In Situ Dehydroxylation in Eu^{3+}-Doped Sol−Gel Silica

Brandon T. Stone, Vilma C. Costa, and Kevin L. Bray*

Department of Chemical Engineering, University of Wisconsin−Madison,
Madison, Wisconsin 53706

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Fluorescence line narrowing and lifetime measurements are used to characterize the extents of clustering and hydroxyl quenching, respectively, in Eu^{3+}-doped sol−gel silica glasses prepared using europium trifluoromethanesulfonate (triflate). A triflate ($(CF_3SO_3)_3$-Eu) rather than a traditional nitrate ($Eu(NO_3)_3 \cdot 6H_2O$) precursor is used as the rare earth ion dopant in order to determine the feasibility of effecting chemical dehydroxylation via in situ fluorination by incorporating fluorine directly as a ligand substituent of the Eu^{3+} precursor. In samples doped only with Eu^{3+}, the use of the triflate precursor leads to no noticeable differences in hydroxyl quenching of Eu^{3+} fluorescence or Eu^{3+} aggregation relative to samples prepared with a nitrate precursor. Beneficial effects are observed, however, in samples codoped with Al^{3+} or Sr^{2+}. When Al^{3+} or Sr^{2+} is included in the synthesis, a reduction in hydroxyl quenching of Eu^{3+} is observed when the triflate precursor is used relative to the nitrate precursor. In addition, $(CF_3SO_3)_3Al$ is found to be as effective at inhibiting Eu^{3+} clustering as the previously reported $Al(NO_3)_3 \cdot 9H_2O$ and $(C_4H_9O)_2Al{-}O{-}Si(OC_2H_5)_3$ precursors. The effect of incoporating fluorine via $FSi(OC_2H_5)_3$ is also briefly considered and gives mixed results which differ for nitrate and triflate Eu^{3+} precursors.

Introduction

There is considerable interest in the optical properties of luminescent species in sol−gel glasses for applications as laser materials,[1,2] chemical sensors,[3−5] chromogenic materials and devices,[6−8] and waveguides.[9,10] The sol−gel process provides a convenient technique for preparing luminescent glasses because of the wide range of compositions that is achievable and the ability to systematically study relationships among glass composition, structure, and optical properties of luminescent dopants. More intelligent design of optical sol−gel materials based on rare earths, organic dyes, and other luminescent dopants requires a better understanding of structure−property relationships, better control of the spatial distribution of dopants in porous and densified systems, and more complete knowledge of the effects of doping and dopant precursors on the mechanism and kinetics of sol−gel reactions.

The optical properties of luminescent dopants in a sol−gel sample are also useful in characterizing the chemical and physical changes that occur in the sample as the initial solution evolves into a wet gel and is then densified through heat treatment to produce a glass. Rare earth ions are commonly used as probes of the sol−gel process because of their small size and the sensitivity of their luminescent transitions to their local environment. Among the rare earths, Eu^{3+} has been used most extensively to monitor sol−gel synthesis of glass.[11−15] The main conclusion of these studies is that the rare earth ions are in an aqueous environment at the porous wet gel stage and attain an amorphous solid-state environment similar to that observed in melt-derived glasses upon densification.

Other studies of Eu^{3+},[16,17] Er^{3+},[18,19] and Nd^{3+} [2,20,21] in sol−gel glasses have shown that the ions have a tendency to be segregated or form clusters rather than to be uniformly distributed throughout the glass. At the wet gel stage, the ions move freely in the liquid pore phase and are not incorporated into the evolving rigid silica gel phase. This ion mobility coupled with weak interactions between the ions and the rigid gel phase promotes the formation of clustered metal ions (localized regions in the glass rich in metal ions) as the pores shrink during drying and thermal densification. Rare

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* To whom correspondence should be addressed: Department of Chemical Engineering, 1415 Engineering Drive, Madison, WI 53706-1691. Phone: (608) 262-9053. Fax: (608) 262-5434. E-mail: bray@engr.wisc.edu.

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earth ion clusters are undesirable in most optical materials because they lead to a reduction in luminescence efficiency and a shortening of lifetimes due to enhanced concentration quenching.[22,23] Reduction of luminescence efficiency due to hydroxyl quenching has also been problematic in rare earth doped sol−gel glasses.[2,17] The problems of rare earth ion clustering and hydroxyl quenching must be eliminated to achieve practical optical devices based on rare earth ion-doped sol−gel glasses.

The incorporation of aluminum in rare earth-doped sol−gel glasses has been found to reduce the extent of rare earth ion clustering,[2,17,19,20,24] but unfortunately the presence of Al^{3+} also leads to more severe hydroxyl quenching.[13,17,25] Luminescence peak position shifts[16,17] and changes in the relative intensities of phonon sidebands[26] provide evidence of the interaction of Al^{3+} and Eu^{3+} in sol−gel glasses. It has been proposed that Al^{3+}, with its high ionic field strength and strong interaction with the silica network, has the ability to penetrate rare earth clusters and provide a more uniform distribution of rare earth ions in sol−gel glasses.[27] The enhanced hydroxyl quenching is believed to be due to a strong tendency for Al^{3+} to attract and retain hydroxyl groups in a densified glass.[27] Other proposed methods for reducing rare earth clustering include co-doping with other metal ions,[27] rare earth ion encapsulation by chelating ligands,[28,29] and use of acetate precursors.[30]

