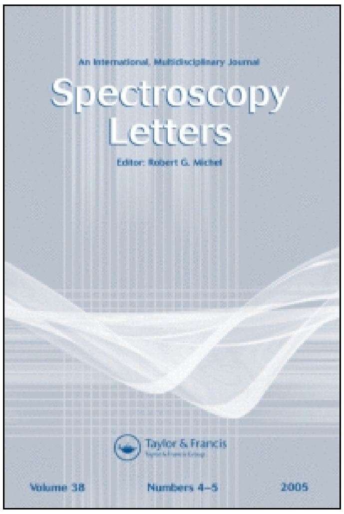

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EXCITATION TRANSFER BETWEEN THE TWO SITES IN THE NANOMETRIC SCALE X_1-Y_2SiO_5:Eu

Key words: Excitation transfer, Lifetimes, Site selective photoluminescence spectra, X_1-Y_2SiO_5:Eu

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ABSTRACT

We have measured the photoluminescence spectra of nanometric scale X_1-Y_2SiO_5:Eu_x. The spectra were recorded at 15K and room temperature using site selective excitation by a dye laser in addition to conventional UV excitation. We found that at low temperature there is a pronounced excitation transfer from site 2→1. The transfer rate increases rapidly with increasing concentration and for x=0.7 no fluorescence from site 2 can be observed. Decaycurve measurement revealed this transfer process directly. The lifetimes of the $^5D_0$ levels of the two sites were also measured as a function of Eu^{3+} concentration. The results show that the lifetimes of the $^5D_0$ level of site 2 decreases with increasing concentration. The

mechanism of the excitation transfer is discussed. Wavelengths of the $^5D_0 \rightarrow ^7D_{0-4}$ transitions of the two sites were also tabulated.

1. INTRODUCTION

Y_2SiO_5 can crystallizes in the two different structures: X_1 type of space group $P2_1/c$ and X_2 type of space group B2/b, depending upon the synthetic temperature [1,2]. In both structures, there are two crystallographically non-equivalent RE (RE=rare earth) sites of the low symmetry C_1, which differ in its coordination to oxygen: 7 and 9 for X_1 type; 6 and 7 for X_2 type [3]. In an earlier paper, we investigated certain spectroscopic properties of nanometric scale X_1-Y_2SiO_5:$Eu_{0.1}$ [4]. Specifically we measured excitation and emission spectra and found some interactions between the two sites. In this paper we present our work on excitation transfer between the two sites at different concentrations and temperatures. It is shown that the excitation transfer process from site 2 (the higher energy site) → site 1 (the lower energy site) can be seen directly by measuring the decaycurves. At low temperature and high concentration, the transfer enables the fluorescence of site 2 to disappear entirely.

2. EXPERIMENT

Compounds of the X_1-Y_2SiO_5:Eu_x with x=0.01, 0.1, 0.2, 0.4 and 0.7 were prepared by sol-gel method according to [4]. X-ray checks (Cu Kα radiation) of the resulting white products showed all samples crystallize in the X_1 type. The average particle size is about 50nm.

The experimental apparatus is basically the same as described in [4]. Briefly, the luminescence of X_1-Y_2SiO_5:Eu nanometric powder samples was measured under both UV and dye laser excitation at 300 and 15K. The 254nm radiation from a mercury lamp was selected by a wide band filter, and this excitation corresponds to the strong absorbing charge transfer state of Eu^{3+} in X_1-Y_2SiO_5. A rhodamine 6G dye laser was employed to excite selectively the $^5D_0$ level of Eu^{3+} ions in the two sites. The $^5D_0 \rightarrow {}^7D_{0\text{-}4}$ transitions between 565 and 725nm were considered in detail.

The decaycurves (and the fluorescent lifetimes of the $^5D_0$ level) were measured by using a oscilloscope interfaced with a computer.

3. RESULTS

3.1 Site Selective Photoluminescence

Under UV excitation X_1-Y_2SiO_5:Eu shows strong red luminescence between 565--725nm (fig.1). The five groups of sharp lines can easily be attributed to $^5D_0 \rightarrow {}^7D_{0\text{-}4}$ transitions of Eu^{3+} ion. Owing to the absence of inversion symmetry in the RE^{3+} sites, strong electric dipole transitions to the $^7D_{2,4}$ crystal field sublevels are recorded around 620 and 700nm. The strongest emission peaks at 614.7nm. The $^5D_0 \rightarrow {}^7D_1$ transitions induced by magnetic dipole interaction around 590nm have strengths almost equal to those of electric dipole transitions. Their strongest peak locates at 587.4nm. The $^5D_0 \rightarrow {}^7D_0$ transition also has significant intensity. The strength of this transition depends on the amount of the contributions from the other $^7D_{JM}$ wavefunction to the $^7D_{00}$ one.

