

Thermoanalysis and Emission Properties of $\text{Eu}^{3+}/\text{Eu}^{2+}$ in Eu^{3+} -Doped Xerogels

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A series of Eu^{3+} -doped silica sol–gels are prepared under various conditions: (1) pH values of the sols are controlled at 3.0, 5.5, and 7.5; (2) the counterions of dopants are selected from acetate, chloride, and nitrate of europium (III) compounds; (3) two chelating agents, namely ethylenediaminetetraacetic acid (EDTA) and ethylenediaminetriacetic (HEDTA) are used for complexing the europium (III) dopants; (4) a sol–gel matrix containing low O–H functionality is synthesized by using deuterated solvents (D_2O and $\text{C}_2\text{D}_5\text{OD}$) and under an extremely dry N_2 environment; and (5) a mixture of 1% of aluminum or antimony alkoxide and 99% of silicon alkoxide is adopted as precursors. The conditions that these differences have on the network structures of a gel matrix are examined in order to determine the optimal conditions for the creation of structural defects in an SiO_2 network, generation of electron–hole centers and utilization of them to reduce Eu^{3+} to Eu^{2+} during the sol–gel processing. Both differential scanning calorimetric (DSC) measurements and thermogravimetric and differential thermal analysis (TG/DTA) are employed to illustrate which gel samples are the most liquidlike and have the greatest cross-linking density. The results from thermoanalysis are then correlated to the emission intensity and lifetimes of each Eu^{3+} -doped sample. The relative emission intensity of $\text{Eu}^{2+}/\text{Eu}^{3+}$ gives the degree of conversion of Eu^{3+} to Eu^{2+} which is produced from the defect electron–hole pair generation. The absolute emission intensity of Eu^{3+} and Eu^{2+} is strongly quenched by the presence of OH groups in xerogels and is shown to be enhanced by laser irradiation due to water evaporation. The results show that a basic gel prepared by the mixed metal alkoxides most efficiently converts Eu^{3+} to Eu^{2+} because of its liquidlike nature, reduced cross-linking density, and low OH quenching.

Introduction

It has been shown¹ that in fused silica samples, thermally generated defect electrons in the O^{2-} matrix are ejected from a storage of preexisting defects. The defects probably appear as peroxy radicals, nonbridging-oxygen hole centers, or self-trapped holes.² These defect electrons are present in sol–gel silicate structures. Yoldas³ reported that in sol–gel systems, not only by dopants but also by thermochemical means, a massive concentration of electron–hole (e^- – h^+) carriers can be created at low temperatures. The evidence has recently been reported on the emission of these e^- – h^+ pairs in the Eu^{3+} -doped xerogel sample.⁴ The defects or ejected electrons that stem from these carriers are free to move about and can be effectively harvested for the reduction of high oxidation state rare-earth metal ions (and transition metal ions) to their corresponding low oxidation state ions. The structural defects or amount of e^- – h^+ pairs generated in xerogels should critically depend on the chemical conditions of sol–gel processing.

Lanthanide ions are energetically preferred as the trivalent state according to their electronic configurations. Some lanthanide ions, however, can also exist as divalent states such as Eu^{2+} , Sm^{2+} , and Yb^{2+} . The Eu^{2+} aqueous solution in air is unstable.⁵ When Eu^{3+} is predispersed in the sol solution, the ejected electrons from the oxygen-associated hole centers react with Eu^{3+} encapsulated in sol–gel matrix to produce Eu^{2+} ions

which have been proposed to become stable at the cation vacancies by forming Eu^{2+} –hole complexes.⁴ Eu^{3+} in gel glasses has emission transitions corresponding to $^5\text{D}_0 \rightarrow ^7\text{F}_j$, where $j = 0, 1, 2, 3, 4$, and displays in wavelengths from 580 to 700 nm. The ratio of the emission intensities of the $^5\text{D}_0 \rightarrow ^7\text{F}_2$ at 610 nm and $^5\text{D}_0 \rightarrow ^7\text{F}_1$ at 590 nm transitions is generally assumed to be an indication of the degree of asymmetry in the surroundings of the Eu^{3+} ion.⁶ Eu^{2+} has a broad emission band corresponding to $4\text{f}^65\text{d} \rightarrow 4\text{f}^7$ at a wavelength ~ 445 nm in porous Vycor glass⁷ and ~ 410 nm in xerogel.⁴ The photophysical properties of lanthanide ions in aqueous solution are sensitive to the number of water molecules in contact with the primary coordination sphere of the metal ion,⁸ owing to a radiationless path for deactivation via coupling to OH vibrational overtones. Sol–gel derived porous supports usually contain large amounts of hydroxyl groups, the presence of which is detrimental to rare-earth luminescence and has been proposed as a major cause for the absence (or low intensity) of luminescence in rare-earth doped gels.^{9,10} Therefore, a sol–gel environment that preserves a strong emission and longer lifetime for the europium ions is one with fewer OH groups.

Sol–gel encapsulation of lanthanides, especially the divalent ions such as Eu^{2+} and Sm^{2+} have become recent areas of research because of their potential for utilization in optical memories,¹¹ solid-state lasers,¹² phosphors for green color display, X-ray phosphor for medical imaging,¹³ and a possible design of single-site catalysts for both organic and inorganic reactions. The divalent lanthanides (e.g., Eu^{2+}) are generally produced from their trivalent ions (e.g., Eu^{3+}) by thermal heating under a mixed gas of H_2/N_2 ,¹⁴ photoreduction with short wavelength (193–222 nm) excitation,¹⁵ and electrochemical

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reduction.¹⁶ It should be more useful if a sol–gel process could be derived to effectively reduce Eu^{3+} and simultaneously stabilize the Eu^{2+} generated in an optically transparent xerogel.⁴

The question is what are the sol–gel processing conditions that could (i) lead to a high concentration of structural defects in the polymeric oxo-bridged SiO_2 network, (ii) generate a large quantity of electron–hole carriers in silica supports, and (iii) reduce effectively the Eu^{3+} to form Eu^{2+} ions by harvesting these e^- – h^+ pairs. In sol–gel chemistry, several experiments have been published that show variations in the processing parameters (such as the $\text{Si}:\text{H}_2\text{O}$ molar ratio, acid or base catalyst, solvent, temperature, etc.) that cause modifications in the network structure of the sol–gel matrix.¹⁷ Evidently, the counterion of the europium salt was proven to affect strongly the photophysical properties of Eu^{3+} in the sol–gel matrix due to inner sphere coordination of the Eu^{3+} by the counterion.¹⁰ The emission of Eu^{2+} incorporated in a sol–gel derived SiO_2 glass was shown to be enhanced by about 250 times by codoping with 1% of aluminum oxide.¹⁴ The metal/ligand complexation of lanthanide ions display a large reduction in the number of coordinated water molecules around the first coordination sphere of the metal ions, yet the ligands do not channel effectively the radiationless deactivation of lanthanide luminescence.¹⁸ Recently, Armendia et al.¹⁹ used differential scanning calorimetry (DSC) with thermogravimetry (TG) attachment and mass spectrometry (MS) to follow the influences of processing parameters on the sol–gel synthesis of sulfated zirconia catalysts.

