

Paper

Improvement in Durability of Red Phosphor Encapsulated by Sol-Gel Glass for Use in White Light-Emitting Diodes

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ABSTRACT

Transparent glass films with homogeneously doped light emissive molecules can be prepared by using the sol-gel process. As part of our work on improving the durability of water-soluble polysilanes against UV light irradiation, we fabricated $\text{Eu}(\text{TTA})_3\text{Phen}$ -doped sol-gel glasses and studied their optical characteristics. Using a three dimensionally dense glass network protects the Eu complex from free oxygen and water in an ambient and also improves the durability without any loss of light output. By adding the $\text{Eu}(\text{TTA})_3\text{Phen}$ beyond the limit of solubility in a starting solution, we demonstrated that the glass encapsulation prevents oxidation of the Eu-complex and also preserves its excitation intensity at a wavelength of 400 nm.

KEYWORDS: sol-gel glass, phosphor, rare-earth complex, hybrid material

1. Introduction

The light-emitting diode has advantages such as high luminous efficacy, low power consumption, and long life compared to the incandescent and fluorescent lamps that have been widely used in our daily life. For example, its conversion efficiency from electricity to light is said to exceed 30% depending upon wavelength. Because of these merits, it is widely used in such applications as the backlights of the electronic devices such as mobile telephones, digital video cameras, personal digital assistants (PDA), and so on, as well as large-scale displays, road indicators, and so on. In the recent years, it has been expected to become widely used as a light source for traffic signals, automotive headlights, and general illumination.

The LED has a basic structure of a p-n junction in which semiconductor layers of p-type and n-type, each of which is a charge carrier of electrons or holes, are stacked. The electrons and holes charged from the electrodes flow through the different energy bands (conduction band and valence band) and their mixture zone is generated in the vicinity of the p-n junction, where they pass through due to the voltage in the positive direction. By recombination of the electrons and holes in this mixture zone, the photons that hold the energy equivalent to the energy level differential between the conducting band and the valence band (the band gap) are emitted. Therefore, light of visible-range wavelengths can be obtained from LEDs by using semiconducting materials

with different band-gap energies in a highly efficient way.

Among LEDs, the white LED especially has been expected to be the solid-state illumination light source that can replace the incandescent lamp. One method to realize a white LED has been the method of creating white by combining the emissions from three LEDs, red, green, and blue, which are the three primary colors of light. However, this method requires three LEDs and has the problem that the emitted color changes depending on the viewing angle. Also, three drive circuits for the LEDs are required, which is a big issue for practical applications in view of cost and size.

Meanwhile, another method of combining a blue LED and a phosphor is becoming common at this time. In this method, the phosphor absorbs the emission from the blue LED and emit the light in the spectrum from red to green, and a pseudo-white emission can be realized by combining this light and the blue light passing through the phosphor. However, this method has the defect in that the variability of color temperature between LEDs is large because of the difficulties during manufacturing of accurately controlling the ratio of the blue light transmitted through the phosphor. Also, the delicate control of the color temperature is linked to difficulties in realizing a white LED with high color rendering properties. Hence, a method to generate a white light by exciting the phosphors to emit red, green, and blue by a near ultra-violet LED, similar to the case

of fluorescent lamps, has been studied recently¹⁾. A group of phosphors in the Eu complex has been known to have red emissions of high purity upon excitation by near ultra-violet LEDs, and especially Eu(TTA)₃Phen, which has a high efficiency in wavelength conversion, has been expected as a phosphor for white LEDs. Here, TTA is 2-thenoyltrifluoroacetone and Phen is 1,10-phenanthroline. However, the Eu complex deteriorates quickly in the air, and this has been a problem for long-term reliability²⁾.

