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DENSIFICATION PROCESS IN SILICA SOL-GEL: MONITORING BY OPTICAL AND RAMAN SPECTROSCOPY


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Résumé - Nous présentons une étude de sol-gels de silice purs (A) et dopés Eu³⁺ (B). Le processus de densification a été suivi au moyen de mesures d’absorption et de spectroscopie Raman (A) ainsi que de fluorescence (B).

Abstract - We present a study of pure (A) and Eu³⁺-doped (B) silica sol-gels. We relate absorption and Raman measurements on sample A with fluorescence spectra of the ion in sample B at different stages of the densification process.

I - Introduction

In alternative to the conventional melting technique the sol-gel method allows one to obtain materials doped with lasing species, which potentially have higher purity and homogeneity. This possibility, and the advantages deriving from the superior physical properties of sol-gel derived silica hosts (i.e. coefficient of thermal expansion close to zero) might produce a new generation of advanced tunable solid state lasers /1/, /2/. It is also well known that the final properties of the sample are quite dependent on the first treatment and on the subsequent dehydration stages. The residual water plays an important role on the spectroscopical properties of the optically active ion embedded in the matrix. For this reason it is worthwhile to follow the modification of the system with the densification process.

II - Experimental

The composition of the samples used in this work and the different heat treatments are reported in Table 1. The samples were successively heated in air from room temperature to different final temperatures at a rate of 0.1 °C/min. For instance, sample A6 was obtained by heating sample A5 at 700 °C. The Raman spectra were recorded with a Dilor monochromator, for the absorption measurements a Cary 2300 Spectrometer was employed. The C.W. excitation was by Xenon-lamp passed through a monochromator. An Excimer laser for pulsed excitation was also employed.

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III Results and Discussion

The room temperature Raman spectra of undoped gel sample A at different heat treatments are show in Fig. 1. The broad band in the region from 3000 cm\(^{-1}\) to 3800 cm\(^{-1}\), with the two interesting structures at 3220 cm\(^{-1}\) and 3440 cm\(^{-1}\) /3/, is characteristic of liquid water. The two sharp peaks at 3750 cm\(^{-1}\) and at 980 cm\(^{-1}\) arise from OH stretching vibration of Si-O \(\leftrightarrow\) H isolated surface silanol groups, and from Si \(\leftrightarrow\) OH stretching vibration of the hydroxyl group relative to the silicon atom, respectively. The double structure at about 2900 cm\(^{-1}\) is due to vibrations of organic groups arising from the original components used for the gel preparation /4/. The other structures at 440, 800, 1070 and 1200 cm\(^{-1}\) are ascribed to Si-O-Si vibrations of the silica network. The low-frequency broad band at 50 cm\(^{-1}\) in the spectrum of the sample A8 is the 'boson peak' characteristic of glasses /5/. The sharp Raman band at 600 cm\(^{-1}\) has been related to the breathing mode of a "defect" in the SiO\(_2\) network that consists of a planar 3-fold siloxane ring /6/. The very intense and sharp peak at 490 cm\(^{-1}\) is due to the symmetric stretching vibration of three symmetrical bonded network oxygens connected to a silicon atom which is decoupled from the network via a terminating hydroxyl group /7/. The intensities of the O \(\leftrightarrow\) H stretching peak at 3750 cm\(^{-1}\) and of the Si \(\leftrightarrow\) OH modes at 980 and 490 cm\(^{-1}\), decrease together with thermal treatment, in agreement with the interpretation of Mulder and Damen /7/. Fig. 1 shows that hydroxyl and organic groups are also present after heat treatment at 900 °C. This is also confirmed from the lifetime measurements in the Eu\(^{3+}\) doped gels, which show also at advanced densification, the presence of non radiative relaxation due to OH stretching, which drastically reduce the quantum fluorescence efficiency. Of course this is very disadvantageous for the use of doped sol-gel in glass lasers /1/. For the wet gel a single exponential decay is observed at room temperature, with a lifetime \(\tau=140\ \mu s\), which is much shorter than the
radiative one estimated to be about 4 ms, and which is comparable to the
lifetimes observed for Eu$^{3+}$ in aqueous solution /8/. By increasing the
annealing temperature the decay profiles become less and less
exponential with a continuous distribution of lifetimes. The lifetime
increases as OH groups are expelled and non radiative transitions become less
efficient but a appreciable amount of hydroxyl groups are retained by the
system even after the high temperature annealing.

