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Energy transfer between Eu^{3+} ions in sol–gel derived silica glasses

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Abstract

Time-resolved fluorescence line narrowing technique has been used to analyse the evolution of the $^5D_0 \rightarrow {}^7F_0$ emission of Eu^{3+} ions in sol–gel derived silica glasses. These samples were doped with 2.5 mol% of Eu^{3+} and heat treated at different temperatures. Background fluorescence, coming from Eu^{3+} ions excited by energy transfer processes, was observed in these experiments. Using a previously proposed equation model, a study of the multipole character of the interaction between Eu^{3+} ions was performed. The annealing process carried out in the samples causes important changes in the efficiency of energy transfer process and in its multipole character, varying from $S=6$ (in a sample treated at 400°C) to $S=10$ (in a sample treated at 600°C), indicating that the environment of Eu^{3+} ions has been modified.

Keywords: Sol–gel silica glass; Eu^{3+}; Time-resolved optical spectroscopies; Energy transfer

1. Introduction

Sol–gel process is a room temperature method for the synthesis of inorganic hosts that permits a homogeneous doping in a silica matrix. This technique is expected to lead new applications in nonlinear optics, solid state tunable lasers, electronics and other field of technology [1]. Broadened luminescence is generated by the existence of different sites for these active ions in the same matrix, due to the disordered nature of the media. In this way, Eu^{3+} ions have been widely used as a crystal field probe to test the ion–ion and ion–matrix interactions in crystals and glasses [2]. The main advantages are the simplicity of its energy level structure, the sensitivity shown by the luminescence to the local surroundings and the fact that the $^5D_0 \leftrightarrow {}^7F_0$ transitions are between non-degenerate levels.

In sol–gel samples, the sites for these active ions change if the silica glass is treated at different temperatures [3,4]. A study of the densification (solidification of the liquid environment) of the gel obtained at different heat treatments were performed by Campostrini et al. [3] and Bouajaj et al. [4]. As the annealing temperature was increased, the densification of the sample becomes higher. This evolution comes from the expulsion of solvent and from the polycondensation of the silica chains. The system goes from a liquid-like environment towards a dry and densified environment.

Interaction between ions of the same species occurs when the distance among them is short enough, inducing energy transfer processes. This kind of process is known as migration. In order to give a view of these energy transfer processes between Eu^{3+} ions, the evolution of the $^5D_0 \rightarrow {}^7F_0$ emission has been analysed using time resolved fluorescence line narrowing (TRFLN) in other different matrixes [5–8]. In this technique an inhomogeneously broadened absorption band is excited, within the high energy side, with a monochromatic pulsed light. Initially, a narrow line emission spectrum coming from ions that were excited by the incident light is observed, besides a broad background fluorescence coming from ions excited by energy transfer. As time passes this background emission becomes more important with respect to the narrow peak. In these experiments, the analysis of the fluorescence spectrum temporal evolution gives information about microscopic transfer processes between ions and different sites occupied by them in the matrix, the homogeneous widths of the transitions, etc.

In this work, the energy transfer between different sites occupied by Eu^{3+} ions in sol–gel derived silica glasses is investigated by TRFLN in the gel to glass transition induced by heat treatments in the range from room temperature to 800°C. Theoretical expressions for the

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evolution of the fluorescence [8,9] are used to analyse the experimental results obtained in samples with different heat treatments. As the multipole energy transfer process depends on the distance between ions, it is possible to obtain information about the distribution of Eu^{3+} ions.

2. Experimental

Silica glasses doped with 2.5 mol% of $Eu(NO_3)_3$ were prepared by sol–gel technique. The molar ratio TEOS (tetraethoxysilane):CH_3CH_2OH:H_2O used was 1:4:4. Treatments at different temperatures up to 800°C were performed on the samples at a heating rate of 3°C/min. Once the final temperature was reached, they were annealed for approximately 24 h.

Broad band emission spectra were obtained by exciting the samples with light from a 250 W incandescent lamp passed through a 0.25 m monochromator. Fluorescence was detected through a 0.25 m double monochromator with a photomultiplier. The spectra were corrected by the instrumental response. For TRFLN spectra a tunable laser operating with Rhodamine 6G, pumped by a Q-switched 532 nm frequency-doubled Nd-YAG laser, was used. The spectral linewidth was 0.15 cm^{-1} and the pulse width 5 ns. The time resolved fluorescence was recorded using the 0.25 m double grating monochromator with a maximum slit of 50 μm and a photomultiplier. In order to avoid the saturation of the detector by direct laser light, a mechanical chopper synchronized with the Q-switching was inserted between the sample and the monochromator. Finally, the temporal evolution of the fluorescence was registered using a digital storage oscilloscope controlled by a PC. For low temperature measurements a helium continuous flow cryostat was used.