One technique for chemical dehydroxylation involves high-temperature treatment of a sol−gel glass with carbon tetrachloride.[31] Direct treatment with chlorine requires special precautions due to the toxicity of chlorine. Thomas et al.[2] raised concerns about the volatility of aluminum and neodymium chlorides that could be byproducts of chlorine treatment. An alternate technique uses fluorine as a dehydroxylation agent through the inclusion of hydrofluoric acid in the initial sol−gel reaction mixture.[32,33] Pope and Mackenzie referred to this technique as “in situ dehydroxylation”.[33] In preliminary work, Costa et al.[34] recently suggested an alternative method for achieving in situ dehydroxylation in Eu^{3+}-doped sol−gel silica by using soluble fluorinated organic europium precursors. This method offers the possibility of incorporating high concentrations of fluorine in the synthesis without significantly affecting the pH of the reaction.

The goals of the current study are to further consider the effect of fluorinated organic europium precursors on clustering and hydroxyl quenching. We also examine whether it is possible to combine the beneficial cluster inhibition properties of Al^{3+} with the beneficial dehydroxylation properties of fluorine in the preparation of Eu^{3+}-doped sol−gel silica. Finally, we briefly consider the effects of using a fluorinated silicon precursor ($FSi(OC_2H_5)_3$) on the clustering and hydroxyl quenching of Eu^{3+}.

Experimental Section

Sample Preparation. Sol−gel silica samples were prepared using tetraethoxysilane (TEOS), deionized water, and ethanol in a 1/4/4 molar ratio. A small amount of concentrated nitric acid was added as a catalyst to each sample. The dopant ions Eu^{3+} and Al^{3+} were added in the form of nitrate ($Eu(NO_3)_3{\cdot}6H_2O$, $Al(NO_3)_3{\cdot}9H_2O$) or trifluoromethanesulfonate (triflate; $(CF_3SO_3)_3Eu$, $(CF_3SO_3)_3Al$) salts. Some samples were prepared using Sr^{2+}, instead of Al^{3+}, as a codopant. In these samples, Sr^{2+} was added in the form of a nitrate ($Sr(NO_3)_2$) or a hexafluoropentanedionate (hfpd; $(CF_3COCHC(CF_3)O)_2Sr$) salt. Samples containing Eu^{3+} and Al^{3+} were prepared with Al/Eu molar ratios of 1 and 3, and both ions were added in the same precursor form (either nitrate or triflate). Samples containing Eu^{3+} and Sr^{2+} were prepared with a Sr/Eu molar ratio of 1. Samples were prepared with each of the four possible combinations of Eu^{3+} (nitrate or triflate) and Sr^{2+} (nitrate or hfpd) precursors. In additional samples doped only with Eu^{3+}, part of the TEOS was replaced with triethoxyfluorosilane ($FSi(OC_2H_5)_3$) to incorporate fluorine in the silica matrix at ($FSi(OC_2H_5)_3$ in initial reaction mixture)/(Eu in the densified sample) molar ratios of 1 and 5. Separate samples based on the two Eu^{3+} precursor types (nitrate or triflate) were prepared.

After thorough mixing, samples were cast in plastic vials and allowed to react at room temperature or at 35 °C. Gel times varied from 2 days to 4 weeks, depending on the sample composition and reaction temperature. After gelation, the samples were aged for 2 days at 60 °C and then 2 days at 90 °C. During aging, the samples cracked into irregularly shaped pieces with characteristic dimensions of 1−5 mm. Samples were heated to a final densification temperature of 800 °C, with 24 h dwell times at 200° intervals. Some samples were heated to 900 °C. Samples heated to 800 or 900 °C were largely transparent, with precipitation present in some pieces. The ratio of cloudy to transparent pieces increased with increasing dopant concentrations and increasing modified alkoxide precursor content. The greatest degree of precipitation was observed in samples doped with strontium hexafluoropentanedionate. All of the samples contain 1.0 wt % Eu_2O_3, based on a fully densified oxide glass free of residual water, fluorine, and organics.[17] After densification, samples were stored under air in sealed glass vials from 1 day to 2 weeks prior to spectroscopic measurements.

Spectroscopic Measurements. All measurements were made with samples heated to 800 or 900 °C. Broadband fluorescence spectra were excited with the 514.5 nm laser emission of an argon ion laser. Sample fluorescence was dispersed by a 1-m monochromator and detected by a photomultiplier tube (PMT). All broadband fluorescence spectra were collected at room temperature. The excitation source used in the fluorescence line narrowing measurements was a tunable dye laser pumped by a Q-switched Nd:YAG laser. The dye laser provided the continuously tunable laser emission from 571 to 581 nm needed for selective excitation of the $^7F_0 \rightarrow {}^5D_0$ Absorption Transition of Eu^{3+}. A shutter was used to prevent exposure of the photomultiplier tube to laser light as