As a method to solve this problem, it is considered that the encapsulation technology with sol-gel glass can be applied, which our group has been studying. So far, we have reported on an improvement in the reliability of the organic thin film of water-soluble polysilane encapsulated with sol-gel glass²⁾. In general, the polysilane is a one-dimensionally chained macromolecule with silicon as the main chain, that has high hole mobility and high oscillator strength when excited owing to the delocalization of the σ bond³⁾⁴⁾, and there are reports on organic EL (electroluminescent) devices with near ultra-violet emissions⁵⁾⁶⁾. Also, we have demonstrated a highly efficient energy acceptor emission that uses the highly efficient resonance energy transfer process between heterogeneous polysilanes⁷⁾ and between polysilane and organic dyes⁸⁾. Furthermore, we have reported on EL devices for the visible range (red, green, blue, and white) made by thin spin-coated films of polysilane and organic dyes mixtures, that utilized the highly efficient energy transfer between the polysilane and the organic dyes⁶⁾⁹⁾. However, when ultra-violet light is continuously radiated, the silicon main chain in this polysilane is easily oxidized due to the reaction with oxygen in the atmosphere, as is the case with the Eu complex. Thus, there are difficulties in its stable use for a long time period in the atmosphere. For this problem, we have demonstrated that the deterioration of its emission properties can be suppressed significantly by means of encapsulating the water-soluble polysilane with sol-gel glass²⁾⁶⁾.

These results show that the sol-gel glass functions to protect the polysilane encapsulated in it from oxygen in the atmosphere. Accordingly, it is considered that a long-term stable Eu complex can be realized if the Eu complex can be enclosed in the sol-gel glass. Thus, we have tried to encapsulate the Eu(TTA)₃Phen, the red emission phosphor, in the sol-gel glass as the initial stage of study. In this paper, the results of suppressing the deterioration of the fluorescence intensity under ultra-violet irradiation by means of encapsulation of the Eu complex in the sol-gel glass are presented.

2. Optical properties of Eu(TTA)₃Phen

2.1 Regarding to the Eu(TTA)₃Phen

In the rare-earth complexes that have Eu and so on as core rare-earth ions, the ligands of the π conjugated system increase the light absorption efficiency and transfer this absorbed energy to the rare-earth ions. Also, highly efficient emission is expected because of the existence of the ligands around the rare-earth ions, which segregate the rare-earth ions in the central portion from the exterior quenching agent and reduce the opportunity of concentration quenching. Especially, since the red phosphor Eu(TTA)₃Phen (molecular weight: 995.7 g/mol) used in this study has a higher absorption efficiency and smaller concentration quenching compared to the simple body of Eu³⁺, it is expected to make a red phosphor with high chromatic purity and high wavelength conversion efficiency capable of excitation by near ultra-violet LEDs. Figure 1 shows the molecular structure of Eu(TTA)₃Phen as well as its photoluminescence (PL) spectrum and photoluminescence excitation (PLE) spectrum. Here, a fluorescence spectrophotometer (JASCO Corporation, FP-777) was used for measuring PL and PLE. The wavelength of the excitation light source for the PL spectral measurement was set at 400 nm. Since the central wavelength of the PL spectra was 612 nm, it is known that this Eu complex shows red emission. Also, the emission wavelength for measuring the PLE spectrum was set at 612 nm. From the PLE spectrum, it is known that strong emission intensity is obtained with an excitation wavelength below 380 nm. In other words, it is considered that high luminous efficacy with this red emission phosphor can be realized when an ultra-violet LED is used for the excitation light source.

The molecular structure of Eu(TTA)₃Phen is composed of ligands with many coordinate positions, such as TTA (2-thenoyltrifluoroacetone) and Phen (1,10-phenanthroline), and this is a metal-chelate compound or a complex in which there are more than two donor

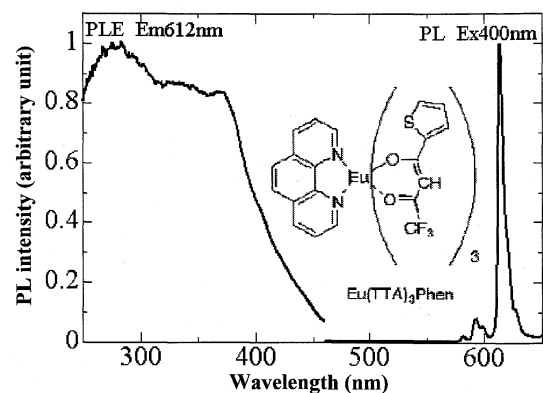


Figure 1 Molecular structure of Eu(TTA)₃Phen and PL/PLE spectra of Eu(TTA)₃Phen powders

atoms in one ligand with certain intervals. Since the stability constant is the equilibrium constant of a balanced reaction, when the stability constant is considered from the standpoint of thermodynamics, the standard free energy difference ΔF^0 between the original series and the formed series of a chemical reaction can be expressed by the following equations (1) and (2).