3. Theoretical background

In TRFLN experiments, the most appropriate quantitative measure of the transfer is the ratio $R(t, E_0)$ of the intensity in the narrow band I_R, coming from ions with energy E_0 excited resonantly, to the total intensity, which includes the background fluorescence I_B. This relation can be expressed as

$$R\,(t,E_0) = \frac{I_R}{I_R + I_B} \tag{1}$$

When we consider asymmetric transfer rates, a reasonable general theoretical approximation to $R(t)$ depending on the energy mismatch between ions, together with an expression for the background fluorescence evolution, was obtained by Huber and Ching [10]. It is necessary to assume an interaction mechanism for the energy transfer processes to obtain an expression that can be compared with experimental results. In a previous paper, the present authors evaluated the expressions given by Huber and Ching for the ratio $R(t, E_0)$ and the background fluorescence assuming a multipole interaction assisted by a phonon [9]. The quantity $R(t, E_0)$ can be expressed, according to the authors [8], by the following expression

$$R(t, E_0) = \exp(-\beta t^{3/S}) \tag{2}$$

with

$$\beta = C_A \frac{4\pi}{3} \Gamma\left(1 - \frac{3}{S}\right) \int \left[C_{DA}^{(S)}(E - E_0)\right]^{3/S} W_+^{(3/S)-1}\, p(E)\, dE \tag{3}$$

where $S = 6, 8, 10, \ldots$ depending on the interaction character (dipole–dipole, dipole–quadrupole, quadrupole–quadrupole, ...), E_0 is the energy of the ions excited by the laser pulse at $t = 0$, C_A is the acceptor concentration, $\Gamma(x)$ is the gamma function, $p(E)$ is the normalized inhomogeneous line shape and $C_{DA}^{S}(E - E_0)$ is the donor–acceptor energy transfer parameter whose dependence on the energy mismatch $(E - E_0)$ for processes with emission or absorption of a phonon is given by

$$\begin{aligned} C_{DA}^{S}(E - E_0) &\propto |E - E_0| \left(\frac{1}{\exp[|E - E_0|/KT]} + 1 \right) \quad & E \le E_0 \\ C_{DA}^{S}(E - E_0) &\propto |E - E_0| \left(\frac{1}{\exp[|E - E_0|/KT]} \right) \quad & E \ge E_0 \end{aligned} \tag{4}$$

and

$$W_+ = 1 + \exp\left(\frac{E - E_0}{KT}\right) \tag{5}$$

In this way, the transfer probability from ions with energy E_0 to ions with energy E is expressed by

$$W_{OR} = \frac{C_{DA}^{(S)}(E - E_0)}{R^S} \tag{6}$$

where R is the donor–acceptor distance. The processes with high values for the parameter S are more favoured when the distance R decreases.

The critical radius R_C, defined as the distance between ions for which the energy transfer probability equals the radiative decay probability, can be calculated from the equation

$$\frac{1}{\tau} = \frac{C_{DA}^{S}}{(R_C)^S} \tag{7}$$

The evolution of the background fluorescence after the excitation pulse can also be evaluated assuming a multipole interaction mechanism assisted by a phonon. The obtained result can be expressed, according to Martín et al. [9], by the following equation

$$I(t,E,E_0) = \frac{[1 - R(t,E_0)]p(E)}{\ln R(t,E_0)} \Big[- C_{\mathrm{A}} \frac{4\pi}{3} \Gamma(1 - 3/S) [C_{\mathrm{DA}}^{S}(E - E_0)t]^{3/S} W_{+}^{3/S-1} \Big] \tag{8}$$

where $R(t, E_0)$ is given by Eq. (2).

4. Results and discussion

Lifetimes corresponding to the $^5D_0$ level obtained in sol–gel derived silica glasses doped with 2.5 mol% of Eu^{3+} are presented in Fig. 1. A very low value of about 100 μs is obtained for the as made sample, but a notable enhancement is observed with the increase of the annealing temperature. This effect was also observed in similar sol–gel silica matrixes by Campostrini et al. [3] and Bouajaj et al. [4]. This result can be explained considering the vibrational modes of the silica network involved in non radiative deexcitation processes. In the as made samples low quantum efficiency is found due to the high vibrational energy of the present OH groups. With the annealing these groups are expelled and nonradiative transition become less efficient, therefore an enhancement of lifetime is obtained. In this way, in the sample heat treated at 800°C, a value of 717 μs for the $^5D_0$ lifetime was measured, close to the value of about 1 ms that Brecher et al. [11] obtained in silica glasses by melt.