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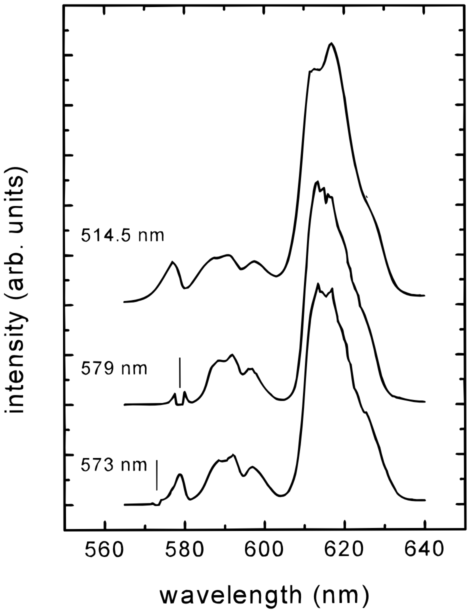

Figure 1. Site selective excitation of a densified sol−gel silica sample containing 1.0 wt % Eu_2O_3 prepared using $(CF_3SO_3)_3$-Eu. The spectra in the two lower traces were measured at 9.0 K, and the spectrum in the upper trace was measured at room temperature. The spectra show the $^5D_0 \rightarrow {}^7F_0$ (572−581 nm), $^5D_0 \rightarrow {}^7F_1$ (581−605 nm), and $^5D_0 \rightarrow {}^7F_2$ (605−635 nm) transitions of Eu^{3+}. The individual traces were normalized to a $^5D_0 \rightarrow {}^7F_1$ emission peak intensity of 1. Excitation wavelengths are indicated above each trace on the left and also by short vertical lines in the lower two traces.

the monochromator scanned past the laser wavelength, resulting in a flat region 2.0 nm wide around the laser wavelength in each spectrum. Low-temperature measurements were obtained by mounting samples in a variable temperature cryostat. All fluorescence line narrowing measurements were made at 9.0 K, the lowest attainable temperature of the cryostat. The dye laser was also used for lifetime measurements. Fluorescence decays were detected by the PMT and recorded by a digital storage oscilloscope. Lifetimes were measured at both room temperature and 9.0 K. Fluorescence decays were monitored at several wavelengths spanning the $^5D_0 \rightarrow {}^7F_2$ emission band, and excitation was provided at wavelengths within the $^7F_0 \rightarrow {}^5D_0$ absorption band. Sixteen different combinations of excitation and detection wavelengths were used to measure lifetimes. Since the decay curves were slightly nonexponential, average lifetimes were obtained by calculating the area under normalized decay curves.[35] The values obtained from the areas and from the exponential fits were in good agreement. An average lifetime was calculated for each sample from the 16 different measurements to allow comparison between samples.

Results

Fluorescence Line Narrowing Measurements. Fluorescence spectra obtained upon site selective excitation of a densified sol−gel silica sample containing 1.0 wt % Eu_2O_3 prepared using the triflate precursor are shown in Figure 1. The upper trace is a fluorescence spectrum excited with 514.5 nm laser emission; 514.5 nm light is not directly absorbed by Eu^{3+} ions, but it can be absorbed with the release of lattice phonons and leads to excitation of the entire ensemble of Eu^{3+} ions. The lower traces were obtained upon selective excitation at different wavelengths within the inhomogeneously broadened $^7F_0 \rightarrow {}^5D_0$ absorption band of Eu^{3+}. All three spectra were similar, evidence that site selective excitation was not possible with this sample. This finding is similar to the lack of site selective emission observed in Eu^{3+}-doped sol−gel silica glasses prepared using a nitrate precursor.[17]

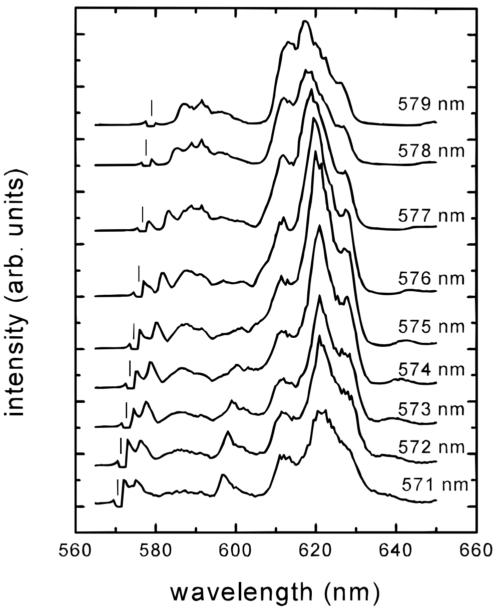

Figure 2. Site selective excitation of a densified sol−gel silica sample containing 1.0 wt % Eu_2O_3 and codoped with Al^{3+} (Al/Eu = 3). Triflate precursors for aluminum and europium were used. All spectra were measured at 9.0 K. The individual traces were normalized to a $^5D_0 \rightarrow {}^7F_1$ emission peak intensity of 1. Excitation wavelengths are indicated above each trace on the right and also by short vertical lines on the left.

Figure 2 shows fluorescence spectra obtained upon site selective excitation of a densified sol−gel silica sample containing 1.0 wt % Eu_2O_3 and codoped with Al^{3+} at an Al/Eu molar ratio of 3. Triflate precursors for both Eu^{3+} and Al^{3+} were used to prepare this sample. The spectra were measured at 9.0 K. Note that the relative intensities and peak positions within the $^5D_0 \rightarrow {}^7F_1$ and $^5D_0 \rightarrow {}^7F_2$ emission bands varied considerably with excitation wavelength, as different subsets of Eu^{3+} ions within the sample were selectively excited.