$$\Delta F^0 = -RT \ln K_{MA} \dots \dots \dots (1)$$

$$\Delta F^0 = \Delta H^0 - T \Delta S^0 \dots \dots \dots (2)$$

Here, R is the gas constant, T is the temperature, and K_{MA} is the stability constant. Thus, the stability constant of the chelate compound depends upon changes in enthalpy and changes in entropy from the standpoint of thermodynamics. It is considered that the chelate compound is more stable compared to the complex with monodentate coordination because of an entropy increase due to the formation of the chelate ring.

2.2 Fabrication of the Eu(TTA)₃Phen thin film

The Eu(TTA)₃Phen has a problem similar to other Eu complexes in that the fluorescence intensity is reduced by continuous ultra-violet radiation and it is difficult to obtain stable emission for a long time period. Hence, the temporal changes of the thin film spin-coated with Eu(TTA)₃Phen was evaluated. The fabrication conditions of the spin-coated thin film are as follows. First, the Eu(TTA)₃Phen was dissolved in dimethylformamide (DMF). Then, it was dropped on the silica glass after sufficient mixing, and then spin-coated under conditions of 1500 revolutions per minute for 60 seconds. The temporal change in the fluorescent strength of the spin-coated thin film fabricated under such conditions was measured in the condition of being radiated by ultra-violet light of 400 nm and intensity of 0.21 mW/cm².

2.3 Temporal changes of the fluorescence intensity of the Eu(TTA)₃Phen thin film

Figure 2 shows the temporal changes of the fluorescence intensity of the Eu(TTA)₃Phen thin film spin-coated on silica glass under continuous radiation of the ultra-violet. Here, the measurement was made both in air and in a vacuum of 5×10^{-4} Pa separately. The tendency that the fluorescence intensity decreases in a straight line while radiation of the ultra-violet continues was observed under measuring in air. For example, it reduced to 55% of the initial fluorescence intensity level after 80 minutes of ultra-violet radiation. On the other hand, there was no tendency of reduction in the fluorescence intensity over time in measuring of the spin-coated thin film in vacuum, and it was 99% of the initial fluorescence intensity after 60 minutes of elapsed

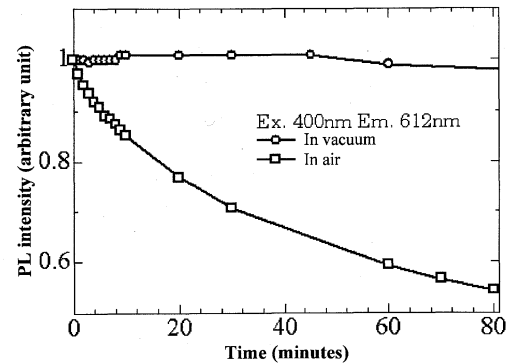


Figure 2 PL intensity change of a spin-coated film of Eu(TTA)₃Phen under 400 nm excitation in air and vacuum

time. From these results, it is considered that oxygen and moisture in the air are the factors that deteriorate the fluorescence intensity of Eu(TTA)₃Phen.

3. Fabrication of the Eu(TTA)₃Phen-doped sol-gel glass

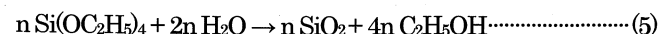
3.1 Regarding the Eu(TTA)₃Phen-doped sol-gel glass

The sol-gel method is started from a liquid solution of organic and inorganic metallic compounds, and the solution is converted to a sol in which fine particles of metal oxide or metal hydroxide are dissolved by means of hydrolysis or polymerization of the compounds in the solution. The reaction is further advanced to make it turn into a gel, and then the porous gel fabricated is heated to obtain an amorphous material, glass, polycrystalline substance, and so on. The sol-gel method enables homogeneity in low-temperature synthesis, improved productivity, synthesis with new compositions, and so on, but it has demerits in the costliness of the raw materials, residual fine pores, residual carbon and hydroxyl, the long time required for the manufacturing process, and so on¹⁰.