In the Judd–Ofelt theory [12,13] the $^7F_0 \leftrightarrow {}^5D_0$ transitions are completely forbidden. Nevertheless, they are allowed if there is an important 'J-mixing' between ^7F_J levels or if the symmetry of crystal field acting on the active ion is low (C_S, C_N or C_{NV} symmetries) [14,15]. These electronic transitions between the $^7F_0$ and the $^5D_0$ non-degenerate levels are unique to apply the fluorescence line narrowing technique, and therefore they are used to study the site distribution and to analyse energy transfer processes between optically active ions. Fig. 2 shows the inhomogeneous excitation spectrum of the $^7F_0 \rightarrow {}^5D_0$ transition in sol–gel silica glasses doped with 2.5 mol% of Eu^{3+} and heat treated at 400°C, obtained at 13 K and detecting at 611 nm ($^5D_0 \rightarrow {}^7F_2$ emission). The asymmetric and inhomogeneously broadened profile observed for this transition is due to the large variation in the local crystal field acting on the Eu^{3+} ion from site to site. A phonon side band can be observed at the high energy side of the excitation band (not shown).

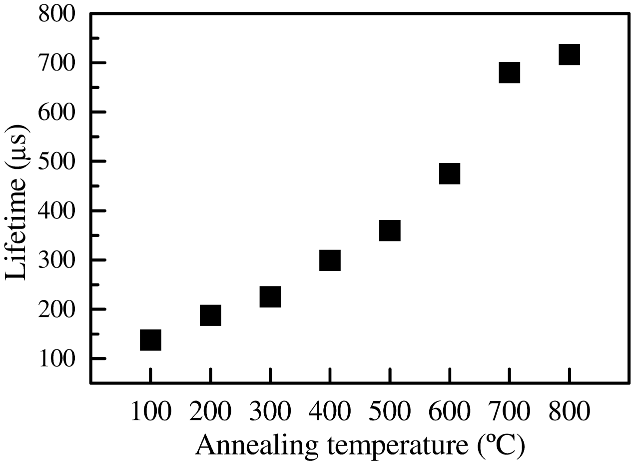

Fig. 1. Lifetime corresponding to the $^5D_0$ level obtained at RT as a function of annealing temperature of the heat treatment for sol–gel silica glasses doped with 2.5 mol% of Eu^{3+}.

The TRFLN spectra at 13 K with a relatively short delay of 200 μs after excitation at the high energy side of the $^7F_0 \rightarrow {}^5D_0$ band, in sol–gel derived silica glasses doped with 2.5 mol% of Eu^{3+} and heat treated at 400, 600 and 800°C are shown in Fig. 2. After heating at 400°C, a resonant emission coming from the subset of ions initially excited is observed, besides a broadband (background fluorescence) indicating the existence of energy transfer