Figure 3 shows fluorescence spectra obtained upon site selective excitation of a densified sol−gel silica sample containing 1.0 wt % Eu_2O_3 and codoped with Sr^{2+} at a Sr/Eu molar ratio of 1. Europium triflate and strontium nitrate were the precursors used. The upper trace is the broadband fluorescence spectrum excited with 514.5 nm laser emission. The traces were all similar in appearance, and little site selectivity in the emission was observed. Only small changes in peak positions and relative peak intensities were also observed in the site selective emission spectra of a Eu^{3+},Sr^{2+}-doped sample with a Sr/Eu ratio of 1 prepared using europium nitrate and strontium nitrate. In a previous study,[27] site selective emission was obtained from a nitrate-based Eu^{3+},Sr^{2+}-doped sample with a Sr/Eu ratio of 9.

Lifetime Measurements. Room-temperature lifetimes for 1.0 wt % Eu_2O_3 sol−gel silica samples prepared using nitrate and triflate precursors are listed in Table 1. Similar trends were observed for both types of samples. The lifetimes increased with decreasing

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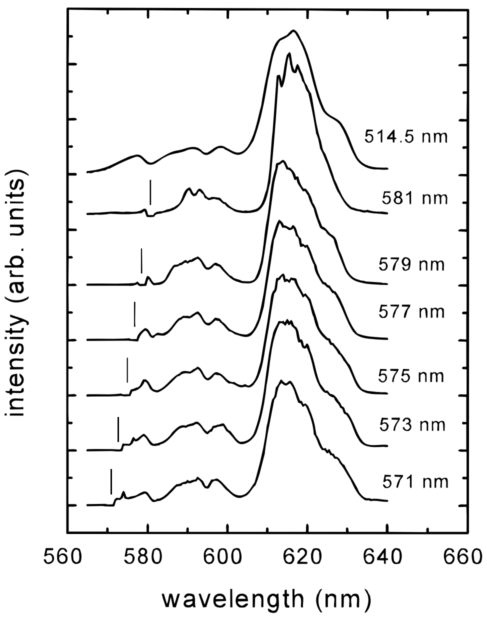

Figure 3. Site selective excitation of a densified sol−gel silica sample containing 1.0 wt % Eu_2O_3 and codoped with Sr^{2+} (Sr/Eu = 1). Strontium nitrate and europium triflate were the precursors used. The spectrum in the upper trace was measured at room temperature, and the spectra in all other traces were measured at 9.0 K. The individual traces were normalized to a $^5D_0 \rightarrow {}^7F_1$ emission peak intensity of 1. Excitation wavelengths are indicated above each trace on the right and also by short vertical lines on the left.

Table 1. Room-Temperature Lifetimes for Densified Sol−Gel Silica Samples Containing 1.0 wt % Eu_2O_3 Prepared with the Nitrate and the Triflate Precursors. The Lifetimes Were Obtained from Areas under Normalized Decay Curves and Are Listed in ms (±0.05 ms)

λ_{mon} (nm) → λ_{exc} (nm)	612.5	617.5	620	630
Nitrate Precursor−Room Temperature (Average $\tau = 1.68$ ms)				
573	1.71	1.73	1.66	1.55
575	1.72	1.71	1.67	1.53
577	1.78	1.75	1.68	1.63
579	1.71	1.74	1.68	1.68
Triflate Precursor−Room Temperature (Average $\tau = 1.66$ ms)				
573	1.71	1.61	1.55	1.43
575	1.74	1.72	1.62	1.44
577	1.80	1.77	1.73	1.57
579	1.78	1.75	1.72	1.66

detection wavelength (λ_{mon}) for all of the excitation wavelengths (λ_{exc}). The range of lifetime values measured at a given excitation wavelength increased with decreasing excitation wavelength. The average lifetimes of the two samples were approximately equal.

Lifetimes at 9.0 K for 1.0 wt % Eu_2O_3 sol−gel silica samples prepared using the nitrate and triflate precursors are listed in Table 2. The trends described above for the room-temperature lifetimes were also observed in the 9.0 K lifetimes. The average lifetimes measured at 9.0 K were slightly longer than the average lifetimes measured at room temperature for each of the samples. Not only the longest but also the shortest lifetimes measured for both samples were obtained at 9.0 K.

Table 3 contains room-temperature and 9.0 K lifetimes for 1.0 wt % Eu_2O_3 sol−gel silica samples codoped with Al^{3+} and prepared with nitrate and triflate precursors. The Al/Eu molar ratio in these samples was 1, and the same precursor type was used for both dopants.