The reaction formula for promoting hydrolysis and polymerization using the tetraethoxysilane (TEOS) as a raw material, which is a representative raw material, is shown by following formulas (3) and (4).



Therefore, from these formulas, the hydrolysis and polymerization reactions of TEOS is expressed by following formula (5).



Also, in the sol-gel method, the silanol group remains in the matrix during the process of fabricating a glass

out of the aqueous solution, and it reduces the property of the glass. A method to solve this problem is to apply heat to the sol-gel glass at the temperature above 800°C. However, heat treatment at high temperature can not be applied to the case in which $\text{Eu}(\text{TTA})_3\text{Phen}$ and so on are contained because they thermally decompose, and a new heat treatment method suitable for the $\text{Eu}(\text{TTA})_3\text{Phen}$ -doped sol-gel glass is required. In the $\text{Eu}(\text{TTA})_3\text{Phen}$ -doped sol-gel glass, the structure, the remaining silanol group, the density of the thin film, and so on of the $\text{Eu}(\text{TTA})_3\text{Phen}$ in the sol-gel glass varies depending upon the difference in composition and heat treatment temperature. Therefore, it is considered that such parameters as the composition of the sol-gel glass and the heat treatment temperature influence the PL and PLE properties and the effect of suppressing the deterioration. The following shows the results of our study on the conditions of heat treatment effective for highly effective emission and for suppression of deterioration.

3.2 Fabrication and evaluation of the $\text{Eu}(\text{TTA})_3\text{Phen}$ -doped sol-gel glass

Figure 3 shows the fabrication process flow of the $\text{Eu}(\text{TTA})_3\text{Phen}$ -doped sol-gel glass. For fabrication of the sol-gel glass, tetramethoxysilane (TMOS), tetraethoxysilane (TEOS), ethanol (EtOH), water (H_2O), ammonium hydroxide (NH_4OH), and dimethylformamide (DMF) were used. Initially, a mixture of raw materials at the ratio of $\text{TMOS} : \text{DMF} : \text{Eu}(\text{TTA})_3\text{Phen} = 1 : 1.4 : 2 \times 10^{-3}$ was prepared. Then, this solution was mixed,

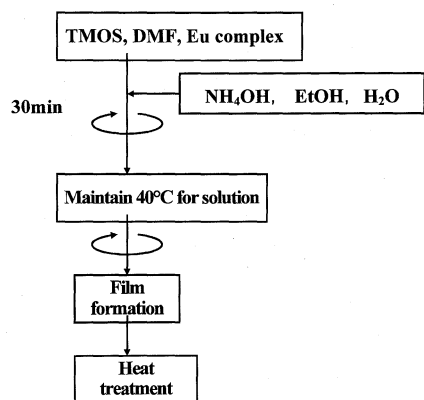


Figure 3 Fabrication process of sol-gel glass-encapsulated $\text{Eu}(\text{TTA})_3\text{Phen}$

Table 1 Composition in volume ratio of sol-gel glass encapsulated $\text{Eu}(\text{TTA})_3\text{Phen}$

Composition	Dopant ratio
TMOS:H ₂ O:EtOH:NH ₄ OH:DMF 1:10:2.7:0.00037:1.4	SiO ₂ :Eu(TTA) ₃ Phen 99.8:0.2

while being stirred, with another solution of a mixture ratio of $\text{EtOH} : \text{H}_2\text{O} : \text{NH}_4\text{OH} = 2.7 : 10 : 0.00037$. After stirring the solution for 30 minutes keeping the temperature at 40°C with a magnet stirrer, a thin film was formed on a glass substrate by dipping. The thickness of the fabricated thin film was around 1 mm. After that, the $\text{Eu}(\text{TTA})_3\text{Phen}$ -doped sol-gel glass was fabricated by heat treatment in air. Here, the composition of the sol-gel glass and the doped density of the $\text{Eu}(\text{TTA})_3\text{Phen}$ are as shown in Table 1.

