Bull. Chem. Soc. Jpn., 73, 251—258 (2000)

ORMOSIL Composite Phosphors Incorporated with Lanthanide Complexes

Hui-hui Li, Satoshi Inoue, Daisuke Ueda, Ken-ichi Machida,* and Gin-ya Adachi*

Department of Applied Chemistry, Faculty of Engineering, Osaka University, 2-1 Yamadaoka, Suita, Osaka 565-0871

(Received June 14, 1999)

Lanthanide complexes, $[Eu(phen)_2]Cl_3$ and $[Tb(bpy)_2]Cl_3$, were doped into organically modified silicate (ORMOSIL) matrices over a wide range of composition. The features and luminescence behavior of the resultant composite products were strongly dependent on the matrix composition. Transparent ORMOSIL composite phosphor disks were obtained under the optimized complex concentration and matrix composition, as well as with careful control of the drying process. Luminescence property varieties of the composites based on various matrix compositions were studied and interpreted from the viewpoint of local chemical environment around the doped complex molecules. Those for composite phosphors incorporated with $[Eu(phen)_2]Cl_3$ were additionally characterized by the $^5D_0$-$^7F_2$ to $^5D_0$-$^7F_1$ emission intensity ratio. Illustrative models of the lanthanide complex-containing sol–gel derived composites were proposed.

Lanthanide complexes such as $[Eu(phen)_2]Cl_3$ and $[Tb(bpy)_2]Cl_3$ have been well known for providing intense red or green emission lines under UV light irradiation.[1,2] The greatly enhanced emission intensities of these complexes compared with those of their corresponding lanthanide simple salts, i.e. $EuCl_3$ and $TbCl_3$, are ascribed to the efficient energy transfer through the intramolecular crossing from the conjugated organic ligands to the central lanthanide metal ions, which undergo subsequent radiative decay from the excited state to the ground one. However, owing to the surrounding quenchers like the solvated H_2O molecules, the complexes usually suffer remarkable decreases in the emission intensity during standing in air, caused by the nonradiative multiphonon decay through the O–H stretching mode of water molecules. Besides, the lanthanide complex solids are usually soft, easily melted, and with few desired mechanical properties. Thus these complexes have been impeded from direct applications as luminescent phosphors. One approach to solve the above problems is to dope the complexes into solid matrices, since the complexes are trapped in the host materials and shielded from the influence of the surrounding substances serving as the quenchers. Meanwhile, the complex-dispersed composite materials should possess many excellent properties originated from the solid host matrices and thus are more promising to be used as light-emitting sources than the complex solids themselves.

On the other hand, the sol–gel process has been established as an excellent method for the preparation of inorganic-organic composite materials under mild conditions.[3] The sol–gel derived ORMOSILs possess hybrid material characteristics, combining the properties which originate from the organic components and those from the inorganic ones,[4] viz. good optical properties and excellent compatibility with organic molecules from the former, and good mechanical strength from the latter. High-performance materials are conveniently obtained by this process, because various modifications of the above properties can be easily realized by simply adjusting the kinds and/or the proportions of the siloxanes as starting materials during the preparation. As a result, recently the sol–gel method has been gaining much attention for the fabrication of organometallic complex-containing composite materials,[5—10] apart from the fact that its applications in the field of hybrid materials incorporated with photoactive organic dopants such as laser and non-linear dyes have been extensively attempted for the developments of tunable solid lasers,[11—15] non-linear optics,[16,17] and other optical devices.[18—20] In our previous reports, the lanthanide complexes, $[Eu(phen)_2]Cl_3$ and $[Tb(bpy)_2]Cl_3$, had been incorporated into silica[6] and ORMOSIL[5,7] matrices via the sol–gel process, and the ORMOSIL matrices have been found to be more favorable for incorporating the larger amounts of the complexes than that with the silica component only. ORMOSIL composite phosphor powders with high emission intensity comparable with commercial lamp phosphors, i.e. ca. 80% for ORMOSIL:$Eu(phen)_2^{3+}$ vs. $Y(P,V)O_4$:Eu and ca. 100 % for ORMOSIL:$Tb(bpy)_2^{3+}$ vs. $LaPO_4$:Tb,Ce, respectively, have been obtained under optimized preparation conditions. In particular, transparent phosphor bulks and films are produced under certain preparation conditions, although the emission intensities of the resultant materials are relatively low. Also, transparent ORMOSIL composite films have been utilized to enhance the output of photovoltaic cells (PVCs) by directly coating them on the silicon solar cell panels,[21,22] based on the excellent "fluorescence wavelength shifting" effect of such composite phosphor films. However, despite all the above developments, to date, preparation of the lanthanide complex-containing ORMOSIL materials is still in the stage of trial and error and thus, a systematic study on the correlation between the composite materials doped with lanthanide complex dopants and the sol–gel derived host matrices needs to be done. The investigation is sure to be of considerable significance for the preparation and design of not only inorganic–organic hybrid materials incorporated with organometallic complexes but also composite materials doped with organic molecules such as dyes as dopants.

