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Site distribution and thermalization effects in europium-doped silica glasses

A. BOUAJAJ, A. MONTEIL*, C. BOVIER**, M. FERRARI*** and A. PIAZZA****

Physico-Chimie des Matériaux Luminescents, URA 442 du CNRS, Université Lyon I, 43 bd du 11 Novembre 1918, 69622 Villeurbanne, France

** Laboratoire POMA, Université d'Angers, 2 bd Lavoisier, 49045 Angers cedex, France*

*** Département de Physique des Matériaux, URA 172 du CNRS, Université Lyon I, 43 bd du 11 Novembre 1918, 69622 Villeurbanne, France*

**** CNR, Centro di Fisica degli Stati Aggregati ed Impianto Ionico, via Sommarive 14, 38050 Povo (TN), Italy*

Abstract: For the no-phonon transition $^5D_0 \rightarrow ^7F_0$ of Eu^{3+} in glasses, obtained by sol-gel route, emission and absorption at low temperature are not resonant. This effect is interpreted by a redistribution of the excitation energy among the different environment for the Eu^{3+} ion. A simple model is used to interpret the temperature evolution of the emission spectra. A good agreement is obtained with experimental results. The experimental emission spectra are simulated using the Boltzmann law and the experimental excitation spectra. The mechanism of redistribution is a phonon-assisted energy transfer process. This is confirmed by temperature dependance of decays and time resolved emission measurements.

Introduction

Because the particular relevance of sol-gel optical materials it is important to control their final properties. For this purpose it is necessary to understand the modifications induced by the densification process [1]. A powerful method to study the local structure and the dynamical processes involved in such systems, is to use the spectroscopical properties of optically active ions. Several works have been devoted to study the densification process of sol-gel with rare-earth ions as probe [2]. Eu^{3+} has been widely used both in crystalline and glassy materials because its optical transitions are very sensitive to the local surroundings and one of its transition: $^5D_0 \leftrightarrow ^7F_0$ is a singlet. In this work we follow the evolution of

this line at different stages of the densification process of acid-catalyzed gels. For sample heated above 500 °C we have found that emission and absorption are not resonant contrary to what it is expected for a no-phonon transition. Finally a model that explains this effect is presented.

Experimental

Gels were prepared by hydrolysis and condensation of tetramethylorthosilicate (TMOS), methanol and water with the following molar ratios: $\text{TMOS/MeOH/H}_2\text{O} = 1/6.2/10$. An acidic aqueous solution of $\text{Eu}(\text{NO}_3)_3$ was then added in order to reach the desired Eu^{3+} concentration: $\text{Eu/Si} = 0.002$. Starting from a wet gel (a) several samples were successively heated 10 h to

200 °C (b) 500 °C (c) 800 °C (d) and 1050 °C (e) with a rate of 0.1 °C/mn.

Excitation spectra were obtained using a Rh6G dye laser pumped by excimer laser. A xenon lamp coupled with a monochromator was used for broadband excitation. The fluorescence was focused onto a model 1401 double Spex monochromator equipped with a cooled RCA C31034A02 photomultiplier tube. The average resolution in the region of interest was 0.3 cm⁻¹.

Results and Discussion

Figure 1 shows the low temperature excitation spectra of the $^5D_0 \leftarrow ^7F_0$ transition for different heat treated samples. In this condition the whole inhomogeneous site distribution is detected. The Full Width Half Maximum (FWHM) of the line varies from 17 cm⁻¹ for the wet gel (Fig. 1a) up to 155 cm⁻¹ for the sample heated to 800 °C (Fig. 1d). This evolution comes from the effect of 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 [3]. For the fully densified we observe a narrower linewidth of 115 cm⁻¹ (Fig. 1e) that reflects a rearrangement of the silica network. For the sample heated to 200 °C (Fig. 1b) two peaks are observed at 17247 cm⁻¹ and 17267 cm⁻¹. The first one is related to the liquid-like environment, as for the peak of Fig. 1a, and the second one is related to the dry environment [4].

Fig. 1: $^5D_0 \leftarrow ^7F_0$ excitation spectra at 10 K for different heat treatments.

Figure 2 shows the low temperature emission spectra for the $^5D_0 \rightarrow ^7F_0$ transition. The main feature consists in a displacement of the barycenter towards the lower energies, from 17245 cm⁻¹ for the wet gel (Fig. 2a) to 17212 cm⁻¹ for the fully densified sample (Fig. 2e). The positive shift of few wavenumbers observed for the gel treated to 200 °C (Fig. 2b) is due to an increase of the number of "dry" sites as observed in the excitation spectra. In heated samples we can remark that the linewidth is narrower for emission spectra than for excitation spectra. For instance we get a FWHM of 55 cm⁻¹ for the sample heated to 800 °C (Fig. 2d).

Fig. 2: $^5D_0 \rightarrow ^7F_0$ emission spectra at 10 K for different heat treatments. Excitation with a Xenon lamp at 395 nm.

This value has to be compared with the 155 cm^{-1} observed in the excitation spectrum. Since the transition is a no-phonon line, it is expected that both emission and absorption or excitation lines are identical. The observed differences must be interpreted considering the inhomogeneous nature of the line. In fact the 5D_0 energy level varies from site to site due to the different strengths of the local crystal field around the europium ions. The excitation is redistributed between the ions by a phonon-assisted energy transfer. The relative population of the 5D_0 states follows a Boltzmann thermodynamic law. In fact at room

temperature emission and excitation spectra are well superimposed. This thermal dependance is confirmed by a simple model that we have applied to the fully densified sample. We have calculated the emission spectra $f_{em}(E)$ at different temperatures as:

$$f_{em}(E, T) = f_{ex}(E) \times \exp - \left[\frac{(E - E_0)}{kT} \right]$$

where f_{ex} is the experimental excitation spectrum recorded at $T = 10\text{ K}$ shown in Fig. 1e, E_0 is the lowest energy in the inhomogeneous distribution of the 5D_0 states taken at 17192 cm^{-1} as obtained in the excitation spectra f_{ex} .

Fig. 3: $^5D_0 \rightarrow ^7F_0$ experimental and simulated emission spectra at different temperatures for the full densified sample e.

Simulated spectra with experimental emission spectra are shown on Fig. 3 for different tem-

peratures. Simulated spectra are in good agreement with experimental ones.

Preliminary measurements in time resolved Fluorescence Line Narrowing experiments show that energy transfer between different sites is active. Its efficiency increases with the densification of the sample. In fact it becomes more important thanks to the vibrational modes of the silica network involved in the process. Moreover it is inferred from the temperature dependence that the process is mainly phonon-assisted. Demonstration and analysis of the energy transfer process present in this system will be the subject of a future paper [5].

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