In this paper, we prepare a series of Eu^{3+} -doped silica sol–gels using various pH values of the sols, different counterions of the dopants, two chelating agents (EDTA and HEDTA), the deuterated solvents (D_2O and $\text{C}_2\text{D}_5\text{OD}$) and under an extremely dry N_2 environment, and two mixed precursors of metal (Al or Sb)–silicon alkoxides. A detailed thermal analysis of Eu^{3+} -doped xerogels prepared is conducted to obtain the engineering conditions that optimize the liquidlike nature, reduce cross-linking density of the oxo-bridged SiO_2 network, and minimize the OH quenching of europium emission. The photophysical properties (emission intensity and lifetime) of both Eu^{3+} and Eu^{2+} species in xerogels are investigated to support the claims based on the thermal analysis. A complete set of sol–gel processing conditions is then illustrated to offer a maximum yield of $\text{Eu}^{3+} + \text{e}^- \rightarrow \text{Eu}^{2+}$ at room temperature.

Experimental Section

Chemicals. Tetramethyl orthosilicate (TMOS), $\text{Eu}(\text{CH}_3\text{COO})_3\cdot\text{hydrate}$, $\text{Eu}(\text{NO}_3)_3\cdot\text{hydrate}$, $\text{EuCl}_3\cdot\text{hydrate}$, N-(2-hydroxyethyl)ethylenediaminetriacetic acid (HEDTA), ethylenediaminetetraacetic acid (EDTA), aluminum isopropoxide, antimony(III) ethoxide, and ethanol (spectroscopic grade) were purchased from Aldrich Chemical Co. D_2O and $\text{C}_2\text{D}_5\text{OD}$ were obtained from Merck & Co., Inc. All chemicals are used as received. Deionized water is employed to prepare the sols.

Sol–Gel Processing. All of the sols began with a 1:4:4 molar ratio of precursor (TMOS or a mixed metal/silicon alkoxides)/ethanol/water, and sometimes adding a small amount (2 drops) of 0.04 M HCl as a catalyst. For the control gel, to which all other processing conditions will be compared, the sol was prepared by using TMOS as precursor and doped during the introductory stages with $\text{Eu}(\text{CH}_3\text{COO})_3\cdot\text{hydrate}$, based on the total volume of the reagents, to produce a 1.0×10^{-3} M Eu^{3+} sol at pH = 5.5. This sol mixture was then sonicated for 10 minutes and transferred to 4.0 mL polystyrene cuvettes and covered with parafilm. Gelation occurred within 24 h; gels were

allowed to develop and dry at room temperature until stabilization of the weight has been completed. Monolithic transparent rectangular xerogels of 2.0 cm in length and 0.4 cm in width were produced.

To investigate the effects of pH on the microstructure of xerogel which may result in different concentration of structural defects, the same amount of $\text{Eu}(\text{CH}_3\text{COO})_3\cdot\text{hydrate}$ (i.e., 1.0×10^{-3} M Eu^{3+}) was doped into two separate sol mixtures of 1:4:4 molar ratio of TMOS/ethanol/ H_2O . In one sol, acid was added to produce an acid gel at pH = 3.0 and base was added into the other sol to generate a basic gel at pH = 7.5. To study the effects of counterions of europium salts on the emission properties of $\text{Eu}^{3+}/\text{Eu}^{2+}$ encapsulated in xerogels, enough $\text{Eu}(\text{NO}_3)_3\cdot\text{hydrate}$ and $\text{EuCl}_3\cdot\text{hydrate}$ were doped into two separate sols to give 1.0×10^{-3} M Eu^{3+} initial sols based on the total volume of the reagents. An attempt was made to reduce the number of OH groups surrounding the $\text{Eu}^{3+}/\text{Eu}^{2+}$ ions in a sol–gel matrix: one sol was prepared using D_2O and $\text{C}_2\text{D}_5\text{OD}$ doped with $\text{Eu}(\text{NO}_3)_3\cdot\text{hydrate}$ and processed in a glovebag under constant N_2 flow.

To study the effects that a chelating reagent has on the reduction factor of Eu^{3+} to form Eu^{2+} during the sol–gel processing, the above procedure of sol–gel processing was modified. The $\text{Eu}(\text{CH}_3\text{COO})_3\cdot\text{hydrate}$ was complexed in an EDTA or HEDTA sample which was prepared using the disodium salt in a phosphate buffer. Both EDTA and HEDTA form a 1:1 complex with Eu^{3+} , the total concentration of the ligand in solution is slightly higher than the Eu^{3+} ion concentration, and as a result the concentration of the free Eu^{3+} ion in solution is negligible. Each $\text{Eu}^{3+}/\text{EDTA}$ or $\text{Eu}^{3+}/\text{HEDTA}$ complex was then doped into the separate sols of 1:4:4 molar ratio of TMOS/ethanol/water, where the complex concentration is 1.0×10^{-3} M and pH of the sol is 5.5. To investigate the effects of mixed metal/silicon alkoxides as precursors on the structural evolution and chemical bond formation of the oxo-bridged SiO_2 network, 1.0×10^{-3} M Eu^{3+} (europium acetate hydrate) was prepared in two separate sol mixtures of 1:4:4 molar ratio of precursor/ethanol/ H_2O . A mixture of 1% aluminum isopropoxide and 99% TMOS was used in one precursor and the other precursor was composed of 1% antimony(III) ethoxide and 99% TMOS. For comparison, the pH of the resultant sol was maintained at 5.5 as the control gel.