In the present paper, the lanthanide complexes, $[Eu(phen)_2]Cl_3$ and $[Tb(bpy)_2]Cl_3$, were doped into the ORMOSIL matrices derived from tetraethoxysilane (TEOS) and diethoxydiphenylsilane (DEDPS) over a wide matrix composition range. Luminescence characteristics of the resultant composite phosphors were investigated and the varieties in intensity were interpreted.

Experimental

Lanthanide(III) complexes, $[Eu(phen)_2]Cl_3$ and $[Tb(bpy)_2]Cl_3$, were prepared according to the procedures described elsewhere.[6] Mixtures of TEOS (99.9% in purity, Wako Pure Chemical Industries, Ltd.), DEDPS (99.9% in purity, Kanto Chemical Co., Inc.), ethanol (99.9% in purity), and deionized water with molar ratios of $1-x:x:8:5$ (x = 0—1) containing a few drops of diluted hydrochloric acid used as a catalyst were refluxed for 1 h to produce the ORMOSIL sol precursor solutions. Then, appropriate amounts of respective lanthanide complex dissolved in *N,N'*-dimethylformamide (DMF, 99.9% in purity) were added to the above homogeneous sol precursor solutions until the desired concentration (1—10 mol% vs. silane ingredient) was reached. In most cases a molar ratio of complex/Si = 0.03 was used in this work, unless otherwise indicated. The lanthanide complex-doped sol solutions were thereafter casted into polystyrene cuvettes and kept in wrapped containers with a few pores at 50—80 °C. Generally, solidified ORMOSIL phosphors were obtained after a few days to several weeks except in the cases when the DEDPS content was too high. Heat treatments for the composite glass phosphors were conducted at various temperatures (100—300 °C) for 5 h in air.

Refractive indices of the ORMOSIL composite samples were measured by refractometry, and the luminescence spectra were recorded on a Hitachi Model 850 fluorescence spectrophotometer, using the "front face" orientation. The relative emission intensities were calculated from the integrated areas of the emission bands recorded under the optimum excitation wavelength for each sample by comparison to that of $Y(P, V)O_4$:Eu or $LaPO_4$:Ce, Tb (commercially available lamp phosphors, Nichia Chemical Industries, Ltd.). The transmittance and absorption spectra were obtained on a Shimadzu UV 2200 double beam spectrophotometer.

Results and Discussion

Preparation and Characterization. A series of inorganic–organic glass phosphors with various matrix compositions incorporated with 3 mol% of $[Eu(phen)_2]Cl_3$ or $[Tb(bpy)_2]Cl_3$ were prepared via the sol–gel method. Designations of the matrix compositions and times for setting on of the gelation of the precursor sol solutions are summarized in Table 1, together with the appearance of the final products after curing at 50 °C. It should be noted that the compositions of the matrices as presented in Table 1 are designated according to the nominal ratios of the network-forming ingredients TEOS and DEDPS just for simplification. The solidification rate of the transparent homogeneous sol solutions doped with complexes was found to become gradually slower with decreasing the ratio of TEOS : DEDPS, suggesting that the formation of three-dimensional matrix networks became more difficult when the content of organosiloxane DEDPS was increased, since the polycondensation reaction was probably impeded by the phenyl groups connecting to the Si atoms. Furthermore, the appearance of the obtained products was also strongly dependent on the matrix composition. Transparent ORMOSIL solid composite phosphors were obtained over the composition range TEOS : DEDPS $\geq 3:7$, while only highly viscous liquids were produced when the TEOS : DEDPS ratio was lower than the above value. Meanwhile, the plasticity of the materials increased with the DEDPS component, due to the increased flexibility originating from the organic modifiers in the matrices. In particular, transparent monolithic bulk phosphor disks based on the matrices with a composition between TEOS : DEDPS = 7 : 3 and 3 : 7 were obtained by controlling the drying processes carefully, and intense red or green emissions from the composite disks were observed upon UV light irradiation. Spectrum measurements indicated that the transmittance of the resultant ORMOSIL phosphor disks (ca. 2 mm in thickness) was very high ($>$ 92%) in the visible region (400—800 nm), as indicated in Fig. 1. In addition, the

Table 1. Matrix Compositions, Gelation Times, and Appearances of the ORMOSIL Composite Phosphors Incorporated with 3 mol% of the Lanthanide Complexes as Obtained at 50 °C in Air

TEOS:DEDPS/molar ratio	Gelation time/days	Appearance of the final product
10:0	3	Transparent solid, cracked, brittle
9:1	4	Transparent solid, cracked, brittle
8:2	6	Transparent solid, partially cracked
7:3	8	Transparent bulk
6:4	15	Transparent bulk
5:5	20	Transparent bulk, slightly flexible
4:6	26	Transparent bulk, slightly flexible
3:7	50	Transparent bulk, rubbery
2:8	—	Highly viscous liquid
1:9	—	Highly viscous liquid
0:10	—	Highly viscous liquid

