OPTICAL CHARACTERIZATION OF SOL-GEL GLASSES DERIVED FROM Eu^{3+} COMPLEX-FORMING PRECURSORS

Vilma C. Costa
Centro de Desenvolvimento da Tecnologia Nuclear - CDTN - Rua Mário Werneck s/n - Cidade Universitária - Pampulha - Belo Horizonte - MG
Wander L. Vasconcelos
Depto. Eng. Metalúrgica - UFMG - Rua Espírito Santo, 35 - 2º andar - 30160-030 - Belo Horizonte - MG
Kevin L. Bray
Department of Chemical Engineering - University of Wisconsin - Madison - WI 53706

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Fabrication of new optical devices based upon the incorporation of rare earth ions via sol-gel method depends on elimination of dopant ion clusters and residual hydroxyl groups from the final material. The optical absorption and/or luminescence properties of luminescent rare earth ions are influenced by the local bonding environment and the distribution of the rare-earth dopants in the matrix. Typically, dopants are incorporated into gel via dissolution of soluble species into the initial precursor sol. In this work, Eu^{3+} is used as optical probe, to assess changes in the local environment. Results of emission, excitation, fluorescence line narrowing and lifetimes studies of Eu^{3+}-doped gels derived from $Si(OCH_3)_4$ and fluorinated/chelate Eu^{3+} precursors are presented. The precursors used in the sol-gel synthesis were: tris (6,6,7,7,8,8,8-heptafluoro-2,2-dimethyl-3,5-octanedionate) Eu(III), Eu (III) trifluoromethanesulfonate, Eu(III) acetylacetonate hydrate, Eu (III) trifluoroacetate trihidrate, tris (2,2,6,6-tetramethyl-3,5- heptanedionate) Eu(III) and $Eu(NO_3)_3.6H_2O$. The results were interpreted in terms of the evolution of the Eu^{3+} fluorescence in systems varying from solution to the gels densified to 800ºC. The lifetimes studies indicate that the fluorinated precursors are effective at reducing the water content in densified gels.

Keywords: Eu^{3+}; sol-gel; complex-forming precursors.

INTRODUCTION

The sol-gel process is among the most promising of the developing techniques for synthesizing new optical materials. Some of the applications for these optical materials are optical fibers and gradient-index waveguides, antireflection coatings, solid state lasers, non-linear optics, luminescent solar concentrators and photochromic glasses[1-3]. The potential advantages of the sol-gel method for preparing optical materials include obtaining new chemical compositions, better purity and more convenient processing conditions.

The rare earth ions have interesting emission properties for laser applications and have been studied as luminescent ions when incorporated inside sol-gel matrices. Sol-gel glasses doped with rare earth are an important kind of materials with applications including solid-state laser, fiber amplifiers and optical waveguides. The optical spectroscopy of rare earth ions can also be useful for characterization of glasses[4,5]. Eu^{3+} has been most often used as an optical probe because of its particularly informative luminescence spectrum[6].

The luminescence efficiency of rare earth in sol-gel host materials is compromised due to the tendency of rare earth ions to form clusters and by the presence of hydroxyl ions and remnant organic. Clustering results in concentration quenching of fluorescence due to nonradiative energy transfer between rare earth cations within the clusters. This effect is undesirable for application of sol-gel materials based on luminescence properties.

Hydroxyl quenching and dopant clustering are two complications that currently limit the luminescence efficiency of rare earth ions in sol-gel host materials[7,8]. Hydroxyl quenching is caused by residual water, solvents, and silanol groups present in sol-gel glasses and leads to an enhancement of non-radiative decay pathways of rare earth ions. Dopant clustering is deleterious because it leads to concentration quenching of luminescence through cross-relaxation and energy transfer processes. In previous work, it was shown a method for detecting rare earth clustering in sol-gel glasses based on Eu^{3+} fluorescence line narrowing spectroscopy[9]. Fluorescence line narrowing (FLN) is a site-selective spectroscopy designed to combat inhomogeneous spectral broadening in glass. It was reported that the addition of metal cations co-dopants leads to some inhibition of the tendency for Eu^{3+} to aggregate in a gel-derived SiO_2 matrix[9]. Dopant ion encapsulation by complex-forming ligands has been achieved in order to inhibit clustering of the dopant ions[10,11]. Some ligands, such as TTFAH (thenoyltrifluoroacetone), are highly asymmetric, reducing the local-field symmetry of the metal ion and making the radiative transitions somewhat more allowed[10]. Brecher et al. demonstrated that organometallic complexes of europium show intense fluorescence in a variety of solutions[11].