The unsplit $^5D_0 \rightarrow {}^7D_0$ transition can be used to deduce the number of RE sites in luminescent crystalline samples. There are three sharp $^5D_0 \rightarrow {}^7D_0$ transitions in figure 1 with peaks locating at 577.7, 579.7 and 580.9nm respectively. Since the 580.9nm peak originates in the $^5D_0 \rightarrow {}^7D_0$ transition of Eu^{3+} in Y_2O_3 [4], the figure indicates the presence of two Eu^{3+} sites of low symmetry in X_1-Y_2SiO_5, which is in agreement with structure data. For convenience, we refer to lines at 579.7nm and 577.7nm as sites 1 and 2 respectively. It should be pointed out that the existence of

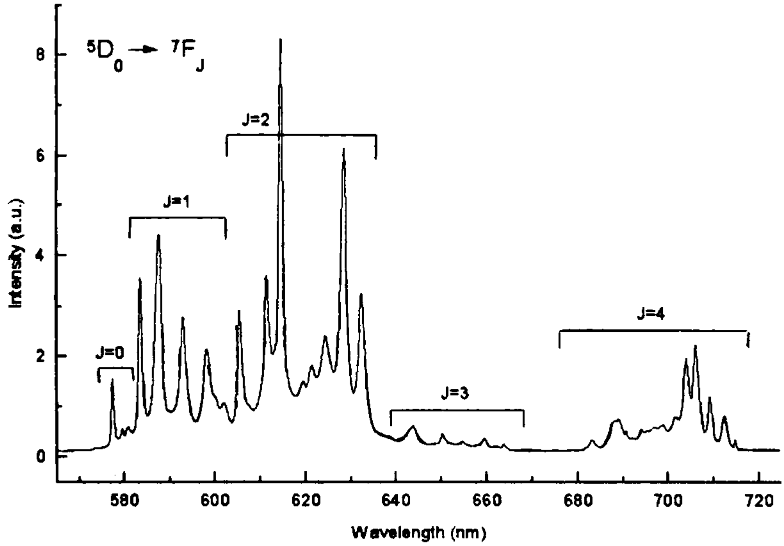

FIG.1 Emission spectrum of X_1-Y_2SiO_5:$Eu_{0.01}$ under 254nm excitation at room temperature.

small amount Y_2O_3 mixed in Y_2SiO_5 is normal in powder samples, as stated by their phase diagram [5].

Using a dye laser to excite the two sites of Eu^{3+} ions selectively, two different photoluminescence (PL) spectra (15K) were obtained (fig.2), where figure (a) is for site 1 and (b) for site 2. The wavelength values of the $^5D_0 \rightarrow {}^7D_{0\text{-}4}$ transitions for the two sites were given in table 1.

It is well known that Eu^{3+} is a non-Kramers ion, its electric energy-level degeneracy can be completely lifted by the crystal field. Thus the 2J+1 emission lines are expected for the transition of $^5D_0 \rightarrow {}^7D_J$. In some cases the total number of lines exceeds the maximum 2J+1 (see table 1), indicating the possibility of structure disorder, due to, for example, the different orientation of the SiO_4 group [6,7]. The

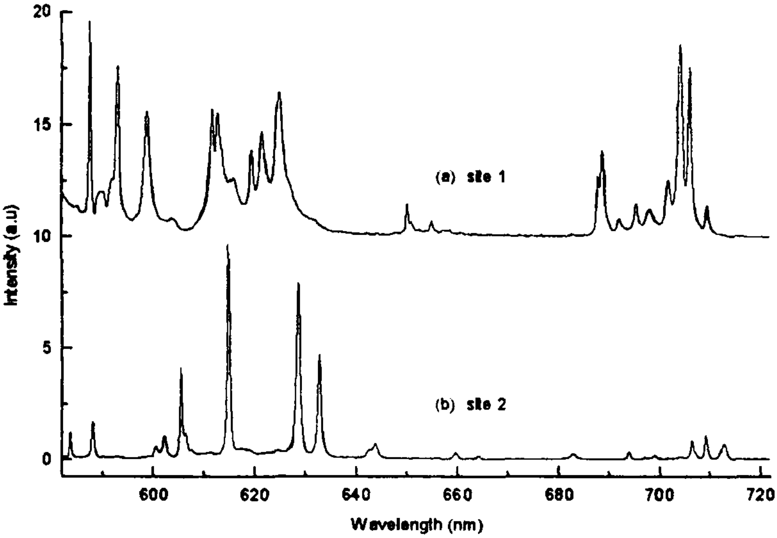

FIG.2 Emission spectra of X_1-Y_2SiO_5:$Eu_{0.01}$ obtained at 15K by exciting (a) site 1 and (b) site 2.

