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Photo-reduction behavior of sol–gel derived silica materials doped with europium(III) crown ether complex

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Abstract

Silica-based composite glasses doped with europium(III) crown ether complex, SiO_2:[Eu(15C5)]$^{3+}$, which were prepared by the conventional sol–gel method, showed the red line emissions based on f–f transitions of Eu^{3+} ion and also gave the f–d blue band emission of Eu^{2+} ion at 425 nm after irradiating with UV lights around 320 nm for several minutes even in air. The peak intensity of blue emission band increased with prolonging the duration of irradiation, and furthermore such enhancement in intensity still continued even after stopping the UV light irradiation. The 15-crown-5 ether ligands and silanol groups (–Si–OH) in the silica-based matrices played special roles for stabilizing the Eu^{2+} ion generated by the photo-reduction and the subsequent reduction of Eu^{3+} ion without any light irradiation.
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Keywords: Europium complex; Organic–inorganic composites; Divalent europium; 15-Crown-5 ether; Photo-reduction

1. Introduction

Recently, the sol–gel method has been attracting attentions as the typical way to prepare functional materials, e.g. optical glasses, dielectric ceramics and so on, at the lower temperature than the conventional solid state reactions [1–5]. In addition, it is easy to produce the functional materials is the ease of fabrication to produce the materials with complicated shapes by it, owing to the fluidity of gel solutions under the mild processing conditions, such as low temperature and atmospheric pressure.

Many organic–inorganic composites have been prepared by using such sol–gel method, since such composite materials can incorporate the organic components without any decomposition of them. Moreover, the composition of organic and inorganic compounds can be controlled to optimize their physical properties such as optical and electrical ones. Therefore, the sol–gel method has a great potential for creating new functional materials.

The sol–gel derived silica-based glasses doped with some europium(III) or terbium(III) complexes show the strong red or green line emissions and good stability at the temperature around 473–573 K [6–10]. Furthermore, the excellent persistent spectral hole burning (PSHB) properties have been observed on the SiO_2:[Eu(15C5)]$^{3+}$ composite glasses [11]. The fast formation of hole has been ascribed to the rapid photo-reduction from Eu^{3+} to Eu^{2+} ion and the hole is stable even at room temperature [12].

In this study, the SiO_2:[Eu(15C5)]$^{3+}$ composite glasses were prepared by the sol–gel method and the photo-reduction behaviors were studied on the basis of their photoluminescence, ESR and FT-IR measurements. In addition, their good PSHB properties were elucidated by discussing the mechanisms for the photo-reduction of Eu^{3+} ion.

2. Experimental

2.1. SiO_2:[Eu(15C5)]$^{3+}$ composites

The organic–inorganic composite glasses of SiO_2:[Eu (15C5)]$^{3+}$ were prepared by following procedures: the solution containing tetramethoxysilane (TMOS), deionized

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water, ethanol, anhydrous europium(III) chloride and 15-crown-5 ether with a molar ratio of 1:5:10:0.03:0.09 was stirred vigorously to obtain the transparent and homogeneous sol solution. A few drops of diluted HCl solution as a catalyst were added to the above sol solution, and then the solution was cast to a polystyrene cup and dried at 323 K for 1 week. In order that the gelation takes place completely, furthermore, the resultant gels were kept at 363 K for 1 week additionally.

The surface modification was made for a part of SiO_2:[Eu(15C5)]$^{3+}$ composite glasses. The SiO_2:[Eu(15C5)]$^{3+}$ gel solids were ground to the powders by an agate mortar and exposed to the vapor of 1,1,1,3,3,3-hexamethyldisilazane ($(CH_3)_3SiNHSi(CH_3)_3$) at 363 K for 12 h in each sealed reactor tube. The reaction was performed as follows:

$$2(\text{–Si–OH})\,(\text{glass surface}) + (CH_3)_3SiNHSi(CH_3)_3 \rightarrow 2(\text{–Si–O–Si}(CH_3)_3)\,(\text{glass surface}) + NH_3.$$

2.2. *PMMA: [Eu(15C5)]$^{3+}$ composite*

An appropriate amount of polymethylmethacrylate (PMMA: $n \fallingdotseq 1000$) (10 g) was dissolved into 70 g of acetone, and then a part of the solution (23.5 g) was mixed with anhydrous europium chloride (0.0930 g), 15-crown-5 ether (0.237 g) and dimethylformamide (2.00 g) and stirred vig-

