Inorganic and Organically Modified Rare-Earth-Doped Silica Gels

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The fluorescence properties of inorganic and organically-modified rare-earth-doped sol-gel silica are presented. Eu^{3+}-doped ormosils were prepared from $Si(OCH_3)_4$ and $CH_3Si(OCH_3)_3$, $(CH_3)_2Si(OCH_3)_2$, $(CH_3)_2Si(OC_2H_5)_2$, or $(n\text{-}C_3H_7)Si(OCH_3)_3$ in various proportions. Er^{3+}-doped ormosils were prepared using $Si(OC_2H_5)_4$ and $CH_3Si(OC_2H_5)_3$, $(CH_3)_2Si(OC_2H_5)_2$, or $C_2H_5Si(OC_2H_5)_3$. Gels derived from $Si(OCH_3)_4$ were also doped with the fluorinated Eu^{3+} precursors $Eu(fod)_3$, $(CF_3SO_3)_3Eu$, and $(CF_3CO_2)_3Eu \cdot 3H_2O$. The effect of metal ion codopants, which are known to inhibit clustering of Eu^{3+} in sol-gel silica, on Er^{3+} fluorescence is also considered. Fluorescence line-narrowing studies of Eu^{3+}-doped samples indicated that significant Eu^{3+} clustering occurs in both the ormosils and fluorinated precursor compositions. Lifetime measurements of the Eu^{3+}- and Er^{3+}-doped ormosils showed longer lifetimes at low heat treatment temperatures relative to purely inorganic sol-gel silica, but no significant difference remained in fully densified samples. The longest lifetimes were observed for samples doped with the fluorinated precursors, indicating that the fluorinated ligands are effective at reducing the water content in densified gels.

Introduction

Rare-earth ion-doped glass devices are of great interest for a wide range of applications, including laser materials, waveguides, and optical amplifiers (Hanna, 1993; DiGiovanni, 1992). In particular, Er^{3+}-doped glasses are being considered for use as infrared laser materials (Gapontsev et al., 1982) and as amplifiers for optical communications (Ainslie, 1991). The interest in Er^{3+} is strong because the $^4I_{13/2} \rightarrow {}^4I_{15/2}$ electronic transition in Er^{3+} produces infrared light (~ 1.54 μm) that is close to the wavelength of lowest signal attenuation in silica glass fiber (Miya et al., 1979). The $^4I_{13/2} \rightarrow {}^4I_{15/2}$ emission is also outside the range of wavelengths of light focused on the retina of the human eye and is therefore eye-safe (Winburn, 1985). Additionally, Er^{3+}-doped glasses codoped with Yb^{3+} are being investigated as upconversion laser materials providing laser wavelengths in the blue and green regions of the visible spectrum (Jackel et al., 1992).

Sol-gel synthesis has been used to produce solid-state inorganic materials with a variety of compositions (Brinker and Scherer, 1990). An important area of emphasis has been the preparation of optical materials. The properties of optical sol-gel materials have been studied extensively and several applications have been demonstrated or proposed. These include solid-state lasers, nonlinear optics, chemical sensors, waveguides, ferroelectrics, and photochromic glasses (Mackenzie, 1994; Reisfeld and Jørgensen, 1992; Cheetham et al., 1994). Many of these applications are based on the useful luminescence properties of rare-earth dopants that have been introduced into the composition. In addition, the sensitivity of rare-earth luminescence to the local rare-earth ion coordination environment in both the liquid and solid phases, makes rare-earth ions effective probes of chemical and physical changes that occur during the sol-gel reaction and postreaction processing (Ferrari et al., 1992; Matthews et al., 1994).

Most technological applications require highly efficient

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rare-earth luminescence. Currently, the luminescence efficiency of rare-earth ions in sol-gel host materials is limited by the tendency of rare-earth ions to aggregate and form clusters and by the presence of residual water and hydroxyl groups. Clustered rare-earth ions lead to concentration quenching through cross-relaxation or energy-transfer processes and result in lower luminescence efficiencies and shorter lifetimes (Quimby et al., 1994; Nilsson et al., 1995). Previous work (Lochhead and Bray, 1995) indicates that clustering occurs in Eu^{3+}-doped silica sol-gel glasses even at low concentration. Residual water and hydroxyl groups lower the luminescence efficiency of rare-earth ions in sol-gel glasses through a nonradiative phonon quenching mechanism (Berry and King, 1989).

Strategies for inhibiting rare-earth clustering include codoping with Al^{3+} (Lochhead and Bray, 1995; Sen and Stebbins, 1995; Thomas et al., 1992) or other metal ions (Costa et al., 1996) and rare-earth ion encapsulation by chelating ligands (Matthews et al., 1994; Sabbatini and Guardigli, 1992). Metal-ion codoping has been shown to inhibit rare-earth ion clustering and promote a more uniform distribution of rare-earth ions in silica gels and silicate glass matrices. Dopant ion encapsulation protects individual rare-earth ions and increases the distance between ions to prevent clustering.