In order to minimize the hydroxyl content of sol-gel matrices, the use of organically modified alkoxide sol-gel precursors[12], dopant ion encapsulation and the addition of fluorine as dehydroxylating agent[13], have been tried and demonstrated to reduce hydroxyl content in silica gel glasses.

In this work the spectroscopy of Eu^{3+} ions is used as probe of structural changes in sol-gel silica glasses to investigate the effect of the use of different Eu^{3+} precursors, some of them are fluorinated and/or chelate precursors, on clustering and quenching of Eu^{3+} ions. The fluorescence characterization consisted of measuring broadband fluorescence spectra, excitation spectra, fluorescence line narrowing and fluorescence lifetimes.

E-mail: vilma@prover.com.br

EXPERIMENTAL PROCEDURE

Sample Preparation. The gels were prepared by mixing TMOS and the solutions in which the europium precursors were previously dissolved. The Eu^{3+} precursors (from Aldrich) studied were: tris (6,6,7,7,8,8,8-heptafluoro-2,2-dimethyl-3,5-octanedionate) Eu(III) ($Eu(fod)_3$), Eu (III) trifluoromethanesulfonate ($(CF_3SO_3)_3Eu$), Eu(III) acetylacetonate hydrate ($Eu(acac)_3$), Eu (III) trifluoroacetate trihidrate ($(CF_3CO_2)_3Eu.3H_2O$), tris (2,2,6,6-tetramethyl-3,5- heptanedionate) Eu(III) ($Eu(thd)_3$) and $Eu(NO_3)_3.6H_2O$. DMF was used to dissolve the $Eu(fod)_3$ and methanol was the solvent for $Eu(thd)_3$ and $Eu(acac)_3$. The molar ratio solvent to TMOS was 4. The water to TMOS molar ratio was 16. HNO_3 was added to low the pH to 1.5. The samples contained 1 and 5 wt% Eu_2O_3. The europium concentration in a sample is expressed in terms of the weight percent of Eu_2O_3 that would be present in a fully densified SiO_2 glass in which water and organics are absent. Reaction and gelation occurred at room temperature. After gelation the gels were aged and dried at 60°C and 90°C for two days. Further heat treatment in air was carried out in a box furnace. The samples were ultimately heated to 800°C.

All precursors were studied in solution (prepared with a precursor concentration of 0.1M). In all cases, the solvents and solutions were prepared immediately before the use. Spectra are presented for the sol or initial mixing stage (before gelation), the wet gel (corresponding to the material after aging at room temperature in the ambient atmosphere) and the gels heated to 90°C and 800°C.

The Eu^{3+} precursors studied that involved fluorinated ligands were: $Eu(fod)_3$, $(CF_3SO_3)_3Eu$, (CFS) and $(CF_3CO_2)_3Eu.3H_2O$, (CFC) and the chelate ligands were: $Eu(fod)_3$, $Eu(thd)_3$ e $Eu(acac)_3$.

Spectroscopic Measurements. The broadband emission spectra were obtained, at room temperature, by exciting samples with the 466 nm and 514.5 nm lines of a Coherent Innova Series 70-5 argon ion laser. Luminescence was collected on a 1-meter monochromator and detected by a photomultiplier tube.

Fluorescence line narrowing measurements were carried out using a pulsed tunable dye laser pumped by a Q-switched Nd:YAG. The dye laser provided the tunable emission from 571-580 nm to selectively excite the $^7F_0\varnothing^5D_0$ transition of Eu^{3+}. Spectra were normalized to the $^5D_0\varnothing^7F_1$ peak intensity and were collected at 77 K. Excitation spectra were measured by scanning the dye laser across the $^7F_0\varnothing^5D_0$ transition while the strongest fluorescence band was detected. Luminescence decay measurements were recorded using a digital storage oscilloscope. The lifetime were obtained by calculating the area under the normalized decay curve.