Thermal Analysis. The thermal analysis of Eu^{3+} -doped silica xerogels was conducted by thermogravimetric and differential thermal analysis (TG/DTA) and differential scanning calorimetry (DSC) measurements. All data were obtained on a Seiko DSC 220C (Seiko Scientific Instruments, Inc.) and a Seiko TG/DTA 320 equipped with a Seiko SSC5200H disk station for scanning program manipulation and data analysis. The xerogel specimen (~ 10 mg) broken into tiny pieces with a mortar and pestle was placed into an aluminum sample pan while the reference was an empty Al pan. The xerogel sample was either weighed with an analytical balance or in the TG/DTA's internal balance. For DSC scans, the sample was lidded and the sample chamber was cooled with liquid nitrogen. The specimens were subjected to temperature scan from -50 °C to 600 °C at a heating rate of 10 °C/min and the thermal data were recorded and analyzed. To erase the thermal history and release the stress resulting from the mechanical sampling, the DSC samples were first annealed at 75 °C. For TG/DTA, the sample was maintained in an open aluminum pan and was heated from 24 °C to 600 °C at a rate of 10 °C/min while the data were recorded.

The DSC heat flow may be expressed, in mathematical form, by the equation

$$dQ/dt = -C_p(dT/dt) + K(T,t)$$

where dQ/dt = DSC heat flow, dT/dt = heating rate, C_p = sample (complex) heat capacity, t = time, T = temperature, and $K(T,t)$ = kinetic DSC response. This equation shows that the parent, total DSC heat flow signal is comprised of two distinct components (C_p and kinetic) which can be separated by the great power of the oscillating DSC technique. The C_p component gives characterization information on reversible thermal events such as T_g which is displayed in Figure 1B and Table 1. The kinetic component provides data on the irreversible aspects of thermal transitions, such as the evolution of moisture, decomposition, crystallization, or curing. The percentage of moisture (liquidlike components) evolved from a xerogel sample (i.e., the weight loss in percentage = $1 - \text{TG}\%$) and the temperature at which the weight loss levels off (T_{LO}) are reported in Figure 1A and Table 1.

Photophysical Properties of Eu³⁺/Eu²⁺ in Eu³⁺-Doped Xerogels. The luminescence spectra and lifetimes of europium species encapsulated and reduced in the sol-gel matrix were recorded by using a Q-switched Nd:YAG laser (Continuum, Powerlite 8050, 50 Hz) pumped dye laser (Continuum, ND 6000) system. The dye laser of Rhodamine 6G was frequency doubled with a second harmonic generation module to isolate the 280 nm light which was employed as the excitation source. The emission spectra were scanned 500 times and averaged by using an optical multichannel analyzer (EG&G PARC OMA4 with CCD detection). The transient luminescence signal was focused onto a monochromator (Shimadzu GV-50) and detected by a 1P28 photomultiplier tube. A nanosecond signal processor (EG&G, model 4400) in combination with a boxcar integrator was used to measure the emission decay.

Results and Discussion

pH Effect. There was a potential for investigating the effect of pH values on sol-gel processing because the gelation times for different pH of sol vary drastically. At low pH the sol takes several days to gel while at higher pH the sol gels in a matter of minutes.¹⁷ This behavior occurs because the condensation rate increases continuously with the pH of sol.^{17,20} When europium-doped xerogels of differing pH were examined by TG analysis, the results indicated that the condensation rate is not the only factor that changes as a result of the pH. As shown in Figure 1A, all three types of xerogels, (a) pH = 5.5, (b) pH = 3.0, and (c) pH = 7.5, have a substantial weight loss from room temperature to about 100 °C. This loss is primarily attributed to the loss of physically adsorbed water and possibly residual alcohol evaporation.¹⁷ Above 100 °C, the additional weight loss is due to the loss of organics and non-cross-linked gel oligomers.¹⁷ The pH = 7.5 gel has the sharpest weight loss ($1 - \text{TG}\% = 20.0\%$) and the lowest temperature ($T_{LO} = 132.7$ °C) at which the weight loss levels off. The corresponding values for pH = 3.0 and 5.5 gels are % weight loss = 16.9% and 17.3% and $T_{LO} = 168.5$ °C and 157.8 °C, respectively. This indicates that of the three europium-doped xerogels the pH = 7.5 gel is the most liquidlike in nature. This observation confirms the relationship between the rate of condensation and pH of the sol. Since the pH = 7.5 sol gelled so quickly, there was little time for hydrolysis to take place, leaving behind a large quantity of unreacted water. As condensation continued these water molecules were being filled with many small clusters of "gel" or oligomers of silica that dissolve in basic conditions.²⁰ Eventually, these oligomers interconnect and span the sol, thus gelling the sol. As the gel dried, not all of the abundant water

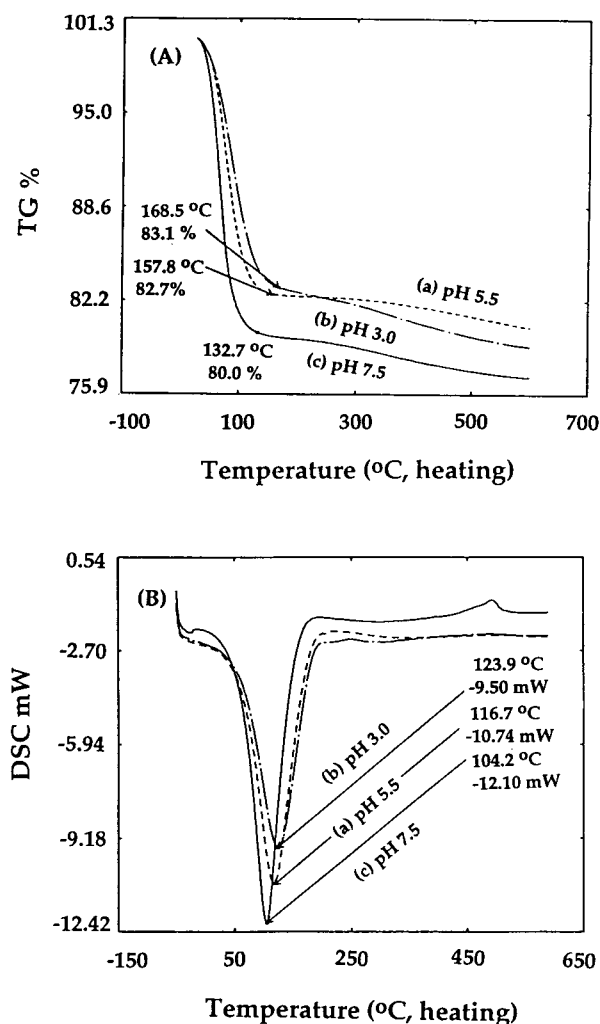


Figure 1. (A) TG (percent weight) and (B) DSC (heat flow) in mW as a function of temperature (heating) in 1×10^{-3} M Eu³⁺-doped xerogels processed at different pH values. The points labeled on each TG curve correspond to the temperature and percent weight at which the weight loss levels off.