Samples A and B both show a very broad and strong absorption band in the
region between 300 nm and 500 nm which evolves with the heat treatment. We
think that this trend is most probably due to organic species produced by
hydrolysis and polymerization reactions during the stabilization steps /4/.
Note that the band intensity increases and shifts towards higher energy from
the wet gel to the sample heated at 500 °C, and drastically falls down at
higher treatments because decomposition of organic residuals is active up to
about 400 °C /9/. The related fluorescence band is also very broad and
masks the Raman signal in the samples treated at temperatures below
500 °C. Nevertheless, this band plays an important role on the fluorescence
efficiency for the B doped gel as we will see later. To avoid the band
effects on the first dehydration stages we have used the near infrared
absorption. The spectra from 1 to 2 μm are shown in Fig.2. Two strong and
broad bands are observed at 1.37 and 1.92 μm for samples A1,A2,A3. The
highest energy band corresponds to the first overtone of the vibration modes
of water molecules as can be seen in Fig.1a. The absorption band at 1.920
μm is also related to the hydroxyl groups which are associated with
physical pore water. During the dehydration process we observe a
continuous modification of the absorption spectra with expulsion of free
water and solvent after treatment at 250 °C (Fig.2d). At higher
treatments, a sharp peak at 1.37 μm (which is assigned to Si – O ↔ H
vibration) and a broad structure at 1.895 μm appear. The latter is a
combination vibration of the stretching mode of a Si – O ↔ H bond at 3550
cm$^{-1}$, which is hydrogen bonded to water, plus 2 times the bending
frequency of Si – O ↔ H bond at 870 cm$^{-1}$. For the samples A5, A6, A7 we
observe in Fig.2 another structure at 1.4 μm related to the first
overtone of the stretching vibrations at 2.817 μm. These results show that
from the wet gel up to heat treatment at 150 °C a large amount of physical
water is present in the environment. Above 250 °C the chemisorbed water
decreases but a considerable number of hydroxyl groups is still inside the
gel and, with the residual organic groups, plays a relevant role in the
relaxation processes in glass derived sol–gel doped with fluorescent ions.

In Fig.3 we show the fluorescence spectra at $T=77$ K for the sample B at
different heat treatments. In the energy region below 17500 cm$^{-1}$ one
observes the transitions from the "D$_{0}$ state of Eu$^{3+}$ to the lowest F$_{j}$
multiplets ($j=0,1,2,3,4$). The broad band at higher energy arises from
organic species and its behavior was described above. The main features observed are: i) the broadening of the lines and the increase of the Stark splitting with the dehydration process; ii) the increase of the fluorescence efficiency when the absorption band shifts towards lower energy. Effect i) depend from the evolution of the Eu\textsuperscript{3+} environment. First the ion is coordinated with water and solvent molecules and its environment is typically aqueous; the sites are not very different one from the other, and this is reflected in a relatively sharp gaussian like shape of the lines. When the dehydration process proceeds the coordination bonds of Eu\textsuperscript{3+} ions are progressively and partially substituted by the hydroxyl and methoxyl groups. This process practically finishes at 250 °C. At higher heat treatments, as a result of shrinkage and sintering across pores related to a reduction of hydroxyl groups, the europium ions are more and more embedded in the network in different sites and with stronger low-symmetry components in the local environment. Effect ii) is related to a transfer process between the organic species and the europium ion. A very strong absorption band of Eu\textsuperscript{3+}, assigned to the F\textsubscript{6} \rightarrow L\textsubscript{6} transition, is observed at 395 nm. We observe an increase of the fluorescence when the organic band emission shifts towards lower energy and the overlap with the absorption band of Eu\textsuperscript{3+} increases. In this case the excitation energy can be transferred to europium. In samples heated above 500 °C, where the luminescence band due to organic species is strongly reduced, we observe luminescence only from the directly excited ions. The same results are obtained after exitation at 308 nm with pulsed laser.

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REFERENCES