Optical characterization of Eu^{3+}-doped sol-gel hybrid thin film prepared with various conditions

E.O. Oh · Y.H. Kim · C.M. Whang

Abstract Good optical quality Eu^{3+}-doped silica-polyethyleneglycol (PEG) hybrid films with covalent bonds between the inorganic (silica) and organic (PEG) phases were prepared by the sol-gel process. These materials are transparent, flexible and show high Eu^{3+} luminescence output. Their luminescence properties, local environment around europium ion and structure have been investigated as a function of dopant concentration, molecular weight of PEG, PEG content and water content. Photoluminescence spectra of the samples prepared by different europium ion concentration showed that increasing the Eu^{3+} concentration induces a decrease in the intensity of the host broad band in the green-blue spectral region and an increase in the intensity of a series of Eu^{3+} intra 4f^6 yellow-red sharp lines. However, the sample with higher Eu^{3+} concentration was found to exhibit concentration quenching of luminescence due to dopant clustering. Photoluminescence spectra of the samples with shorter polymer chains indicated that the distance between the hybrid's emitting centers and the metal ions is large enough to allow efficient energy-transfer mechanisms. It was noted that luminescence intensity and sharpness were increased by increasing polymer concentration and decreasing water content.

Keywords Europium · Inorganic-organic hybrid · Photoluminescnece · Optical properties · Lanthanide ion

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1 Introduction

Rare-earth ions are characterized by long excited state lifetimes and narrow-band, practically monochromatic, emission due to their unique f-f electronic transitions. They have attracted considerable interest due to their potential application as solid state laser, lamp and optical communication amplifiers [1–3]. In this context, recent studies deal with materials prepared by reacting silicon-alkoxide with polyethers [2, 3]. Polyethyleneglycol (PEG) presents certain liquid-like features, the polymer acting as an immobile solvent for many metallic salts, while the presence of a silica network allows the transparent materials to be obtained, resulting in better mechanical properties than pure PEG systems.

However, they are also characterized by two serious disadvantages, such as hydroxyl quenching and dopant clustering [4–6]. Hydroxyl quenching is caused by residual water, solvents and silanol groups which are present in sol-gel glasses. Dopant clustering is deleterious because it leads to concentration quenching of luminescence through cross-relaxation and energy transfer processes.

This investigation aims at preparing europium ion doped inorganic-organic sol-gel thin films possessing good luminescent properties and also at controlling their optical properties by varying experimental variables, namely, molecular weight of organic component, content of organic component, water content and europium content.

2 Experimental

TEOS(Tetraethylorthosilicate) and PEG(Polyethyleneglycol) were chosen as the precursors of inorganic and organic component, respectively. Hydrocholoric acid (HCl, 1 M) and ethanol (EtOH) were used as catalyst and solvent. For the
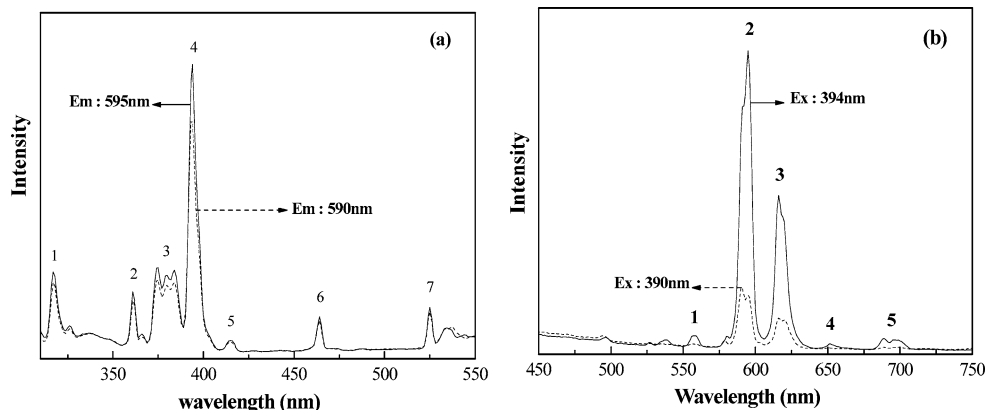
Table 1 The composition of the samples