TABLE 1: Thermodynamical Data of Eu(III)-Doped Xerogels Prepared under Various Conditions

sol-gel processing conditions		TG/DTA		
		DSC T_g (°C)	% weight loss ($1 - \text{TG}\%$)	T_{LO} (°C)
pH	3.0	123.9	16.9	168.5
	5.5 (ref)	116.7	17.3	157.8
	7.5	104.2	20.0	132.7
solvents	ref	116.7	17.3	157.8
	deuterated	147.2	18.0	204.1
chelating agents	ref	116.7	17.3	157.8
	EDTA	113.1	21.3	150.6
	HEDTA	122.0	16.6	170.5
counterions	ref	116.7	17.3	157.8
	Cl ⁻	118.5	18.3	152.4
	NO ₃ ⁻	125.7	16.2	158.5
mixed metal precursors	ref	116.7	17.3	157.8
	Al	102.8	20.0	143.7
	Sb	89.1	22.9	134.5

evaporated, therefore the pH = 7.5 gel was more liquidlike and had a greater weight loss than the pH = 5.5 or 3.0 gels that had more time to hydrolyze and condense. The more acidic gels had time to react with the water to form an $\equiv\text{Si}-\text{OH}$ group, but the condensation process never went to 100% completion. As a result, some of these $\equiv\text{Si}-\text{OH}$ functionalities and the

original $\equiv\text{Si}-\text{OR}$ groups remain, thus lowering the amount of water and alcohol that are regenerated via condensation. This explains that the pH = 5.5 and pH = 3.0 gels are less liquidlike as shown in Figure 1A and do not have as much a weight loss as the pH = 7.5 gel.

The cross-linking density and liquid or solid structure of xerogels cannot be directly determined by the TG and DSC curves. However, by extrapolating from the interpretation of TG/DTA data, it shows that the gel with the smallest initial weight loss, pH = 3.0, is the least liquidlike. This interpretation can be extended to say that the pH = 3.0 gel is not only the least liquidlike but also the gel with the highest cross-linking density. The cross-linking density of a polymeric system is, in general, related to its glass transition temperature (T_g)²¹ which can be detected from the Cp component in the oscillating DSC measurements. Normally, the T_g of these gels and glasses composed of silica network structure is one at which the glass transforms into the viscous one and its viscosity corresponds to $\sim 10^{13}$ poise. Since the pH = 3.0 sol took the longest to gel, it had the most time for the oligomers to polymerize and cross-link, thus forming an expansive SiO_2 network of bonds that are not easy to break. Figure 1B shows the DSC (heat flow) in mW as a function of temperature in $^\circ\text{C}$ for europium-doped xerogels of different pH values: (a) pH = 5.5, (b) pH = 3.0, and (c) pH = 7.5. The T_g values (corresponding to the reversible thermal events) for gels of pH 3.0, 5.5, and 7.5 are determined as 123.9, 116.7, and 104.2 $^\circ\text{C}$, respectively. The pH = 3.0 gel displays the highest T_g value, indicating the SiO_2 network of this gel has the largest molecular weight as resulted from the highest density of cross-linking. This result is in agreement with the statement made by Brinker and Scherer¹⁷ that acidic gels are more "polymeric" while basic gels are more "particulate".

The pH = 5.5 gel has an intermediate liquidlike nature (TG/DTA curve in Figure 1A) and cross-linking density (DSC curve in Figure 1B). In Figure 1A, after 150 $^\circ\text{C}$ both the pH = 3.0 and 7.5 gels experience a further, though not as rapid, weight loss. However, the pH = 5.5 gel remains relatively stable at high temperature. This suggests that the pH = 5.5 gel (which is referred to as the reference gel in this investigation) is the most thermally stable gel of the three. This observation is important because the rest of the effects (e.g., $\text{D}_2\text{O}/\text{C}_2\text{D}_5\text{OD}$ solvents, counterions, chelating agents, and mixed metal/silicon alkoxide precursors) are studied using gels with a pH ~ 5.5 (i.e., the reference gel). This is to ensure that any further change in the thermal and optical properties of europium-doped xerogels can be attributed to factors other than a pH-caused instability.

The emission intensity and lifetimes of both Eu^{3+} and Eu^{2+} species in the Eu^{3+} -doped xerogels are very sensitive to the amount of OH oscillators (e.g., water and alcohol in contact with the primary sphere of the metal ion) preserved in the sol-gel matrix. On the other hand, the efficiency of converting the trivalent Eu^{3+} ion to divalent Eu^{2+} ion during the sol-gel processing should depend on the concentration of electron-hole (e^- - h^+) carriers generated (i.e., the structural defects of the oxo-bridged SiO_2 network formed that ejected the defects electrons) and also the redox yield of harvesting of these e^- - h^+ pairs in the presence Eu^{3+} ions. The pH = 7.5 sol forms many tiny coagulates very quickly that result in a low cross-linking density of SiO_2 network, produce many structural defects, and generate a high concentration of e^- - h^+ carriers. It was proposed⁴ that the ejected electrons from the oxygen-associated hole centers can react with Eu^{3+} encapsulated in the sol-gel matrix to produce Eu^{2+} ions that are stabilized at the cation vacancies by forming Eu^{2+} -hole complexes. Figure 2A shows

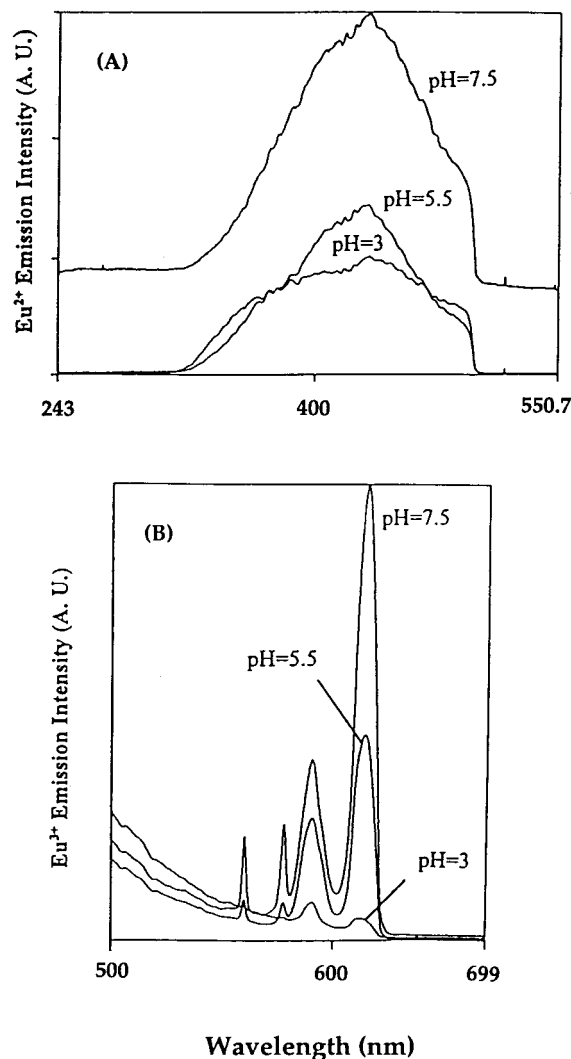


Figure 2. Fluorescence spectra of (A) Eu^{2+} at 410 nm and (B) Eu^{3+} at 580, 590, and 610 nm in 1×10^{-3} M Eu^{3+} -doped xerogels processed at different pH values. ($\lambda_{\text{exc}} = 280$ nm).