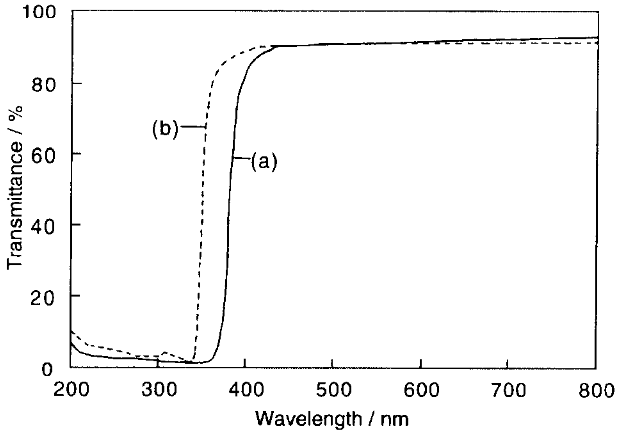


Fig. 1. Transmittance spectra of ORMOSIL (TEOS : DEDPS = 6 : 4) composite phosphor disks (thickness = ca. 2 mm) incorporated with 3 mol% of (a) $[Eu(phen)_2]Cl_3$ and (b) $[Tb(bpy)_2]Cl_3$, respectively.

transparency of the composite materials changed little even after heat treatment up to 300 °C, although in some cases the ORMOSIL composites cracked due to the shrinkage during the process. However, the absorption edge of the matrices in the UV region demonstrates a red shift to the long wavelength side with increasing the content of organic modifier, as shown in Fig. 2, suggesting a decrease in the intensity of the UV lights absorbed by the lanthanide complex dopant molecules for excitation with an increase of the modifier content in the matrices. Refractive indices of the ORMOSIL composite glass matrices were measured by refractometry and were found to vary continuously from n = 1.38 to 1.45 with raising the SiO_2 content over the composition region from TEOS : DEDPS = 3 : 7 to 10 : 0.

Luminescence Properties. Strong excitation and emission bands were observed on the luminescence spectra of all samples. Typical excitation and emission spectra of the ORMOSIL:$Eu(phen)_2^{3+}$ phosphors as incorporated with 3 mol% of $[Eu(phen)_2]Cl_3$ into the matrices with various compositions are shown in Fig. 3. The excitation bands are characteristic of the π–π^* transition of the conjugated 1,10-phenlanthroline (phen) ligands. However, broader bands of the excitation spectra (230—370 nm) are observed on ORMOSIL glass phosphors based on matrices consisting of higher amounts of SiO_2, while the phosphors derived from the matrices of the lower content of SiO_2 provide sharper profiles of the excitation ones (300—370 nm). In other words, the excitation spectrum portions below 300 nm are weakened with decreasing the TEOS : DEDPS ratio. This must be ascribed to the increased absorbance of the host matrix below 300 nm with elevating the organic modifier content, as seen in Fig. 2. Furthermore, it is of interest that the emission spectrum profiles vary drastically with the matrix composition. As can be seen from Fig. 3, the $^5D_0$-$^7F_2$ transition of Eu^{3+} ions provides split lines in the emission spectra of the composite samples with matrix compositions of TEOS : DEDPS $\leq$ 5 : 5, with the main line peaking at 615 nm and a shoulder peak at ca. 623 nm. The peak split becomes more distinct with increasing the organosiloxane content of the matrix and the shoulder peak is weakened with standing in air. This phenomenon is due to the two kinds of complex molecules which exist in different coordination states in the matrices. As observed during the experiments, the $^5D_0$-$^7F_2$ emission line generally peaks at 619 nm when the Eu(III) complex exists as the hydrous $[Eu(phen)_2]Cl_3{\cdot}2H_2O$, while two sharper split peaks (at 615 and ca. 623 nm, respectively) can be observed in the emission spectrum of the corresponding anhydrous complex after heat treatment at 200 °C (see

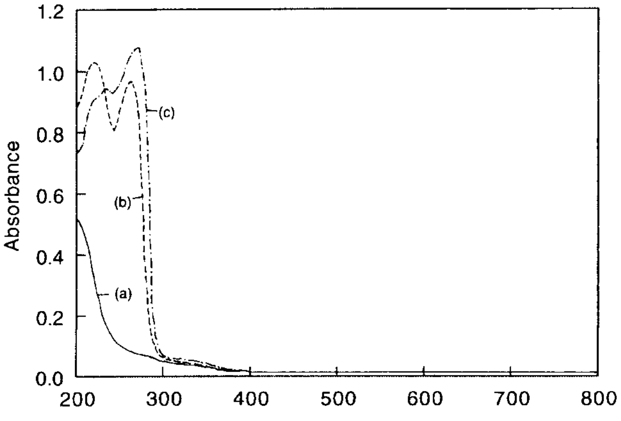


Fig. 2. Absorption spectra of the sol–gel derived matrices with various compositions: (a) TEOS : DEDPS = 10 : 0, (b) TEOS : DEDPS = 8 : 2, and (c) TEOS : DEDPS = 5 : 5.