The use of organically modified silicon alkoxide sol-gel precursors (Capozzi and Seddon, 1994) and the addition of fluorine as a dehydroxylating agent (Pope and Mackenzie, 1993) have been demonstrated to reduce the hydroxyl content in silica-gel glasses. Organically modified precursors contain hydrophobic alkyl groups that act to inhibit water and hydroxyl retention (Zhang et al., 1995), while the presence of fluorine induces chemical reactions upon heat treatment that act to remove water and hydroxyl groups from sol-gel silica (Rabinovich et al., 1986). Encapsulation also inhibits hydroxyl quenching by physically shielding dopant ions from water and hydroxyl groups.

We are interested in improving rare-earth luminescence efficiency in sol-gel glasses through chemical modifications of the compositions. Our approach is to use the particularly informative luminescence properties of Eu^{3+} as a probe of clustering and hydroxyl quenching. Our goals are to use Eu^{3+} as a model of rare-earth ions in general and to identify reaction conditions and compositions conducive to high luminescence efficiency. Once we optimize conditions for Eu^{3+}, we apply them to systems doped with more technologically useful rare-earth ions.

In this study, Eu^{3+} fluorescence is used to probe the effect of organic modification of silicon alkoxide precursors and the presence of fluorine on clustering and hydroxyl quenching of rare-earth ions. We introduce fluorine into the composition in a new way; namely, as a substituent on ligands incorporated into the Eu^{3+} source precursor. This method provides a simple way of introducing fluorine and permits high F/Eu ratios to be achieved. Eu^{3+} fluorescence line-narrowing spectroscopy and lifetime measurements will be used to examine the effects of organic modification and fluorine incorporation on clustering and hydroxyl quenching, respectively. We also discuss preliminary extensions of this and previous Eu^{3+} work to Er^{3+}-doped sol-gel silica. We specifically consider the effects of organic modification and codoping with Al^{3+} or Yb^{3+} on the luminescence properties of Er^{3+}.

Experiment

Eu^{3+}-doped samples

Eu^{3+}-doped gels were derived from $Si(OCH_3)_4$ (TMOS) in separate combinations with each of the following organically modified silicon alkoxides: $CH_3Si(OCH_3)_3$ (MTMS), $(CH_3)_2$-$Si(OCH_3)_2$ (DMDMS), $(CH_3)_2$-$Si(OC_2H_5)_2$ (DMDES), and $C_3H_7Si(OCH_3)_3$ (PTMS). The organically modified silica gels were prepared by mixing TMOS, the modified silicon alkoxide and an aqueous solution in which $Eu(NO_3)_3 \cdot 6H_2O$ was previously dissolved. The molar ratio of water to the combined silicon precursor content (TMOS + modified silicon precursor) was 16. The molar ratios of TMOS to modified alkoxide were 19:1, 9:1, and 3:1. No ethanol was used in the initial reaction mixture. The reaction mixtures were cast in cylindrical plastic vials, which were then sealed, and left to react at room temperature. Gel times ranged from one to two weeks, depending on the sample composition.

After gelation the gels were aged and dried at 60°C for two days and at 90°C for two days. The samples were ultimately heated to 800°C, with 24 h dwell times at 200° intervals. Samples began cracking during aging. Upon heating to 800°C, some samples broke into pieces and others maintained their cylindrical shape, but developed a network of internal cracks. After heating to 800°C, all samples were transparent and colorless. Final products were flat, cracked disks, 1–2 mm thick and 1–1.5 cm in diameter, or irregularly shaped pieces broken away from such disks, with characteristic dimensions of 1–5 mm.

All samples contained 1.0 wt. % Eu_2O_3. The rare-earth ion concentration of all samples investigated in this study is expressed in terms of the weight percent of RE_2O_3 (RE = Eu or Er) that would be present in a fully densified SiO_2 glass in which residual water and organics are absent and reaction has gone to completion. Weight loss during heat treatment was not measured for any of the samples. In a previous work the properties of rare-earth-doped sol-gel silica heated to 800°C were found to be similar to the properties of melt-derived rare-earth-doped silica glass (Sun et al., 1987). Only trace amounts of water, organics, and unreacted starting materials are expected to remain after heating to 800°C (Yamane et al., 1979). Most of the organic groups in the hybrid gels have decomposed after heating to 800°C (Babonneau et al., 1992), but to distinguish these samples from those prepared with TMOS only, they are still referred to as hybrid gels, or ormosils. The densities of the samples heated to 800°C ranged from 1.6 g/mL to 2.2 g/mL, depending on the sample composition, and were similar to previously reported densities (Moreshead et al., 1990; Laczka, 1991).

A series of samples prepared from fluorinated Eu^{3+} precursors and TMOS were also studied. The Eu^{3+} precursors used were: tris (6,6,7,7,8,8,8-heptafluoro-2,2-dimethyl-3,5-octanedionate)Eu(III)(Eu(fod)$_3$), Eu(III) trifluoromethanesulfonate ($(CF_3SO_3)_3Eu$), and Eu(III) trifluoroacetate ($(CF_3CO_2)_3Eu \cdot 3H_2O$). The Eu^{3+} precursors were dissolved in water [$(CF_3SO_3)_3Eu$, $(CF_3CO_2)_3Eu \cdot 3H_2O$) or DMF-methanol (Eu(fod)$_3$] and combined with an aqueous solution of TMOS (water: TMOS = 16). HNO_3 was added to lower the pH to 1.5. Samples containing 1.0 and 5.0 wt. % Eu_2O_3 were prepared. The heat-treatment procedure for these samples was the same as that used for the organically modified samples.

