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Preparation and luminescence characteristics of the europium and terbium complexes incorporated into a silica matrix using a sol-gel method

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Abstract

A series of silica-based composite materials incorporating lanthanide bipyridyl (bpy) and phenanthroline (phen) complexes, $SiO_2:Ln(bpy)_2^{3+}$ and $SiO_2:Ln(phen)_2^{3+}$ (Ln = Eu, Tb), was prepared by the sol-gel method with luminescence properties studied before and after heat treatment up to 873 K. For the $SiO_2:Ln(bpy)_2^{3+}$ and $SiO_2:Ln(phen)_2^{3+}$ composites heated at appropriate temperatures, the energy transfer from the bpy or phen ligands to Ln^{3+} ions took place smoothly, as for the original complexes, and consequently strong red or green emissions based on Eu^{3+} and Tb^{3+} ions were observed. Emission outputs from the lanthanide complexes incorporated into silica gel matrices were intensified by optimizing the concentration of complexes and heat treating at individual temperatures, and the maximum relative emission intensities (vs. Y(P,V)O_4:Eu and LaPO_4:Ce,Tb phosphors, as practically used) were ca. 15% and 45% for $SiO_2:Eu(phen)_2^{3+}$ and $SiO_2:Tb(bpy)_2^{3+}$ composite materials. Furthermore, thermal stability of $Ln(bpy)_2^{3+}$ complexes was effectively improved compared with the original lanthanide complexes by incorporation into an SiO, matrix.

Keywords: Lanthanide complexes; Sol-gel method; Composite materials; Luminescence characteristics; Relative emission intensity

1. Introduction

Compounds containing optically active lanthanide ions, e.g. Eu^{3+} and Tb^{3+} , have long been used as phosphors and laser materials because of their sharp and intense emissions based on f-f electronic transitions. Among such trivalent lanthanides, the Eu³⁺ ion provides five narrow emission lines corresponding to a series of ${}^{5}D_{0} - {}^{7}F_{i}$ transitions, i = 0, 1, 2, 3 and 4, and the strongest emission line assigned to the transition ${}^{5}D_{0}-{}^{7}F_{2}$ appears at about 610 nm. In a similar manner to the Eu³⁺ ion, the Tb³⁺ ion has four narrow emission lines corresponding to ${}^{5}D_{4} - {}^{7}F_{4}$ transitions, where j = 2, 3, 4 and 5, and the strongest line for the transition ${}^{5}D_{4} - {}^{7}F_{5}$ is observed at about 540 nm as a green emission light with high purity [1]. These lanthanide ions form stable crystalline complexes with heterocyclic ligands, such as bipyridyl (bpy) and phenanthroline (phen), which exhibit efficient energy transfer from the absorbing coordinated ligands to the chelated lanthanide ions [2-4]. The feasibility of application of these compounds is based on the fact that they can absorb ultraviolet radiation with the organic portions of complex molecules, followed by intramolecular energy transfer to Ln³⁺ ions, and can emit

rivalent organic compounds containing lanthanide ions have been excluded from such applications because of their poor thermal resistivity, moisture stability and mechanical strength, although they also have good light emitting characteristics for use as phosphors [14], laser devices b^{3+} ion [15,16] and biomimetic materials [17]. Although the composite materials of lanthanide complexes incorporated into polymer matrices have been studied, when attempting to solve the above mentioned problems [18,19] it is difficult to apply such materials as phosphors for the same reasons that most plastics are considerably limited in their use as host matrices, that is their low photostability and poor thermal stability.

However, the sol-gel method can provide glasses and ceramics via the transition states of viscous gels produced by polymerization of raw materials such as metal alkoxides under much more gentle conditions than those of the conventional high-temperature melting technique [20,21]. Therefore, the sol-gel process has great potential to provide unique inorganic light-emitting solid materials

visible light at individual wavelengths in the red or green region with higher efficiency than unchelated lanthanide

ions [5-10]. However, the phosphors [11,12] and laser devices [13] made for practical use up to date are limited

almost to inorganic solids. Therefore, the complexes or

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hybridized with organic compounds, e.g. luminescent materials [22], solid-state tunable dye laser media [23], etc., which are typically incorporated into gel hosts via dissolution of the active organic compounds into the initial precursor sol. In this work, the silica-based composite materials incorporating lanthanide bpy and phen complexes were prepared according to the sol–gel method and their luminescence properties studied together with their thermal stability.