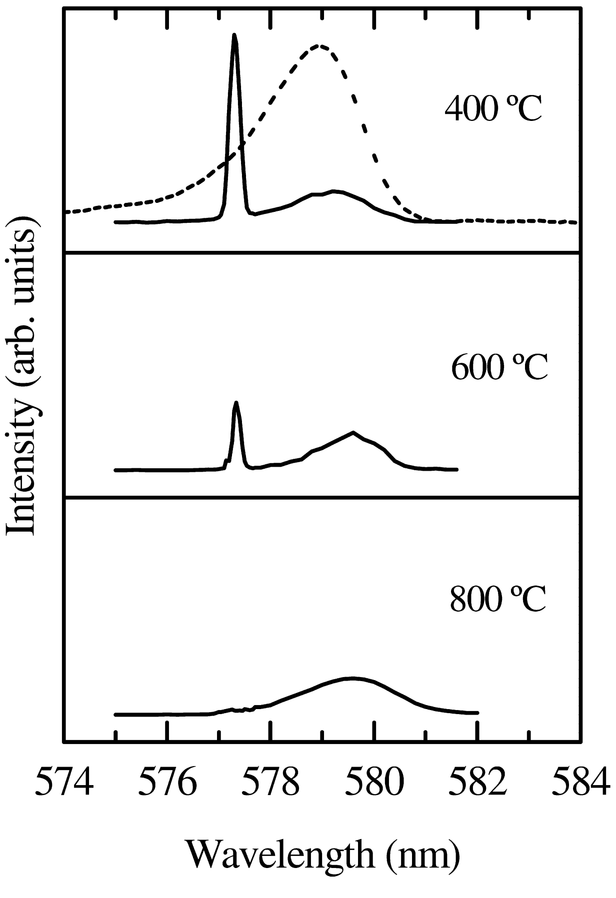

Fig. 2. Inhomogeneous excitation spectrum corresponding to the $^7F_0 \rightarrow {}^5D_0$ transition (----) and $^5D_0 \rightarrow {}^7F_0$ TRFLN spectra (—) for sol–gel silica glasses doped with 2.5 mol% of Eu^{3+} and heat treated at 400, 600 and 800°C, obtained at 13 K with a delay of 200 μs after laser excitation at 577.35 nm (spectra have been normalized to the maximum intensity of the background emission).

processes between Eu^{3+} ions. When the temperature of heat treatment is increased the background fluorescence becomes more important. So, the sample heat treated at 800°C only shows background emission. These results indicate that energy transfer processes are strongly enhanced by the thermal treatment. The energy transfer efficiency between Eu^{3+} ions is much more efficient in these samples than in diborate glasses with 23 mol% of Eu^{3+}, where a critical radius of 4.2 Å was obtained [8]. The spectrum of the sample treated at 800°C points out that the distance between the Eu^{3+} ions is shorter than the critical radius. Therefore, a clustering process of these ions has to be claimed to explain these results. Moreover, these results justify why Campostrini et al. [3] obtained, in the high temperature treated samples, emission spectra independent on the excitation wavelength. In these samples the very efficient energy transfer prevents the observance of narrowed emission spectra.

Exciting at the low energy side of the $^7F_0 \rightarrow {}^5D_0$ band, background fluorescence, caused by energy transfer towards Eu^{3+} sites of higher energies, was not observed, indicating that the processes with absorption of phonons are less probable than those with emission, therefore the transfer between Eu^{3+} ions is assisted by phonons and asymmetric. On these conditions Eq. (2), proposed by the authors [8], is expected to be adequate to describe the temporal evolution of the ratio $R(t, E_0)$. This ratio, given by Eq. (1), has been calculated from TRFLN measurements. The values obtained for this parameter, with laser excitation at 577.35 nm, are presented in Fig. 3 as a function of delay time for sol–gel silica glasses doped with 2.5 mol% of Eu^{3+} and heat treated at different temperatures (400 and 600°C). The fits of $R(t, E_0)$ to Eq. (2) are also included in this figure as solid lines. The values calculated for S and β from these fits and for 500°C are included in Table 1.

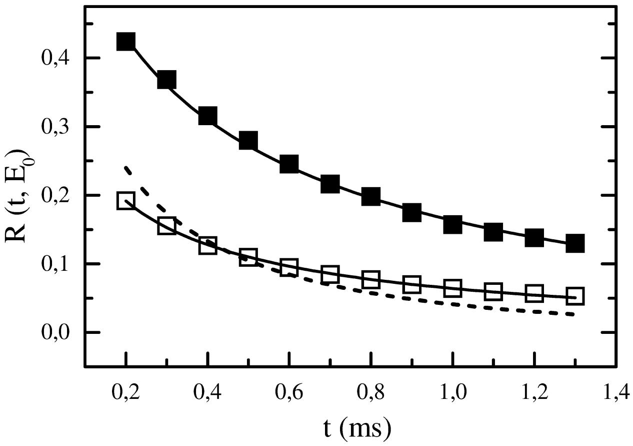

Fig. 3. Values obtained for $R(t, E_0)$ as a function of delay time after laser excitation at 577.35 nm at 13 K in a sol–gel silica glass doped with 2.5 mol% of Eu^{3+} heat treated at 400 (■) and 600°C (□). The solid lines correspond to the fits to Eq. (3). The fit for $S=6$ for the sample heat treated at 600°C is also presented (dashed line).