The PL and PLE spectra as well as the temporal changes of the fluorescence intensity under continuous ultra-violet radiation were measured on the fabricated thin film of $\text{Eu}(\text{TTA})_3\text{Phen}$ -doped sol-gel glass. The PL and PLE spectra were measured with a fluorescence spectrophotometer (JASCO Corporation, FP-777). Also, the temporal changes in the fluorescence intensity under ultra-violet radiation were measured with the same measuring device, in which the fluorescence intensity was measured continuously while the thin film was constantly radiated with ultra-violet.

3.3 PL/PLE Spectra of the $\text{Eu}(\text{TTA})_3\text{Phen}$ -doped sol-gel glass

Figure 4 shows the measuring results of the PL spectra of the $\text{Eu}(\text{TTA})_3\text{Phen}$ -doped sol-gel glass thin films that were fabricated with varied heat treatment conditions. Here, the heat treatment conditions were set as four kinds: 2 hours at 80°C, 1 hour at 100°C, 1 hour at 120°C, and 1 hour at 140°C.

The central wavelength of the PL spectra was 612 nm in any thin film with different heat treatment condition, and it is considered that this emission is attributable to a transition of ${}^5\text{D}_0 \rightarrow {}^7\text{F}_2$ in Eu^{3+} (13). Also, the results showed that the PL intensity of a thin film heat-treated for 1 hour at 100°C showed the highest level. It is considered that the PL intensity was decreased in the case of the lower temperature due to insufficient removal of the silanol group. Also, it is assumed that the PL intensity was decreased with the higher temperatures due to changes in the $\text{Eu}(\text{TTA})_3\text{Phen}$ structure.

Then, Figure 5 shows the measuring results of the PLE spectra of $\text{Eu}(\text{TTA})_3\text{Phen}$ -doped sol-gel glass thin films on which the heat treatment was applied based on the four kinds of conditions. Here, the emission wavelength at the time of PLE spectra measuring was set at 612 nm.

From the results of the PLE spectra, it was known that the fluorescence intensity increased drastically below 400 nm in the fabricated $\text{Eu}(\text{TTA})_3\text{Phen}$ -doped sol-gel glass thin films and that they are sufficiently applicable as a red emission phosphor to be excited by ultra-violet LEDs. Also, it resulted that the thin film that was heat treated for one hour at 100°C showed the

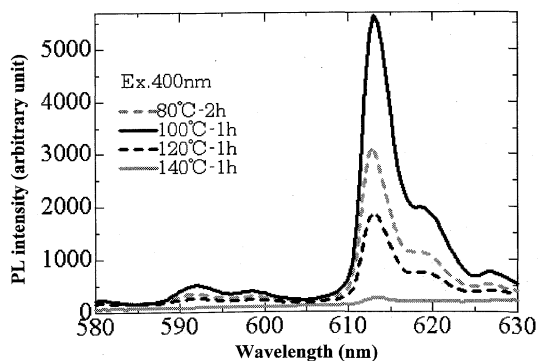


Figure 4 PL spectra of glass encapsulated $\text{Eu}(\text{TTA})_3\text{Phen}$ films annealed at different conditions

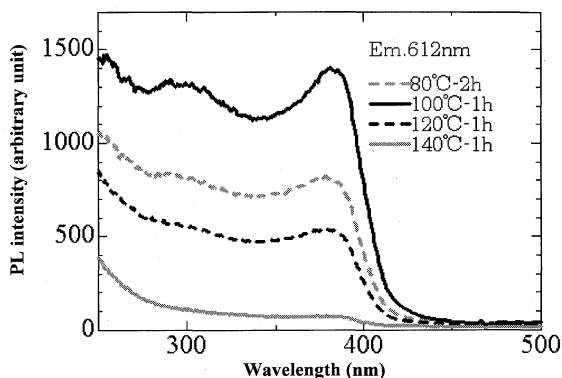


Figure 5 PLE spectra of glass encapsulated $\text{Eu}(\text{TTA})_3\text{Phen}$ films annealed at different conditions

highest fluorescence intensity, similar to the results of the PL spectra. There was no tendency observed that the PLE spectra shifted to shorter wavelengths in any case of the heat treatment condition, and this suggests that the thin films effectively converted the wavelength even with an excitation light near ultra-violet.