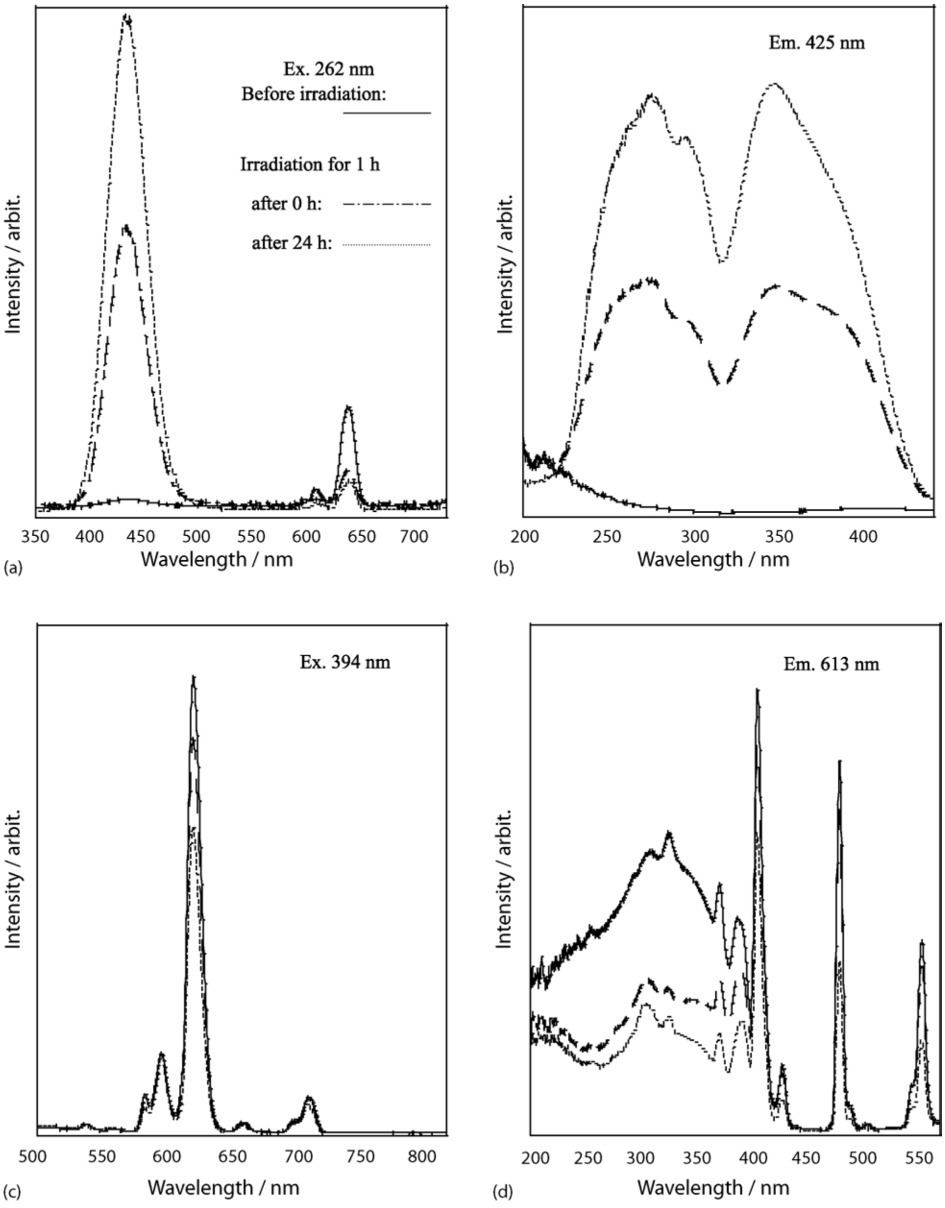

Fig. 1. Photo-luminescence spectra of the SiO_2:[Eu(15C5)]$^{3+}$ composite glass monoliths before and after UV light (320 nm) irradiation for (a) emission and (b) excitation spectra of Eu^{2+} ion, and (c) emission and (d) excitation spectra of Eu^{3+} ion.

orously. The resulting transparent solution was cast into a cuvette and dried at 323 K for 1 week in air, followed by drying additionally at 363 K for 1 week.