2. Experimental details

2.1. Sample preparation

The lanthanide phen complex was conventionally prepared by addition of 1,10-phenanthroline (99.9%, Wako Chemical Co., Ltd.) to an ethanol solution containing the lanthanide chloride $LnCl_3 \cdot 6H_2O$, which was obtained by chlorination of lanthanide oxides (Eu₂O₃ or Tb₄O₇, 99.9%, Shin-Etsu Chemical Co., Ltd.) with NH₄Cl (99.9%, Kanto Chemical Co., Ltd.), and the sample was used without further purification. After stirring overnight, the resulting white precipitate was filtrated. A hydrous complex Ln(phen)₂Cl₃2H₂O was obtained from the solid by washing with ether and drying in vacuo at room temperature. The bpy complex was prepared by addition of 2,2'bipyridyl (99.9%, Wako Chemical) to the ethanol solution containing LnCl₃ in a similar manner as the Ln(phen)₂Cl₃ complex.

The appropriate amount of each lanthanide complex was dissolved in the mixed solution of water, ethanol and tetraethoxysilane (TEOS, 99.9%, Wako Chemical) with molar ratio 11:7:1 by stirring thoroughly. In our study, hydrochloric acid or ammonia was not added because the sol solutions prepared here were sufficiently polymerized to gels without any catalyst. After aging at room temperature for 2–10 days, transparent gel solutions were formed and dried at 323 K for several days. The final composite materials SiO₂:Ln(phen)₂³⁺ and SiO₂:Ln(bpy)₂³⁺ were obtained by heating at 373–873 K for 5 h in air and grinding to a particle size less than 50 μ m with sieving.

2.2. Measurements

The resulting organolanthanide complexes and silica gel-based composite materials incorporating them were identified on the basis of elemental analysis and IR absorption spectrum measurements. Thermogravimetric analysis (TG) of the lanthanide complexes and composite materials was performed up to 873 K in air on a Rigaku thermal analysis apparatuses (Rigaku Thermoflex TG 8110 and DSC 8240). The excitation and emission spectra were recorded with a Hitachi 850 spectrofluorophotometer at room temperature. The sample was mounted in a front face holder and measurements carried out under UV–vis excitation light. The relative emission intensity was calculated from the area of the emission spectrum recorded under an optimum excitation condition by normalizing that of $Y(P,V)O_4$:Eu or LaPO₄:Ce,Tb phosphor as 100%. Measurements of IR spectra for the composite materials were carried out using the conventional KBr pellet technique. The average error of the observed values in this paper was less than 3%.

3. Results

3.1. Europium complexes and their composite materials

The excitation and emission spectra of the $Eu(bpy)_2Cl_3$. 2H₂O complex are shown in Fig. 1, together with the excitation spectrum of EuCl₃. Although an original absorption band $({}^{7}F_{0} - {}^{5}L_{6}$ transition) of the Eu³⁺ ion was usually observed at around 394 nm, such absorption scarcely reflects on the excitation spectrum of the $Eu(bpy)_2Cl_3$. 2H₂O complex and the broad and wide absorption curve was dominated by a band at about 340 nm. This band is assigned to the efficient $\pi - \pi^*$ transition based on the conjugated double bond of the bpy ligand. Consequently, a strong red emission was observed from the chelated Eu³⁺ ion via efficient energy transfer from the surrounding bpy ligands. In the case of EuCl₃, however, the emission intensity was considerably weaker than that of the Eu(bpy)₂Cl₃ complex itself, because no such energy transfer took place.