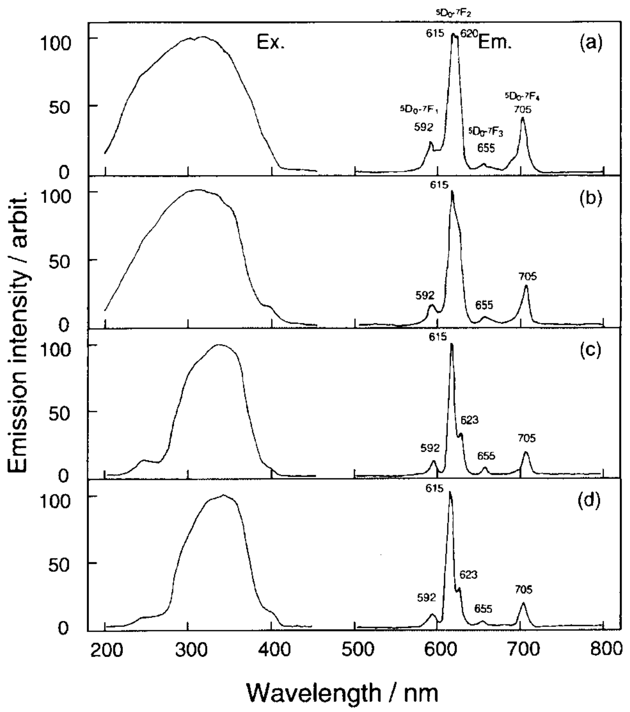


Fig. 3. Excitation and emission spectra of ORMOSIL composite phosphors incorporated with 3 mol% of $[Eu(phen)_2]Cl_3$ based on the matrices of various compositions: (a) TEOS : DEDPS = 10 : 0, (b) TEOS : DEDPS = 7 : 3, (c) TEOS : DEDPS = 3 : 7, and (d) TEOS : DEDPS = 0 : 10. Heat treatment: 200 °C, 5 h in air.

Fig. 4). Therefore, the above observation indicates that the Eu(III) complex tends to take the hydrous form in the SiO_2-rich ORMOSIL network, while on the contrary, it prefers to exist as the anhydrous form $[Eu(phen)_2]Cl_3$ when the organic component in the matrix is enriched. This discrepancy suggests that the local chemical environment around the complex molecules and/or the interaction between the trapped complex molecules and the matrix are closely related to the composition and structure of the host matrices.

The emission intensity of the ORMOSIL composite phosphors incorporated with 3 mol% of $[Eu(phen)_2]Cl_3$ was found to be strongly dependent on the matrix composition. The relative emission intensity maximized at ca. 60% vs. $Y(P,V)O_4$:Eu by optimizing the matrix composition to TEOS : DEDPS = 3 : 7 and heating at 200 °C for 5 h, as shown in Fig. 5a. This observation is attributed to the following factors. First, the complex molecules trapped in the matrices of the lower TEOS : DEDPS ratio are more likely to take the anhydrous form, as mentioned above, and thus the probability of the nonradiative multiphonon relaxation via the O–H stretching mode is relatively low for the corresponding ORMOSIL phosphors. Besides, the local symmetry around Eu^{3+} ions seems to be another significant factor that plays an role in this observation. The emission peak based on the $^5D_0$-$^7F_2$ electric dipole transition (615 nm) of Eu^{3+} ions involving no change in parity is generally forbidden and the resultant luminescence intensity is strongly dependent on the degree of mixed parity arising from the lack of a symmetry center,[23] while the $^5D_0$-$^7F_1$ transition (590 nm) is a magnetic one and almost independent of the local symmetry. Peak intensity ratios of the emission, based on the $^5D_0$-$^7F_2$ transition to $^5D_0$-$^7F_1$, were calculated to clarify the local symmetry of the Eu^{3+} ions. The results are plotted against the matrix composition, as shown in Fig. 5b. Obviously, the curve b is roughly in accordance with the curve a, suggesting a close correlation between the local asymmetry of the Eu^{3+} ions and the emission intensity of the resultant ORMOSIL glass phosphors. At the beginning, the I_{615}/I_{590} ratio gradually increases with raising the DEDPS content, indicating that an increase in the organosiloxane content to form the ORMOSIL matrix lowers the local symmetry around Eu^{3+} ions. However, the I_{615}/I_{590} ratio is saturated to a maximum and maintained at the value after the DEDPS : TEOS ratio exceeds 6 : 4. The slight difference between the two curves reveals the influences from other factors besides the local asymmetry. The absorption of the ORMOSIL matrix at ca. 280 nm increases with elevating the DEDPS component, indicating a consequential decrease in the intensity of the UV light absorbed by the lanthanide complex molecules for excitation. As a result, the emission intensity of the composite materials tends to decrease with elevating the DEDPS : TEOS ratio. The overall influences from these factors leads to the observation that the emission intensity maximized at TEOS : DEDPS = 3 : 7.