the relative emission intensity of Eu^{2+} generated in the sol-gel processing of Eu^{3+} -doped xerogels at different pH values (3.0, 5.5, and 7.5) of sols. Since the initial europium ions prepared and encapsulated in sol solution was the trivalent Eu^{3+} only, it is evident that the observed Eu^{2+} emission peak at 410 nm in Figure 2A should be originated from the sol-gel assisted reduction of $\text{Eu}^{3+} + e^- \rightarrow \text{Eu}^{2+}$. The gel with pH = 3.0 has the lowest fluorescence intensity of Eu^{2+} (a broad band maximum at 410 nm) with pH = 5.5 having an intermediate intensity and pH = 7.5 having the highest intensity. This observation implies that the higher cross-linking density of the SiO_2 oxo-bridged network has the fewest defect electrons produced in acid gel. Thus, the redox efficiency of $\text{Eu}^{3+} + e^- \rightarrow \text{Eu}^{2+}$ is reduced and lowers the emission intensity of Eu^{2+} .

It is important to verify that the broad band emission at 410 nm is not due to the neat or photochemical products of silicon alkoxides during the sol-gel processing. A control study was conducted on an undoped xerogel (i.e., the xerogel sample that does not contain europium ions) prepared and excited under the same conditions as the europium-doped sample. The fluorescence band for the undoped xerogel was observed at 354 nm (see Figure 3 in ref 4) which is 56 nm higher in energy than the observed emission band of Eu^{2+} at 410 nm. Moreover, the emission intensity of undoped sample is at least 50% smaller as compared to the Eu^{2+} band at 410 nm of the europium doped

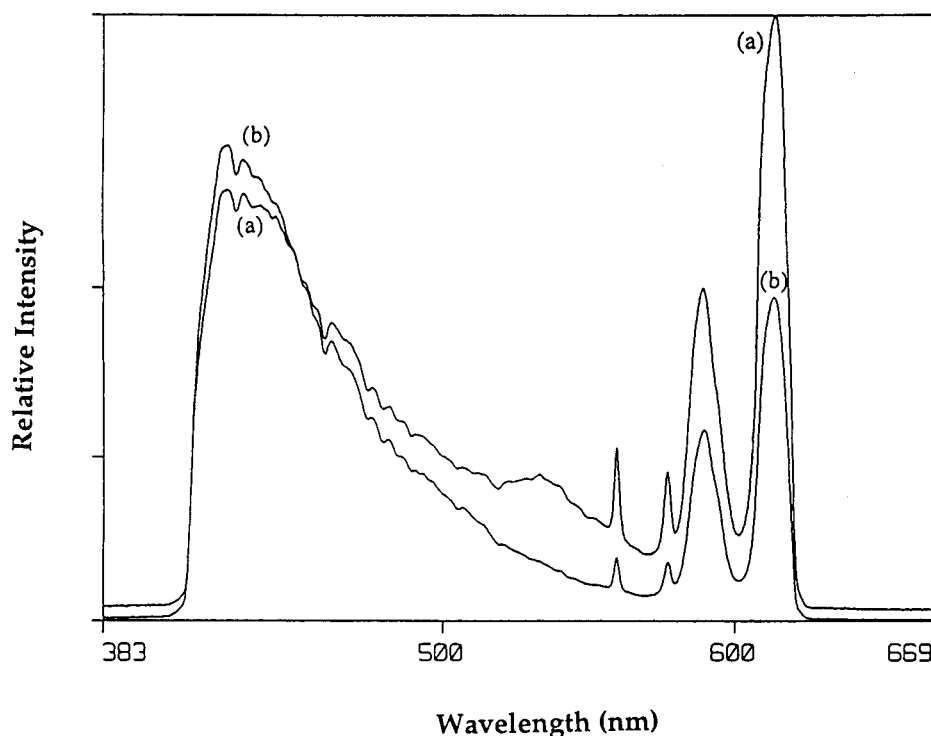


Figure 3. Emission spectra of Eu²⁺/Eu³⁺ in 1×10^{-3} M Eu³⁺-doped xerogels prepared by using (a) D₂O and C₂D₅OD and (b) H₂O and C₂H₅OH as solvents.

xerogel. The effect of laser irradiation on the undoped xerogel did not alter the original fluorescence band or induce other emission bands.

McDonagh et al. reported²² that more O–H groups are active in the acidic gel than in the basic gel as predicted from the gelation behavior of hydrolysis and condensation as a function of pH.¹⁷ Owing to a radiationless path for deactivation via coupling to O–H vibrational overtones, the O–H quenching of Eu³⁺ emission should decrease as the pH of the xerogel increases. Figure 2B shows the relative emission intensity of the residual Eu³⁺ species that did not react with defect electrons and that are preserved in xerogels processed at different pH values (3.0, 5.5, and 7.5) of sols. Under our experimental conditions, the fluorescence decay times of Eu³⁺ in xerogels prepared at pH = 3.0, 5.5, and 7.5 were measured as 0.165, 0.219, and 0.268 ms, respectively. Thus, the pH = 7.5 gel (or basic gel) had the least amount of OH quenching and pH = 3.0 gel (or acidic gel) had the most. The residual water content in a Eu³⁺-doped gel can be removed by thermal heating or laser-induced thermal processing which will reduce the amount of OH oscillators in contact with the primary sphere of europium ion. It was observed that the fluorescence of Eu³⁺ and Eu²⁺ intensifies and the emission lifetime of Eu³⁺ lengthens after the Eu³⁺-doped gel has been subjected to laser irradiation.

