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Stability of sol-gel derived glass coated Eu-complex using deuterated methanol

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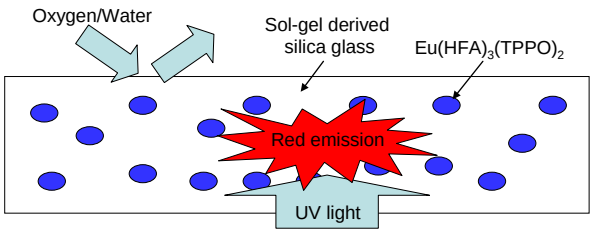
A high-stability Eu-complex has been achieved by coating with a silica glass via a low temperature sol-gel process using deuterated methanol. A three-dimensional glass network protects Eu-complex from free-oxygen and/or water to change the ligand structure. In addition, the chemical bond of deuterated Eu-complex is more stable than that of the conventional Eu-complex. Therefore, we achieved the high-thermal stability Eu-complex encapsulated by a sol-gel derived silica glass using deuterated methanol instead of ethanol.



1. Introduction White light-emitting diodes (LEDs) have attracted much attention as many lighting applications due to their low power consumption and brightness compared to a conventional fluorescent lamp. In general, a white LED consists of a blue LED and a yellow phosphor for practical use. However, the controllability of emissive color is not high enough to achieve various color temperature. Therefore, the white LED with the combination of an ultraviolet (UV) LED and several phosphors was investigated to realize various white LEDs.

Previous studies made on red phosphors indicated that these phosphors generate the red emission by irradiating UV light [1]. However, the optical characteristics of reported materials need to improve for a practical white LED application. In these red phosphors, Eu-complex is most attractive from the point of view of several optical characteristics, such as sharp red emission peaks, high absorption coefficient at the UV wavelength region, and high PL quantum efficiency [2,3]. The organic ligand of Eu-complex absorbs the UV light and photo-induced exitons move to the Eu ion. As a result, the Eu complex generates the red emission corresponding to the $^5D_0$-$^7F_2$ transition of Eu^{3+} ion by the UV light irradiation [3].

One important problem with Eu-complexes is the stability in the presence of UV light irradiation [4, 5] and high temperature annealing [6]. The strength of bond between the Eu ion and the organic ligand is lower than that of a conventional inorganic material. Therefore, the chemical structure of Eu-complex changes easily. As a result, the PL intensity decreases by the decomposition of organic ligand.

There exits much literature on encapsulation techniques using the sol-gel process to solve the above-mentioned problem [7-9]. The previous research indicated that the high thermal stability up to 140 ℃ was realized by encapsulating the sol-gel derived silica glass around Eu-complex [6]. However, the further increase of thermal stability is necessary for practical use. This is because the fabrication process of white LED needs approximately 150 ℃, and Eu-complex will be decomposed during the fabrication process.

In this letter, we demonstrated the high-thermal stability of a hybrid organic-inorganic emitting film combining Eu-complex and sol-gel derived silica glass. The PL quantum efficiency was almost same up to 180 ℃, and the

higher thermal stability was achieved. The most important finding is that deuterated methanol is an available organic solvent for the sol-gel encapsulation. The Eu-complex is deuterated by adding deuterated methanol, and it suppressed the vibration of organic ligand during the annealing process [10, 11]. As a result, thermal decomposition of the Eu-complex does not occur by the deuterated chemical bond of Eu-complex, resulting in the high-thermal stability.

2. Experimental At first, phenyltrimethoxysilane (PTMS) and diethyldimethoxysilane (DEDMS) were mixed with a magnetic stirrer. Then, bis-triphenylphosphine oxide)(tris-hexafluoroacetylacetonato) europium(III) ($Eu(HFA)_3(TPPO)_2$) powder was injected in the above-mentioned solution, and the solution was mixed for 30 minutes to dissolve completely. Finally, the resulting solution was mixed with distilled water and deuterated methanol. The concentrations of PTMS:DEDMS: distilled water:deuteraterd methanol:$Eu(HFA)_3(TPPO)_2$ was 1:0.5:25:5:0.0015. The synthesis process for $Eu(HFA)_3(TPPO)_2$ was described in a previous paper [12].

The solution was mixed at 25 °C for 72 hours, and it was further mixed at 100 °C for 3 hours to remove distilled water and deuterated methanol. The rotation speed was maintained at 400 rpm by a magnetic stirrer for all the mixing processes. Finally, the solution was spin-coated at a rotation speed of 2000 rpm for 60 second. For comparison, we used ethanol instead of deuterated methanol, and other fabrication conditions were same as the above-mentioned encapsulated sample.