Room temperature broad-band (nonselective) emission spectra were obtained by exciting samples with the 514.5-nm line of an argon ion laser. Luminescence was collected with a 1-m monochromator and detected by a photomultiplier tube. Fluoroescence line-narrowing measurements were completed with a tunable dye laser pumped by a Q-switched Nd:YAG laser. Sample pieces of varying sizes were used in the fluorescence measurements and the results obtained were independent of the size of sample used. The dye laser provided the tunable emission from 571 nm to 580 nm needed to selectively excite the $^7F_0 \rightarrow {}^5D_0$ transition of Eu^{3+}. Spectra were normalized to the $^5D_0 \rightarrow {}^7F_1$ peak intensity and were collected at 77 K. Luminescence decay measurements were recorded using a digital storage oscilloscope. Since the decay curves were slightly nonexponential, average lifetimes were obtained by calculating the area under normalized decay curves (Armagan et al., 1989). The uncertainty in the lifetime values was approximately ±0.05 ms.

Er^{3+}-doped samples

Er^{3+}-doped hybrid organic/inorganic silica sol-gel samples were prepared using $Si(OC_2H_5)_4$ (TEOS) with each of $CH_3Si(OC_2H_5)_3$ (MTES), $(CH_3)_2Si(OC_2H_5)_2$ (DMDES), or $C_2H_5Si(OC_2H_5)_3$ (ETES). $Er(NO_3)_3 \cdot 5H_2O$ was used as the source of Er^{3+}. Solutions were made with 10:1 and 5:1 ratios of TEOS:modified alkoxide. Deionized water and ethanol were added to achieve a 1/4/4 molar ratio of (total Si)/water/ethanol. The initial sols were mixed until homogeneous, cast-in-plastic vials that were then sealed and left to react at 35°C. HNO_3 was added as a catalyst to the initial sol. The sources of Al^{3+} and Yb^{3+} in the codoped sol-gel silica samples were $Al(NO_3)_3 \cdot 9H_2O$ and $Yb(NO_3)_3 \cdot 5H_2O$. These samples were prepared using a 1/4/4 molar ratio of TEOS/water/ethanol and left to react at room temperature in sealed plastic vials.

Gel times ranged from one to five weeks, depending on the reaction temperature, the alkoxides used, and the amount of salt in the initial sol. After gelation, the gels were aged for two days at 60°C, followed by two days at 90°C. Samples shattered during aging, forming irregularly shaped pieces with characteristic dimensions ranging from 1 mm to 5 mm. Some of the individual pieces contained cracks, while others were crack-free. Samples were then heated in air to a final densification temperature of 800°C, with 24-h dwell times at 200° intervals. Very little further cracking or shrinkage was observed after aging at 90°C during heat treatment to 800°C. Er^{3+}-doped sample pieces heated to 800°C were transparent and had the faint pink color characteristic of Er^{3+}. All of the Er^{3+} fluoroescence spectra and fluorescence lifetimes presented in this article were measured with samples heated to 800°C. The densities of the samples heated to 800°C ranged from 1.6 to 2.2 g/mL, depending on the sample composition.

Fluorescence spectra and lifetimes were measured with sample pieces of varying sizes using the 488 nm line of an argon ion laser ($^4I_{15/2} \rightarrow {}^4F_{7/2}$ excitation). Laser power densities ranging from 0.5 to 2.5 W/cm^2 were used for the fluorescence measurements. Sample fluorescence was focused on the entrance slit of a 1-m monochromator. Infrared fluorescence was detected with a germanium detector and measured using standard lock-in amplifier techniques. The spectra are uncorrected. Fluorescence decay traces of the 1.54-μm $^4I_{13/2} \rightarrow {}^4I_{15/2}$ emission were recorded on a digital oscilloscope from the output of a fast (~ 200-μs rise time) germanium detector. The 488-nm radiation of an argon-ion laser was chopped at a frequency of 10 Hz to simulate pulsed excitation. Average lifetimes were obtained by calculating the area under normalized decay curves, as previously. Low-temperature measurements were made using a variable-temperature cryostat.

Results and Discussion

Organically modified compositions — Eu^{3+} doping

Figure 1 presents broad-band fluorescence spectra for several 1.0 wt. % Eu_2O_3-doped ormosils densified at 800°C. The spectra observed for the different compositions were similar. Enlargement of the nondegenerate $^5D_0 \rightarrow {}^7F_0$ transition near 578 nm revealed slight differences in the linewidth of the transition for the different compositions. Larger $^5D_0 \rightarrow {}^7F_0$ linewidths were observed in the organically modified compositions relative to the unmodified composition, a result that indicates a wider range of bonding sites for Eu^{3+} in the organically modified systems (Weber, 1986). The linewidth broadening occurred on the high-energy side of the transition and became more pronounced as the amount of organically modified precursor used in the preparation was increased. For a given TMOS:modified alkoxide ratio, the $^5D_0 \rightarrow {}^7F_0$ linewidth decreased as DMDES > MTMS > DMDMS.

