Luminescence Behavior of Inorganic and Metalorganic Europium(III) Dopants Incorporated into Silica and Epoxy-Diol ORMOSIL Sol-Gel Hosts

LOWELL R. MATTHEWS, XIAO-JUN WANG AND E. T. KNOBBE

Department of Chemistry and the University Center for Laser Research, Oklahoma State University, Stillwater, Oklahoma 74078-0447, U. S. A.

Abstract. The narrow, intense emission bands of europium (III) make its compounds of interest for various optical source applications. Previous studies have indicated that complexes like tris(4,4,4-trifluoro-1-(2′-thienyl)-1,3-butanedionato-O, O′)europium(III), Eu(tfa)₃, have superior fluorescence properties in select media with respect to comparable inorganic salts like EuCl₃. It has been shown that such complexes are readily incorporated into solid-state matrices via the sol-gel process. The present research examines the luminescence behavior of Eu(tfa)₃ and EuCl₃ doped into a sol-gel-derived “epoxy-diol” ORMOSIL host, and extends our earlier work involving doped silica and acrylate ORMOSIL gel materials. The present study focuses on the effects of dopant-matrix interactions and seeks to compare the emission behavior of Eu(tfa)₃ and EuCl₃ in silica and epoxy-diol ORMOSIL gel host materials.

Keywords: europium(III) complex, epoxy-diol ORMOSIL, luminescence, sol gel

1. Introduction

In our earlier work, [1–7] we reported the incorporation of europium(III) thienyltrifluoro-acetate complexes into silica and acrylate-silica ORMOSIL gel hosts via the sol-gel method. These dopants are of interest for use in solution-derived matrices as they have been shown to exhibit intense fluorescence and laser emission in solution [3]. Similarly, gels doped with the rare earth metalorganic complex were previously shown to possess intense fluorescence characteristics, especially with respect to comparable gels doped with inorganic europium(III) salts such as the chloride [1–2, 4–6] or nitrate [7].

Silica xerogels tend to possess mechanical properties which largely preclude optical shaping and polishing operations. ORMOSIL materials, in contrast, are compatible with various optical grinding and polishing operations [8–9]. Thus, there is interest in the investigation of additional organoeuropium complex-doped gel systems, as novel optical media may be prepared in useful embodiments via this route. The study of alternate compositions is especially salient if guest-host interactions are found to make an important contribution to the overall luminescence behavior of these systems, as the chemical environment is readily modified within ORMOSIL media. The research presented herein extends our earlier work on the silica and acrylate ORMOSIL gels to include an “epoxy-diol” ORMOSIL composition. Present efforts are focused on the assessment of dopant chemistry, dopant concentration, and dopant-matrix interaction effects in rare-earth doped silicate materials.

2. Syntheses and Characterization

The tris(4,4,4-trifluoro-1-(2′-thienyl)-1,3-butanedionato-O, O′)europium(III) trihydrate, Eu(tfa)₃·3H₂O, Eu(tfa)₃, was obtained from Kodak and used without further purification. The structure of the complex [10] is shown in Figure 1.

The epoxy-diol ORMOSIL host (matrix E) was prepared under mild acidic conditions using tetramethoxysilane (TMOS), 3-glycidoxypropyltrimethoxysilane (GPTMS), ethylene glycol, and water as previously described [1–2, 11–12]. Molar ratios of 4.5 H₂O:1 TMOS:1 GPTMS:1 ethylene glycol were employed. Silica (matrix S) specimens were prepared,
Fig. 1 Chemical structure of Eu(tta)₃·3H₂O (modified from ref. 5).

according to the "sonogel" procedure described by Esquivias and Zarzycki [11], using mild acid catalysis and a 4 H₂O:1 TMOS molar ratio. Prior to doping, the precursor ORMOSIL sol was hydrolyzed overnight; the silica sol was hydrolyzed for only approximately 10 minutes. Doping was achieved by the addition of aliquots of EuCl₃ or Eu(tta)₃ dissolved in methanol at five times the desired concentration. The resulting solutions were cast into transparent polystyrene cuvettes and kept in covered containers at room temperature until the onset of gellation. Aging and drying were allowed to proceed under ambient conditions over a period of several weeks. Matrix E and matrix S specimens were found to retain approximately 60% and 30%, respectively, of their initial volumes. Solid-state samples, having final calculated number densities of approximately 2 x 10¹⁸ cm⁻³, were selected from a pair of concentration series for study.