2.3. Characterization of the composite materials

Fluorescence spectra of the SiO_2:[Eu(15C5)]$^{3+}$ composite monoliths or glass powder were measured on a fluorescence spectrophotometer (Hitachi F-4500) equipped with a xenon lump as the light source. Electron spin resonance (ESR) spectra were measured by using an electron spinning resonance spectrometer (BRUKER ESP-300) at room temperature, and MgO:Mn^{2+} was used as an internal standard material to evaluate the g values of specimens. The IR spectra were recorded on a FT-IR-430 spectrometer (JASCO) using the KBr method in a range of 400–4000 cm^{-1}.

3. Results and discussion

Fig. 1 shows the photo-luminescence spectra measured before and after the UV light ($\lambda = 320$ nm) irradiation for the monolith samples of SiO_2:[Eu(15C5)]$^{3+}$. Before the irradiation, the spectra were composed of the several peaks corresponding to the f–f transition of Eu^{3+} ion. For the irradiated samples, however, the blue band emission characteristic of Eu^{2+} ion was observed and the peak intensity increased with prolonging the irradiation time. Consequently, the red line emissions were inversely weakened. In addition, this reduction reaction from Eu^{3+} to Eu^{2+} ion was still continued even for 24 h after stopping the UV light irradiation. This continuous reduction suggests that some defects such as oxygen-associated hole center (Si–O^{-}–Si) [13] are generated in silica-based matrices during the UV light irradiation, and the successive photo-reduction of Eu^{3+} ion is caused by an electron transfer from such defects as a negative charge. However, the existences of hole centers and increases or decreases of them were confirmed in detail.

The ESR spectrum of SiO_2:[Eu(15C5)]$^{3+}$ after the UV light irradiation for 1 h is shown in Fig. 2. The g value of spectrum was in good concordance with the previous work ($g = 2.0057$) [14]. This shows the existence of Eu^{2+} ion in the silica-based composite matrices.

Fig. 3(A) shows time dependences of the emission peak (425 nm) intensity based on Eu^{2+} ion for the SiO_2:[Eu(15C5)]$^{3+}$, PMMA:[Eu(15C5)]$^{3+}$ and SiO_2:Eu^{3+} (free from 15-crown-5 ether ligand) composite materials. All the materials were excited by the UV light at 320 nm. The blue band emission derived from Eu^{2+} ion was observed on the SiO_2:[Eu(15C5)]$^{3+}$ composite, but not obviously detected on the other PMMA:[Eu(15C5)]$^{3+}$ and SiO_2:Eu^{3+} composite materials.

Concentration dependences of the blue emission peak intensities (excited at 320 nm) for the SiO_2:[Eu(15C5)]$^{3+}$ composite monolith containing the various amounts of 15-crown-5 ether ligand are shown in Fig. 3(B) and the compositions of starting materials and solvents employed are summarized in Table 1. The transparent composite solids were obtained from the gel solutions of SiO_2:[Eu(15C5)]$^{3+}$ with the four composition ratios of (a–d). The blue emission peak intensity of Eu^{2+} ion was enhanced with increasing the

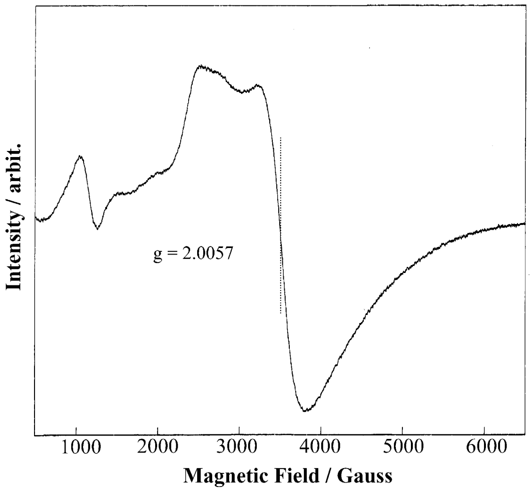

Fig. 2. An ESR spectrum of SiO_2:[Eu(15C5)]$^{3+}$ sample after the UV light irradiation.