Table 2. Lifetimes at 9.0 K for Densified Sol−Gel Silica Samples Containing 1.0 wt % Eu_2O_3 Prepared with Nitrate and Triflate Precursors. The Lifetimes Were Obtained from Areas under Normalized Decay Curves and Are Listed in ms (±0.05 ms)

λ_{mon} (nm) → λ_{exc} (nm)	612.5	617.5	620	630
Nitrate Precursor−9.0 K (Average $\tau = 1.72$ ms)				
573	1.83	1.75	1.70	1.47
575	1.83	1.75	1.71	1.43
577	1.83	1.77	1.74	1.55
579	1.82	1.81	1.76	1.70
Triflate Precursor−9.0 K (Average $\tau = 1.69$ ms)				
573	1.85	1.74	1.60	1.29
575	1.96	1.78	1.72	1.29
577	1.98	1.77	1.75	1.37
579	1.84	1.67	1.74	1.63

Table 3. Room-Temperature and 9.0 K Lifetimes for Densified Sol−Gel Silica Samples Containing 1.0 wt % Eu_2O_3 and Codoped with Al^{3+} (Al/Eu = 1) Prepared with Nitrate and Triflate Precursors. The Same Precursor Type Was Used for Both Dopants in a Given Sample. The Lifetimes Were Obtained from Areas under Normalized Decay Curves and Are Listed in ms (±0.05 ms)

λ_{mon} (nm) → λ_{exc} (nm)	612.5	617.5	620	630
Nitrate Precursors, Al/Eu = 1, Room Temperature (Average $\tau = 0.99$ ms)				
573	1.12	0.99	0.91	0.85
575	1.12	0.95	0.83	0.84
577	1.12	0.96	0.92	0.94
579	1.18	1.09	1.08	0.98
Nitrate Precursors, Al/Eu = 1, 9.0 K (Average $\tau = 1.06$ ms)				
573	1.25	1.11	0.95	0.85
575	1.26	1.05	0.88	0.83
577	1.26	1.02	0.94	0.91
579	1.29	1.12	1.10	1.10
Triflate Precursors, Al/Eu = 1, Room Temperature (Average $\tau = 1.07$ ms)				
573	0.96	0.87	0.84	0.83
575	1.43	1.14	0.85	0.82
577	1.58	1.26	1.13	0.87
579	1.51	1.19	0.94	0.91
Triflate Precursors, Al/Eu = 1, 9.0 K (Average $\tau = 1.25$ ms)				
573	1.64	1.27	1.17	1.01
575	1.59	1.22	1.08	1.07
577	1.51	1.15	1.04	1.16
579	1.39	1.28	1.13	1.28

In both the nitrate- and triflate-based samples, the lifetimes decreased upon addition of Al^{3+}. Most of the lifetimes measured at 9.0 K were longer than the lifetimes measured at room temperature for both of the samples. At room temperature, the lifetimes for the nitrate- and triflate-based samples are comparable within experimental error, except at $\lambda_{mon} = 612.5$ nm and $\lambda_{exc} > 573$ nm, where the lifetimes of the triflate-based sample are longer. At 9.0 K, however, the lifetimes for the triflate-based sample were all longer than the corresponding lifetimes for the nitrate-based sample. At room temperature and at 9.0 K, there is a bigger difference between the average lifetimes of the triflate- and nitrate-based samples doped with both Al^{3+} and Eu^{3+} than between the average lifetimes of samples doped only with Eu^{3+}.

Table 4 contains 9.0 K lifetimes for 1.0 wt % Eu_2O_3 sol−gel silica samples codoped with Sr^{2+}. The Sr/Eu molar ratio in both samples was 1. The two samples

Table 4. Lifetimes at 9.0 K for Densified Sol−Gel Silica Samples Containing 1.0 wt % Eu_2O_3 and Codoped with Sr^{2+} (Sr/Eu = 1) Prepared with Europium Nitrate and Triflate Precursors. The Source of Sr^{2+} in Both Samples Was the Hexafluoropentanedionate (hfpd) Salt. The Lifetimes Were Obtained from Areas under Normalized Decay Curves and Are Listed in ms (±0.05 ms)

λ_{mon} (nm) → λ_{exc} (nm)	612.5	617.5	620	630
Europium Nitrate + Strontium hfpd, Sr/Eu = 1, 9.0 K (Average τ = 1.75 ms)				
573	1.97	1.89	1.90	1.58
575	1.82	1.82	1.82	1.54
577	1.73	1.82	1.74	1.49
579	1.75	1.85	1.66	1.56
Europium Triflate + Strontium hfpd, Sr/Eu = 1, 9.0 K (Average τ = 1.93 ms)				
573	2.05	2.09	2.12	1.67
575	1.85	1.85	1.96	1.46
577	1.82	1.89	1.94	1.48
579	2.01	2.50	2.30	1.96

Table 5. Lifetimes at 9.0 K for Densified Sol−Gel Silica Samples Containing 1.0 wt % Eu_2O_3 Prepared with Nitrate and Triflate Precursors and a $FSi(OC_2H_5)_3$/Eu Molar Ratio of 1. The Lifetimes Were Obtained from Areas under Normalized Decay Curves and Are Listed in ms (±0.05 ms)

λ_{mon} (nm) → λ_{exc} (nm)	612.5	617.5	620	630
Nitrate Precursor, $FSi(OC_2H_5)_3$/Eu = 1, 9.0 K (Average τ = 1.77 ms)				
573	1.89	1.76	1.71	1.37
575	1.93	1.88	1.80	1.35
577	1.95	1.90	1.85	1.70
579	1.94	1.81	1.78	1.65
Triflate Precursor, $FSi(OC_2H_5)_3$/Eu = 1, 9.0 K (Average τ = 1.46 ms)				
573	1.53	1.46	1.45	1.21
575	1.49	1.45	1.42	1.23
577	1.54	1.49	1.48	1.35
579	1.59	1.55	1.50	1.54