Sample no.	n ([Eu]/[O])	TEOS (M)	EtOH (M)	HCl (M)	PEG M_n	PEG wt%	H_2O (M)
			various Eu^{3+} concentration				
E1	0.000						
E2	0.010						
E3	0.020						
E4	0.040	1	2	0.001	400	15	2
E5	0.080						
E6	0.120						
E7	0.240						
		various average molecular weight of PEG					
P200					200		
P400					400		
P600	0.020	1	2	0.001	600	15	2
P1000					1000		
		various PEG weight%					
W10						10	
W20						20	
W30	0.010	1	2	0.001	400	30	2
W40						40	
		various water content					
H1							1
H2	0.010	1	2	0.001	400	15	2
H4							4
H8							8

M_n(g/mole) denotes average molecular weight of PEG

lanthanide ion, Europium (III) (Trifluromethanesulfonate, $Eu(CF_3SO_3)_3$) was chosen. The molar ratio of TEOS:EtOH:HCl was 1:2:0.001. Average molecular weight of PEG(M_n) was varied from 200 to 1000 g/mole, content of PEG was changed from 10 to 40 wt% and molar ratio of H_2O/TEOS was changed from 1 to 8. The dopant ion concentration, $n =$ [Eu]/[O] representing the ratio of $Eu(CF_3SO_3)_3$ ion group per (OCH_2CH_2) monomer unit, was changed from 0 to 0.24. The composition of the starting materials for the prepared samples are collected in Table 1.

The excitation and emission spectra of the samples were recorded using a SHIMADZU Spectrofluorometer (model RF-5301, Japan) with pulsed Xe arc lamp. The photoluminescence spectra of the samples were recorded using a Photoluminescence Spectrometer (model SPEX 1403, U.S.A) with pulsed He-Cd laser (325 nm).

3 Results and discussion

Figure 1(a) shows the excitation spectra of the E6 sample with different emission wavelength. Excitation spectra are monitored with the $^5D_o \rightarrow ^7F_1$ transition wavelength. The narrow lines denoted by 1,2,3,4,5,6 and 7 correspond to transitions between the $^7F_0$ and $^5H_4$, $^5D_4$, $^5G_{J=3,4,5}$, $^5L_6$, $^5D_1$, $^5D_2$ and $^5D_3$ levels, respectively. The presence of narrow spectra will be ascribed to a ligand-to-metal charge transfer (LMCT) transition resulting from the interaction between the ligands and the lanthanide ions. Figure 1(b) shows the emission spectra of the E6 sample with different excitation wavelength with the $^7F_0 \rightarrow ^5L_6$ transition wavelength, 390–394 nm. The lines denoted by 1,2,3,4 and 5 are assigned to the Eu^{3+} intra-4f^6 transitions between the $^5D_0$ and $^7F_{0-4}$ levels. The intensities of these emission spectra depend on the selected excitation wavelength [4, 7, 8].

Photoluminescence spectra of the prepared samples excited under 325 nm were given in Fig. 2. The spectra are composed of a large broad band in the green-blue spectral region, already observed in the undoped hybrid composites E1, and a series of Eu^{3+} intra 4f^6 yellow-red sharp lines. These sharp lines correspond to the following transitions: $^5D_o \rightarrow ^7F_o$ (575 nm), $^5D_o \rightarrow ^7F_1$ (586–592 nm), $^5D_o \rightarrow ^7F_2$ (611–617 nm), $^5D_o \rightarrow ^7F_3$ (647 nm) and $^5D_o \rightarrow ^7F_4$ (685–695 nm). The large broad band clearly presents two components: a main band in the blue spectral region, peaking between 410–425 nm and a shoulder in the green spectral region, peaking around 446 nm. Only the energy of the former component depends on the selected excitation wavelength [4, 7–9].
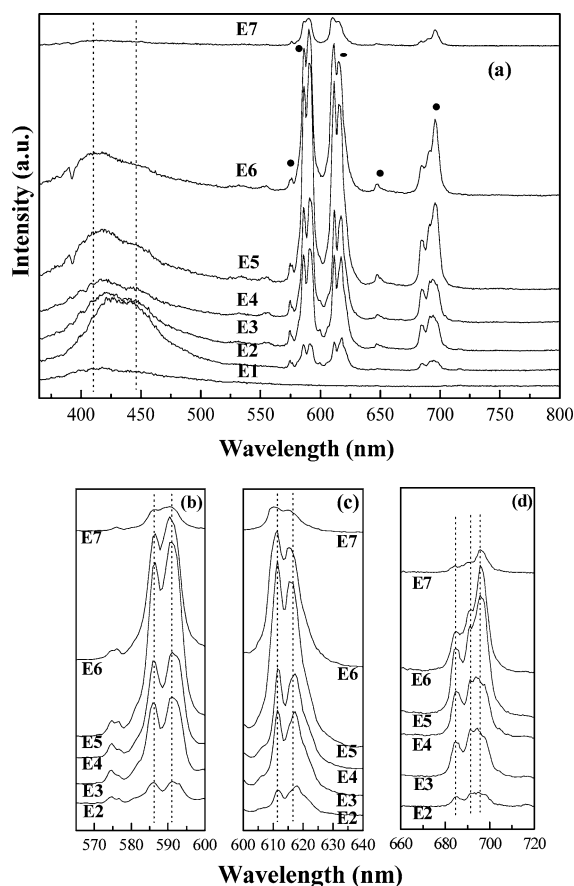