Table 1
Values obtained for S, β, C_{DA} and R_C in sol–gel silica glasses doped with 2.5 mol% Eu^{3+} heat treated at different temperatures. Results found by Lavín et al. [8] for Eu^{3+} doped calcium diborate glasses are also presented

T (°C)	S	β ($s^{-3/S}$)	C^S_{DA} ($cm^S s^{-1}$)	R_C (Å)
400	6.3	48.6	$4.97*10^{-42}$	7.6
500	7.4	47.1	$4.66*10^{-49}$	10.1
600	9.5	24.3	$1.52*10^{-63}$	10.9
Diborate glasses [8]	10	9.3	$9.5*10^{-72}$	4.2

The energy transfer parameter $C^S_{DA}(E-E_0)$ and the critical radius calculated for an energy mismatch $|E-E_0|$ of 50 cm^{-1}, corresponding to the mismatch between the ions excited at 577.35 nm and the maximum of the excitation band to the $^5D_0$ level, are also presented in Table 1.

The values obtained for S vary from about 6 (i.e. dominant dipole–dipole character for the interaction) for the sample heated up to 400°C to about 10 (i.e. dominant quadrupole–quadrupole character) for the sample heated up to 600°C. In order to enhance the change suffered by the multipole character of the sample heat treated at 600°C, the fitting curve taking $S=6$ is also presented in Fig. 3 (a value of $\beta=101$ $s^{-1/2}$ is obtained from the fit). The increase of S with the annealing temperature indicates that the interionic Eu^{3+}–Eu^{3+} distance decreases with the heat treatment. This result supports the preceding suggestion about a clustering process of the Eu^{3+} ions. On the other hand, tendency to cluster of trivalent rare earths has been observed in other matrix [16]. Assuming clustering is occurring, the energy transfer parameters and the critical radii in Table 1 for sol–gel silica glasses would be overestimated because they have been calculated considering the averaged concentration of 2.5 mol% of Eu^{3+}.

In order to analyse the dependence of the transfer probability with the energy mismatch $(E-E_0)$, the ratio between the TRFLN spectrum, obtained exciting at 577.35 nm ($E_0=17\ 320$ cm^{-1}) the sample heat treated at 400°C with a delay of 200 μs, and the inhomogeneous excitation spectrum (both showed in Fig. 2) is presented in Fig. 4. The fitting to the ratio $I(t, E, E_0)/p(E)$, obtained from Eq. (8) with $S=6$, is also presented in Fig. 4. As it can be observed, a good agreement is obtained confirming that the transfer toward different sites is assisted by acoustic phonons with energies up to 90 cm^{-1}.

5. Conclusions

Efficient energy migration between Eu^{3+} ions is observed in sol–gel derived silica glasses after excitation to the $^5D_0$ level. The energy transfer is notably enhanced in the gel to glass transition. The experimental results, about the evolution of the luminescence after pulsed excitation and the shape of the background emission, are well

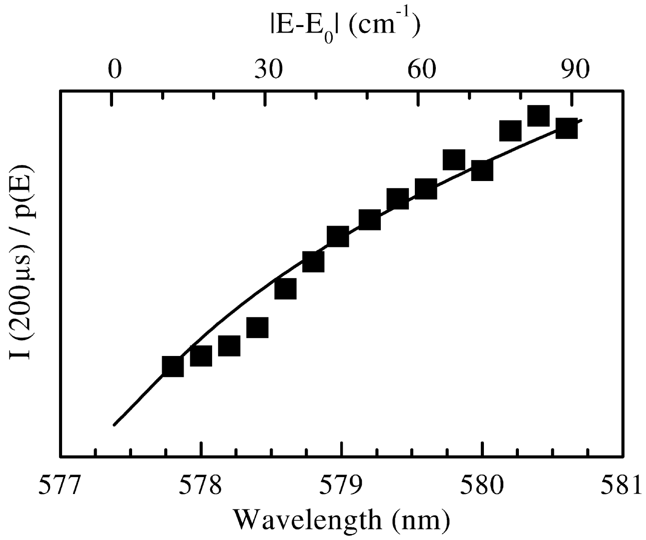

Fig. 4. Ratio between the TRFLN spectrum, obtained exciting at 577.35 nm ($E_0 = 17\,320$ cm^{-1}) with a delay of 200 μs a sol–gel derived silica glass doped with 2.5 mol% of Eu^{3+} heat treated at 400°C, and the inhomogeneous excitation spectrum (both showed in Fig. 2). The solid line corresponds to the fit to the ratio $I(t, E, E_0)/p(E)$ obtained from Eq. (8) with $S = 6$.

accounted by a model previously proposed by the authors. An energy dependent phonon assisted and asymmetric multipole interaction between Eu^{3+} ions is found. In order to explain the high efficiency of the energy transfer as well as the change from dipole–dipole to quadrupole–quadrupole interaction with the thermal treatment of the samples, a clustering process of the Eu^{3+} ions is invoked.

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