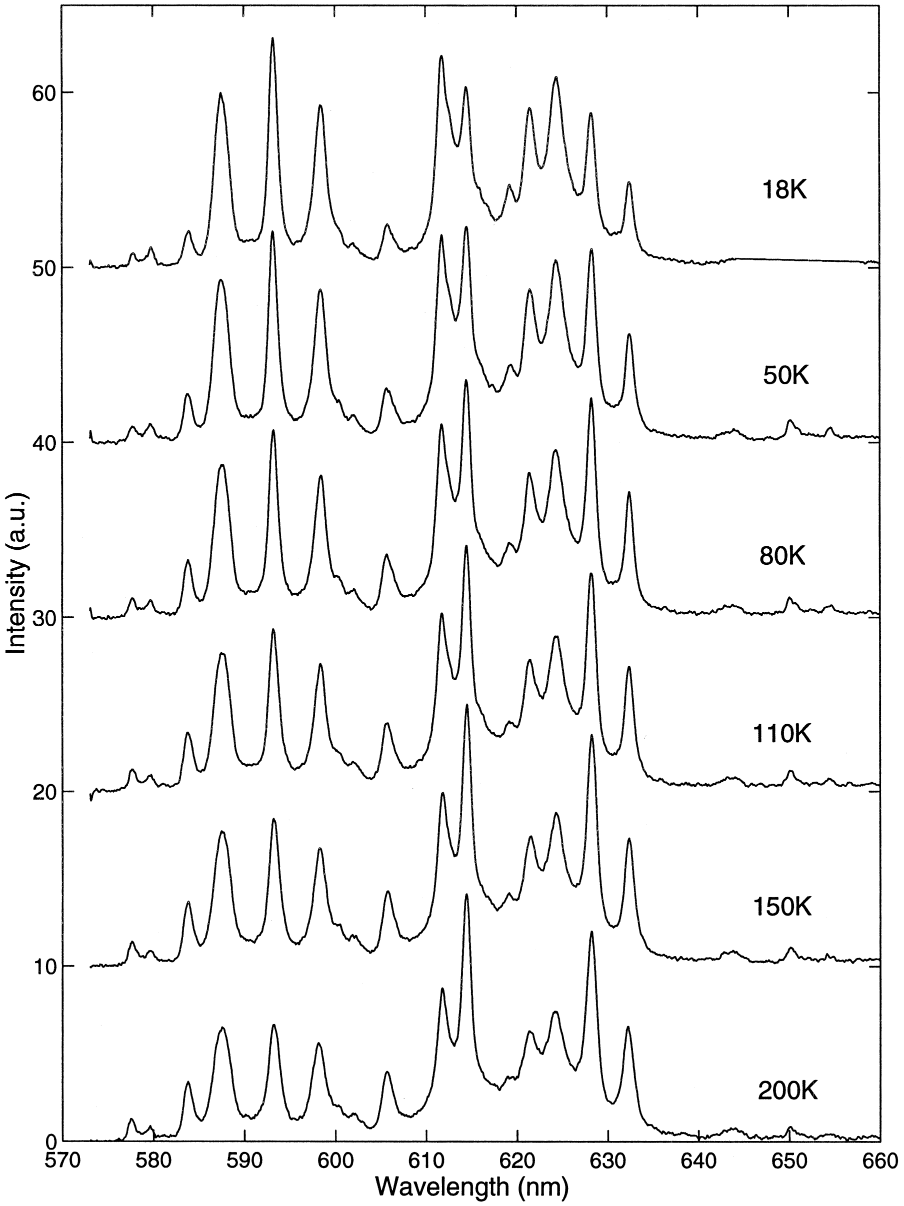

Fig. 2. Variation with temperature of photoluminescent intensity of nanocrystalline $Y_{2-x}Eu_xSiO_5$ with $x=0.4$ under cw 254 nm UV excitation.

between inequivalent sites involves absorption or emission of a phonon and since the energy of site 2 is higher than that of site 1 by $\Delta E \approx 80$ K, the transfer rates [8] are:

$$\begin{aligned} X_{ij}(2 \rightarrow 1) &= \eta W(R_{ij})[n(|\Delta E|)+1] \\ X_{ji}(1 \rightarrow 2) &= \eta W(R_{ji}) n(|\Delta E|), \end{aligned} \tag{2}$$

where $n(E) = (\exp(E/kT) - 1)^{-1}$ is the number of phonons per mode, $W(R)$ is the resonant transfer rate, and η is a positive constant related to electron–phonon coupling.