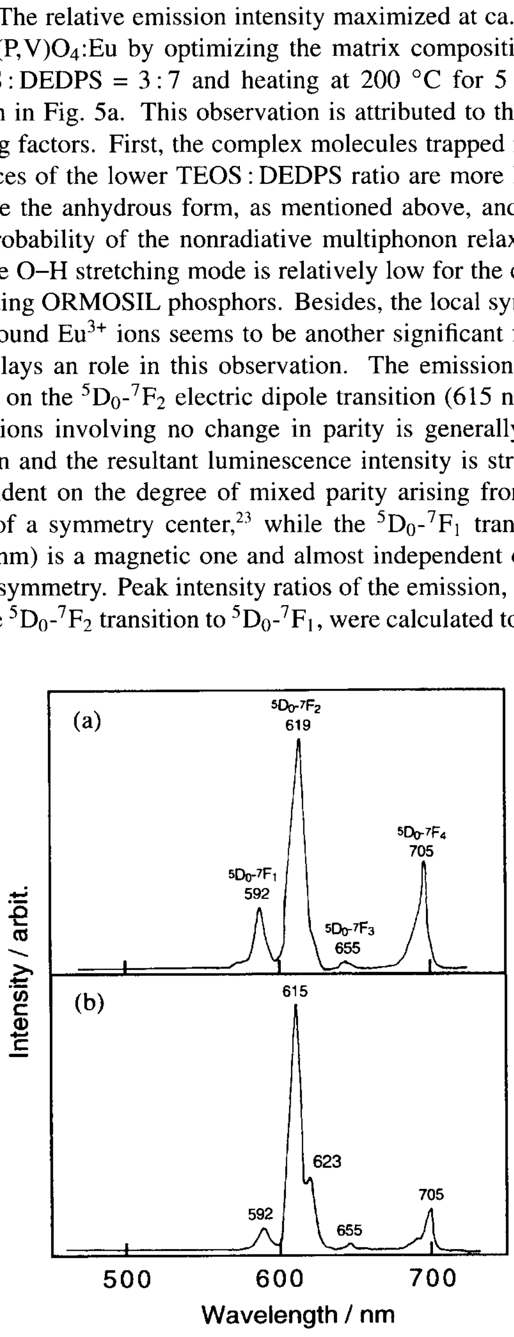


Fig. 4. Emission spectra of the $[Eu(phen)_2]Cl_3$ complex recorded (a) without any heat treatment and (b) after a heat treatment at 200 °C for 5 h in air.

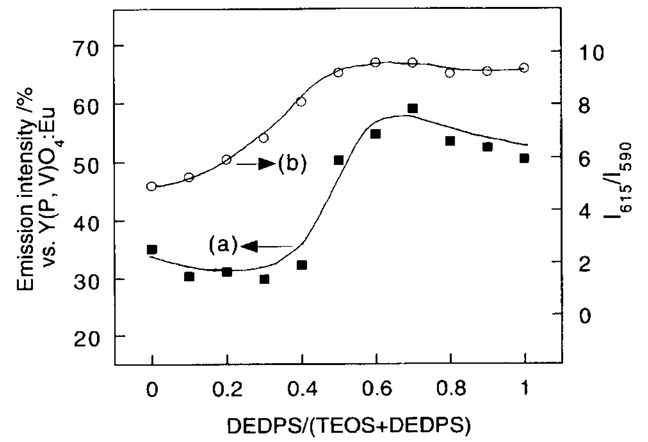


Fig. 5. Matrix composition dependencies of (a) the relative emission intensity and (b) the peak intensity ratio of the $^5D_0$-$^7F_2$ emission line to that of the $^5D_0$-$^7F_1$ one (I_{615}/I_{590}) for the ORMOSIL:$Eu(phen)_2^{3+}$ (3 mol%) phosphors. Heat treatments: 200 °C, 5 h in air.

Complex concentration dependencies of the ORMOSIL: $Eu(phen)_2^{3+}$ composites with various matrix compositions are presented in Fig. 6. It can be seen that the emission intensity maximizes at a complex concentration of 3 mol% for the ORMOSIL:$Eu(phen)_2^{3+}$ phosphors with a matrix composition of TEOS : DEDPS = 3 : 7, whereas the emission intensity of those composite phosphors based on matrix compositions of TEOS : DEDPS = 7 : 3 and 5 : 5 steadily increases with the complex concentration, suggesting different interactions between the complex molecules and the local chemical environment as the matrix composition is varied. In addition, luminescence life times of the samples have been measured; the results are summarized in Table 2. It is of interest that two components of the life time are evaluated on each sample, and both of them become longer with an increase in the

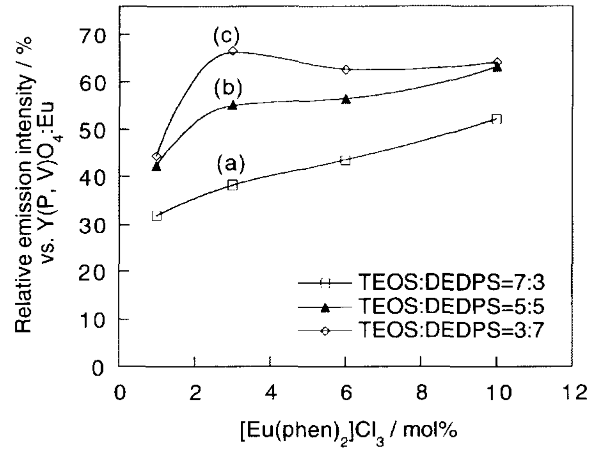


Fig. 6. Complex concentration dependencies of the relative emission intensity for the ORMOSIL:Eu(phen)$_2$$^{3+}$ composite phosphors based on the matrices of various compositions: (a) TEOS : DEDPS = 7 : 3, (b) TEOS : DEDPS = 5 : 5, and (c) TEOS : DEDPS = 3 : 7. Heat treatment: 200 °C, 5 h in air.