Luminescence (emission and excitation) spectra were measured using a Spex Industries Model F112 spectrofluorimeter. Absorption spectra were determined using a Cary 5 spectro-photometer. All spectra were corrected for instrumental response. Fluorescence lifetimes were measured by exciting the samples, while positioned in the spectrofluorimeter sample chamber, with radiation from a Lambda Physik LPD 500 fs dye laser (pumped by a Lambda Physik LEXTRA 200 excimer laser oscillating at 308 nm). Two excitation wavelengths were utilized: 441 nm and 543 nm. Temporally-resolved luminescence transients were characterized through the use of a Tektronix model 2440 digital storage oscilloscope (500 MHz bandwidth) in conjunction with the spectrofluorimeter’s R928 PMT output. Relative quantum efficiencies were calculated by the reference technique described elsewhere [1].

3. Discussion of Results

Figure 2 through 5 show representative emission spectra for EuCl₃ and Eu(tta)₃ in the different host matrices. Relative emission intensities have been normalized with respect to that of Eu(tta)₃ in the epoxydiol ORMOSIL host, Eu(tta)₃·3E, excited at 408 nm (Fig. 5). The spectra shown in Figures 2 and 3 represent emission upon excitation at 464 nm, corresponding to the ⁷F₀ → ⁵D₂ absorptive transition of Eu³⁺; this wavelength was chosen because it lies outside the main absorption band of the (tta)⁻ ligand, thereby facilitating the direct comparison of europium-only transitions as a function of the local chemical environment. In Figures 4 and 5, the samples were excited at higher photon energies; EuCl₃ (Fig. 4) was excited at 393 nm, corresponding to the “E” band of Dickie and Crosswhite [13] (later designated ⁷F₀ → ⁵L₆ [14]) which was found to be the most intense excitation band of the inorganic salt. The emission spectrum of Eu(tta)₃ (Figure 5) was recorded using an excitation wavelength (λₑₓ) of 408 nm, which corresponds to the maximum of the organo-rare earth complex excitation peak. This decay mechanism is associated with excitation of the organic ligand and subsequent radiative relaxation from the incorporated Eu³⁺ ion following ligand-to-metal energy transfer (LMET) [3, 15]. This emission is the most intense observed in the present study and has therefore been assigned the value of 1.00 normalized relative emission intensity units. The 393 and 408 nm excitation wavelengths were selected so that maximum luminescence intensities could be quantified as a function of ligand and matrix interactions. In all cases the observable emission peaks result from relaxation out of the ⁵D₀ excited state of Eu³⁺ to the first five levels of the ⁷F ground manifold; the ⁵D₀ → ⁷F₂ emission is the one typically associated with laser behavior in Eu³⁺-based systems [13].

Changes in the local chemical environment, either by variation of the ligand or gel matrix composition, were found to leave the essential spectral features of europium(III) essentially unchanged as a function of the local conditions, although distinct perturbations to the radiative branching ratios were observed. There were, however, pronounced chemistry-related effects on the relative emission intensity characteristics. Under a given set of conditions (matrix composition and excitation band), the Eu(tta)₃ complex’s emission was found to be at least 30 and as much as
Fig. 2. Fluorescence emission spectrum of EuCl₃, 2.2 × 10¹⁹ cm⁻³⁻³ in epoxy-diol ORMOSIL (E) and 2.1 × 10¹⁹ cm⁻³⁻³ in silica (S) gels, excited at the ⁷F₀ → ⁵D₂ transition of Eu³⁺ near 464 nm. Spectrum E is offset 0.001 normalized relative intensity units. All emission spectra in Figure 2-5 are normalized to Eu(tfa)₃ in matrix E, excited at 408 nm (Fig. 5).