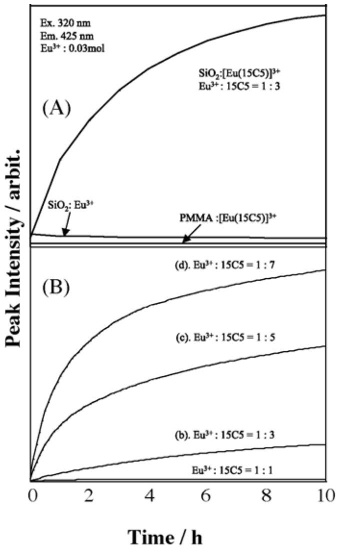

Fig. 3. Dependences of (A) time and (B) concentration dependence (15-crown-5 ether) on the emission peak (425 nm) intensity for the SiO_2:[Eu(15C5)]$^{3+}$, PMMA:[Eu(15C5)]$^{3+}$ and SiO_2:Eu^{3+} glass monoliths under the excitation at 320 nm.

Table 1
Starting materials and solvents for SiO_2:[Eu(15C5)]$^{3+}$ composite glasses (molar ratio)

	TMOS	H_2O	EtOH	$EuCl_3$	15C5	Sample condition
(a)	1	5	10	0.03	0.03	Transparent
(b)	1	5	10	0.03	0.09	Transparent
(c)	1	5	10	0.03	0.15	Transparent
(d)	1	5	10	0.03	0.21	Transparent
(e)	1	5	10	0.03	0.30	Opaque

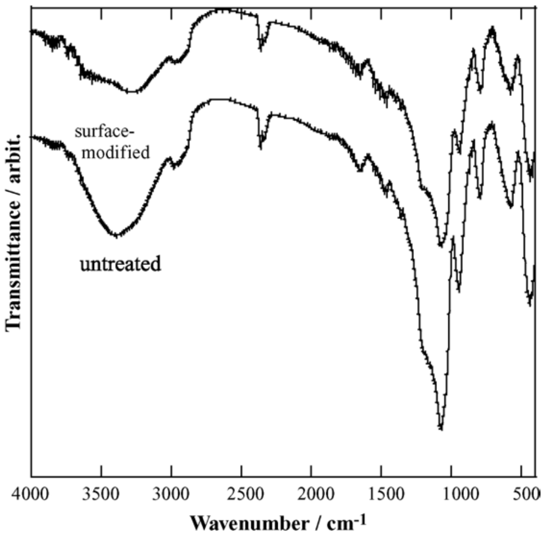

Fig. 4. FT-IR spectra of the SiO_2:[Eu(15C5)]$^{3+}$ composite glass powders before and after the surface modification.

molar ratio of 15-crown-5 ether to Eu^{2+} ion. The opaque and inhomogeneous specimen, however, finally formed from the gel solution with the composition (e). These results indicate that the silica-based glass network and the 15-crown-5 ether ligand strongly affect to the photo-reduction behavior of Eu^{2+} ion of the SiO_2:[Eu(15C5)]$^{3+}$ composite glasses. Also, the Eu^{3+} ions re-oxidized from the Eu^{2+} ions were always observed on a series of our experiments.

A FT-IR spectrum of the SiO_2:[Eu(15C5)]$^{3+}$ composite glass powder modified by 1,1,1,3,3,3-hexamethyldisilazane is shown in Fig. 4, together with that of the untreated SiO_2:[Eu(15C5)]$^{3+}$ composite one. The absorption peak derived from O–H stretching mode at around 3300 cm^{-1} was decreased by the surface modification with $-Si(CH_3)_3$ group, suggesting that the H atom of –OH group in SiO_2 matrix was adequately changed to $-Si(CH_3)_3$.

Fig. 5 shows time dependences observed on the untreated and surface-treated SiO_2:[Eu(15C5)]$^{3+}$ composite glass powders by successively monitoring the emission intensity at 425 nm under the excitation at 320 nm. Compare to the untreated SiO_2:[Eu(15C5)]$^{3+}$ composite, the photo-reduction from Eu^{3+} to Eu^{2+} ion was suppressed for the surface-modified SiO_2:[Eu(15C5)]$^{3+}$ composite glass. The photo-reduction caused by residual silanol groups, however, was observed on the surface-modified sample. This means that the silanol group is one of the important factors for the photo-reduction of Eu^{3+} ion induced by the UV light irradiation.