RESULTS AND DISCUSSION

Fluorescence Spectra. Figures 1 and 2 presents broadband fluorescence spectra for the 5.0 wt% Eu_2O_3 doped samples prepared from the different Eu^{3+} precursors, in different stages of sol-gel reaction. The precursors used are indicated in the figures.

Important spectral changes related to the emission peaks relative intensity are observed. Lifetime shortening and the relative weakness of the $^5D_0\varnothing^7F_0$ and $^5D_0\varnothing^7F_2$ emission bands reflect a symmetric solvation shell of the Eu^{3+} bonding environment.

The spectra of samples prepared from $Eu(fod)_3$, show that the effect of this ligand is significant. The spectra show marked enhancement of the $^5D_0\varnothing^7F_2$ fluorescence, indicative of low symmetry sites. Changes in intensity are more pronounced and the $^5D_0\varnothing^7F_0$ emission, which is almost unobservable in the absence of chelating agent, becomes very significant upon chelation. The presence the chelate organic ligands in the inner-coordination shell reduces the nonradiative decay probability. This increased intensity comes from a reduction in the symmetry on the europium species that makes the transition 'more allowed'. The same considerations can be made for $Eu(thd)_3$, but in this case, the effect is not so pronounced.

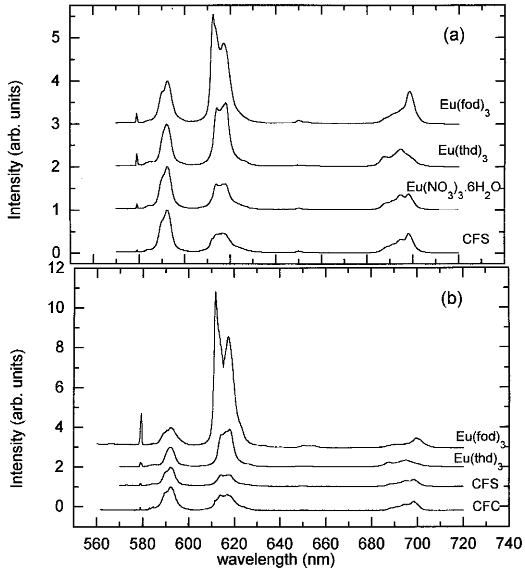

Figure 1. *Fluorescence spectra (77 K) of some* Eu^{3+} *precursors: (a) solution, (b) sol. The precursor is indicated in each spectrum. Intensities were normalized to the* $^5D_0\varnothing^7F_1$ *emission.*

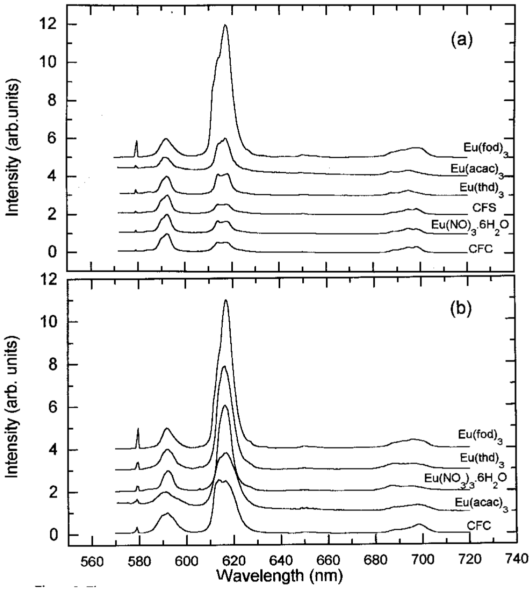

Figure 2. *Fluorescence spectra (77 K) of some* Eu^{3+} *precursors: (a) wet gel, (b) gel heated to 90 °C . The precursor is indicated in each spectrum.*