Fig. 2 shows temperature dependences for the weight loss (TG) and relative emission intensity of the original Eu(bpy)₂Cl₃·2H₂O complex. The initial weight loss in the region $-\Delta w_1$ beginning at 373 K was 6.7% and was assigned to the loss of solvated water. It is clear that the emission intensity increases with decreasing weight due to the loss of water. The second and third weight losses in the regions $-\Delta w_2$ and $-\Delta w_3$ at 473–573 K were ca. 30% respectively. These reductions were caused by the elimination and/or decomposition of bpy ligands. At temperatures



Fig. 1. Excitation and emission spectra of $Eu(bpy)_2Cl_3 \cdot 2H_2O$ (solid line) and $EuCl_3$ (dashed line).



Fig. 2. Temperature dependences of the relative emission intensity and weight loss (TG curve) for $Eu(bpy)_2Cl_3 \cdot 2H_2O$. Heating rate for TG, 3 K min^{-1} .

above 603 K, Eu(bpy)₂Cl₃·2H₂O was completely decomposed to EuClO. The relative emission intensity of Eu(bpy)₂Cl₃·2H₂O remained constant up to ca. 420 K, but was drastically decreased by heat treatment above this temperature. This is due to the decomposition of Eu(bpy)₂Cl₃ itself by the elimination and/or decomposition of ligands. In contrast, europium β -diketone complexes such as Eu(acac)₃·*n*H₂O also provide strong emission spectra, but decompose only by heating to around 373 K.

The excitation and emission spectra of Eu(phen)₂Cl₃· 2H₂O heated at 423 K is shown in Fig. 3, together with the excitation spectrum of EuCl₃. The excitation spectrum was observed as a broad band peaking at ca. 330 nm, and the strong emission spectrum consisted of three main lines at 590 nm (${}^{5}D_{0}{}^{-7}F_{1}$), 615 nm (${}^{5}D_{0}{}^{-7}F_{2}$) and 700 nm (${}^{5}D_{0}{}^{-7}F_{4}$) based on the Eu³⁺ ion. As well as the case of the Eu(bpy)₂Cl₃ complex, the absorption at 330 nm is due to the $\pi - \pi^{*}$ transition of the phen ligand. This means that the energy transfer occurs from the phen ligand to the Eu³⁺ ion. For the complex heated at 623 K, however, the



Fig. 3. Excitation and emission spectra of $Eu(phen)_2Cl_3 \cdot 2H_2O$ (solid line) and the complex after heat treatment at 873 K (dashed line).

broad band disappears in the excitation spectrum and the corresponding three emission lines were also weakened. This indicates that most of the $Eu(phen)_2Cl_3 \cdot 2H_2O$ complex was completely decomposed and hence the emission intensity was decreased.

Fig. 4 shows temperature dependences of the weight loss and relative emission intensity of the original $Eu(phen)_2Cl_3 \cdot 2H_2O$ complex. The initial weight loss in the region of $-\Delta w_1$ of Eu(phen)₂Cl₃·2H₂O at 373 K was about 6.3%. This is assigned to the vaporization of solvated water from the complex. The large weight loss in the region of $-\Delta w_2$ starting at about 573 K was evaluated to be ca. 60%, attributed to the elimination and/or decomposition of the phen ligand as well as Eu(bpy)₂Cl₃. 2H₂O. Above 623 K, the complex was completely decomposed. The relative emission intensity of $Eu(phen)_2Cl_3 \cdot 2H_2O$ was increased by raising the heating temperature up to 423 K, and a maximum value of ca. 80% was obtained at this temperature. This indicates that the material derived from Eu(phen)₂Cl₃2H₂O is also a good phosphor, with luminescence ability comparable with that of $Y(P,V)O_4$:Eu, which is used as a lamp phosphor. Furthermore, from the result of this maximum value being maintained up to about 573 K, it is concluded that the material derived from Eu(phen)₂Cl₃ possesses good thermal stability. However, the emission intensity decreased on raising the heating temperature up to 623 K, and the complex was finally completely decomposed with only a weak emission spectrum similar to that of EuCl₃ observed, as mentioned above. This is due to the decomposition and/or elimination of phen ligands in the above temperature region, as supported by the TG result that the $Eu(phen)_2Cl_3 \cdot 2H_2O$ complex is completely decomposed at 623 K.