With limited experimental data a complete solution of Eq. (1) is not possible. However, we can simplify the problem by assuming that the energy transfer between equivalent sites is resonant, and therefore much faster than transfer between inequivalent sites. If we assume that that the excitation is always equally distributed amongst equivalent ions then we can write rate equations for the average excitation probabilities of sites of types 1 and 2 ($\bar{P}_1$ and $\bar{P}_2$) as follows:

$$\begin{aligned} \frac{d\bar{P}_1}{dt} &= g_1 - \gamma_1 \bar{P}_1 + \bar{X}(2 \rightarrow 1)\frac{\bar{P}_2}{N_1} - \bar{X}(1 \rightarrow 2)\frac{\bar{P}_1}{N_1} \\ \frac{d\bar{P}_2}{dt} &= g_2 - \gamma_2 \bar{P}_2 + \bar{X}(1 \rightarrow 2)\frac{\bar{P}_1}{N_2} - \bar{X}(2 \rightarrow 1)\frac{\bar{P}_2}{N_2}, \end{aligned} \tag{3}$$

where N_1 and N_2 are the proportion of centers of sites 1 and 2, respectively, and $\bar{X}(\alpha \rightarrow \bar{\alpha})$ is the total transfer rate from site α to $\bar{\alpha}$. Under cw excitation we have $d\bar{P}_1/dt = d\bar{P}_2/dt = 0$ and the ratio of the intensities of luminescence from site 2 and site 1 is:

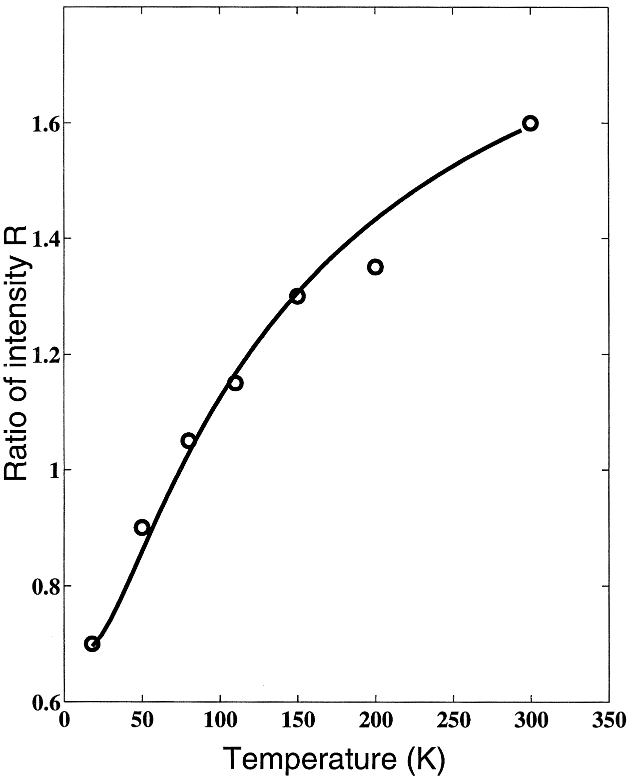

Fig. 3. Variation with temperature of the ratio of luminescence intensity from site 2 to site 1 in nanocrystalline $Y_{2-x}Eu_xSiO_5$, with $x = 0.4$ under UV excitation. The experimental results are shown as dots and the fitted results are plotted as a solid line.

$$R = \frac{I_2}{I_1} = \frac{\gamma_2 N_2 P_2}{\gamma_1 N_1 P_1} = C\frac{An(|\Delta E|) + \beta\gamma_1}{A[1 + n(|\Delta E|)] + (1 - \beta)\gamma_2}, \tag{4}$$

where $C = N_2\gamma_2/N_1\gamma_1$, $\beta = g_2/(g_1 + g_2)$ (we assume $g_1 = g_2$ for UV excitation), and the transfer coefficient

$$A = \left(\frac{\beta}{N_2} + \frac{1-\beta}{N_1}\right)\sum_{ij}\eta W(R_{ij}). \tag{5}$$

A fit to our experimental results gives $A = 0.28\ (\text{ms})^{-1}$ and $C = 2.1$. The former value shows that at room temperature the effective transfer rate between the two sites is about five times that of the radiative decay rate. From the latter value we deduce that $N_2/N_1 = 1.5$. N_1 would be equal to N_2 if the Eu^{3+} ions were randomly distributed. Our result indicates that Eu^{3+} ions preferentially occupy site 2 rather than site 1. The fit to the experimental results is shown in Fig. 3. Agreement is reasonable considering that experimental uncertainties are approximately 10% and the theoretical approximations are quite crude.