Comparision of figures 1 and 2 reveals that the spectra of $(CF_3SO_3)_3Eu$, $(CF_3CO_2)_3Eu$ and $Eu(NO_3)_3.6H_2O$ show very similar intensity and behavior. Previous work[14] has shown that the NO_3^- ion has the ability to form an inner sphere complex with Eu^{3+}. In the nitrate solution, coordination will be shared by the NO_3^- ions and water molecules, resulting in increased asymmetry compared to coordination only by water. For $(CF_3SO_3)_3Eu$ and $(CF_3CO_2)_3Eu$, the Eu^{3+} bonding environment most likely consists of coordinated water molecules and the organic ligands, in the first coordination sphere, as evidenced by the similarity between the wet gel and sol spectra and the aqueous solution.

The spectra of the wet (unheated) gel shows a ($^5D_0\varnothing^7F_2$)/($^5D_0\varnothing^7F_1$) peak height ratio less than one, supporting arguments of a higher symmetry solvation shell.

Figure 2(b) shows the spectra after heating 2 days at 90°C.

Heating leads to increased solvent and water evaporation. The spectra, for all precursors, show a significantly enhanced $^5D_0\varnothing^7F_2$ intensity, indicating the presence of low symmetry sites. Furthermore, the effect of line broadening with thermal treatment indicates a progressive increase in the distribution of site symmetries for Eu^{3+}.

From figures 1 (a) and (b) and figure 2, it can be seen that the emission profile observed is very similar before and after gelation. This suggests that although the material is macroscopically rigid, the Eu^{3+} ions retains partial coordination by a liquid-like environment. This result can be supported by the lifetime values obtained.

Lifetime Measurements. Room-temperature luminescence lifetime of the $^5D_0$ state are presented in table I. Lifetime values are extremely sensitive to the constitution of the metal ion coordination sphere. Particularly, the lifetime of the $^5D_0$ level of the Eu^{3+} site is very sensitive to the hydroxyl groups concentration. These species lead to enhanced nonradiative decay of luminescent ion through hydroxyl quenching and so lifetime shortening is expected.

Table 1. Lifetime values (μs) measured at room temperature. Excitation is at maximum of $^7F_0\varnothing^5D_0$ absorption band. $^5D_0$ luminescence was monitored at 617 nm.

Precursor	solution	sol	wet gel	90°C
$Eu(NO_3)_3$	136.56	120.21	133.68	154.03
$(CF_3CO_2)_3Eu$	153.49	109.02	139.1	330.68
$(CF_3SO_3)_3Eu$		140.04	131.55	193.57
$Eu(acac)_3$	115.89	108.43	111.39	385.0
$Eu(thd)_3$	133.02	183.12	157.98	362.85
$Eu(fod)_3$	235.38	415.05	627.07	575.7

The lifetimes obtained for samples prepared from Eu $(thd)_3$ and $Eu(fod)_3$ were longer than the lifetimes obtained using the other precursors. The organic ligand shell shields the Eu^{3+} ion from immediate local surroundings and the fluorinated ligand in $Eu(fod)_3$ impart hydrophobic character to that precursor. This can be seen from the emission spectra and the lifetime value in all samples prepared. For the other precursors, the lifetime is not affected until some heat treatment is performed. Although the sample is not dehydrated at 90°C, water and solvent concentrations are decreased. The heat treatment lead to lenghtening of lifetime. The lifetime values for all precursors are longer if compared to lifetime of the sample prepared from europium nitrate.

Excitation Spectra. The $^7F_0\varnothing^5D_0$ excitation spectroscopy can be used as diagnostic of the bonding environment of Eu^{3+} [15]. Figure 3 presents the $^7F_0\varnothing^5D_0$ excitation spectra taken at room temperature for all Eu^{3+} precursors studied in the sol stage.

Figure 3 shows that the peak positon for $Eu(NO_3)_3$, $(CF_3SO_3)_3Eu$ and $(CF_3CO_2)_3Eu$ are sharp and centered 579.1 nm. That peak has been atributed to an aqueous europium complex containing one inner-sphere NO_3^-, for the nitrate precursor[14].