2000 times more intense than that of EuCl₃ in equivalent matrices (compare Figure 2 with Figure 3 and Figure 4 with Figure 5). This behavior is consistent with previously described observations, and arises from the alteration of the immediate local environment of Eu³⁺ by the highly asymmetric chelating ligands and from the relatively efficient LMET mechanism [1–2].

Regarding matrix effects, Eu(tfa)₃ luminescence was observed to be at least twice as intense in the ORMOSIL matrix as in the silica matrix (see Figure 3 and 5). This indicates that the dense, organically modified
silicate host tends to promote radiative decay from the metal-organic complex to a greater extent than when it is entrapped in a lower density, purely inorganic host; this was observed, however, to be a relatively small effect. The radiative intensity of EuCl$_3$ was found to be much more heavily influenced by matrix effects, as shown in Figure 2 and 4. The relative luminescence intensities of the salt increased by factors ranging from 25 to nearly 100 upon incorporation into the ORMOSIL host, a much greater difference than that observed in the case of the metalorganic complex (Fig. 7). This discrepancy has been attributed to a fundamental difference between the guest-host interactions associated with the two dopant species. Eu(tfa)$_3$, by nature of
its bulky, shielding ligands, is substantially less sensitive to the local environment than EuCl$_3$, whose free Eu$^{3+}$ ion may interact to a much greater extent with the surrounding matrix. In the case of EuCl$_3$:S, there is extensive quenching which is presumably due to the presence of abundant hydroxyl species. EuCl$_3$:E, however, is substantially less quenched, despite the large hydroxyl activity in such materials. It appears that chelation between the Eu$^{3+}$ and select groups of the epoxy-diol ORMOSIL may make an important contribution in this system. It is likely that interactions with $\alpha,\beta$-dioxyl or other $\alpha,\beta$-dioxy groups, present in the matrix E medium, may be responsible for such behavior. Similar effects were not observed in the case of EuCl$_3$:doped acrylate ORMOSIL hosts [2], indicating that an inherently different dopant-matrix interaction exists in the EuCl$_3$:E material.

Figures 6 and 7 show the excitation spectra of EuCl$_3$ and Eu(tta)$_3$ associated with emission from the $^5$D$_0 \rightarrow ^7$F$_2$ transition of Eu$^{3+}$ ($\lambda_{em} = 612$ nm). In contrast to Figures 2–5, which indicate that the Eu$^{3+}$ emission processes in the two dopant species are fundamentally similar (although again subject to perturbations in the branching ratios), Figures 6 and 7 indicate that the excitation processes which populate the Eu$^{3+}$ $^5$D$_0$ level in the two dopants are distinctly different at wavelengths shorter than 450 nm. The broad, strong excitation band of Eu(tta)$_3$ has been found to correspond to the red-most edge of the complex's intense ligand absorption band, which is shown in the case of a thin film in Figure 8. The absorption band of the thin film contains at least two components, centered at 341 nm and approximately 350 nm, but in bulk samples the red edge extends out to well beyond 400 nm. Europium(III) fluorescence from excitation of Eu(tta)$_3$ in this region reportedly originates from the ligand-to-metal energy transfer (LMET) mechanism, [3, 10]. The LMET band nearly obscures Eu$^{3+}$ features in this region, including the strong $^7$F$_{5} \rightarrow ^5$I$_{6}$ transition (393 nm) clearly visible in the case of EuCl$_3$:doped gels (Fig. 6). Outside this region, however, the $^7$F$_{0} \rightarrow ^5$D$_{0,-2}$ Eu$^{3+}$ features are visible and subject to similar matrix effects—both dopants are clearly more luminescent in the epoxy-diol ORMOSIL than in the silica gel. Significantly, the Eu(tta)$_3$ spectra (Fig. 7) show that, as noted above, matrix composition affects overall excitation intensity but causes little or no perturbation to spectral features as the (ttf)-ligands largely shield the Eu$^{3+}$ ion from the surrounding matrix.