Table 2. Luminescence Lifetimes and Relative Emission Intensities of the ORMOSIL Composite Phosphors Incorporated with Various Amounts of [Eu(phen)$_2$]Cl$_3$, after Heat Treatment at 200 °C for 5 h in Air

TEOS/DEDPS	[Eu(phen)$_2$]Cl$_3$/mol%	τ_1/μs[a]	τ_2/μs[a]	I/%[b]
7/3	1	293	826	32
	3	371	954	38
	6	389	931	43
	10	422	1039	52
5/5	1	454	1106	42
	3	459	1077	55
	6	594	1118	56
	10	560	1130	63
3/7	1	395	867	44
	3	638	1058	66
	6	647	1068	63
	10	659	1065	64

a) Luminescence lifetime. b) Relative intensity vs. Y(P, V)O$_4$:Eu.

emission intensity of the corresponding composite phosphor. This fact reveals that the doped complex molecules actually exist as different forms in the matrices and are surrounded by remarkably different local environments. This is another piece of supportive evidence for the above assumption: The [Eu(phen)$_2$]Cl$_3$ complex exists as hydrous and anhydrous forms in the sol–gel derived host materials, although the proportion of the two forms varies with the matrix composition. The hydrous complex molecules have short life times, while the anhydrous ones are supposed to experience slower decays than those in the hydrous form.

In addition, ORMOSIL:Tb(bpy)$_2$$^{3+}$ composite phosphors incorporated with 3 mol% of [Tb(bpy)$_2$]Cl$_3$ were prepared and their luminescence spectra were measured. Excitation and emission spectra of the ORMOSIL:Tb(bpy)$_2$$^{3+}$ based on the matrices derived from a series of siloxane mixtures of various DEDPS : TEOS ratios after a heat treatment at 200 °C are shown in Fig. 7. Likewise, strong broad bands peaking at ca. 320 nm are observed in the excitation spectra of all the ORMOSIL:Tb(bpy)$_2$$^{3+}$ phosphors, assigned to the π–π* transition of bpy ligands, and the excitation spectrum profiles similarly become sharper with enriching the organic component of the matrices, owing to the increase of the absorbance of the matrix at around 280 nm on raising the organic modifier content in the matrix network. Four emission lines corresponding to $^5D_4$-^7F_i (i = 6—3) are observed in the emission spectra of the ORMOSIL:Tb(bpy)$_2$$^{3+}$ phosphors based on the matrices derived from siloxane mixtures with the compositions of TEOS : DEDPS ≥ 5 : 5, with the strongest line peaking at 545 nm corresponding to the $^5D_4$-$^7F_5$ transition, while five distinct emission lines could be observed on those of TEOS : DEDPS ≤ 6 : 4, with an extra emission line peaking at ca. 702 nm in the longer wavelength side, as assigned to the $^5D_4$-$^7F_0$ transition of Tb^{3+}. The appearance of this line with the increase of the DEDPS component may be ascribed to the lowered probability of multiphonon relaxation caused by the –OH groups as the [Tb(bpy)$_2$]Cl$_3$ complex tends to exist as the anhydrous form. The phonon-assisted nonradiative decay via the O–H stretching mode or the lattice vibration of matrix is common for the luminescent complexes and generally several phonons are involved in this nonradiative relaxation process. The larger

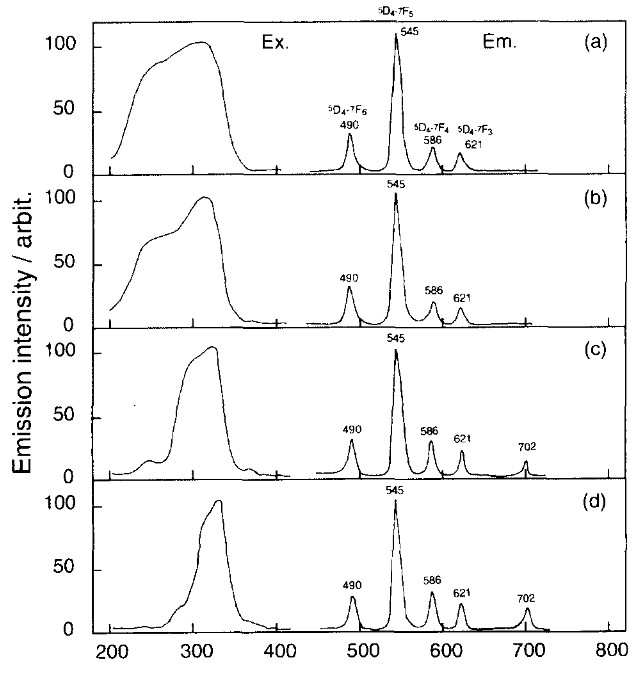


Fig. 7. Excitation and emission spectra of ORMOSIL composite phosphors doped with 3 mol% of [Tb(bpy)$_2$]Cl$_3$ based on the matrices of various compositions: (a) TEOS : DEDPS = 10 : 0, (b) TEOS : DEDPS = 7 : 3, (c) TEOS : DEDPS = 3 : 7, and (d) TEOS : DEDPS = 0 : 10. Heat treatment: 200 °C, 5 h in air.

the number of phonons needed to assist the decay, the less the probability of this process.[24] Since the $^5D_4$-$^7F_0$ transition of Tb^{3+} involves the lowest energy during the crossing, it is assumed that it suffers from the phonon-assisted decay more than other transitions. As a result, although the emission line based on the transition is negligible when the influence of –OH groups is significant, it becomes appreciable as the local environment surrounding Tb^{3+} ions becomes hydrophobic and the undesired influence from the –OH groups is alleviated on raising the DEDPS content, just like the case of the ORMOSIL:Eu(phen)$_2^{3+}$ phosphors stated above.

