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Site Selection Spectroscopy of SiO_2:Eu^{3+} Gels

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Abstract. Silica gels doped with Eu^{3+} ions were studied at temperatures between 10 K and 300 K by site selection spectroscopy in samples heated up to 200°C. The $^5D_0 \rightarrow {}^7F_0$ transition shows internal structures due to the different environments of the europium ions. Lifetimes, energy levels and homogeneous linewidths are site dependent. In the wet gel the Eu^{3+} ions prefer a liquid-like environment and only when the liquid is removed by heat treatment, the ion is linked more strongly to the silica network.

Keywords: optical spectroscopy, fluorescence line narrowing, Eu^{3+}, silica xerogel

Optical spectroscopy of Eu^{3+} ions was shown to be a good technique to study the process of densification from gel to glass [1–4]. In this work we follow the evolution of the gel local structure in the early stages of the gel-xerogel transition.

The samples studied are gels obtained by hydrolysis and copolymerization of diethoxydimethylsilane (DEDMS) and tetraethoxysilane (TEOS) with molar ratio DEDMS/TEOS = 5/95, Eu/Si = 0.01:1 and $Si/EtOH/H_2O/H^+ = 1/2/4/0.001$. The addition of DEDMS to TEOS helps in obtaining cracking-free monolithic samples, suitable for optical studies [2]. The samples were heated for 48 hours at different temperatures in the range 60–200°C.

In Figure 1 we show the spectra of the $^5D_0 \rightarrow {}^7F_0$ transition at room temperature, obtained by exciting in the $^5L_6$ state with a broad band Xenon lamp source. The wet gel presents a relatively narrow band (FWHM = 20 cm^{-1}) centered at about 17260 cm^{-1}. After heating, a broader band (FWHM = 50 cm^{-1}) centered at 17295 cm^{-1} appears and becomes dominant for the samples heated at temperatures above 160°C, while the first component (17260 cm^{-1}) becomes less and less important. For heat treatment above 200°C, the second band broadens and tends to shift to higher frequency as shown in the spectra of a sample treated at 550°C. It is evident that two kinds of environments are present in these samples: a wet environment which produces the emission at about 17260 cm^{-1}, and a dry one, which produces the band at higher energy. These assignments were mainly based on the behavior of the luminescence spectra as a function of the temperature [2, 3]. In particular, the band at 17260 cm^{-1}, which occurs at about the same value as the $^5D_0 \rightarrow {}^7F_0$ transition of Eu^{3+} in solutions [5], broadens at temperatures lower than about −30°C. This increasing of the inhomogeneous linewidth is due to the freezing of a liquid environment in unequal configurations [3].

In order to have more information on these two groups of sites, we studied the sample treated at 100°C (which has both components) by performing high resolution measurements with different excitation or detection frequencies within the inhomogeneous profile. For these measurements we used a pulsed dye laser with linewidth of 0.2 cm^{-1}. The experimental details are described in [2].

In Figure 2f we show the excitation spectra taken by detecting at 16200 cm^{-1} (maximum of $^5D_0 \rightarrow {}^7F_2$ transition). The spectra are taken at 11 K to avoid ther-