A series of IR spectrum patterns observed on the $Eu(bpy)_2Cl_3 \cdot 2H_2O$ complex and $SiO_2:Eu(bpy)_2^{3+}$ composite materials is shown in Fig. 5. For $SiO_2:Eu(bpy)_2^{3+}$ composite materials, additional absorption peaks in the regions of A (C=C and C=N stretching) and B (C-H



Fig. 4. Temperature dependences of the relative emission intensity and weight loss (TG curve) for $Eu(phen)_2Cl_3 \cdot 2H_2O$. Heating rate for TG, 3 K min^{-1} .



Fig. 5. IR spectra of (a) the original $\text{Eu}(\text{bpy})_2\text{Cl}_3 \cdot 2\text{H}_2\text{O}$ complex, and (b–e) $\text{SiO}_2:\text{Eu}(\text{bpy})_2^{3+}(x \mod \%)$ composite materials with various contents *x* of $\text{Eu}(\text{bpy})_2^{3+}$: (b) x = 0 (SiO₂ alone), (c) x = 1, (d) x = 3 and (e) x = 10. Heat treatment: in air, 523 K, 5 h.

out-of-plane bend) were superimposed on the original pattern of SiO₂, and their intensity enhanced with increasing concentration of Eu(bpy)₂Cl₃, although the SiO₂ matrix provided a simple, strong absorption band based on the Si-O stretch in a wavenumber region of C. This indicates that the Eu(bpy)₂Cl₃ complex is incorporated into the SiO₂ matrix without any decomposition or serious modification, according to the nominal concentration of the complex. However, the uniform and transparent material of $SiO_2:Eu(bpy)_2^{3+}$ was not obtained from sol solutions containing a larger amount of Eu(bpy)₂Cl₃ than 10 mol%. This is due to the segregation of the lanthanide complex in the silica matrix. When the concentration of $Eu(phen)_2Cl_3$. $2H_2O$ in the silica matrix was below $3 \mod \%$, SiO_2 :Eu(bpy)³⁺₂ composite materials with good transparency and uniformity were obtained with good reproducibility. The same results as for the $Eu(bpy)_2Cl_2 \cdot 2H_2O$ complex and its composite materials were also observed for Eu(phen)₂Cl₃·2H₂O and its derivatives.

The excitation and emission spectra of the composite materials doped with 1 mol% Eu(bpy)₂Cl₃·2H₂O complex [SiO₂:Eu(bpy)₂³⁺(1 mol%)], heated at 523, 723 and 873 K, are shown in Fig. 6. The measured emission profile was very similar to that of the original Eu(bpy)₂Cl₃·2H₂O complex. The red emission spectra were observed even for the composite materials incorporating a small amount of Eu(bpy)₂Cl₃·2H₂O, such as SiO₂:Eu(bpy)₂³⁺(0.1 mol%), and were assigned to the Eu(bpy)₂³⁺ complex cation incorporated into the silica matrix (see Fig. 6(a) Fig. 6(b)).



Fig. 6. Excitation and emission spectra of SiO_2 :Eu(bpy) $_2^{3+}(1 \text{ mol}\%)$ composite materials heated at various temperatures for 5 h in air: (a) 523 K, (b) 723 K and (c) 873 K.

In particular, the fact that the absorption band based on the $\pi - \pi^*$ band also reflects the excitation spectrum pattern indicates that the $Eu(bpy)_2^{3+}$ complex cations exist in the SiO₂ matrix and maintain the original molecular composition and structure. Furthermore, the strong red emission was still observed for the SiO_2 :Eu(bpy)³⁺₂ composite material heated at higher temperatures than that at which the Eu(bpy)₂Cl₃·2H₂O complex was almost decomposed (above 450 K). This means that the thermal stability of $Eu(bpy)_2Cl_3 \cdot 2H_2O$ is improved by incorporation into the silica gel matrix. However, the excitation spectrum based on the bpy ligand at ca. 310-330 nm disappeared with heat treatment at 873 K. Consequently, the emission spectra of the composite materials were significantly weakened compared with that of the sample heated to 723 K, and only weak emission lines ascribed to the free Eu³⁺ ion derived via decomposition of the complex was observed (see Fig. 6(c)).