To investigate the thermal stability of the sol-gel derived glass coated $Eu(HFA)_3(TPPO)_2$, the fabricated sample was annealed at the temperature range from 120 to 220 °C with a hotplate for 2 hours. For comparison, $Eu(HFA)_3(TPPO)_2$ powder was dissolved in tetrahydrofuran (THF), and the solution was also spin-coated and annealed under the same conditions as the encapsulated samples.

The photoluminescence/photoluminescence excitation (PL/PLE) spectra were measured with a luminance spectrometer (FluoroMax, Horiba Jovin Yvon). In addition, the PL quantum yield was estimated by a luminance quantum yield measurement system (QEMS-2000, Systems Engineering Inc.), which consists of an integrated sphere and an excited UV LED with a center wavelength of 375 nm. In this approach, the quantum yield was given by the integrated PL intensity of the sample excited by the UV-LED divided by the decrease in the excitation intensity caused by inserting the sample into the integrated sphere. The optical degradation characteristics were estimated as the PL intensity change while irradiating with UV with a center wavelength of 350 nm and the optical intensity of 6.95 mW/cm^2.

3. Results and discussion Figure 1 shows the PL and PLE spectra of $Eu(HFA)_3(TPPO)_2$ encapsulated by a sol-gel process. The annealing tepmperatures of both samples was 120 ℃. The excitation wavelength of the PL spectrum was 350 nm. The PL spectra of all the samples clearly indicate that the sol-gel derived glass encapsulated $Eu(HFA)_3(TPPO)_2$ generated sharp red emission with a center wavelength of 614 nm. The peak wavelength of the PL spectrum corresponds to the transition between $^5D_0$ and $^7F_2$ [2].

The PLE spectrum was monitored at 613 nm, corresponding to the peak wavelength of the measured PL spectrum. Both encapsulated samples showed a broad PLE spectrum below 400 nm compared to the spin-coated sample, suitable for white LEDs with near-violet excitation. In general, the PLE spectrum of Eu-complexes is affected by the energy transfer from the organic ligand to the Eu^{3+} ion [13]. Therefore, this result indicates that the molecular structure of $Eu(HFA)_3(TPPO)_2$ was not changed during the sol-gel process even though deutrated methanol was used in the starting solution of sol-gel process. As a result, the broad PLE spectrum was obtaiend for the sol-gel derived silica glass encapsulated $Eu(HFA)_3(TPPO)_2$.

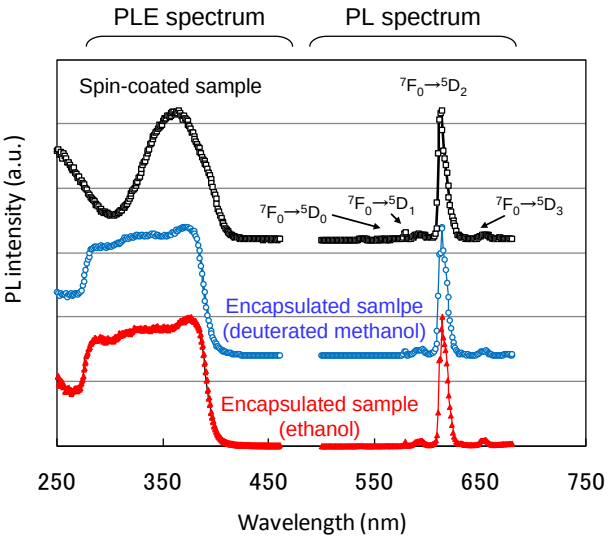


Figure 1 PL and PLE spectra of spin—coated and encapsulated sample using deuterated methanol and ethanol, respectively.

In Fig. 2, we show the relationship between the PL quantum yield for 375 nm excitation and the annealing temperature. Since the organic ligands in $Eu(HFA)_3(TPPO)_2$ are decomposed by the annealing process, the PL quantum yield will decrease due to the low energy-transfer efficiency between the organic ligand and the Eu^{3+} ion. Therefore, we can estimate the thermal stability of $Eu(HFA)_3(TPPO)_2$ by measuring the PL quantum yield.

The PL quantum yield of the spin-coated sample was found to rapidly decrease with increasing annealing temperature due to oxidization of the organic ligand structure in the ambient air. On the other hand, both encapsulated samples exhibited enhanced thermal stability compared to the spin-coated sample. It is noted that the sol-gel derived silica glass protects to oxidize the organic ligand, resulting in the high-thermal stability.