Table 6. Average Lifetimes (ms) of Various Densified Sol−Gel Silica Samples Containing 1.0 wt % Eu_2O_3 with and without Codopants Prepared with Nitrate, Triflate, or Hexafluoropentanedionate (hfpd) Precursors. Samples Marked with an Asterisk (*) Were Heated to 900 °C. All Other Samples Were Heated to 800 °C

Eu^{3+}, Al^{3+}, and Sr^{2+} Nitrate	295 K	9.0 K
Eu^{3+} only	1.68	1.72
Al/Eu = 1	0.99	1.06
Al/Eu = 1*	0.99	
Al/Eu = 3*	0.97	1.02
Sr/Eu = 1	1.62	1.64
$FSi(OC_2H_5)_3$/Eu = 1	1.25	1.77
Eu^{3+} nitrate and Sr^{2+} hfpd	295 K	9.0 K
Sr/Eu = 1	1.70	1.75
Eu^{3+} and Al^{3+} triflate, and Sr^{2+} nitrate	295 K	9.0 K
Eu^{3+} only	1.66	1.69
Al/Eu = 1	1.07	1.25
Al/Eu = 3	1.18	1.28
Sr/Eu = 1	1.62	1.77
$FSi(OC_2H_5)_3$/Eu = 1	1.32	1.46
Eu^{3+} triflate and Sr^{2+} hfpd	295 K	9.0 K
Sr/Eu = 1	2.00	1.93

were prepared using different europium precursors and strontium hfpd. Comparing the Sr^{2+} codoped samples, the lifetimes measured in the europium triflate-based sample were generally longer than the corresponding lifetimes of the europium nitrate-based sample.

The average lifetime in the Sr^{2+},Eu^{3+}-doped sample is slightly longer than the average lifetime in the Eu^{3+}-only sample when europium nitrate is the Eu^{3+} precursor. When europium triflate is the Eu^{3+} precursor, however, the average lifetime in the Sr^{2+},Eu^{3+}-doped sample is much longer than the average lifetime in the Eu^{3+}-only sample. The longest lifetime obtained for any of the samples was 2.50 ms, measured for the Sr^{2+},Eu^{3+}-doped sample prepared using europium triflate and strontium hfpd.

Lifetimes at 9.0 K for 1.0 wt % Eu_2O_3 sol−gel silica samples with fluorine incorporated by the use of $FSi(OC_2H_5)_3$ are listed in Table 5. The $FSi(OC_2H_5)_3$/Eu ratio in these samples is 1. Phase separation occurred in the samples prepared with F/Eu ratios of 5. The lifetimes measured in the europium nitrate-based sample were all longer than the lifetimes measured in the europium triflate-based sample. In general, the lifetimes measured for these two samples increased with decreasing detection wavelength and increasing excitation wavelength.

The incorporation of fluorine via $FSi(OC_2H_5)_3$ had different effects on the measured Eu^{3+} lifetimes, depending on the europium precursor used. In the triflate-based system, a large decrease in the average lifetime measured at room temperature (1.32 ms) and at 9.0 K (1.46 ms) was observed relative to samples prepared from the europium triflate precursor and no $FSi(OC_2H_5)_3$ (1.66 ms (295 K), 1.69 ms (9 K)). On the contrary, the analogous comparison for europium nitrate based samples indicated little change in average lifetime at 9.0 K (1.77 and 1.72 ms in the presence and absence of $FSi(OC_2H_5)_3$, respectively) and a decrease in the lifetime at room temperature (1.25 and 1.68 ms in the presence and absence of $FSi(OC_2H_5)_3$, respectively).

Table 6 contains the average lifetimes for the samples considered in this study, most of which were discussed in detail in preceding paragraphs. The average Eu^{3+} lifetime of a nitrate-based 1.0 wt % Eu_2O_3 sample with an Al/Eu ratio of 1 was the same for samples heated to 800 and 900 °C. An increase in the Al/Eu ratio from 1 to 3 led to a slight decrease in the average lifetime in the nitrate-based system. In the triflate-based system, however, the average Eu^{3+} lifetime increased with an increase in the Al/Eu ratio from 1 to 3. The 9.0 K and room-temperature lifetimes of the Eu^{3+},Sr^{2+} codoped samples prepared with europium nitrate or europium triflate and strontium hfpd are similar within the uncertainty of the lifetime measurement. When europium nitrate is the Eu^{3+} source, the identity of the strontium precursor has less influence on the average Eu^{3+} lifetime in Eu^{3+},Sr^{2+} codoped samples than when europium triflate is the Eu^{3+} source. The lifetime in the europium triflate-based Eu^{3+},Sr^{2+} codoped samples is much longer when strontium hfpd is the Sr^{2+} source than when strontium nitrate is used.

Discussion

Eu^{3+} Clustering. The extent of rare earth ion clustering can be gauged qualitatively by fluorescence line narrowing measurements. Glass is an amorphous host, providing dopant ions with a distribution of unequivalent bonding sites. Ions in unequivalent bonding sites have slightly different energy level positions, leading to inhomogeneously broadened absorption and emission spectra. In the absence of energy transfer between ions, a narrow band excitation source such as a laser can be tuned across an inhomogeneously broadened absorption band to excite subsets of ions within the entire distribution to obtain emission spectra with properties characteristic of the selected sites. Energy transfer among ions becomes possible when the spatial separation between ions decreases sufficiently and prevents site selective emission from being observed by providing a pathway for the excitation of ions not intentionally excited by the laser. The probability of energy transfer and the number of unintentionally excited sites increase as the distance between ions decreases. Site selective emission will only be observed when the ions are separated sufficiently within the glass to reduce or eliminate the probability of energy transfer. As a result, site selective emission spectra are a useful local probe of rare earth clustering in glass.