The SiO₂:Eu(phen)³⁺₂(1 mol%) composite materials also provided somewhat different excitation and emission spectra from those of the SiO₂:Eu(bpy)³⁺₂ composite materials (see Fig. 7). The excitation spectrum pattern consisted of a broad declining curve with several shoulder peaks, and the shape was similar to that of the original Eu(bpy)₂Cl₃· 2H₂O complex rather than Eu(phen)₂Cl₃·2H₂O. In addition, the relative emission intensity of SiO₂:Eu(phen)³⁺₂ was greater than that of SiO₂:Eu(bpy)²⁺₂. This is due to the



Fig. 7. Excitation and emission spectra of $SiO_2:Eu(phen)_2^{3+}(1 \text{ mol}\%)$ (solid line) and $SiO_2:Eu^{3+}$ (dashed line) composite materials.

efficient $\pi - \pi^*$ transition from the phen ligand to the chelated Eu³⁺ ions, indicating that the Eu(phen)₂Cl₃· 2H₂O complex is incorporated into the silica gel matrix with its original molecular structure maintained, which contributes to the strong emission.

The heat treatment temperature dependences of the $SiO_2:Eu^{3+}$ and $SiO_2:Eu(bpy)_2^{3+}$ composite materials with various concentrations of complex are shown in Fig. 8. The relative emission intensities of the $SiO_2:Eu(bpy)_2^{3+}$ composite materials were higher than those of the $SiO_2:Eu^{3+}$ material. In the case of composite materials doped with 0.1 and 1 mol% $Eu(bpy)_2Cl_3\cdot 2H_2O$, the relative intensity was maximized by heating at the relatively high temperature of 680–730 K. Therefore, the resulting $SiO_2:Eu(bpy)_2^{3+}$ composite materials incorporating approximately 1 mol% $Eu(bpy)_2Cl_3\cdot 2H_2O$ were concluded to possess good thermal stability. In particular, since the lanthanide complex incorporated into the silica gel matrix was effectively protected from moisture by the surrounding SiO_2 units, their luminescence property was



Fig. 8. Temperature dependences of the relative emission intensities of SiO₂:Eu³⁺(0.1 mol%) (\bigcirc) and SiO₂:Eu(bpy)₂³⁺(*x* mol%) with various concentration values *x* of Eu(bpy)₂³⁺: *x* = 0.1 (\blacktriangle), *x* = 1 (\spadesuit), *x* = 3 (\triangle), *x* = 10 (\square). Heat treatment: in air, 5 h.

very stable after standing in air. The emission intensity of SiO_2 :Eu(bpy)₂³⁺ increased with amount of complex incorporated, e.g. 6.5% and 7.5% for samples with x = 3 and 10 mol% (treatment temperature 523 K); the thermal stability became poor with increasing concentration of Eu(bpy)₂Cl₃·2H₂O beyond x = 3, because an excess amount of Eu(bpy)₂Cl₃·2H₂O was segregated in the grain boundary of the SiO₂ matrix.

Fig. 9 shows heat treatment temperature dependences of the emission intensity for SiO_2 :Eu(phen)³⁺₂ composite materials. In the low temperature region, the emission intensity of complexes was increased with increasing heat treatment temperature, as well as for the original $Eu(phen)_2Cl_3 \cdot 2H_2O$ complex and SiO₂:Eu(phen) $_{2}^{3+}$ composite materials. This is due to the removal of solvated water from both the complex and silica matrix. The emission intensity for each composite material (1 mol%) was maximized at 523-573 K, providing a relative intensity value of about 15%. It can be noted that the specific intensity value per complex formula unit for $SiO_2:Eu(bpy)_2^{3+}$ is several times higher than that of the original Eu(phen)₂Cl₃·2H₂O.