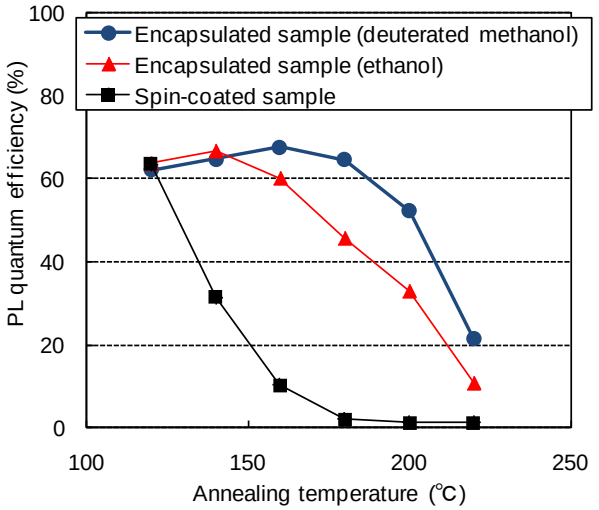


Figure 2 Relationship between the PL quantum yield for 375 nm excitation and the annealing temperature.

In addition, the thermal stability was further improved by using deuterated methanol, as shown in Fig. 2. The experimental result indicates that the Eu-complex was deuterated by mixing with deuterated methanol in the starting solution of the sol-gel process. In previous papers, the high frequency vibration of C-H and O-H bonds are suppressed by the deuteration of organic ligand [14], and the deuterated $Eu(HFA)_3(TPPO)_2$ has no high-frequency vibration mode of C-H and O-H bonds [10]. Therefore, we obtained the thermally stable Eu-complex in combination with the encapsulation using the sol-gel derived silica glass and the low vibration of organic ligand via a deuterated chemical structure.

The most important finding is that the PL quantum yield remained equal to the original value of approximately 60 % below annealing temperature of 180 °C, and monotonously decreased with increasing the annealing temperature above 200 °C. The fact that no degradation occurred at temperatures less than 180 ℃ indicates that the sol-gel glass protects the $Eu(HFA)_3(TPPO)_2$ against oxygen.

Figure 3 shows the change in the PL intensity for the spin-coated sample and the encapsulated sample using deuterated methanol under 350 nm excitation. The annealing temperature of encapsulated sample was ranged from 120 to 180 ℃. The most important result is that the encapsulated sample annealed at 120 ℃ was achieved the highest stability in this study, with a relative PL intensity of 0.81 following 90 min of emission. However, the PL intensity of the spin-coated sample was rapidly decreased by the UV light irradiation and a relative PL intensity was 0.46 after the 90 min emission. The fact indicates that the chemical structure of $Eu(HFA)_3(TPPO)_2$ was decomposed by the UV light irradiation.

Similar to the annealing temperature dependence of PL quantum yield, the long-term stability against UV light irradiation was also improved by encapsulating using sol-gel derived glass. This is because the sol-gel derived silica glass protects the chemical reaction between the organic

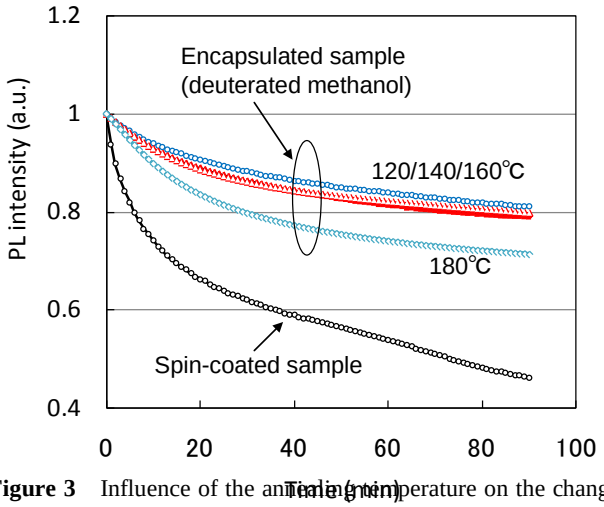


Figure 3 Influence of the annealing temperature on the change in PL intensity for the encapsulated sample under 350 nm excitation at 6.95 mW/cm^2.

ligand of $Eu(HFA)_3(TPPO)_2$ and oxygen with the UV light irradiation. In addition, the encapsulated sample annealed at 180 ℃ had lower stability than other samples annealed at the low temperature due to structural changes to $Eu(HFA)_3(TPPO)_2$ caused by the high temperature annealing.

In summary, We demonstrated an organic-inorganic composite film composed of $Eu(HFA)_3(TPPO)_2$ encapsulated by sol-gel glasses, and studied its thermal and long-term stability against UV light irradiation. Improved thermal stability was successfully achieved by adding deuterated methanol to suppress the vibration oriented non-radiative recombination, resulting in the efficient energy transfer to Eu^{3+} ion. The PL quantum yield was almost independent of the annealing temperature below 180 ℃. In addition, the reduction of PL intensity during UV light irradiation was also suppressed by encapsulating in sol-gel glass, which was fabricated using deuterated methanol.

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