Figure 2 shows 77 K fluorescence line-narrowing (FLN, also referred to as selective excitation) spectra for a 1.0 wt. % Eu_2O_3-doped sample made from a 3:1 molar ratio of TMOS: DMDES and densified at 800°C. The conventional broad-band luminescence spectrum is shown at the top of the figure for comparison. The spectra obtained upon selective excitation were similar to the nonselective broad-band spectrum.

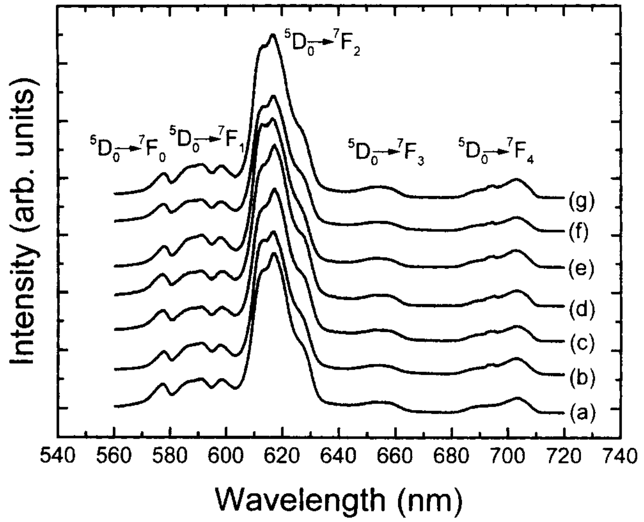

Figure 1. Room temperature fluorescence spectra (nonselective, $\lambda_{exc} = 514.5$ nm) of 1.0 wt. % Eu_2O_3-doped ormosils.

Eu^{3+} transitions are labeled on the figure. (a) TMOS only; (b) TMOS/DMDMS = 9; (c) TMOS/MTMS = 9; (d) TMOS/DMDES = 9; (e) TMOS/DMDES = 3; (f) TMOS/MTMS = 3; (g) TMOS/MTMS = 19.

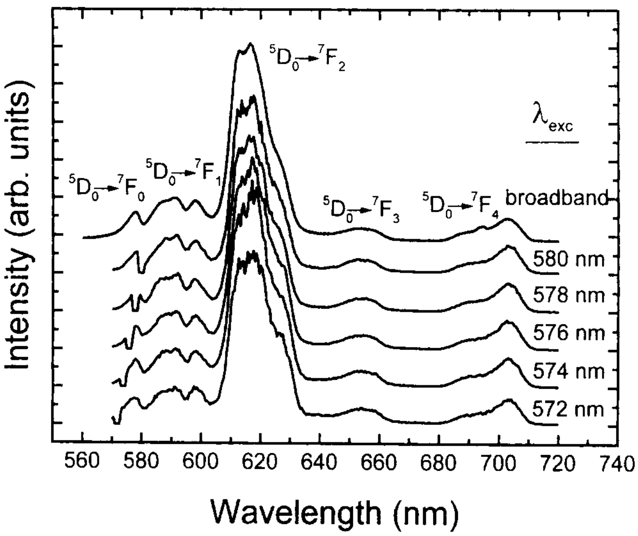

Figure 2. FLN spectra at 77 K of 1.0 wt. % Eu_2O_3-doped ormosil (molar ratio TMOS/DMDES = 3) heated to 800°C.

Eu^{3+} transitions are labeled on the figure. Intensities were normalized to the $^5D_0 \rightarrow ^7F_1$ emission at each pump wavelength. Upper spectrum, fluorescence spectrum at 300 K ($\lambda_{ex} = 514.5$ nm).

The lack of spectral sensitivity to excitation wavelength reflects an inability to obtain fluorescence from selectively excited subsets of Eu^{3+} ions within the inhomogeneous distribution of bonding sites. We attribute the finding to efficient energy transfer among Eu^{3+} ions (Weber, 1986). Since efficient energy transfer occurs only when Eu^{3+} ions are spatially close to each other, we are led to conclude that Eu^{3+} ions aggregate or cluster in the matrix. This indicates that the distribution of Eu^{3+} ions in the material is nonuniform. Similar results were obtained for the other organically modified compositions considered in this study and were also obtained previously for unmodified Eu^{3+}-doped materials derived from TMOS and TEOS (Lochhead and Bray, 1995).

The lifetime of Eu^{3+} is highly sensitive to the hydroxyl concentration in sol-gel materials, and is a useful probe of whether chemical modification influences the residual hydroxyl content of sol-gel materials. This is because hydroxyl groups have high phonon energies and introduce an efficient nonradiative decay pathway for rare-earth ions that acts to shorten lifetimes. We measured lifetimes of several compositions at different heat-treatment temperatures in order to examine the effect of organic modification on the hydroxyl content. Representative results are shown in Table 1. At the wet-gel stage, before any heat treatment, the organically modified systems show slightly longer lifetimes than the unmodified control sample. The difference in lifetime increases with heating temperature up to 200°C, but is no longer evident in samples heated to 800°C. These results indicate that the presence of organically modified precursors affects the hydroxyl content in the vicinity of Eu^{3+} in the gels. The longer lifetimes at low heating temperatures are evidence of lower hydroxyl content and are consistent with the expected hydrophobic character of the alkyl groups incorporated in the precursors. The organic substituents appear to facilitate removal of water from the matrix at low heating temperatures. At high heating temperatures, the alkyl groups decompose, are driven from the matrix, and the moisture-inhibiting effects of the alkyl groups are lost.