3.2. Terbium complexes and their composite materials

The excitation and emission spectra of the complex $Tb(bpy)_2Cl_3 \cdot 2H_2O$ are shown in Fig. 10. The excitation spectrum for $Tb(bpy)_2Cl_3 \cdot 2H_2O$ consists of a broad curve with a shoulder peak at ca. 340 nm, assigned to the $\pi-\pi^*$ absorption of bpy ligands, and thus a strong green emission of the Tb^{3+} ion was observed via the energy transfer. The complex residue heated at 873 K showed only the simple excitation spectrum based on the unchelated Eu³⁺ ion, and hence the corresponding five emission lines were considerably weakened.

The temperature dependences of the weight loss and emission intensity of the original $Tb(bpy)_2Cl_3 \cdot 2H_2O$ complex are shown in Fig. 11. The first weight loss was observed at about 373 K, with value estimated as about



Fig. 9. Temperature dependences of the relative emission intensities of $SiO_2:Eu(phen)_2^{3+}(x \mod \%)$ with two concentration values x of $Eu(phen)_2^{3+}: x = 1$ (\bullet), x = 3 (\bigcirc). Heat treatment: in air, 5 h.



Fig. 10. Excitation and emission spectra of the $Tb(bpy)_2Cl_3 \cdot 2H_2O$ complex (solid line) and $TbCl_3$ (dashed line).

6.3%. This is due to the vaporization of solvated water. The weight loss values in the second and third steps, $-\Delta w_2$ and $-\Delta w_3$ observed at 473–623 K, were approximately 30% and attributed to the elimination and/or decomposition of bpy ligands in a similar manner as the case of Eu(bpy)₂Cl₃·2H₂O. Above 623 K, the Tb(bpy)₂Cl₃2H₂O complex was completely decomposed because a weight loss was no longer observed even in the higher temperature region.

In contrast, interesting emission intensity behavior was observed for Tb(bpy)₂Cl₃·2H₂O. The relative emission intensity of Tb(bpy)₂Cl₃·2H₂O was significantly increased with temperature for heat treatment up to 423 K, and the relative intensity evaluated against that of LaPO₄:Ce,Tb used as a standard phosphor attained the highest value of 112.7% (see Fig. 11). This surprising enhancement of the emission intensity may be due to the elimination of solvated water which inhibits the energy transfer via the $\pi-\pi^*$ transition of the bpy ligand to the lanthanide ion. Above 423 K, however, the emission intensity was significantly depressed because of the elimination and/or



Fig. 11. Temperature dependences of the relative emission intensity and weight loss (TG curve) for $\text{Tb}(\text{bpy})_2\text{Cl}_3 \cdot 2\text{H}_2\text{O}$. Heating rate for TG, 3 K min^{-1} .

decomposition of bpy ligands. The elimination of one ligand in the $Tb(bpy)_2Cl_3$ complex takes place at 573 K, and this destruction of the molecular structure is responsible for the steep decrease in emission intensity.

A series of IR spectrum patterns observed for the $Tb(bpy)_2Cl_3 \cdot 2H_2O$ and $SiO_2:Tb(bpy)_2^{3+}$ composite materials is shown in Fig. 12. In analogy with the case of $Eu(bpy)_2Cl_3$, the absorption peaks assigned to the terbium bpy complex, C=N and C=C stretching in the region A and C-H out-of-plane bending in the region B, were intensified with increasing amount of complex, apart from the Si–O stretch in wavenumber region C. However, the uniform and transparent material of $SiO_2:Tb(bpy)_2^{3+}$ was not obtained from mixtures containing more than 10 mol% $Tb(bpy)_2Cl_3 \cdot 2H_2O$.