An emission intensity profile of the ORMOSIL:Tb(bpy)$_2^{3+}$ phosphors against matrix composition is presented in Fig. 8. The emission intensity is obviously dependent on the initial TEOS : DEDPS ratio of the sol solution, and maximizes to ca. 53% vs. $LaPO_4$:Ce, Tb at the ORMOSIL matrix composition of TEOS : DEDPS = 8 : 2. However, it is noted that the dependency for the emission intensity of ORMOSIL:Tb(bpy)$_2^{3+}$ and ORMOSIL:Eu(phen)$_2^{3+}$ on the matrix composition is quite different, and this is attributed to the different properties of the complex dopants. Unlike Eu^{3+} ions, the emission intensity of the Tb^{3+} ions is not influenced by the variety in their asymmetry and thus is less sensitive to the deformation of the electric field surrounding the lanthanide ions, which is induced by the interaction between the complex molecules and the local environment. Therefore, the emission intensity of the ORMOSIL : Tb(bpy)$_2^{3+}$ phosphors is primarily determined by the nonradiative decay through the O–H stretching mode of silanol groups or water molecules as well as the absorbance of the ORMOSIL matrices.

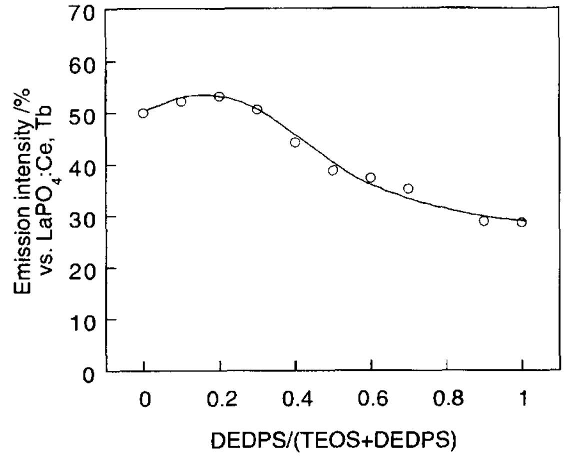
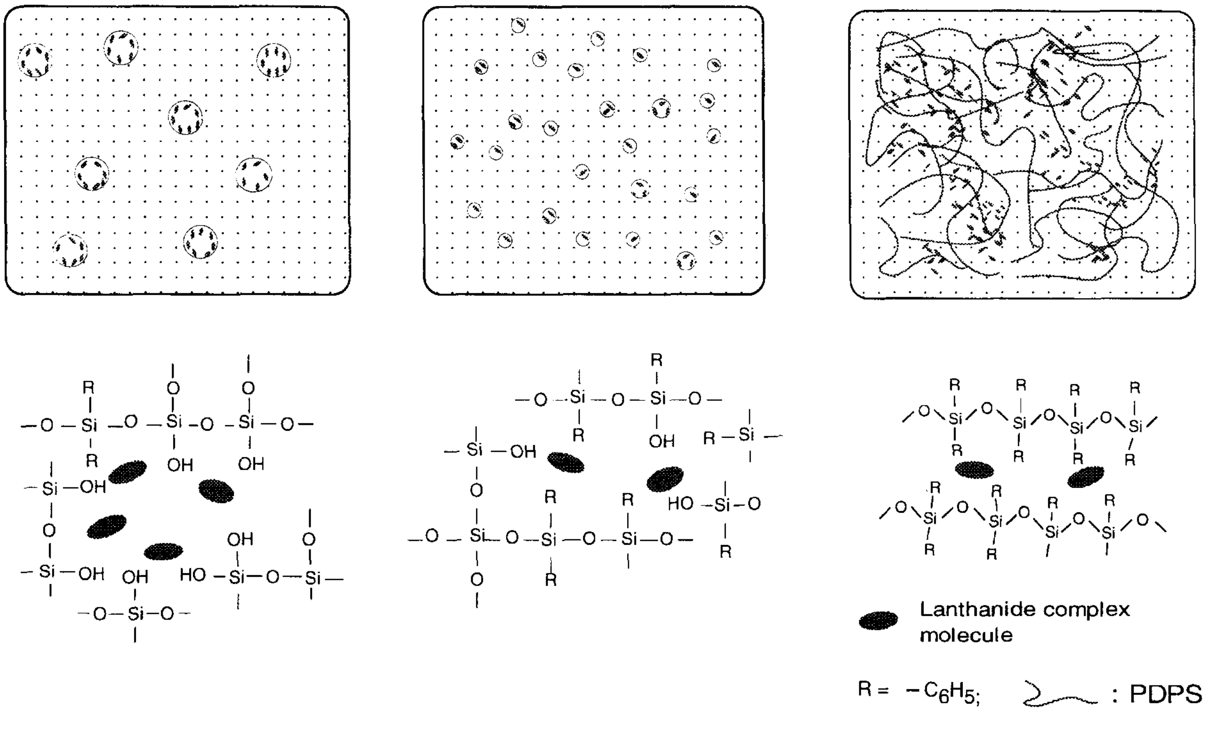


Fig. 8. Matrix composition dependencies of the relative emission intensity for the ORMOSIL glass phosphors doped with 3 mol% of [Tb(bpy)$_2$]Cl$_3$. Heat treatment: 200 °C, 5 h in air.