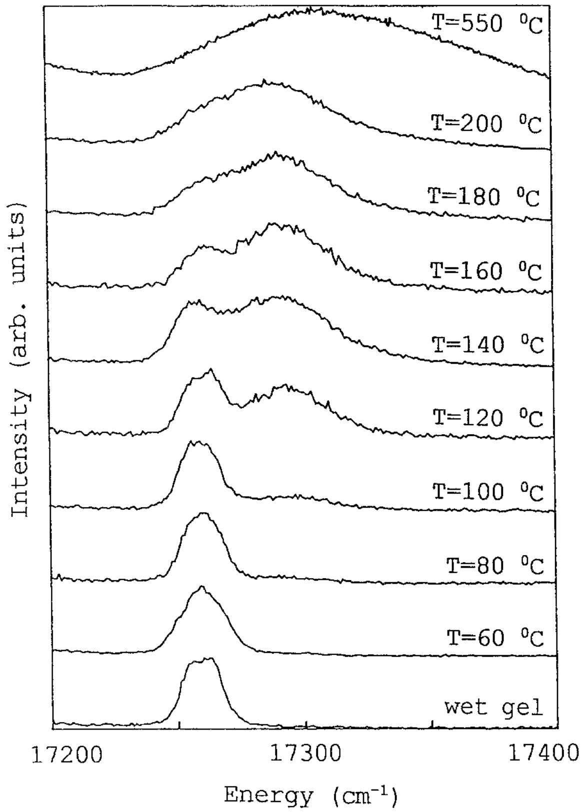

Fig. 1. Room temperature luminescence spectra of the $^5D_0 \rightarrow {}^7F_0$ transition obtained by continuous broad band excitation at 395 nm.

mal population of the $^7F_1$ state. We observe the two bands discussed before and a sideband at distance of about 200 cm^{-1}. In Figs. 2a–e we present site selection spectra obtained by exciting at different frequencies, which are labelled on the excitation spectrum of Fig. 2f. The three components of the $^7F_1$ state are well resolved in all spectra. Four of the five components of the $^7F_2$ state are resolved, at least in the spectra with large splittings. We observe that the Stark splittings of the transitions $^5D_0 \rightarrow {}^7F_{1,2}$ increase (a, b, c) as the excitation energy in the $^7F_0 \rightarrow {}^5D_0$ transition increase. When the excitation is inside the broad band centered at about 17450 cm^{-1}, we are not able to obtain efficient site selection, as expected for the excitation in a phonon sideband (Figs. 2d, e). In Figure 3 we report the excitation spectra at 11 K, in the frequency range of the $^7F_0$-> $^5D_0$ transition, obtained by detecting the luminescence at different energies within the $^5D_0 \rightarrow {}^7F_0$ profile. The three components of the $^7F_0 \rightarrow {}^5D_1$ transition are well resolved in all spectra. We observe that by increasing the detection energy, the Stark splittings of the $^5D_1$ increases as for the $^7F_1$ state in Fig. 2.

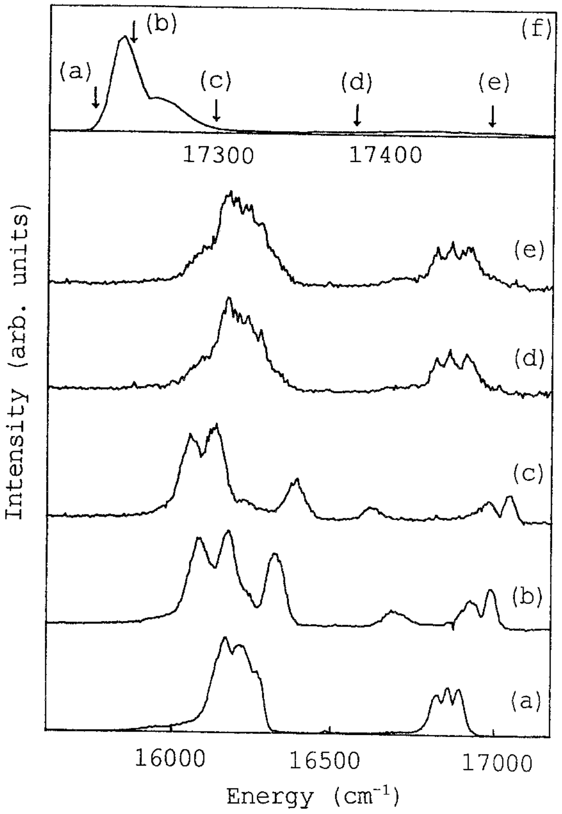

Fig. 2. Luminescence spectra at $T = 11$ K, for the sample heated at 100°C, obtained with different excitations within the inhomogeneous profile of the $^5D_0 \rightarrow {}^7F_0$ line (a, b, c) and its phonon sideband (d, e). The excitation energies are indicated by arrows (f) in the excitation spectrum taken by detecting at 16200 cm^{-1} in the $^5D_0 \rightarrow {}^7F_2$ luminescence band.