complete lifting of degeneracy is consistent with the low point symmetry of the site occupied by the Eu^{3+} ion.

3.2 Excitation Transfer between the Two Sites

Figure 3(a) gives the PL spectra of X_1-Y_2SiO_5:Eu_x (x=0.1, 0.2, 0.4, and 0.7) at room temperature. The excitation is the same as figure 1. There is no so much difference among the spectra of different concentration samples, even between the most diluted sample (x=0.01 in fig.1) and the most concentrated sample (x=0.7 in fig.3(a)). The strongest peak is always located at 614.7nm corresponding to the $^5D_0 \rightarrow {}^7D_2$ transition of site 2. At low temperature (15K), the situation is quite different. The spectrum features of X_1-Y_2SiO_5:Eu_x change rapidly with concentration (fig.3(b)). For x=0.1, the spectrum remains nearly the same as

TABLE 1

Wavelengths of the $^5D_0 \rightarrow ^7F_{0\text{-}4}$ Transitions Observed in Site Selective Excited Luminescence of X_1-Y_2SiO_5:$Eu_{0.01}$ at 15K

Transitions	Site 1	Site 2
$^5D_0 \rightarrow ^7F_0$	579.7	577.7
$^5D_0 \rightarrow ^7F_1$	587.4	583.5
	590.1	587.9
	591.9	
	592.9	
	598.7	600.4
	603.5	602.1
$^5D_0 \rightarrow ^7F_2$	611.5	605.3
	612.6	606.3
	615.9	614.7
	619.4	
	621.4	628.5
	624.8	632.7
$^5D_0 \rightarrow ^7F_3$	650.1	642.7
	650.8	643.8
	654.8	659.8
		664.0
$^5D_0 \rightarrow ^7F_4$	687.8	682.9
	688.6	
	692.1	693.9
	695.4	
	698.1	699.0
	701.7	
	704.1	706.4
	706.0	709.2
	709.5	712.8

All values in nm units

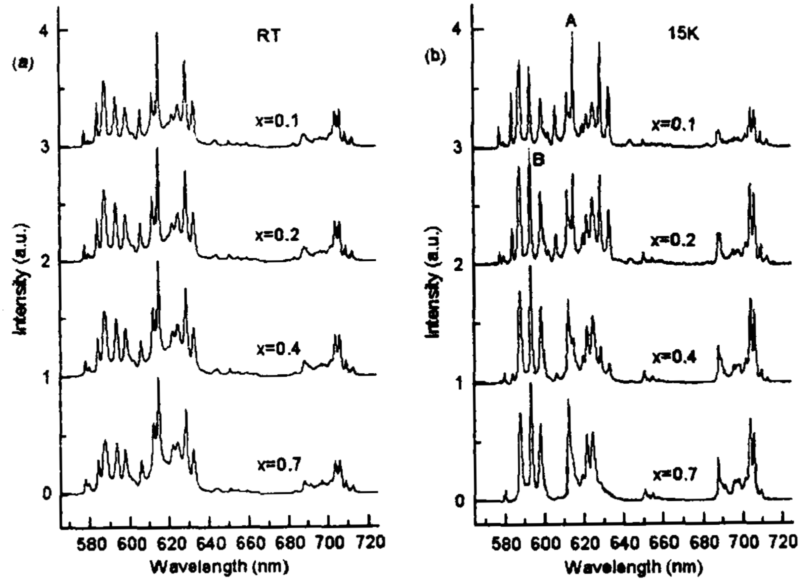

FIG.3 Emission spectra of X_1-Y_2SiO_5:Eu_x with x=0.1, 0.2, 0.4 and 0.7 under 254nm excitation at (a) RT and (b) 15K.

that of at room temperature. The strongest emission peak still located at 614.7nm (referred as A). While for x=0.2, the strongest one is no longer the main peak A of site 2 and becomes the 592.9nm line (referred as B) of $^5D_0 \rightarrow {}^7D_1$ transitions belonging to site 1 (see table 1). At the same time, the transitions of $^5D_0 \rightarrow {}^7D_4$ become stronger too. As the concentration increases further, line A becomes weaker and weaker. For x=0.4, only a small peak can be seen. Correspondingly, the fluorescence of site 1 becomes more and more dominant. For x=0.7 sample, peak A disappears entirely. In fact, not only peak A, all the peaks originate in site 2 disappear totally. This can be seen by comparing figure 2(b) and the PL spectrum of x=0.7 sample in figure 3(b). These results bring such a fact that under UV excitation, at low temperature and high concentration, only fluorescence of site 1 were left.