Incorporation Models for the Lanthanide Complexes. Based on the above experimental results, three structure types of the ORMOSIL composites doped with the lanthanide complexes are proposed, as shown in Fig. 9. Model a stands for the case when the TEOS content is high during the preparation. Since porous materials are generally obtained via the sol–gel method, especially when the SiO_2 content and the solidification rate of gel solution are high, the complex molecules are supposed to be mainly dispersed in the pores of the three-dimensional network of the ORMOSIL host ma-



(a) (b) (c)

Fig. 9. Schematic models of the ORMOSIL composite materials incorporated with lanthanide complexes.

terials. The interfaces between the pores and the network are assumed to be terminated primarily by –OH groups, and the local environment which surrounds the lanthanide complexes is thus hydrophilic and the complex molecules tend to take the hydrous form. Consequently, the multiphonon relaxation through the O–H stretching mode of water molecules inflicts strong influence on the samples, leading to the low emission intensity of the composites. Meanwhile, the emission lines of these composite samples are more characteristic of the hydrous lanthanide complex molecules, as indicated in Fig. 3.

On the other hand, the lanthanide complex molecules doped into the ORMOSIL matrices with the intermediate TEOS : DEDPS ratio seem to be dispersed in numerous fine pores in the matrices, surrounded by both –OH and –R (R = phenyl) groups, see Model b as illustrated in Fig. 9. Compared with the case shown in Model a, more anhydrous lanthanide complex molecules exist in the system, and therefore, emissions characteristic of the anhydrous complex molecules become appreciable in the emission spectrum profiles. The complex molecules are more homogeneously dispersed in these ORMOSIL matrices. Moreover, as the concentration of the lanthanide complex dopant increases, it is easy for the numerous fine pores to accommodate the complex molecules in the matrices and, as a result, the emission intensity of the phosphors increases with raising the complex dopant concentration, as shown in Figs. 6a and 6b.

However, when the DEDPS component is further increased, the hydrolyzed species derived from TEOS which are more reactive in terms of polycondensation under the acid condition might be consumed first; after that, mobile polydiphenylsiloxane (PDPS) molecules, derived from the polycondensation of hydrolyzed product of DEDPS during the evolution of the sol–gel process, are produced in the system. Since cross-linking is more difficult to be accomplished for the PDPS chains, consequently a considerable number of flexible PDPS may exist in the gel solution, leading to the observation that only viscous liquids are obtained at 50 °C when TEOS : DEDPS $\leq 2:8$ and the increased flexibility of the resultant samples with raising the DEDPS concentration after a heat treatment at 200 °C. Meanwhile, it is supposed that far fewer or even no pores are present in such matrices containing many PDPS modifiers (see Fig. 9c), as the PDPS components must have acted as fillers in the system. The lanthanide complex molecules are mainly surrounded by the PDPS chains and take the anhydrous form in the matrices. As a result, the nonradiative decay process via the O–H stretching mode tends to be drastically impeded because of the hydrophobic environment around the lanthanide complex molecules. Thus, he emission peak of the $^5D_0$-$^7F_2$ electron transition is characteristic of that of the anhydrous complex. However, as the complex dopant concentration increases, the aggregation of the lanthanide complex molecules becomes significant due to the limitation of pores in the matrices.

Conclusions

The composite phosphors emitting intense red or green lights upon UV light irradiation are prepared by incorporation of europium(III) or terbium(III) complexes into a series of ORMOSIL matrices. Features and luminescence properties of the resultant composite materials are strongly dependent on the matrix composition. The varieties of emission intensity are related to the local structure or chemical environment around the lanthanide complex molecules, as well as to the absorbance of the matrices for the excitation light in the UV region. In addition, in the case of the ORMOSIL : Eu(phen)$_2^{3+}$ composite phosphors, the asymmetry around the Eu^{3+} ions plays an important role in determining the fluorescence properties.

The structure of the lanthanide complex-dispersing ORMOSIL phosphors is also dependent on the matrix composition. The complex molecules tend to disperse mainly in the pores and to exist as the hydrous form in the SiO_2-rich matrices, while as the organic modifier content increases, they primarily take the anhydrous form and are dispersed more homogeneously in the numerous fine pores of the matrices, leading to a gradual enhancement of the emission intensity as the complex dopant concentration is increased. However, when the DEDPS component is further increased, the lanthanide complex molecules are probably primarily surrounded by flexible hydrophobic PDPS chains in the matrices and exist as the anhydrous form. The aggregation of the complex in this case results in the consequential deteriorated emission intensity of the organic modifier-rich ORMOSIL composite phosphors.

This work was mainly supported by "Research for the Future" Program, "Photoscience" from the Japan Society for the Promotion of Science and Grant-in-Aid for Scientific Research Nos. 09229235, 10123217, and 10874093 from the Ministry of Education, Science, Sports and Culture.

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