Table 1. Selected 77 K Eu^{3+} $^5D_0$-Level Lifetimes (μs) in Organically Modified Gels at Various Heat Treatment Temperatures*

Modified Precursor	TMOS: Modified Precursor	Wet Gel	90°C	200°C	800°C
None	—	107	152	298	1,065
MTMS	9	133	195	342	
DMDMS	9	125	182	327	1,048
DMDES	3		190	376	1,102
DMDES	9	119	195	340	1,001
PTMS	9		178	370	856

*Excitation and detection wavelengths were 579 ± 0.5 nm and 616 ± 1 nm, respectively. The small changes in these wavelengths were needed to account for the evolution of the spectrum upon heat treatment.

Organically modified compositions — Er^{3+} doping

Figure 3 depicts the infrared fluorescence of a 1.0 wt. % Er_2O_3 silica gel sample and 1.0 wt. % Er_2O_3 hybrid samples. The individual traces are normalized to a peak intensity of 1. The width of the fluorescence band was similar in all of these spectra. The similarity in the widths of the spectra obtained for 1.0 wt. % Er_2O_3-doped silica and hybrid silica samples indicates that, similar to what was observed for Eu^{3+}, the use

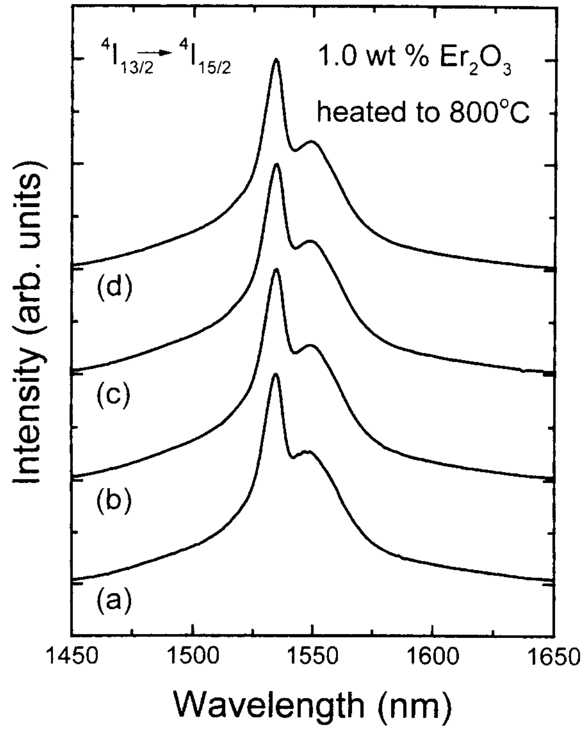

Figure 3. Room temperature Er^{3+} $^4I_{13/2} \rightarrow ^4I_{15/2}$ fluorescence in hybrid organic/inorganic silica gels.

The letter under each trace indicates the silicon alkoxides used to prepare each sample: (a) TEOS only; (b) TEOS/MTES = 10; (c) TEOS/DMDES = 10; (d) TEOS/ETES = 10.

Table 2. Er^{3+} $^4I_{13/2}$-Level Lifetimes (ms) at Various Measurement Temperatures in 1.0 wt. % Er$_2$O$_3$-Doped Inorganic and Hybrid Silica Gels Densified at 800°C

	$T = 12$ K	$T = 100$ K	$T = 200$ K	$T = 295$ K
TEOS only	8.49	8.06	7.17	7.19
TEOS/MTES				
10	5.30	5.05	4.69	5.22
5	5.95	5.58	5.28	5.77
TEOS/DMDES				
10	5.14	5.16	5.18	5.64
5	7.13	6.93	6.74	—

Table 3. Lifetime Values (ms) Measured at 77 K for 5.0 wt. % Eu$_2$O$_3$-Doped Silica Gels Prepared from Eu(NO$_3$)$_3$·6H$_2$O and Three Fluorinated Eu^{3+} Precursors

	$\lambda_{exc} = 577$ nm		$\lambda_{exc} = 579$ nm	
λ_{em} (nm) →	610	625	610	625
Eu(NO$_3$)$_3$·6H$_2$O	1.17	1.14	1.16	1.17
(CF$_3$CO$_2$)$_3$Eu·3H$_2$O	1.63	1.44	1.69	1.61
(CF$_3$SO$_3$)$_3$Eu	1.63	1.63	1.74	1.67
Eu(fod)$_3$	1.60	1.63	1.67	1.64

of organically modified precursors does not improve the dispersion of Er^{3+} in the glass.

Fluorescence lifetimes of the Er^{3+} $^4I_{13/2}$ level in 1.0 wt. % Er$_2$O$_3$-doped hybrid samples are listed in Table 2. The lifetimes listed are from areas under normalized decay curves, but the decay curves were only slightly nonexponential and were also fit using single exponential functions. The values obtained from the areas and from the exponential fits were in good agreement.