Conversely, the EuCl$_3$ spectra (Fig. 6) show that relatively free Eu$^{3+}$ ions can interact extensively with the host matrix. In the EuCl$_3$:S sample spectrum, all the observable features correspond to transitions from the $^7$F$_{0}$ ground state to well-documented Eu$^{3+}$ energy
Fig. 7. Fluorescence excitation spectrum of Eu(tfa)$_3$, $2.2 \times 10^{19}$ cm$^{-3}$ in matrix E and $2.1 \times 10^{19}$ cm$^{-3}$ in matrix S, viewed at the $^5D_0 \rightarrow ^7F_2$ transition of Eu$^{3+}$ near 612 nm. Spectrum E is offset 0.2 normalized relative intensity units.

levels [13–14], most notably the $^5L_6$ "E"-band. The EuCl$_3$:E sample spectrum also shows the predominant $^7F_0 \rightarrow ^5D_{0-3}$ and $^7F_0 \rightarrow ^5L_6$ transitions, with an increased intensity indicative of reduced quenching effects. More interesting, however, is the appearance of a new, broad, intense excitation band centered at approximately 350 nm. This band resembles the LMET band of Eu(tfa)$_3$, yet does not completely overwhelm the sharp Eu$^{3+}$/$f$ transition features; in particular, the $^5D_4$ and $^5H_6$ peaks are still discernible. It appears that the epoxy-diol ORMOSIL matrix either (a) transfers energy to the Eu$^{3+}$/$D_0$ level by LMET (or some related mechanism) or (b) it activates Eu$^{3+}$ levels in this region (330–390 nm) which are not normally associated with transitions from the ground state (i.e., $^5G_{2-3}$, $^5L_{7-10}$, and $^5H_{9-5,7}$). In either case, as indicated by emission spectroscopy, chelation between Eu$^{3+}$ and oxygen-containing groups on the side chains of matrix E is a probable cause of this new excitation band.

Table 1 displays the optical parameters of quantum efficiency, relative emission intensity, and fluorescence lifetime for the four dopant-matrix compositions. Each composition was excited at the Eu$^{3+}$/$F_0 \rightarrow ^5D_2$ peak (464 nm) and at two higher energies (408 and 393 nm), as before. Quantum efficiency values indicate that both dopants are significantly less quenched in matrix E than in matrix S, as expected from the luminescence spectroscopy data. The quantum efficiencies of Eu(tfa)$_3$:E were found to be quite high for materials of this sort, and appear to have some promise in terms of potential optical source applications.

A description of the integrated emission intensity values under consideration as they more effectively quantify the radiant or "brightness" of the specimens. Such comparisons are particularly useful in the case, for example, of materials to be used as phosphors. When excited at 464 nm, where the only differences in energy absorption between Eu(tfa)$_3$ and EuCl$_3$ arise from
Table 1. Optical parameters for all four dopant-matrix compositions. Quantum efficiency and normalized relative integrated emission intensity for each sample at two excitation values, the first at 5 F_0 → 5 D_2 transition of Eu^{3+} near 464 nm, and the second at the "E" band or 5 F_0 → 5 L_4 transition of Eu^{3+} near 393 nm for EuCl_3 or at the maximum value of the LMET band (≈408 nm) for Eu(tfa)_3. The fluorescence lifetimes and rise times of the 5 D_0 → 7 F_2 emission were measured by laser excitation. EuCl_3 was excited at 543 nm, roughly corresponding to the relatively weak 7 F_0 → 5 D_1 transition of Eu^{3+}. Eu(tfa)_3 was excited at 441 nm, which lies just within the red wing of the LMET band.