The Eu³⁺ fluorescence transition, $^5D_0 \rightarrow ^7F_1$ at 590 nm is magnetic dipole in character and is not sensitive to site symmetry, while that of $^5D_0 \rightarrow ^7F_2$ at 610 nm is mainly electric dipole in nature and its emission intensity increases as the site symmetry surrounding the Eu³⁺ ion becomes more asymmetrical. The fluorescence intensity ratio of these two transitions, $^7F_2/^7F_1$ (see Figure 2B) was measured to the values of 0.6, 0.6, 1.8, and 3.1 for Eu³⁺ in solution, pH 3.0 gel, pH 5.5 gel, and pH 7.5 gel, respectively. The result indicates that the Eu³⁺ in acidic gel experiences a similar site symmetry as that in solution, i.e., a highly symmetrical environment. On the other hand, the basic gel condenses quickly and forms an inhomogeneous microenvironment at a molecular scale. Thus, the site symmetry

of the Eu³⁺ in pH 7.5 gel is the most asymmetrical that leads to a large intensity ratio of $^7F_2/^7F_1 = 3.1$.

Deuterated Solvent (D₂O/C₂D₅OD) Effect. Under a fixed concentration of Eu³⁺ encapsulated in sol–gel matrix and a constant laser excitation (wavelength, density, and geometry), the observed reduction in the emission intensity of Eu³⁺ can result from two sources: (1) a surface-assisted reduction of Eu³⁺ to form Eu²⁺ by harvesting the electron–hole carriers generated during the sol–gel processing, and (2) a radiationless deactivation of the excited Eu³⁺ species via energy transfer to OH overtones, where a large amount of hydroxyl groups is usually contained in the sol–gel derived porous supports. An attempt was made to minimize the possible presence of OH oscillators around the first coordination sphere of the europium ions by using D₂O and C₂D₅OD as solvents (referred to as D-sample) and under an extremely dry atmosphere (a glovebag blowing with nitrogen gas) to process xerogels. If the amount of defect electron–hole pairs generated in the Eu³⁺-doped gels prepared by using the deuterated and hydrogenated (H-sample) solvents is similar, then the source (2) that leads to the emission quenching of europium ions can be identified separately. Unfortunately, the Eu³⁺-doped sols in D-sample (at pH = 5.5, the same conditions that the reference gel was prepared) gel at a much slower rate than that in the H-sample. This observation suggests that D₂O and C₂D₅OD solvents slow the polycondensation rate of sol–gel networking and do not promote the creation of defect electrons. These suggestions have been verified in Table 1 by DSC and TG/DTA measurements. The D-sample has higher cross-linking density ($T_g = 147.2$ °C) and is less liquidlike ($T_{LO} = 204.1$ °C, the temperature at which the weight loss levels off) compared to the H-sample.

Figure 3 gives the relative emission intensity of Eu³⁺ and Eu²⁺ in the Eu³⁺-doped D-sample (spectrum a) and H-sample (spectrum b). The low emission intensity of Eu²⁺ at 410 nm in spectrum (a) (shown only in the beginning portion) indicates that the D-sample has a low transformation yield of Eu³⁺ + (e[−]–h⁺ pairs) \rightarrow Eu²⁺ due to a small structural defects created

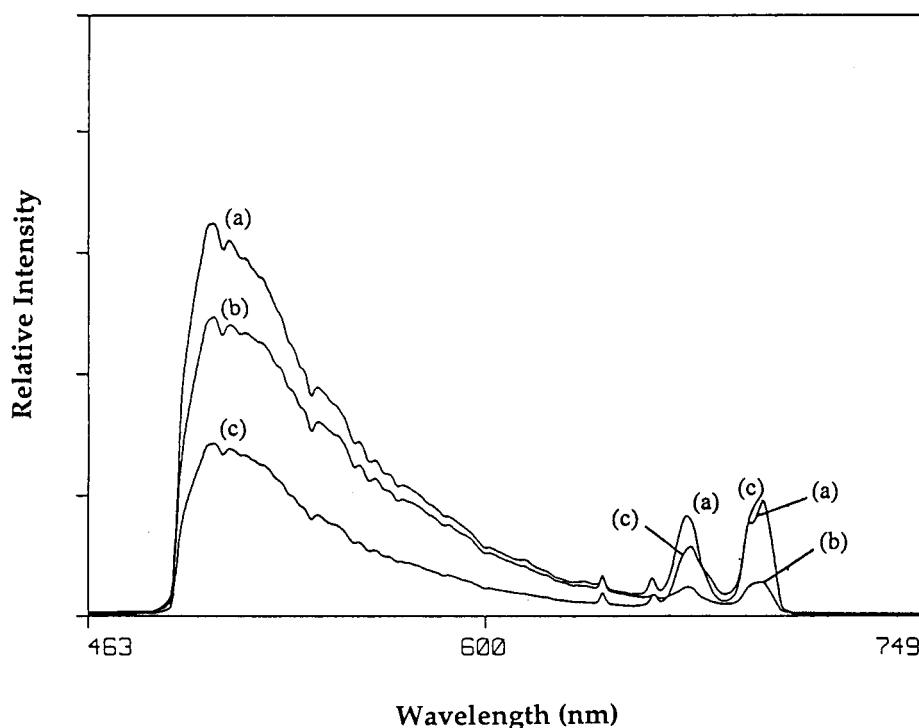


Figure 4. Emission spectra of $\text{Eu}^{2+}/\text{Eu}^{3+}$ in 1×10^{-3} M Eu^{3+} -doped xerogels prepared by using (a) $\text{EuCl}_3 \cdot 6\text{H}_2\text{O}$, (b) $\text{Eu}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$, and (c) $\text{Eu}(\text{CH}_3\text{COO})_3 \cdot \text{hydrate}$ as dopants.

in the sol–gel network. On the other hand, the high emission intensity of Eu^{3+} at 580–700 nm in spectrum 3a supports a low nonradiative OH quenching as a result of the presence of O–D functionality surrounding the first coordination sphere of the europium ions. The low OH quenching of Eu^{3+} emission in the D-sample gives a longer fluorescence lifetime of 0.473 ms as compared to that of 0.219 ms in the H-sample.