The lifetimes obtained from 1.0 wt. % Er$_2$O$_3$-doped hybrid gels are shorter than the corresponding lifetime from a purely inorganic gel for all modified alkoxides used in this study and for ratios of TEOS:modified alkoxide of 10:1 and 5:1. In each hybrid system, the lifetime increases with decreasing TEOS: modified alkoxide ratio. The hydroxyl content of the densified hybrid silica sol-gel samples is expected to be lower or at least similar to that in the purely inorganic samples based on the Eu^{3+} lifetime results. This suggests that the decrease in the lifetime relative to the unmodified silica samples is due to an increase in concentration quenching, rather than a hydroxyl quenching effect, and that Er^{3+}-ion clustering is more extensive in the hybrid samples than in the purely inorganic samples. The results indicate that using organically modified precursors has an overall negative effect on the optical properties of Er^{3+} in sol-gel silica glasses. This observation suggests that ionic Er^{3+} may be incompatible with the nonionic organic part of the hybrid matrix during gelation and may preferentially segregate away from the organic groups to produce a nonuniform, high local concentration domain in the inorganic part of the matrix. This effect appears to be more pronounced for Er^{3+} than for Eu^{3+}, an observation that may be related to the higher charge density of Er^{3+}. Further work is needed to clarify these points.

Nonorganically modified compositions — fluorinated Eu^{3+} precursors

Room temperature broad-band fluorescence spectra of 1.0 wt. % Eu$_2$O$_3$-doped samples prepared from three fluorinated Eu^{3+} precursors and densified at 800°C were measured and compared to the spectrum of a sample prepared from Eu(NO$_3$)$_3$·6H$_2$O, the traditional Eu^{3+} precursor. The spectrum of the sample prepared from (CF$_3$CO$_2$)$_3$Eu was similar to that of the nonfluorinated sample prepared from Eu(NO$_3$)$_3$·6H$_2$O. The other two samples had spectra that differed in two important ways from the spectrum of the nonfluorinated sample. First, the $^5D_0 \rightarrow {}^7F_0$ transition was broader, and second, the $^5D_0 \rightarrow {}^7F_2$ transition intensity was much stronger. The first observation suggests that a wider range of Eu^{3+} bonding sites is present in the samples prepared from Eu(fod)$_3$ and (CF$_3$SO$_3$)$_3$Eu, and the second observation implies that more highly distorted (less symmetrical) Eu^{3+} bonding environments are present. Selectively excited fluorescence spectra measured at 77 K for the samples prepared from the fluorinated Eu^{3+} precursors revealed no line-narrowing effect. As in the case of organically modified systems, this result indicates that fluorinated Eu^{3+} precursors do not inhibit Eu^{3+} clustering.

The principal reason for preparing samples from fluorinated Eu^{3+} precursors was to examine the effect of fluorinated ligands on the lifetime of Eu^{3+}. We found that the fluorinated precursors had a pronounced positive effect on the Eu^{3+} lifetime. Table 3 summarizes 77 K lifetime results of samples containing 5.0 wt. % Eu$_2$O$_3$ heated to 800°C for two excitation (λ_{exc}) and two detection (λ_{em}) wavelengths. A clear increase in lifetime was observed when fluorinated precursors were used. Since the fluorescence line-narrowing spectra indicate that appreciable clustering is present, the longer lifetimes indicate that the use of fluorinated Eu^{3+} precursors leads to lower hydroxyl content in the densified gels. These findings indicate that the *in-situ* dehydroxylation effect observed previously upon HF addition (Pope and Mackenzie, 1993) or postdensification fluorination (Rabinovich et al., 1986) can be achieved by directly incorporating fluorine into the rare-earth precursor.

Nonorganically modified compositions — Er^{3+}-doped silica codoped with Al^{3+} or Yb^{3+}

The visible and infrared fluorescence spectra measured for the Er^{3+}-doped silica gels codoped with Al^{3+} or Yb^{3+} were all similar in general appearance to those measured previously for silica gels doped only with Er^{3+} (Stone and Bray, 1996). Er^{3+} $^4I_{13/2} \rightarrow {}^4I_{15/2}$ fluorescence in 1.0 wt. % Er$_2$O$_3$ silica-gel samples containing only erbium, and containing Al/Er and Yb/Er ratios of 1 are shown in Figure 4. The individual traces are normalized to a peak intensity of 1. The addition of both Al^{3+} and Yb^{3+} caused a broadening of the $^4I_{13/2} \rightarrow {}^4I_{15/2}$ emission, with the influence of Al^{3+} being more pronounced than that of Yb^{3+}. The broadening of Er^{3+} fluorescence suggests a wider distribution of Er^{3+} bonding sites and that both codopant ions act to disperse Er^{3+} in the glass, with Al^{3+} being more effective than Yb^{3+}. Evidence that Al^{3+} directly influences the Er^{3+} bonding environment is found in the small shift of the more intense peak to shorter wavelengths. This shift suggests that Er–O bonding is more ionic in the presence of Al^{3+} (Albin and Horrocks, 1985).