The excitation and emission spectra of the SiO_2 :Tb(bpy)³⁺₂(1 mol%) composite material heated at 423, 573 and 873 K are shown in Fig. 13, together with those of SiO_2 :Tb³⁺. The shoulder peaks at about 310 nm, observed on the excitation spectra of as the SiO_2 :Tb(bpy)³⁺₂ composite materials heated to 423 and 573 K (see Fig. 13(a) Fig. 13(b)), are assigned to the $\pi - \pi^*$ transition of the bpy ligand. Therefore, it is concluded that the chelated Tb^{3+} ions, that is the $\text{Tb}(\text{bpy})_2\text{Cl}_3$ complex, still exist in the silica matrix prepared via the sol-gel process, and the same molecular structure as for the original Tb(bpy)₂Cl₃·2H₂O complex is maintained even after heat treatment up to 573 K. However, the composite



Fig. 12. IR spectra of (a) the original $\text{Tb}(\text{bpy})_2\text{Cl}_3 \cdot 2\text{H}_2\text{O}$ complex and (b–e) $\text{SiO}_2:\text{Eu}(\text{bpy})_2^{3+}(x \mod \%)$ composite materials with various contents x of $\text{Tb}(\text{bpy})_2^{3+}$: (b) x = 0 (SiO₂ alone), (c) x = 1, (d) x = 3 and (e) x = 10. Heat treatment: in air, 523 K, 5 h.



Fig. 13. Excitation and emission spectra of SiO_2 :Tb(bpy)₂³⁺(1 mol%) composite materials heated at various temperatures for 5 h in air: (a) 423 K, (b) 573 K and (c) 573 K.

material heated to 873 K provided no shoulder band at about 310 nm on the excitation. This means that the $Tb(bpy)_2^{3+}$ complex is also decomposed at 873 K. The emission spectrum pattern of SiO_2 :Tb(bpy)₂³⁺ composite materials consisted of four main lines at 489 nm (${}^{5}D_{4}$ - ${}^{7}F_{6}$), 545 nm (${}^{5}D_{4}-{}^{7}F_{5}$), 586 nm (${}^{5}D_{4}-{}^{7}F_{4}$) and 622 nm $({}^{5}D_{4} - {}^{7}F_{3})$, and among these the emission lines at 545 nm was the strongest. The emission intensities of the SiO_2 :Tb(bpy)₂³⁺ composite materials were considerably greater than those of TbCl₃ and SiO₂:Tb³⁺ (doped with TbCl₃). However, the emission intensity for the composite material heated to 873 K decreased to the same level as that of SiO_2 :Tb³⁺, and there was no contribution to the energy transfer between the bpy ligand and the Tb^{3+} ion. These results indicate that the energy transfer from the bpy ligand to the chelated Tb³⁺ ion is essential to the enhancement of the emission intensity of the Tb^{3+} ion.

The relationships between the treatment temperature and the emission intensity for SiO_2 :Tb(bpy)²³⁺ and SiO_2 :Tb(phen)₂³⁺ composite materials are shown in Fig. 14. In the lower temperature region, the emission inten-



Fig. 14. Temperature dependences of the relative emission intensities of SiO_2 :Tb(phen)₂³⁺(1 mol%) (\bigcirc) and SiO_2 :Tb(bpy)₂³⁺(*x* mol%) with various concentration values *x* of Tb(bpy)₂³⁺: *x* = 1 (\bullet), *x* = 3 (\triangle), *x* = 10 (\Box). Heat treatment: in air, 5 h.

sities of the terbium complexes increased with temperature of heat treatment by incorporation into the silica matrix. This is due to dehydration from both the complexes and the silica matrix, which contributes to a depression of the non-radiative process via water. This effect could be explained by the fact that the multiphonon relaxation will decrease due to loss of water. The emission intensity for the composite material incorporating 1 mol% bpy complex, SiO_2 :Tb(bpy)³⁺₂(1 mol%), was maximized at 573 K, indicating that the thermal stability of $Tb(bpy)_2Cl_3 \cdot 2H_2O$ was improved by surrounding with SiO₂ units in a manner similar to SiO_2 :Eu(bpy)³⁺₂. In particular, the emission intensity of the SiO_2 :Tb(bpy)₂³⁺(1 mol%) composite material was maximized at 673 K, providing a value of 44%. It is concluded from this value that the specific emission intensity value per Tb(bpy)₂Cl₃ formula unit is several tens of times higher than that of the original complex. In addition, the mechanical properties of the lanthanide complexes were improved by incorporation into the silica matrix. However, the emission intensity was also decreased by heat treatment above 573 K.