Fig. 1 (a) Excitation spectra of the E6 sample monitored with the $^5D_0 \rightarrow ^7F_1$ transition wavelength, 590–595 nm. The numbers 1,2,3,4,5,6 and 7 denote the intra-4f^6 transitions: $^7F_0$ and $^5H_4$, $^5D_4$, $^5G_{J=3,4,5}$, $^5L_6$, $^5D_3$, $^5D_2$, and $^5D_1$, respectively. (b) Emission spectra of E6 sample monitored with the $^7F_0 \rightarrow ^5L_6$ transition wavelength, 390–394 nm. The numbers 1,2,3,4 and 5 denote the intra-4f^6 transition : $^5D_0 \rightarrow ^7F_{J=0-4}$, respectively

Fig. 2 Photoluminescence spectra of the prepared samples with various Eu^{3+} concentration: (a) monitored with entire wavelength ($^5D_0 \rightarrow ^7F_{J=0-4}$), (b) $^5D_0 \rightarrow ^7F_0$ and $^5D_0 \rightarrow ^7F_1$ transition (575–595 nm), (c) $^5D_0 \rightarrow ^7F_2$ transition (610–630 nm) and (d) the $^5D_0 \rightarrow ^7F_4$ transition (680–700 nm). The dots(·) denote the intra-$4f^6$ transitions ($^5D_0 \rightarrow ^7F_{J=0-4}$).

The energy-transfer mechanisms between the host matrixes and the europium ions arise from two different and independent processes: a charge-transfer band, resulting from the interaction between the Eu^{3+} and the first ligands, and energy transfer from the hybrid's backbone emitting center. The energy-transfer processes depend on the Eu^{3+} local coordination. The relative intensity between the hybrid host's emission band and the Eu^{3+} cation lines strongly depends on the selected excitation wavelength and on the Eu^{3+} content. As Fig. 2 demonstrates, in the most dilute hybrid E1, the broad band and the Eu^{3+} lines can be clearly observed when the 325 nm excitation wavelength is used. Increasing the Eu^{3+} concentration induces a decrease in the intensity of the host broad band associated with the cation lines, in such a manner that for $n = 0.240$ the hybrid host emission could hardly be detected. However, it is also obvious from the Fig. 2(a) that the increase in europium ion concentration resulted in a decrease in peak intensity and sharpness, which has been attributed to the deactivation process by the intermolecular energy transfer orig-

inating from coupling with vibrational modes of the host environment. In particular, solvents containing –OH (e.g., water or oxide matrixes, like SiO_2) and Eu^{3+} local coordination extensively reduce luminescence emission intensity and decay time.

Figure 2(b)–(d) show in detail the Eu^{3+} emission for the prepared samples. It leads us to the conclusion that changes in the energy, maximum splitting, full width at half maximum (FWHM), and number of components occurs as Eu^{3+} content increases. It is suggested that more than one Eu^{3+}-local coordination site might exist. For the diluted samples, E2 - E4, the $^5D_o \rightarrow ^7F_{1,2,4}$ transition peaks actually consist of three, two, five components, respectively. These components of the crystal-field are present when the rare earth ion occupies a crystallographic site without inversion symmetry. These uneven components mix a small amount of opposite-parity wave functions (like 5d) into the 4f wave functions of europium ions. In this way the intraconfigurational $4f^n$ transitions obtain at least some intensity. Spectroscopists say it in the following way: the (forbidden) 4f-4f transition steals some intensity from the (allowed) 4f-5d transition [9].