Weak fluorescence at 980 nm (Figure 5) corresponding to the $^4I_{11/2} \rightarrow {}^4I_{15/2}$ transition of Er^{3+} was observed in samples

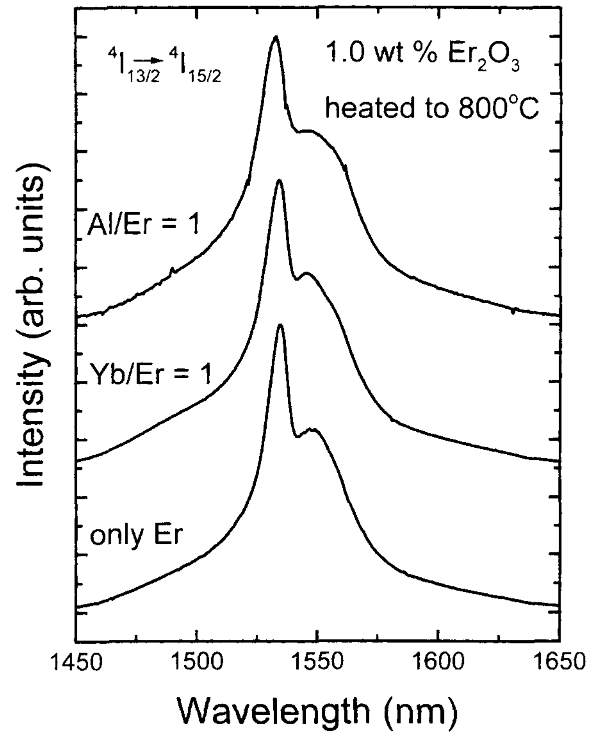

Figure 4. Room temperature Er^{3+} $^4I_{13/2} \rightarrow {}^4I_{15/2}$ fluorescence in purely inorganic silica gels; codopants and amounts are indicated on the figure.

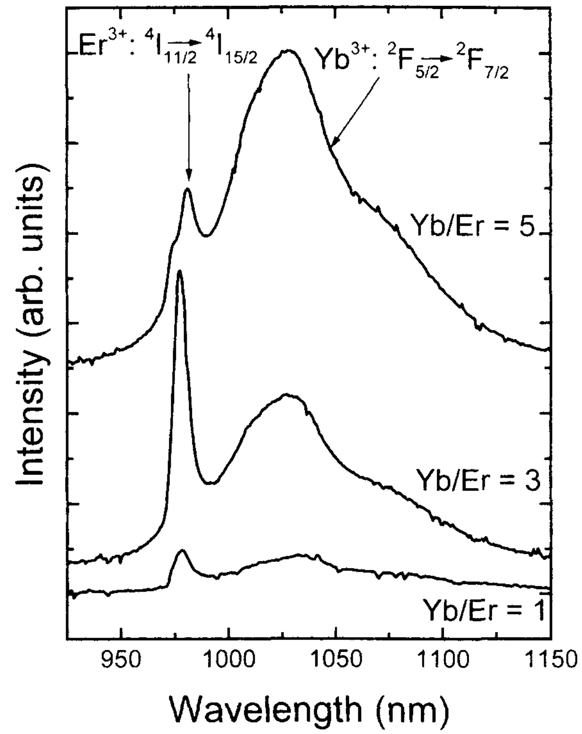

Figure 5. Room temperature Er^{3+} $^4I_{11/2} \rightarrow {}^4I_{15/2}$ fluorescence and Yb^{3+} $^2F_{5/2} \rightarrow {}^2F_{7/2}$ fluorescence in purely inorganic silica gels densified at 800°C.

containing Yb^{3+}. This is the first observation of this emission in an Er^{3+}-doped sol-gel material. The broad fluorescence peak centered at about 1030 nm corresponds to the $^2F_{5/2} \rightarrow {}^2F_{7/2}$ electronic transition of Yb^{3+}. This peak was found to increase in overall intensity as the Yb/Er ratio was increased, as shown in Figure 5. The traces are not normalized, but are on the same scale. Since Yb^{3+} is not directly excited with 488-nm excitation, the Yb^{3+} fluorescence is due solely to nearly resonant transfer from the $^4I_{11/2}$ level of Er^{3+} to the $^2F_{5/2}$ level of Yb^{3+}. The presence of $Er^{3+} \rightarrow Yb^{3+}$ energy transfer is direct evidence for close association of some of the Er^{3+} and Yb^{3+} ions in the matrix.

The $^4I_{13/2}$-level lifetime in Er^{3+}-doped silica gels decreased with increasing Er_2O_3 concentration, and decreased with increasing temperature, as shown in Table 4. The $^4I_{13/2}$-level lifetime is decreased by the effects of hydroxyl quenching (Berry and King, 1989) and concentration quenching via energy transfer (Quimby et al., 1994; Nilsson et al., 1995). The effect of energy transfer is expected to be enhanced by clustering of Er^{3+} ions in a glass. We attribute the decrease in the lifetime of Er^{3+}-doped silica samples with increasing Er^{3+} content to the increasing importance of concentration quenching. The decrease in the lifetime with increasing temperature is attributed to the increasing importance of nonradiative decay due to hydroxyl groups and thermally activated Er^{3+} energy transfer. At room temperature, both hydroxyl and concentration quenching are important in Er^{3+}-doped silica samples.