Counterion Effect. The thermal properties of 1×10^{-3} M Eu^{3+} -doped xerogels prepared by using acetate (reference gel), chloride, and nitrate as counterions, in a molar ratio 1:4:4 = TMOS/ethanol/ H_2O , and at pH 5.5 are expected to be very similar, since all three sols of different counterions gelled at almost the same time. Table 1 shows that the xerogel containing chloride counterion in $\text{EuCl}_3 \cdot 6\text{H}_2\text{O}$ is the least thermally stable (the lowest $T_{\text{LO}} = 152.4^\circ\text{C}$) and has the greatest weight loss (19.3%), thus it is the most liquidlike among the three xerogels. On the other hand, the xerogel containing nitrate counterion in $\text{Eu}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ has the least weight loss (16.2%), so it has the least liquidlike nature. These results are also shown in the DSC measurements where the xerogel with NO_3^- counterion displays the highest $T_g = 125.7^\circ\text{C}$ and thus has the highest cross-linking density. The T_g values in Table 1 indicate that the effect of metal counterions in the creation of structural defects in SiO_2 network (i.e., the generation of electron–hole carriers) during the sol–gel processing follows the order of $\text{CH}_3\text{COO}^- \approx \text{Cl}^- > \text{NO}_3^-$. It is expected that the xerogel doped with $\text{Eu}(\text{CH}_3\text{COO})_3 \cdot \text{hydrate}$ or $\text{EuCl}_3 \cdot 6\text{H}_2\text{O}$ should give a higher degree on the defect electron activated reduction of $\text{Eu}^{3+} + \text{e}^- \rightarrow \text{Eu}^{2+}$ than that doped with $\text{Eu}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$.

Figure 4 shows the relative emission intensity of Eu^{3+} and Eu^{2+} in the 1×10^{-3} M Eu^{3+} -doped xerogels prepared by using acetate (spectrum c), chloride (spectrum a), and nitrate (spectrum b) as counterions. A higher Eu^{2+} emission intensity in spectrum (a) than in spectrum (b) confirms the expectation established from the DSC measurements that a larger amount of defect electrons is generated in chloride-doped xerogel than in the nitrate-doped sample. A relatively low Eu^{2+} emission intensity

in spectrum (c) strongly suggests that the efficiency of surface-assisted reduction of Eu^{3+} to form Eu^{2+} depends not only on the amount of e^- – h^+ carriers created during the sol–gel processing but also on the affinity strength that protects the Eu^{3+} species by its counterion from such a transformation. The evidence of inner-sphere complexation of europium(III) with nitrate, chloride, and perchlorate counterions in gel matrix has been reported.¹⁰ Evidently, the NO_3^- ions have an affinity for the inner coordination sphere of Eu^{3+} which is greater than the affinity of Cl^- . The NO_3^- ions effectively replace water molecules for inner-sphere coordination of Eu^{3+} that can result in less effective nonradiative decay through O–H oscillators and, hence, a longer observed luminescence lifetime. The luminescence lifetime of Eu^{3+} was recorded as 0.125, 0.135, and 0.219 ms for xerogel doped with $\text{EuCl}_3 \cdot 6\text{H}_2\text{O}$, $\text{Eu}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$, and $\text{Eu}(\text{CH}_3\text{COO})_3 \cdot \text{hydrate}$, respectively. This demonstrates that acetate ion attracts more effectively to the Eu^{3+} ion, then nitrate, followed by chloride ion. This would explain why, in Figure 4, the intensity in spectrum (c) for the Eu^{2+} band is the weakest and that for the Eu^{3+} peak is the strongest. In short, the acetate ions more effectively protect the encapsulated Eu^{3+} from the reducing electrons generated in the sol–gel matrix than do the chloride or nitrate ions.

Effect of Chelating Agents. The effectiveness of utilizing electron–hole carriers to reduce the entrapped Eu^{3+} ion to form Eu^{2+} species during the sol–gel processing was observed to depend on the degree of affinity between Eu^{3+} and its counterion. This observation is further illustrated in this section by using two chelating reagents, HEDTA and EDTA. At pH 7.38 and 25°C , the formation constant ($\log K$) of $\text{Eu}^{3+}/\text{EDTA}$ and $\text{Eu}^{3+}/\text{HEDTA}$ complexes was determined to be 17.2 and 15.45, respectively.²³ In Table 1, the $\text{Eu}^{3+}/\text{EDTA}$ -doped xerogel gives the greatest weight loss (21.3%) at $T_{\text{LO}} = 150.6^\circ\text{C}$ and the least amount of cross-linking density ($T_g = 113.1^\circ\text{C}$), while the $\text{Eu}^{3+}/\text{HEDTA}$ -doped xerogel has the smallest weight loss (16.6%) at $T_{\text{LO}} = 170.5^\circ\text{C}$ and the highest cross-linking density ($T_g = 122.0^\circ\text{C}$). In reference to the unchelated sample, the

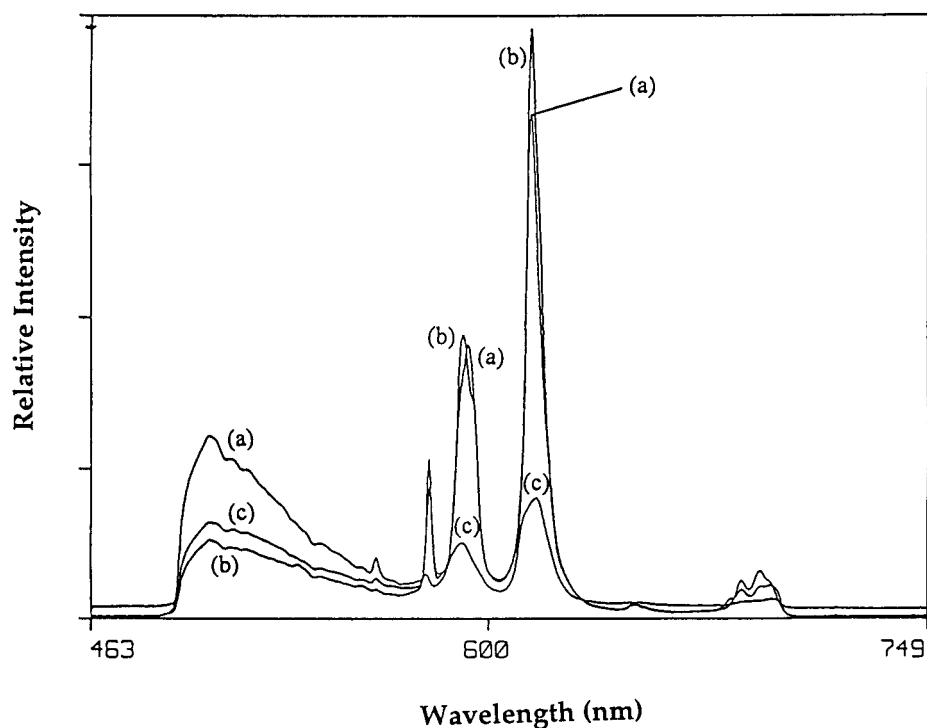


Figure 5. Emission spectra of Eu²⁺/Eu³⁺ in 1×10^{-3} M Eu³⁺-doped xerogels prepared by using (a) Eu(CH₃COO)₃ hydrate/EDTA complex, (b) Eu(CH₃COO)₃ hydrate/HEDTA complex, and (c) Eu(CH₃COO)₃ hydrate as dopants.

addition of EDTA makes the xerogel more liquidlike in nature, but the resulting xerogel with the addition of HEDTA gives the least structural defects. Following a careful examination of TG/DTA curves, it is noticed that both Eu³⁺/EDTA and Eu³⁺/HEDTA-doped xerogels display an additional marked weight loss at around 300 °C. This is probably related to the loss of organics associated with the chelating reagents, and thus the further weight loss at high temperature makes the unchelated sample the most thermally stable.