In order to understand better the fluorescent features of the two sites at low temperature, we measured the PL spectra (15K) corresponding to the two sites by exciting each site selectively. The results are shown in figure 4. Under exciting site 1, we got almost the same spectrum for different concentration X_1-$Y_2SiO_5:Eu_x$ (x=0.1, 0.2, 0.4 and 0.7) samples (fig.4(a)). Whereas if we excite site 2, different results were obtained, as seen in figure 4(b). For x=0.1, all the strong emission lines belong to site 2, but some weak peaks attributed to site 1 also appear (This is different from that of x=0.01, see fig.2(b)). As the concentration increases, emission peaks of site 1 become more and more strong. For x=0.4, the emissions of site 1 have the strength equal to or even larger than those of site 2. For x=0.7, almost no lines from site 2 is recorded. Please pay attention that here only site 2 is excited. These results suggest that the interaction between the two sites increases with increasing concentration. This interaction induces an excitation transfer from site 2 to site 1.

Now we can understand the results shown in figure 3(b). Under 254nm excitation, ions were pumped into the charge transfer state. Then the $^5D_0$ level of the two sites were fed from there and the $^5D_0 \rightarrow {}^7F_{0\text{-}4}$ transitions take place. As the concentration increases, the interaction between the two sites increases. The excitation transfer rate from site 2 to site 1 also increases. And this results in the emission of site 1 more and more dominant.

The most straightforward and the most efficient method to investigate excitation transfer is to measure the decaycurves of related transition and the lifetimes of corresponding levels. Some results are given in figure 5. Curves (a) and (b) are the decaycurves of the $^5D_0 \rightarrow {}^7F_1$ transition of site 1 under exciting site 1 and site 2 respectively. When we excite site 1, the curve is a very good single exponential one and gives the lifetime of 2.9ms for x=0.2 sample. While we excite site 2, the curve rises first and then decays. It shows clearly the presence of excitation transfer from site 2→1.

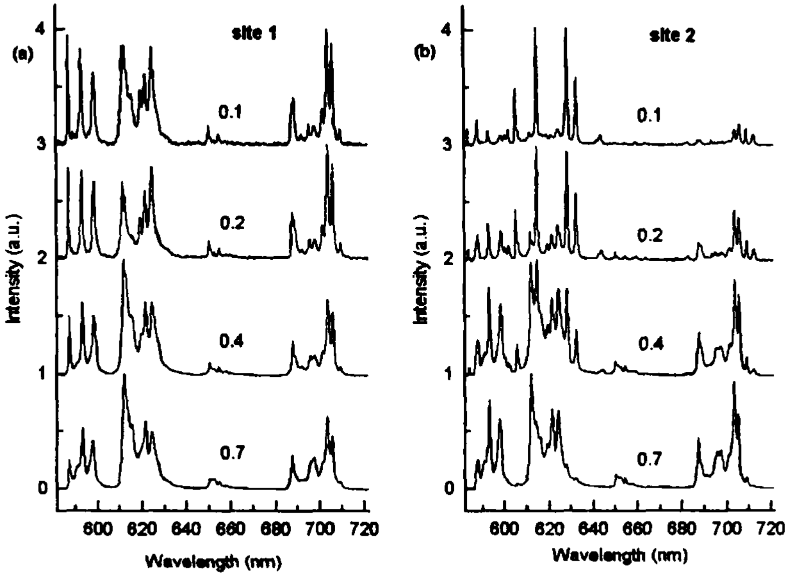

FIG.4 Emission spectra of X_1-Y_2SiO_5:Eu_x with x=0.1, 0.2, 0.4 and 0.7 obtained at 15K by exciting (a) site 1 and (b) site 2.