A series of experimental results allow us to propose the photo-reduction mechanism of Eu^{3+} ions of the SiO_2:[Eu(15C5)]$^{3+}$ composite materials as follows: at first, the electron in the ground state of Eu^{3+} ion is excited to the charge transfer band by UV light irradiation [15]. This excited Eu^{3+} ion receives one electron of the unshared electron pairs from the O atom of neighboring silanol group, so that the reduction from Eu^{3+} to Eu^{2+} ion takes place. The 15-crown-5 ether ligand contributes to stabilize the resultant Eu^{2+} ion by forming the Eu(15C5)$^{2+}$ complex, of which the oxidation potential has found to shift to the positive side compared to the free Eu^{2+} ion [16,17]. The values of redox potential for the free Eu$^{3+/2+}$ and complexed Eu(15C5)$^{3+/2+}$ ion pairs are −150 and −60 mV (versus SCE), respectively [17]. This is due to the good size fitting effect to accommodate such large Eu^{2+} ion in the center cavity of 15-crown-5 ether ligand. Meanwhile, the silanol group generates the radical cation such as [–Si–OH]$^{\bullet+}$, and Eu^{3+} ion is reduced by combining with the neighboring radical cations to form the –Si–O–Si– network. The following equation is the proposed whole reaction:

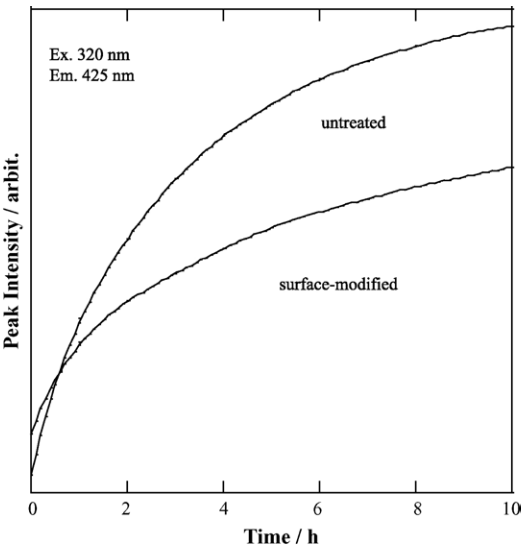

Fig. 5. A time dependence of the emission peak (425 nm) intensity for the SiO_2:[Eu(15C5)]$^{3+}$ composite glass powders before and after the surface modification under the excitation at 320 nm.

$$2[\mathrm{Eu(15C5)}]^{3+} + 2[\text{–Si–OH}]^{\bullet+}(\text{radical cation})$$
$$\to 2[\mathrm{Eu(15C5)}]^{2+} + \text{–Si–O–Si–} + 2\mathrm{H}^{+} + \tfrac{1}{2}\mathrm{O}_2$$

The chain reaction-like reduction mechanism of Eu^{3+} ion after stopping the UV light irradiation for the SiO_2:[Eu(15C5)]$^{3+}$ composite is ascribed to migrate the negative charge from the defect, viz. so-called oxygen-associated hole center (Si–O^{-}–Si) [13].

4. Conclusions

The silica-based organic–inorganic composite glasses of SiO_2:[Eu(15C5)]$^{3+}$ easily generate and stabilize the photo-reduced Eu^{2+} ion under the irradiation of UV lights. The ESR measurements directly demonstrate the formation of Eu^{2+} ion in the SiO_2:[Eu(15C5)]$^{3+}$ composite glasses. In addition, such photo-reduction still proceeds successively after stopping the UV light radiation for the monolith samples of SiO_2:[Eu(15C5)]$^{3+}$. The mechanisms for such photo-reduction of Eu^{3+} ion are certainly elucidated by the electron donation of silanol group and stabilization of crown ether ligand. The Eu^{3+} ion is reduced by receiving an electron from the O atom with unshared electron pairs of silanol group, and furthermore the resultant Eu^{2+} ion is stabilized by the complexation with 15-crown-5 ether ligand under the UV irradiation. Moreover, the oxygen associated hole center ($Si–O^{-}–Si$) formed under the UV light irradiation slowly release the electron, by which Eu^{3+} ion is still reduced without any UV light.

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