3.4 Temporal changes of the fluorescence intensity of the $\text{Eu}(\text{TTA})_3\text{Phen}$ -doped sol-gel glass thin film

Figure 6 shows the temporal changes of the fluorescence intensity in the $\text{Eu}(\text{TTA})_3\text{Phen}$ -doped sol-gel glass thin films and in a spin-coated thin films fabricated for comparison purposes with a solution of $\text{Eu}(\text{TTA})_3\text{Phen}$ in DMF, both under continuous ultra-violet radiation. Here, the central wavelength of the excitation light was 400 nm, its intensity was set at 0.30 mW/cm^2 for the $\text{Eu}(\text{TTA})_3\text{Phen}$ -doped sol-gel glass thin films and at 0.21 mW/cm^2 for the $\text{Eu}(\text{TTA})_3\text{Phen}$ with DMF.

In the thin film without encapsulation with sol-gel glass, there was a result that the fluorescence intensity monotonously decreased under continuous ultra-violet radiation and it was lowered to 55% of the initial fluorescence intensity after 80 minutes elapsed. On the other hand, there was no deterioration in the fluorescence intensity observed in the thin film encapsulated

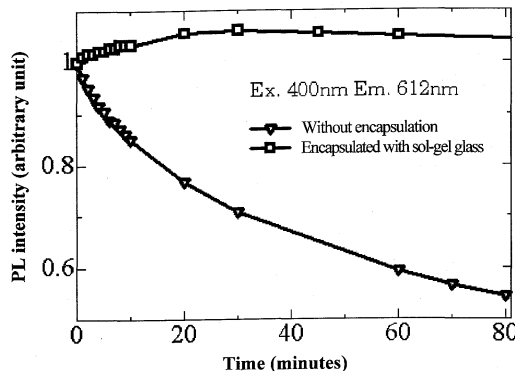


Figure 6 PL intensity change of sol-gel glass-encapsulated and spin-coated $\text{Eu}(\text{TTA})_3\text{Phen}$ films

with sol-gel glass, and it achieved a high fluorescence intensity, 105% of the initial fluorescence intensity, even after 60 minutes elapsed.

It is assessed that, although the initial hydrolysis of the $\text{Si}(\text{OR})_4$ is hard to occur due to an effect of NH_4OH that was used as a catalyst in the sol-gel reactions, when a certain OR group is replaced by an OH group, it becomes vulnerable to hydrolysis and the remaining OR groups are rapidly replaced by OH groups. Since a hydrated silica molecule, which is the main chain of the sol-gel glass, has four positions where polycondensation is feasible, its polymerization progresses three dimensionally to bring about a polymer with remarkable cross-link bonds. That is to say, it can be considered that the reduction in the PL intensity can be suppressed owing to the three dimensional formation of its structure that segregate the Eu complex from the exterior factors such as water and oxygen, which influence its fluorescence properties.

4. Summary

An encapsulating technology using sol-gel glass was studied for the purpose of improving the reliability of the red phosphor $\text{Eu}(\text{TTA})_3\text{Phen}$ of the near ultra-violet excitation type for white LEDs. In the $\text{Eu}(\text{TTA})_3\text{Phen}$ -doped sol-gel glass thin film, the PL and PLE spectra varied depending upon the condition of heat treatment, and the highest PL intensity was obtained under the heat treatment condition of 100°C and one hour. Also it was experimentally confirmed that the $\text{Eu}(\text{TTA})_3\text{Phen}$ has such a high reliability that its fluorescence did not deteriorate under the condition of being radiated by the ultra-violet for 80 minutes.

By using the sol-gel method, an organic molecule was strengthened by inorganic glass without deteriorating its excellent functions, and excellent properties were shown by the fabricated material, which could not be realized by traditional materials. By effectively using this synergistic effect, this technology is expected to

contribute, not only in encapsulation of the phosphor for white LEDs, but also in the expansion of the application potentiality for a wide range of inorganic and organic hybrid materials in the future.

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