<table>
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<tr>
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<th>EuCl_3:E</th>
<th>EuCl_3:S</th>
<th>Eu(tfa)_3:E</th>
<th>Eu(tfa)_3:S</th>
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<tr>
<td>Number Density (cm^{-3})</td>
<td>2.2 \times 10^{19}</td>
<td>2.1 \times 10^{19}</td>
<td>2.2 \times 10^{10}</td>
<td>2.1 \times 10^{19}</td>
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<td>Quantum Efficiency, \lambda_{ex} 464 nm</td>
<td>10.6%</td>
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<td>Quantum Efficiency, \lambda_{ex} 393 or 408 nm</td>
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<td>12.3%</td>
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<tr>
<td>Relative Integrated Emission Intensity, \lambda_{ex} 464 nm</td>
<td>1.15 \times 10^{-2}</td>
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<td>6.72 \times 10^{-2}</td>
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<tr>
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<td>Fluorescence Rise Time (ns)</td>
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ligand modification of the immediate environment of Eu^{3+}, Eu(tfa)_3:E specimens had 7 times greater integrated intensity values than Eu(tfa)_3:S samples, and EuCl_3:E materials were found to have integrated emission intensity values which were 16 times more intense than EuCl_3:S materials. Relative to ligand effects, the Eu(tfa)_3:E specimen had an integrated emission intensity which was 41 times more intense than the comparable EuCl_3:E system. Thus, quenching behavior is much more predominant in the epoxy-diol ORMOSIL host.

The fluorescence lifetime of the 5 D_0 → 7 F_2 relaxation event was also studied in the four dopant-matrix systems. The lifetime of EuCl_3 in matrix S, 116 \mu s, is very close to that reported for crystalline EuCl_3·6H_2O, 122 \mu s [16] In matrix E, however, the lifetime was observed to increase by a factor of 6, up to a value of 710 \mu s, indicating a significantly different chemical environment for the Eu^{3+} ion. This increase is associated with the elimination of one or more pathways for nonradiative decay events out of the S D_0 state. A lifetime of 710 \mu s, in fact, comparable to those reported for similar concentrations of Eu(CIO_4)_3 (775 \mu s) and Eu(NO_3)_3 (680 \mu s) in acetonitrile (CH_3CN) [17], a solvent which lacks the hydroxyl groups which are the most probable quenching agents in aqueous and silicate environments. The lifetime of Eu(tfa)_3 does increase in matrix E relative to matrix S, but the effect is not as dramatic as for EuCl_3. This indicates that the increase is presumably due to the overall reduced level of quenching in matrix E rather than a drastic change in Eu^{3+} environment. This is consistent with other observations indicating that the (tfa)-ligand effectively shields Eu^{3+} from the surrounding matrix.

4. Summary and Conclusions

The luminescence behavior of EuCl_3 and a metalorganic complex, Eu(tfa)_3, doped into sol-gel-derived hosts have been studied. Comparisons between matrix- and ligand-associated interactions have been presented and compared with previously observed results using an acrylate ORMOSIL. In both host matrices, Eu(tfa)_3 exhibits higher quantum efficiencies and greater emission intensities than comparable EuCl_3-doped specimens. These increases are attained without significant changes to the fundamental features of the Eu^{3+} emission spectrum. Introduction of the LMET band, however, makes excitation via broad-band pump source a much more efficient method by which to excite Eu(tfa)_3 than the comparable EuCl_3. These factors make Eu(tfa)_3 an interesting candidate for use as an optical source.

Eu(tfa)_3- and EuCl_3-doped epoxy-diol ORMOSIL hosts featured clear spectroscopic differences with respect to silica systems. In the case of Eu(tfa)_3, the most significant difference is the reduction in quenching interactions as demonstrated by increases in quantum efficiency, integrated intensity, and fluorescence lifetime. For EuCl_3, the preceding effects are augmented by the possible Eu^{3+} ligand-like modification which introduces a new excitation band, offering some of the characteristics noted for the fully complexed Eu(tfa)_3. The anomalously long lifetime observed for
the EuCl₃·E system is not well understood, and bears further study.

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References