Figure 3 (e) shows two unresolved peaks for the $Eu(thd)_3$ sol. The higher energy component coincides with the single sharp line observed in the others precursors (579.1 nm). The existence of two distinct lines in the $^5D_0$ - $^7F_0$ region demonstrates that at least two complex species are present. In this case, probably, the coordination sphere is composed by water and alcohol (solvent) molecules.

Figure 3 (f) shows the excitation spectra for the sol prepared from the florinated and chelate precursor, $Eu(fod)_3$. The bandwidth is broader (~15 Å), that can be an evidence for the presence of different Eu^{3+} environment. DMF is a strong Lewis base used, to coordinate with the chelated Eu^{3+}, which may compete with water molecules for the Eu^{3+} coordination. The bulky ligand groups would tend to keep unbonded molecules comparatively far from the central ion, and, in view of the random spatial arrangement of these molecule, a broader range of bonding environment for Eu^{3+}.

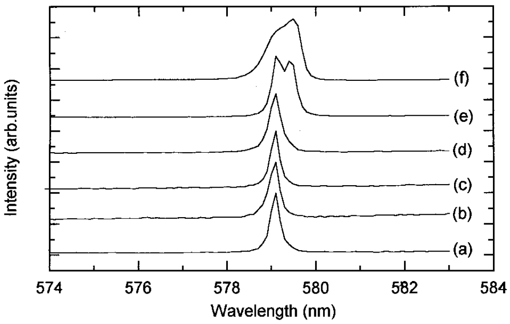

Figure 3. *Excitation spectra of: (a)* $Eu(NO_3)_3.6H_2O$*, (b)* $(CF_3CO_2)_3Eu$*, (c)* $(CF_3SO_3)_3Eu$*, (d)* $Eu(acac)_3$*, (e)* $Eu(thd)_3$*, (f)* $Eu(fod)_3$*. Each spectra was normalized to the maximum emission intensity.*

Figure 3 (d) shows the excitation spectra for $Eu(acac)_3$ precursor. In this case, the presence of only methyl groups on the chelate ligands instead of bulkier groups may allow solvent and water molecules to approach more closely than in the other cases. This can result in less intense fluorescence and in shorter lifetime values than observed for the other chelate precursors.

Eu^{3+} doped silica gel partially densified. Room temperature luminescence broadband spectra of 1 wt% Eu_2O_3 doped samples prepared from the Eu^{3+} precursors and densified at 800°C were measured (Figure 4) and compared to the spectrum of a sample prepared from $Eu(NO_3).6H_2O$. The spectrum of the sample prepared from $(CF_3COO)_3Eu$ (is not presented) was similar to that of the non-fluorinated sample prepared from $Eu(NO_3).6H_2O$. The other two fluorinated samples had spectra that differed in two important ways from the spectrum of the non-fluorinated sample. First, the $^5D_0\varnothing^7F_0$ transition was broader and second, the $^5D_0\varnothing^7F_2$ transition intensity was much stronger. The first observation suggests that a wider range of Eu^{3+} bonding sites is present in the samples prepared from $Eu(fod)_3$ and $(CF_3SO_3)_3Eu$ and the second observation implies that more highly distorted/less symmetrical Eu^{3+} bonding environment are present. Selectively excited fluorescence spectra measured at 77 K for the samples prepared from the fluorinated Eu^{3+} precursors revealed no line narrowing effect. Figure 5 shows broadband and selectively excited emission spectra for 1 wt % silica gel prepared from $Eu(fod)_3$. The FLN spectra of all precursors studied were very similar to those of the $Eu(fod)_3$ precursor and therefore are not presented. This result indicates that the use of fluorinated or chelate Eu^{3+} precursors do not inhibit Eu^{3+} clustering.