Table 2 gives the lifetimes of the $^5D_0$ level of the two sites at 15K for different concentration samples. The table shows that the lifetime of the $^5D_0$ level of site 1 decreases slightly with increasing concentration, while that of site 2 decreases noticeably, from 2.18ms of x=0.01 to 1.34ms of x=0.4. This is also related to the excitation transfer of site 2→1.

4. DISCUSSION

The above experimental results tell us that there is an excitation transfer process from site 2→1, and this transfer can only be seen at low temperature. At room temperature, no transfer process was observed. Now we discuss this problem.

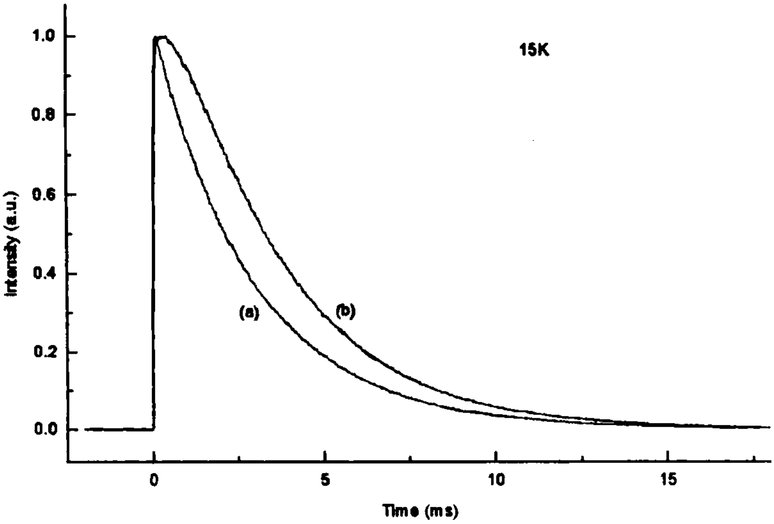

FIG.5 Decaycurves for the $^5D_0 \rightarrow {}^7F_1$ transition of site 1 at 15K by exciting (a) site 1 and (b) site 2.

TABLE 2

Lifetimes of the $^5D_0$ Levels of the Two Sites in X_1-Y_2SiO_5:Eu_x at 15K

x	Lifetime (ms)	
	site 1	site 2
0.01	3.00	2.18
0.1	2.94	1.82
0.2	2.90	1.59
0.4	2.80	1.34
0.7	2.80	

Table 1 shows that the $^5D_0$ level of site 1 and site 2 locates at $17246cm^{-1}$ (579.7nm) and $17305cm^{-1}$ (577.7nm) respectively. The site 2 is higher in energy than that of site 1 with an energy difference of $59cm^{-1}$. Spatial transfer between them required that the phonons make up the mismatch. As the mismatch is large ($|\Delta E_{12}|=59cm^{-1}$), it is enough to consider one-phonon-assisted process. In this case, the energy transfer from site 2→1 creates a phonon and the rate can be described as [8]

$$w_{2\to1}=\frac{J^2(f-g)^2|\Delta E_{12}|}{\pi(h/2\pi)^4\rho}(\sum_s(\frac{\alpha_s}{v_s^5})[n(|\Delta E_{12}|)+1]$$

whilst the process from site1→2 annihilates a phonon and the rate takes the form of

$$w_{1\to2}=\frac{J^2(f-g)^2|\Delta E_{12}|}{\pi(h/2\pi)^4\rho}(\sum_s(\frac{\alpha_s}{v_s^5})[n(|\Delta E_{12}|)]$$

Here J is the matrix element of the site-site coupling Hamiltonian, f (g) is the ground-state (excited-state) coupling strength for the ion at the site, ρ is the mass density, α_s is of order unity, and $n(x)=[\exp(x/kT)-1]^{-1}$. Thus we have

$$\frac{w_{2\to1}}{w_{1\to2}}=\frac{n+1}{n}=\exp(|\Delta E_{12}|/kT)$$

At room temperature (300K), $\Delta E_{12}/kT\approx59/208.5$, $\frac{w_{2\to1}}{w_{1\to2}}\approx1.3$, the transfer rates of 2→1 and 1→2 are comparable. Consequently we can hardly see the excitation transfer phenomenon. While at 15K, $\Delta E_{12}/kT\approx5.6$, $\frac{w_{2\to1}}{w_{1\to2}}\approx270$, site 2→1 dominants the process, the excitation transfer process can be observed clearly.

As to the lifetime results, it can also be easily understood. As the concentration increases, the distance between the two sites decreases. This results in a larger excitation transfer rate [9] and thus a shorter lifetime.

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