As shown in Figure 1, site selective emission was not obtained from a sample containing only Eu^{3+} prepared using a triflate precursor, a result we attribute to rapid energy transfer promoted by short Eu^{3+}–Eu^{3+} separations due to the presence of microscopic Eu^{3+} clusters in the glass. A similar result was obtained previously with a Eu^{3+}-doped sample prepared using a nitrate precursor.[17] The high mobility of ions in the liquid pore phase and weak interaction between the ions and the gel network are believed to be responsible for the spatial localization of Eu^{3+} ions and the formation of clusters (local regions rich in Eu) during densification and pore collapse.

The spectral traces in Figure 2 are of site selective emission obtained from a Eu^{3+},Al^{3+}-doped sample prepared using triflate precursors. The spectral variation with excitation wavelength indicates that different Eu^{3+} bonding sites emit as the excitation wavelength changes. The results indicate that the addition of Al^{3+} leads to increased Eu^{3+}–Eu^{3+} distances and a significant reduction of Eu^{3+}–Eu^{3+} energy transfer. The aluminum triflate precursor is as effective as the aluminum nitrate and aluminum–silicon double metal alkoxide precursors used in a previous study[17] at dispersing Eu^{3+} ions in a silica glass and inhibiting clustering. Whether added as a cation or as part of a double metal alkoxide in silicate compositions, aluminum is a glass network former, and it is incorporated throughout the evolving glass network during the sol–gel process. The association of Eu^{3+} ions with Al^{3+} ions found in the final glass product[17,26] may begin at the wet gel stage. The oxygen coordination of aluminum in rare earth doped silica sol–gel glasses has been found to be four[24] and six[26] in separate studies. The negative charge on the four- or six-coordinate AlO_4^- or AlO_6^{3-} groups found throughout the gel can exert a strong attraction for Eu^{3+} ions in solution. Rather than being confined within the liquid pore phase as in a pure silica gel, Eu^{3+} ions in an aluminosilica gel are much more likely to interact with the evolving network phase because of attraction to the Al^{3+} groups. As the aluminosilica network grows, it can surround the attracted Eu^{3+} ion, isolating it from other Eu^{3+} ions. This is one possible explanation for the action of aluminum in the dispersion of rare earth ions in sol–gel silica.

Little site selectivity was observed in the spectra of a Eu^{3+},Sr^{2+}-doped glass shown in Figure 3, evidence of energy transfer and Eu^{3+} clustering in the glass. Greater spectral differences, although less dramatic than those found in a Eu^{3+},Al^{3+}-doped sample, were observed in site selective excitation spectra of a Eu^{3+},Sr^{2+}-doped sample prepared with a Sr/Eu ratio of 9.[27] The Sr/Eu ratio in the sample used in the present study was 1. The efficiency of Sr^{2+} at dispersing rare earth ions in a glass is much lower than that of Al^{3+}, and the mechanism of dispersion is probably different for Sr^{2+} and Al^{3+}. Sr^{2+} is a glass network modifier, like Eu^{3+}, and remains in the liquid pore phase as the silica gel forms instead of becoming part of the gel network phase. During densification and pore collapse, the presence of Sr^{2+} is probably beneficial only as a diluent for the Eu^{3+} ions.

Eu^{3+} Lifetimes. Sr^{2+} remains an interesting codopant, however, due to its influence on the Eu^{3+} lifetime in sol–gel silica. The Eu^{3+} lifetime in a nitrate-based Eu^{3+},Sr^{2+}-doped sol–gel silica glass prepared with a Sr/Eu ratio of 9 was measured to be 2.50 ms,[27] equal to the longest lifetime reported in the current study. The addition of Sr^{2+} is expected to lead to decreased hydroxyl retention in a doped gel since the ionic field strength of Sr^{2+} is relatively low compared to that of Al^{3+} and Eu^{3+}. A large Sr/Eu ratio leads to an increase in the Eu^{3+} lifetime by diluting Eu^{3+} clusters. We believe that this dilution effect leads to an increased Eu^{3+} lifetime due to reductions in both concentration quenching and local hydroxyl concentration.[27] The longest lifetime in the current study was obtained from a Eu^{3+},Sr^{2+}-doped sample with a Sr/Eu ratio of 1 at 9.0 K prepared using europium triflate and strontium hfpd. The average lifetime of this sample is much longer than that obtained for a Eu^{3+}-doped sample at 9.0 K. The dilution effect of Sr^{2+} on the clustering of Eu^{3+} will be less pronounced at low Sr/Eu ratios. The pronounced increase in Eu^{3+} lifetime at 9 K in the sample with Sr/Eu = 1 suggests that the ability of Sr^{2+} to limit the local hydroxyl concentration in the vicinity of Eu^{3+} is a significant effect.