4. Discussion

The heat-resistance temperatures of $Ln(bpy)_2Cl_3 \cdot 2H_2O$ complexes incorporated into a silica matrix depended strongly on the amount of complexes incorporated, and the temperature for composite materials incorporating 1 mol% $Ln(bpy)_2Cl_3$ was evaluated to be about 573 K for Ln = Tband 723 K for Ln = Eu. This indicates that the segregation of the complexes in the silica matrix tends to lower the temperature at which decomposition starts. The silica matrix formed via the sol-gel route is porous, but the radius of the pores is much smaller than near–UV or visible radiation wavelength (1.5–10 nm) [24]. In addition, since the cage in a silica matrix containing a lanthanide complex is probably even smaller than 1.5 nm, the matrix is consequently transparent [25]. As stated above, lanthanide complexes $Ln(bpy)_2Cl_3 \cdot 2H_2O$ and $Ln(phen)_2Cl_3 \cdot 2H_2O$ are perhaps completely trapped in rigid cages or bottleneck pores [26], separated by channels of diameter smaller than the effective ones of ethanol or water [27]. In the case of SiO₂:Ln(bpy)₂³⁺(1 mol%), each individual Ln(bpy)₂Cl₃·2H₂O complex exists in such a silica gel matrix cage with incorporation of less than 1 mol% complex, and hence the heat-resistance temperature increases to ca. 573 K for SiO₂:Tb(bpy)₂³⁺ and ca. 723 K for SiO₂:Eu(bpy)₂³⁺. However, the Ln(bpy)₂Cl₃·2H₂O complex was segregated in the rigid cage with increasing amount of incorporation, and the heat-resistant temperature was gradually decreased.

The relative emission intensity of SiO_2 :Tb(phen)³⁺₂(1 mol%) composite material was maximized at 573 K, but the value was only 7% (see Fig. 14) and much lower than that of SiO_2 :Tb(bpy) $_2^{3+}(1 \text{ mol}\%)$. This may be caused by the fact that the excited level of the phen ligand was lower than that of the bpy ligand, and in the course of energy transfer from the phen ligand to the Tb³⁺ ion the energy of excitation may return to the phen ligand. Therefore, it is apparent that the $Tb(phen)_2Cl_3$. $2H_2O$ complex and SiO₂:Tb(phen)³⁺₂ composite materials cannot emit more effectively than the $Tb(bpy)_2Cl_3 \cdot 2H_2O$ complex and its composite materials.

5. Conclusions

Some conclusions are obtained as follows.

(1) The relative emission intensities of lanthanide complexes, e.g. $Tb(bpy)_2Cl_3 \cdot 2H_2O$ and $Ln(phen)_2Cl_3 \cdot 2H_2O$ (Ln = Eu and Tb), were considerably increased by heat treatment and were maximized at an optimum temperature. In particular, $Tb(bpy)_2Cl_3 \cdot 2H_2O$ gave a strong green emission with relative emission intensity of 120% versus the LaPO₄:Ce,Tb phosphor, as practically used, on heat treatment at 423 K. However, the emission intensity of the resulting materials derived from the complex was gradually decreased due to moisture in the air.

(2) The lanthanide complexes were incorporated into an SiO_2 matrix with considerable success by the sol-gel method, without any decomposition or serious modifications. In particular, the thermal stability of lanthanide complexes was effectively improved by incorporation into the silica matrix.

(3) The emission spectra of lanthanide complexes were intensified by incorporating them into a silica matrix, and the specific emission intensity per complex formula unit was increased compared with those of the original lanthanide complexes. The composite materials prepared under optimized conditions provide strong red or green emissions with relative intensity values of 17% for $SiO_2:Eu(bpy)_2^{3+}(1 \text{ mol}\%),$ $SiO_2:Eu(phen)_2^{3+}(3 \text{ mol}\%)$ 15% for and 44% for SiO_2 :Tb(bpy)³⁺₂(10 mol%) respectively. Therefore, the relative intensities of the composite materials are expected to be intensified further if the lanthanide complexes are highly dispersed in the matrices.

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