The fluorescence spectrum of the chelated Eu³⁺ species in the xerogel matrix displays a narrower bandwidth, higher emission intensity, and longer lifetime as compared to those of the unchelated Eu³⁺ species. The full width at half-maximum (fwhm) of ⁵D₀ → ⁷F₂ transition of the chelated and unchelated Eu³⁺ ion encapsulated in xerogels is calculated to be 145 and 326 cm⁻¹, respectively. Since the measured emission lifetimes of Eu³⁺/HEDTA, Eu³⁺/EDTA, and unchelated Eu³⁺-doped xerogels are 279, 257, and 219 μs, respectively, one may assume that OH quenching of europium fluorescence is reduced in the chelated sample and this could explain why the observed Eu³⁺ emission peak in spectra 5a and 5b are so intense. The chelating agents, HEDTA and EDTA, are anticipated to displace the coordinated water molecules from the Eu³⁺ ion and thus prevent the nonradiative quenching from the OH groups.

Figure 5 shows a relatively low Eu²⁺ emission intensity for the Eu³⁺/HEDTA-doped xerogels (spectrum 5b). This observation agrees well with the data of thermoanalysis in Table 1, i.e., Eu³⁺/HEDTA-doped xerogel is the least liquidlike with the smallest amount of initial weight loss and the greatest cross-linking density. This indicates that the structural defects or number of defect electrons generated in the Eu³⁺/HEDTA-doped xerogels is low, thus a low yield is expected for the conversion of Eu³⁺ to Eu²⁺. On the contrary, Eu³⁺/EDTA-doped xerogels generate a relatively large number of e⁻-h⁺ carriers which can promote an effective transformation of Eu³⁺ + e⁻ → Eu²⁺ and lead to the observation of a relatively high-intensity band at 410 nm for Eu²⁺ emission as shown in spectrum 5a.

Effect of the Mixed Metal Precursors. A premixing of 1% aluminum isopropoxide (or 1% antimony(III) ethoxide) in 99% TMOS is expected to have different structural evolution during hydrolysis and condensation of multicomponent silicate systems. For example, the resulting xerogels may display various coordinations of Al (or Sb) and comprise different amounts of hetero- versus homo-condensation (and therefore molecular-scale homogeneity). In Table 1, the reversible thermal events of the Cp component in the oscillating DSC measurements show a decrease in *T_g* value from 116.7 °C for a pure TMOS sol (reference gel) to 102.8 °C and 89.1 °C for a premixed sol containing 1% aluminum isopropoxide and 1% antimony(III) ethoxide precursor, respectively. The xerogels of polymeric oxo-bridged aluminosilicate and antimony silicate have a lower cross-linking density than the reference gel, thus they should display a high concentration of structural defects and have a large quantity of electron-hole carriers in the multicomponent silicate systems. These xerogels are also quite unstable thermally and have a liquidlike nature. The antimony-mixed xerogel gives the greatest weight loss 22.9% at *T_{LO}* = 134.5 °C, whereas the aluminosilicate gel displays a 20% weight loss at *T_{LO}* = 143.7 °C. It is important to mention that the thermal properties of xerogels prepared by using the mixed metal precursors are similar to those of basic gel processed at pH = 7.5. Evidently, the Eu³⁺-doped antimony silicate gel shows only a strong fluorescence band at 410 nm for Eu²⁺ with no emission peak corresponding to Eu³⁺. Similarly, Eu³⁺-doped aluminosilicate gel has also shown a strong Eu²⁺ emission band at 410 nm and accompanied by a couple of weak peaks at 590 and 610 nm for Eu³⁺. This observation is in agreement with the results of thermal analysis that the mixed metal precursors can offer an effective way of creating a large quantity of structural defects in an SiO₂ network during the sol-gel processing and producing a high concentration of electron-hole carriers. The observed intense emission band of Eu²⁺ at 420 nm is clearly originated from the defect electron activated reduction of Eu³⁺ + e⁻ → Eu²⁺.

Conclusion

During the sol–gel processing, a large concentration of electron–hole pairs may be created at room temperature due to the structural defects formed in the polymeric oxo-bridged SiO₂ network. In the presence of heavy metal ions (e.g., Eu³⁺), these electron–hole carriers can be harvested for the reduction of high oxidation state Eu³⁺ ion to a corresponding lower oxidation state Eu²⁺ ion. In this paper, we have demonstrated that by selecting the appropriate parameters for sol–gel processing, the transformation and stabilization of a low oxidation state Eu²⁺ ion in an optically transparent xerogel can be optimized.

The basic gels (pH = 7.5) and gels prepared by using the mixed metal precursors (1% aluminum isopropoxide or 1% antimony(III) ethoxide) are more liquidlike in character and have less cross-linking density. These gels display a high concentration of structural defects and should have a large quantity of electron–hole carriers available for promoting the redox transformation. The counterions (or chelating agents) that have a high affinity (or a large complexing constant) to the inner coordination sphere of metal ion (e.g., Eu³⁺) are shown to inhibit the efficiency of surface-assisted reduction of Eu³⁺ to form Eu²⁺. The result of this investigation indicates that EuCl₃·6H₂O is the preferred candidate. Of making divalent lanthanides (e.g., Eu²⁺), doped silica xerogel can offer potential applications in optical memory and high-resolution blue lasers. The basic gels (pH = 7.5) and gels prepared by using the deuterated solvents (D₂O/C₂D₅OD) have shown to reduce substantially the presence of OH oscillators around the first coordination sphere of the europium ions. These gels have a low nonradiative quenching to OH overtones and give an intense emission of Eu³⁺/Eu²⁺ with a long fluorescence lifetime. An ideal Eu³⁺-doped xerogel under these optimal parameters is currently being prepared in our laboratory.

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