4. Concentration quenching

The luminescence of the nanocrystals is very strong and does not show obvious quenching until $x > 0.6$. In Fig. 4 we plot the luminescence intensity of both nanocrystalline and bulk Y_2SiO_5:Eu^{3+} under UV excitation against Eu^{3+} concentration. The quenching concentration is about $x = 0.2$ for normal Y_2SiO_5:Eu^{3+} and about $x = 0.6$ for the nanocrystal. The maximum luminescence intensity of nanocrystalline Y_2SiO_5:Eu^{3+} is more than twice that of the bulk sample and is larger than that of the commercial three-element color luminescent material YVO_4:Eu^{3+}.

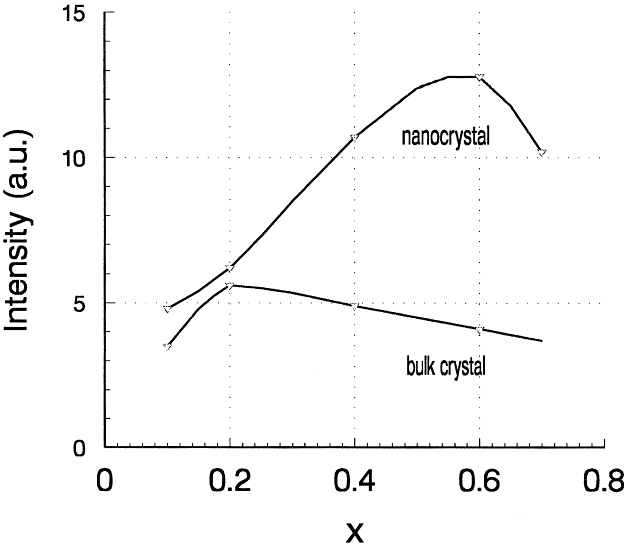

Fig. 4. Variation of luminescence intensity for nanocrystalline and bulk $Y_{2-x}Eu_xSiO_5$ with x at room temperature under UV excitation.

Concentration quenching may occur by cross-relaxation or transfer to nearby quenching centers (traps). For the excited $^5D_0$ levels of Eu^{3+} there are no intermediate energy levels between the excited state and the ^7F_J states to act as a bridge for cross-relaxation, so only the latter mechanism is possible. Due to the partial spin-forbidden character of the transition $^5D_0 \rightarrow {}^7F_J$ the lifetime is several ms and the electric multipole resonant transfer between nearby Eu^{3+} is very slow. It has been argued that interaction between the nearest Eu^{3+} pairs in Y_2O_3:Eu^{3+} is mainly via exchange or super-exchange interactions and thus the interaction distance is very short [9]. We expect a similar case for Y_2SiO_5:Eu^{3+}.

Qualitatively, when the concentration of luminescent centers is small, the luminescent centers can be thought of as 'isolated'. In practical luminescent materials the concentration of traps in the materials is very low and only the few luminescent centers having traps nearby will transfer their energy to the traps. Therefore the luminescent quenching is not significant. For bulk materials, as the concentration of luminescent centers increases, the luminescent centers may be near enough to each other to form a 'resonant energy transfer net' in the crystal and energy can be rapidly transferred to a center near a trap and then hence to the trap. Consequently, most excited centers lose energy non-radiatively and thus concentration quenching occurs. For nanoparticles there is a limited number of primitive cells in any one particle and on average there are only a few traps. Since the traps are distributed randomly there is large fluctuation of the number of traps in each particle. As the concentration of luminescent centers increases, quenching occurs first in particles that contain many traps, while those particles containing few or no traps quench at only high concentration or do not quench at all. Therefore, on average, quenching occurs at higher Eu^{3+} concentrations in nanosize materials than in normal materials. As the luminescent intensity of a nanocrystal is not weaker than that of a normal sample, it seems that the surface contributes little to non-radiative relaxation.

5. Conclusions

We have measured photoluminescence of nanocrystalline $X_1-Y_2SiO_5$:Eu^{3+} as a function of Eu^{3+} concentration and sample temperature with both selective and non-selective excitation. We have shown that the previously uncharacterized site is most likely the luminescence of Eu^{3+} near the surface. The ratio of luminescent intensities of the two major sites in $X_1-Y_2SiO_5$:Eu^{3+} changes with temperature under UV excitation and we have explained this in terms of dynamics taking both transfer and back transfer into account. The quenching concentration increases from $x=0.2$ for the bulk crystal to $x=0.6$ for the nanocrystal. We have given a qualitative explanation of this phenomenon in terms of confinement effects and surface effects.

Acknowledgements

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