In Figure 4 we report the positions of the Stark components observed in Figs. 2 and 3, by plotting the energies of the $^7F_{1,2}$ and $^5D_1$ sublevels, as a function of the energy of $^5D_0 \leftrightarrow {}^7F_0$ transition. The Stark splittings of the $^5D_1$ state are smaller than those of the $^7F_1$ and $^7F_2$ states, as is evident from the different scales. The splittings of all transitions increase almost linearly with the energy of the $^5D_0 \rightarrow {}^7F_0$ transition. It is known that the overall splittings can be assumed as a measure of the distortion of the crystal field at the Eu^{3+} site [2]. The sites which luminesce at low energy and have a liquid-like environment at high temperature, present a relatively highly symmetric crystal field even after freezing. High values of the $^5D_0 \rightarrow {}^7F_0$ transition energies correspond to strongly perturbed sites as expected for ions which are embedded in the growing SiO_2 network.

In spite of the wide site-to-site inhomogeneities observed above, a single exponential decay time is

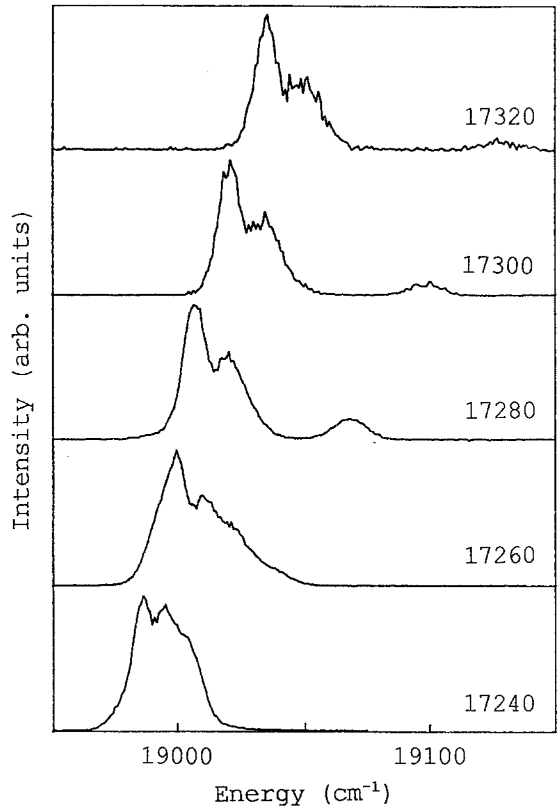

Fig. 3. Excitation spectra at 11 K in the spectral range of the $^7F_0 \rightarrow {}^5D_0$ transition, obtained by detecting at the reported energies, within the inhomogeneous profile of $^5D_0 \rightarrow {}^7F_0$ transition.

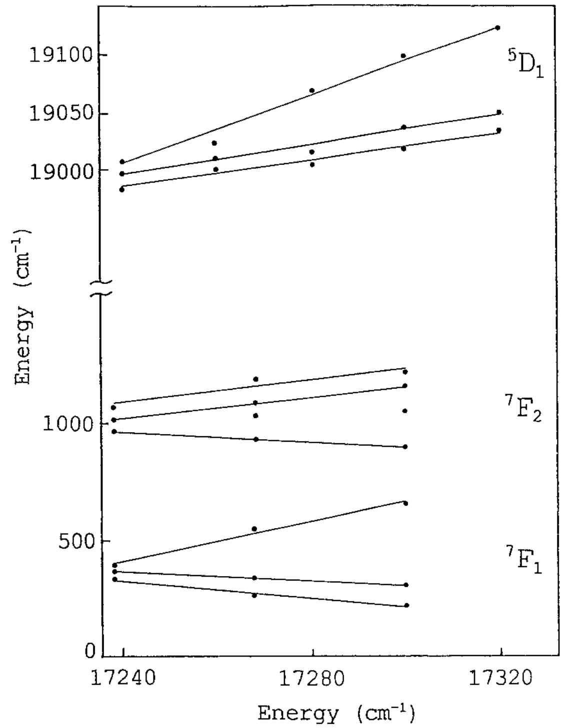

Fig. 4. Peak position of the Stark sublevels of the $^5D_1$ (data from Fig. 3) and of the $^5F_{1,2}$ (data from Fig. 2) as a function of the energy of the $^7F_0 \rightarrow {}^5D_0$ transition.

observed in all samples treated at temperatures below 200°C. The lifetime increases from 135 μs in the wet gel to 240 μs in the sample heated at 200°C, but no important inhomogeneities are observed by exciting or detecting at different energies. This effect cannot be attributed to transfer processes, which are not significantly active in samples heated below 200°C, as the site selection measurements show.