The addition of Al^{3+} or Yb^{3+} caused a decrease in the room temperature lifetimes measured for all Er_2O_3 concentrations, although the decrease for 1.0 wt. % Er_2O_3-doped samples did not occur until a high codopant/Er^{3+} ratio was reached. The addition of Al^{3+} and Yb^{3+} to Er^{3+}-doped silica is expected to reduce the extent of clustering (Costa et al., 1996), and thus is expected to reduce the importance of concentration quenching. Consequently, we believe that the reduction of lifetime in the presence of the codopants is due to increased hydroxyl quenching. The strength of interaction between a metal ion and water correlates with its charge density (ionic charge)^2/(ionic radius) (Bockris and Reddy, 1973). Since Al^{3+} has a much higher charge density than Er^{3+} and

Table 4. Er^{3+} $^4I_{13/2}$-Level Lifetimes (ms) at Various Temperatures in Inorganic Silica Gels Densified at 800°C

Er^{3+}-Doped Silica Samples				
Er_2O_3 Conc.	T = 12 K	T = 100 K	T = 200 K	T = 295 K
1.0 wt. %	8.49	8.06	7.17	7.19
3.0 wt. %	7.24	6.78	6.29	6.21
5.0 wt. %	5.63	5.42	6.21	4.86
10.0 wt. %	—	—	—	4.10
Er^{3+}, Al^{3+}-Doped Silica Samples (Room Temperature Lifetimes)				
Er_2O_3 Conc.	Al/Er = 1	Al/Er = 3	Al/Er = 5	Al/Er = 10
1.0 wt. %	6.95	7.04	6.96	5.10
3.0 wt. %	4.82	3.11	—	—
Er^{3+}, Yb^{3+}-Doped Silica Samples (Room Temperature Lifetimes)				
Er_2O_3 Conc.	Yb/Er = 1	Yb/Er = 3	Yb/Er = 5	Yb/Er = 10
1.0 wt. %	6.97	7.14	5.16	5.03
3.0 wt. %	4.70	3.11	—	—

is expected to be spatially near Er^{3+}, the local hydroxyl concentration in the vicinity of Er^{3+} is expected to be higher in samples codoped with Al^{3+}. A shorter Er^{3+} lifetime is expected under these conditions. Yb^{3+} is similar in size to Er^{3+} and would not be expected to significantly affect the hydoxyl content in the vicinity of Er^{3+}. Understanding the lifetime of Yb^{3+} codoped samples, however, is complicated by the Er^{3+} $\leftrightarrow$ Yb^{3+} energy-transfer processes that occur. These processes will affect the lifetime of both Er^{3+} and Yb^{3+}. Further work is currently underway to better understand these processes.

Conclusions

The effects of organic modification of silicon alkoxide precursors, fluorine incorporation in rare-earth precursors, and metal ion codoping on the aggregation and residual hydroxyl content of sol-gel silica have been considered. Fluorescence line-narrowing studies of Eu^{3+}-doped organically modified gels [derived from TMOS and $CH_3Si(OCH_3)_3$, $(CH_3)_2Si(OCH_3)_2$, $(C_2H_5)_2Si(OCH_3)_2$, or $(n\text{-}C_3H_7)Si(OCH_3)_3$] and unmodified Eu^{3+}-doped TMOS gels prepared using fluorinated Eu^{3+} precursors [$(CF_3CO_2)_3Eu \cdot 3H_2O$, $(CF_3SO_3)_3Eu$, and Eu(fod)$_3$] indicate that significant Eu^{3+} clustering occurs in both types of gels.

Lifetime studies of the organically modified gels suggest that at low heat treatment temperatures, the hydrophobic alkyl substituents lead to lower hydroxyl content in the gels relative to an unmodified sample prepared with the same Eu^{3+} precursor [$Eu(NO_3)_3 \cdot 6H_2O$]. At high heat treatment temperatures, however, the alkyl groups are driven from the gels, and only a small difference in hydroxyl content is present.

Much longer lifetimes were observed in gels heated to 800°C that were prepared with the fluorinated Eu^{3+} precursors, relative to samples prepared from $Eu(NO_3)_3 \cdot 6H_2O$. This result suggests that fluorine introduced into the gel via the rare-earth precursor facilitates the removal of water during heat treatment, probably by a process similar to the previously reported *in situ* dehydroxylation. The results suggest that the use of fluorinated precursors will lead to rare-earth-doped sol-gel materials with higher luminescence efficiencies.

Codoping of Er^{3+}-doped, nonorganically modified silica gels with Al^{3+} or Yb^{3+} leads to a broader distribution of Er^{3+} sites in sol-gel silica. In the case of Al^{3+} codoping, an increase in the local concentration of hydroxyl groups near the Er^{3+} ions and hydroxyl quenching of luminescence was observed. Yb^{3+} codoping resulted in Er^{3+} $\leftrightarrow$ Yb^{3+} energy transfer. This energy transfer provides evidence of the close association of the two sets of ions in a sol-gel glass and permitted the first observation of $^4I_{11/2} \rightarrow {}^4I_{15/2}$ emission in an Er^{3+}-doped sol-gel material. Lifetime studies of Er^{3+}-doped organically modified compositions suggest that Er^{3+} clustering is more pronounced than in unmodified control samples.

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