Photoluminescence spectra of the samples prepared by various conditions excited under 325 nm were given in Fig. 3. As the molecular weight of PEG was decreased from $M_n = 1000$ to $M_n = 200$ (Fig. 3(a)), the main large broad band in the green-blue spectral region originating from the hybrid host matrix is blue shifted. It is known that a shift in the LMCT transition frequencies toward the high energy region of the spectrum relates to an increase in the effective charge of the lanthanide cation and, thus, a decrease in the tendency of the first-shell ligands to bond covalently to the metal ion [8, 9]. Therefore, this suggests that the Eu^{3+} ions experience a more covalent environment in the sample with $M_n = 1000$ than in the sample of $M_n = 200$. This fact is mainly induced by alterations in the type of ligands present in the first coordination shell. In longer polymer chain (Fig. 3(a)-P1000), the Eu^{3+} is coordinated to the carbonyl oxygen atoms. In shorter polymer chain (Fig. 3(a)-P200), the Eu^{3+} is coordinated to the ether oxygen atoms. The oxygen atoms of the carbonyl groups are known to have a greater tendency to bond covalently to the Eu^{3+} ions compared with the ether oxygen atoms [4, 7–9]. For the samples with longer polymer chains, energy transfer occurs as the Eu^{3+} coordination involves the carbonyl-type oxygen atoms of the polymer bridges, which are located near the hybrid's host emitting center. On the contrary, in the samples with shorter polymer chains, the Eu^{3+} ions are coordinated to the polymer chains, and therefore, the distance between the hybrid's emitting centers and the metal ions is large enough to allow efficient energy-transfer mechanisms. Figure 3(b) shows photoluminescence spectra of the samples prepared with different polymer content. We note that increasing oligomer content has a dramatic effect on band shape and intensity. In the case of silica matrixes,
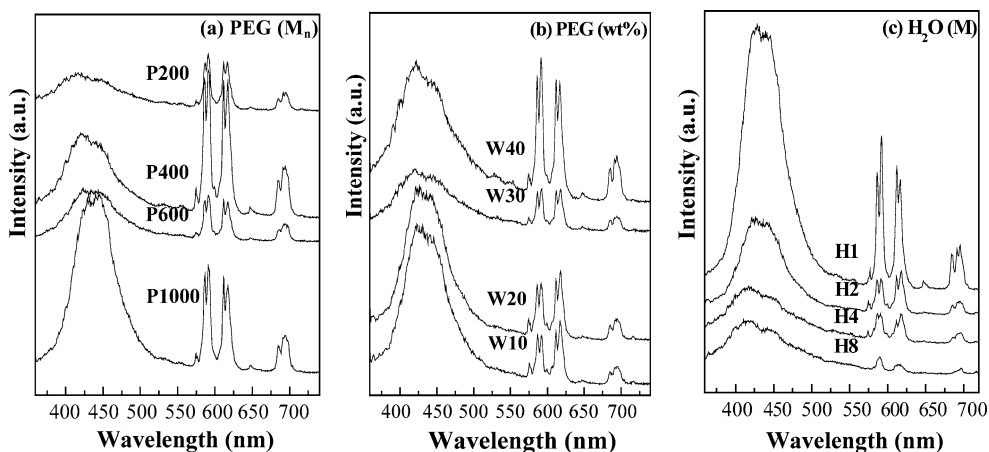
Fig. 3 Photoluminescence spectra excited under 325 nm (He-Cd laser) of the samples prepared with various average molecular weight of PEG (PEG 15 wt%) (a), various PEG content (M_n = 400 g/mole) (b) and various water content (M_n = 400 g/mole) (c).

the 611–617 nm peak was relatively broad at low oligomer concentration, indicating an important interaction with the silica environment. However, the peak became narrow and symmetric at sufficiently high oligomer content (≥40 wt%). Photoluminescence spectra of samples prepared by different water content were given in Fig. 3(c). As the water content increase, the peak intensity and sharpness decrease, which has been attributed to the deactivation process by the intermolecular energy transfer originating from –OH of water. These 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 ions [4, 7–9].

4 Conclusions

The sol-gel method was used to synthesize organic/inorganic hybrid incorporating europium triflate. The effective interaction between the Eu^{3+} ions and the host matrix depends markedly on the host environment and amount of Eu^{3+} incorporated. Photoluminescence spectra of the samples prepared by various conditions showed that increasing the Eu^{3+} concentration, decreasing the polymer chain length, increasing the polymer content and decreasing the water content

induce a decrease in the intensity of the host broad band in the green-blue spectral region and an increase in the intensity of a series of Eu^{3+} intra $4f^6$ yellow-red sharp lines. The control of the energy transfer mechanism is obtained by changing the polymer molecular weight, the Eu^{+3} concentration and the amount of water content.

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