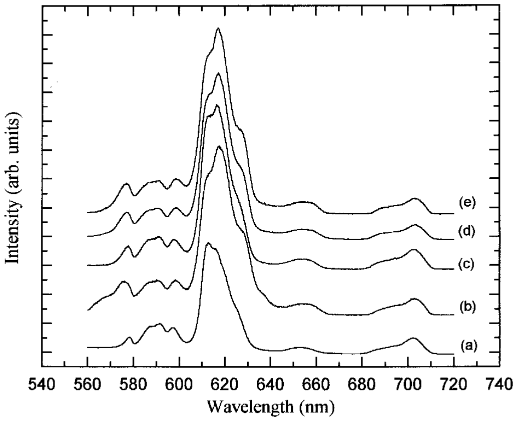

Figure 4. *Room temperature fluorescence spectra of 1.0 wt%* Eu_2O_3 *doped sol-gel silica. (a)* $Eu(NO_3)_3.6H_2O$*, (b)* $Eu(acac)_3$*, (c)* $(CF_3SO_3)_3Eu$*, (d)* $Eu(fod)_3$*, (e)* $Eu(thd)_3$*.*

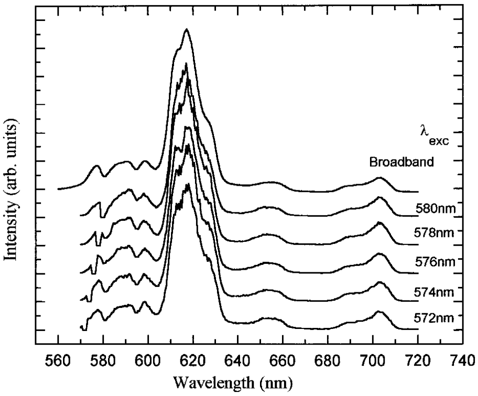

Figure 5. *FLN spectra at 77 K of 1.0 wt% Eu_2O_3 doped sol-gel silica, densified to 800 ^oC, prepared from the $Eu(fod)_3$ precursor. Intensities were normalized to the $^7F_0 \varnothing {}^5D_1$ emission at each pump wavelength. Upper spectrum, fluorescence spectrum at 300 K.*

The fluorinated precursors had a pronounced effect on the Eu^{3+} lifetime. Table 2 summarizes 77 K lifetime results of samples containing 5 wt% Eu_2O_3 heated to 800^{o}C for two excitation (λ_{exc}) and two detection (λ_{em}) wavelengths. A clear increase in lifetime was observed when fluorinated precursors were used. Since the fluorescence line narrowing spectra indicate that appreciable clustering is present, the longer lifetimes indicate that the use of fluorinated Eu^{3+} precursors leads to lower hydroxyl content in the densified gels.

Table 2. Lifetime values (ms) measured at 77 K for 5 wt% Eu_2O_3 doped silica gels. Lifetime values are presented for two excitation wavelenghts (577, 579 nm) and two monitoring wavelenghts (610, 625 nm).

	λ_{exc}=577nm		λ_{exc}=579nm	
λ_{em} (nm)	610	625	610	625
$Eu(NO_3).6H_2O$	1.17	1.14	1.16	1.17
Eu(CFC)	1.63	1.44	1.69	1.61
Eu(CFS)	1.63	1.63	1.74	1.67
$Eu(fod)_3$	1.60	1.63	1.67	1.64
$Eu(thd)_3$	1.52	1.48	1.52	1.49
$Eu(acac)_3$	1.22	1.12	1.26	1.22

CONCLUSIONS

Fluorescence, excitation, fluorescence line narrowing, and lifetime studies were presented during different sol-gel stages of Eu^{3+}-doped TMOS gels prepared using diferent Eu^{3+} precursors. The FLN studies indicate that significant Eu^{3+} clustering occurs in the gels. Much longer lifetimes, relative to samples prepared from $Eu(NO_3).6H_2O$, were observed in gels heated to 800 ^{0}C that were prepared from the fluorinated Eu^{3+} precursors. This result suggests that the presence of fluorine in the pores of the gel significantly facilitates the removal of water during heat treatment and that the use of fluorinated precursors may lead to rare earth doped sol-gel materials with higher luminescence efficiency.

Chelate precursors provide a asymmetric environment and consequently enhanced Eu^{3+} emission and a general increase in a lifetime values for the initial stage of the sol-gel reaction.

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