In contrast with results obtained previously,[34] the switch from europium nitrate to europium triflate did not lead to a longer average lifetime in a sample doped only with Eu^{3+}. The major difference between the samples investigated in the previous[34] and the current study is that in the former study, the water-to-Si ratio, r, in the initial reaction mixture was 16, while in the current study, $r = 4$. A dramatic increase in the Eu^{3+} lifetime was observed by Costa et al.[34] upon switching the precursor from europium nitrate to europium triflate, but all of the lifetimes reported in ref 34 are shorter than the corresponding lifetimes measured in the current study, including those measured at room temperature. Hydroxyl quenching is more pronounced in $r = 16$ samples than in $r = 4$ samples, and while in situ dehydroxylation occurs in both types of samples, it leads to a longer Eu^{3+} lifetime only in the $r = 16$ Eu^{3+}-doped samples.

In the case of the Eu^{3+},Al^{3+}-doped samples, however, in situ dehydroxylation via the incorporation of fluorine did lead to an increase in the Eu^{3+} lifetimes relative to that of samples prepared from nitrate precursors. The lifetimes, however, were still shorter than in a sample containing only Eu^{3+}. In the triflate-based system, the slight increase in average lifetime as the Al/Eu ratio increased from 1 to 3 may be due to a higher local concentration of triflate anions near Eu^{3+} ions in the glass. In the nitrate-based system, the average lifetime decreased slightly as the Al/Eu ratio increased from 1 to 3, probably due to a higher local concentration of hydroxyl groups near Eu^{3+} ions.

Incorporation of fluorine in the silica network via $FSi(OC_2H_5)_3$ led to a slightly longer lifetime in the sample prepared with europium nitrate and a shorter lifetime in the sample prepared with europium triflate at 9.0 K. At room temperature, the addition of $FSi(OC_2H_5)_3$ led to shorter lifetimes in both the nitrate- and triflate-based samples. A longer lifetime in the nitrate-based sample at 9.0 K may be due to replacement of a hydroxyl group in the coordination sphere of Eu^{3+} with a fluorine atom bound to silicon, leading to less effective hydroxyl quenching. This effect did not lead to a longer lifetime in the triflate-based sample, however, or longer lifetimes at room temperature in either sample. In the triflate-based sample, since the extent of hydroxyl quenching is expected to be reduced, the shorter lifetime may be due to an increased importance of concentration quenching, for reasons that we presently do not understand.

Regardless of sample composition, the shortest lifetimes were measured at longer detection wavelengths and shorter excitation wavelengths, conditions representative of Eu^{3+} ions in high crystal field strength sites.[36,37] The longest lifetimes were measured at shorter detection wavelengths and longer excitation wavelengths, conditions representative of low crystal field strength sites. A similar observation was made in a previous study of Eu^{3+},Al^{3+}-doped sol−gel glasses[17] but is extended here to Eu^{3+}-doped and Eu^{3+},Sr^{2+}-doped glasses and Eu^{3+}-doped glasses containing fluorine.

Different trends were observed in the lifetimes of high and low crystal field strength sites with decreasing temperature. In samples doped only with Eu^{3+}, the average lifetime measured at 9.0 K was only slightly longer than the average lifetime measured at room temperature, since the high-field lifetimes decreased and the low-field lifetimes increased. Both the longest and shortest lifetimes measured in a Eu^{3+}-doped sample were obtained with the triflate-based sample at 9.0 K. In Eu^{3+},Al^{3+}-doped samples at room temperature, the high-field lifetimes were longer in the sample prepared with nitrate precursors and the low-field lifetimes were longer in the sample prepared with triflate precursors. At 9.0 K, both the high-field and low-field lifetimes were longer than those measured at room temperature, leading to an increase in the average lifetime of the Eu^{3+}, Al^{3+}-doped samples.

Conclusions

Aluminum triflate is as effective of a precursor as aluminum nitrate and (di-*sec*-butoxyaluminoxy)triethoxysilane at dispersing and inhibiting the clustering of Eu^{3+} ions in sol−gel silica. The increased hydroxyl quenching caused by the addition of Al^{3+} to Eu^{3+}-doped silica is clearly reduced by the use of aluminum and europium triflate precursors compared to that of nitrate precursors. The presence of fluorine on the triflate ligands is proposed to decrease hydroxyl quenching of Eu^{3+} fluorescence by promoting an in situ dehydroxylation process. The reduced hydroxyl quenching was detected as an increase in Eu^{3+} fluorescence lifetime. Lifetimes observed in Eu^{3+},Al^{3+} codoped samples, however, were still shorter than lifetimes observed in samples doped only with Eu^{3+}. The longest average lifetime and longest individual lifetime were measured in a sample doped with europium triflate and strontium hfpd due to a combination of in situ dehydroxylation, Eu^{3+} cluster dilution by Sr^{2+}, and low hydroxyl retention properties of Sr^{2+}. Fluorine incorporated via $FSi(OC_2H_5)_3$ in samples doped only with Eu^{3+} leads to a slightly longer 9.0 K lifetime when $Eu(NO_3)_3{\cdot}6H_2O$ is used as the doping precursor and a shorter 9.0 K lifetime when $(CF_3SO_3)_3Eu$ is used. Further work directed at better understanding the effects of fluorinated metal ion doping precursors on the local structural environments of Eu^{3+} and the effect of local hydroxyl groups on the crystal field properties of Eu^{3+} in sol−gel silica glasses is underway.

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