It is known that the radiative lifetime of Eu^{3+} ions is in the range of a few milliseconds. In the gel samples, the lifetime is reduced by about a factor ten, by non-radiative relaxations. The stretching vibrations of OH groups, due their high energy ($\sim$3500 cm^{-1}), are the most important cause of non-radiative transitions [3]. The observation that the lifetime is practically site independent for a given sample indicates that the number of OH groups surrounding the Eu^{3+} ions is more or less the same.

High site-to-site inhomogeneities are evident in the measurements of the homogeneous linewidths shown in Fig. 5. The sites emitting at high energy present large homogeneous linewidths, showing strong coupling with the vibrational modes of the SiO_2 network. Between 100 K and 300 K their homogeneous linewidths present a T^2 dependence, which is typical of an ion embedded in a solid. The homogeneous linewidths of the sites which luminesce at low energy also present a T^2 dependence for $T < 250$ K. Above 250 K the temperature dependence becomes lower than T^2, indicating a phase change from a solid-like to a liquid-like environment.

In conclusion, wide site-to-site inhomogeneities appear after drying as it results from the inhomogeneous and homogeneous linewidths of the transition bands and in the Stark splittings. Eu^{3+} ions remain in the solution embedded in the gel pores and only when the liquid is removed they tend to enter in the network. In the wet gel the Eu^{3+} ions have a relatively well defined liquid-like environment, which become more and more inhomogeneous as the drying process goes on. Unfortunately, the transfer processes, which are negligible for heat treatment lower than 200°C, become more and more important as the condensation goes on. This makes site selection spectroscopy inefficient.

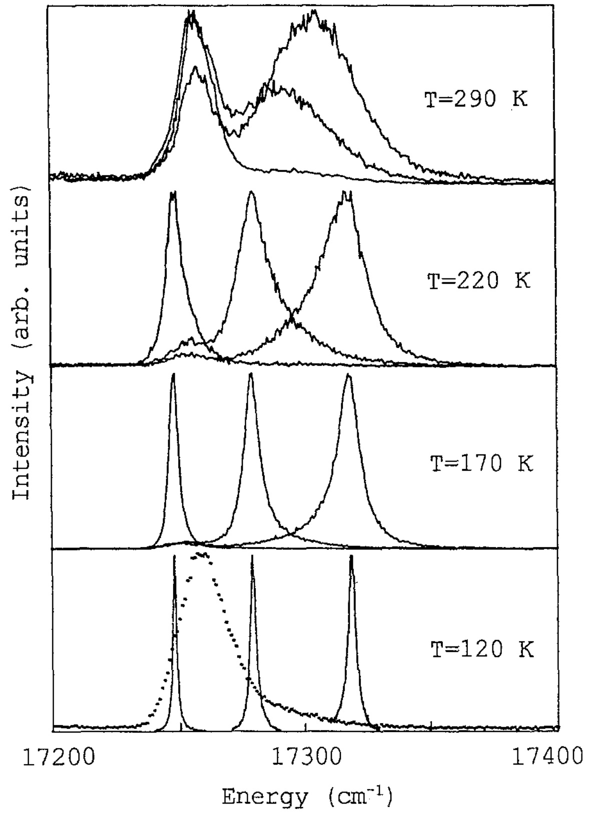

Fig. 5. Fluorescence line narrowing spectra at different temperatures for three excitation energies (17260, 17280 and 17320 cm^{-1}) within the inhomogeneous profile of the $^7F_0 \rightarrow {}^5D_0$ transition shown at $T = 87$ K (dotted line).

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