Preparation and Luminescence Properties of $\text{SiO}_2\text{-ZrO}_2$ and $\text{SiO}_2\text{-Ta}_2\text{O}_5$ Composite Materials Doped with a Terbium(III) Complex

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Tb(III) 錯体を分散した $\text{SiO}_2\text{-ZrO}_2$ 及び $\text{SiO}_2\text{-Ta}_2\text{O}_5$ 系複合体の作製と蛍光特性

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The terbium(III) 2,2'-bipyridyl complex, $[\text{Tb}(\text{bpy})_2]\text{Cl}_3$, was incorporated for the first time into partially metal oxide-substituted silica matrices derived from tetraethyl orthosilicate (TEOS) and metal alkoxides ($\text{M}(\text{OR})_n$, $\text{M}=\text{Zr}$ and Ta) via sol-gel process. The optical properties of the obtained $[\text{Tb}(\text{bpy})_2]\text{Cl}_3$ -dispersed inorganic-organic composite materials were characterized by measurements of photoluminescence, transmittance, infrared spectra and X-ray diffraction patterns. The emission intensity of the $(\text{SiO}_2\text{-M}_x\text{O}_y) : \text{Tb}(\text{bpy})_2^{3+}$ composite phosphors was dependent on the kind and content of metal oxide component in the matrices and maximized at the matrix composition of $\text{Si} : \text{M}=9 : 1$ in molar ratio in either case. In particular, for the $\text{SiO}_2\text{-Ta}_2\text{O}_5$ matrix system with the composition of $\text{Si} : \text{Ta}=9 : 1$, the complex was incorporated into the host media at concentrations up to 20 mol%, which resulted in composite phosphors with a good transparency. Under the optimized preparation conditions, the emission intensity of such organically modified ceramic (ORMOCER) ($\text{SiO}_2\text{-Ta}_2\text{O}_5$) : $\text{Tb}(\text{bpy})_2^{3+}$ phosphors maximized at ca. 75% vs. $\text{LaPO}_4 : \text{Ce,Tb}$ (a commercially available lamp phosphor as the standard substance) with complex concentrations of 10–15 mol%.

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1. Introduction

The lanthanide complexes, such as $[\text{Eu}(\text{phen})_2]\text{Cl}_3$ and $[\text{Tb}(\text{bpy})_2]\text{Cl}_3$, provide intense emission lines under UV light irradiation,^{1,2)} ascribed to the effective intramolecular energy transfer from the organic ligands to the central lanthanide metal ions, which in turn undergo some radiative decay from the excited state to the ground state. However, owing to the influence of the moisture in the surrounding atmosphere, the consequential serious non-radiative multiphonon relaxation based on the O-H stretching mode usually leads to a drastic decrease in the emission intensity of the complexes. Meanwhile, the lanthanide chelate compounds are usually soft, easily melted, and barely with any desired mechanical property to be directly used as luminescent sources. Fortunately, it is to our best knowledge that the above problems may be solved by incorporating them into suitable solid host materials, since the complex molecules should be shielded from the surrounding atmosphere, and the desirable mechanical properties originated from the host media will be obtained on the resultant composites.

On the other hand, the sol-gel process has been established as an excellent candidate for the preparation of various rigid inorganic and inorganic-organic hybrid solid matrices under mild conditions in the last a few decades.³⁾ Since the first report of its application for the preparation of organic dye-doped composites by Reisfeld et al. in 1984,⁴⁾ the sol-gel method has been widely applied in the developments of solid tunable lasers,^{5)–9)} nonlinear optics,^{10,11)} luminescent solar concentrators (LSCs) and other optical materials,^{12)–15)} which mainly deal with organic molecule dopants, with fruitful results having been achieved. Particularly, recent application of the method has been extended to the field of organometallic complex-dispersed composite materials.^{16)–21)} In our previous work, $[\text{Eu}(\text{phen})_2]\text{Cl}_3$ and $[\text{Tb}(\text{bpy})_2]\text{Cl}_3$ complexes have been incorporated into the silica matrix derived from tetraethyl

orthosilicate (TEOS).^{17,18)} The thermal stability of the complexes is improved after the incorporation, and the mechanical properties of the lanthanide complex-dispersed composite materials are also strengthened. However, the emission intensity of the obtained samples is still low, owing to the limitation of the amount of lanthanide complex to be incorporated into the matrices without any apparent phase separation, with the maximum emission intensity achieved for $\text{SiO}_2 : \text{Eu}(\text{phen})_2^{3+}$ at ca. 15% vs. $\text{Y}(\text{P}, \text{V})\text{O}_4 : \text{Eu}$ and ca. 44% for $\text{SiO}_2 : \text{Tb}(\text{bpy})_2^{3+}$ vs. $\text{LaPO}_4 : \text{Ce, Tb}$ under the optimized conditions.¹⁸⁾ Moreover, as suggested by Avnir,²²⁾ SiO_2 is not necessarily the optimal matrix for the purpose of preparing inorganic-organic composite materials, other sol-gel derived matrices, such as TiO_2 , $\text{SiO}_2/\text{ZrO}_2$, Al_2O_3 and so on might also find important applications in this field. Therefore, it is of pretty interest to search for other suitable inorganic or inorganic-organic alternatives which are capable of trapping much more amounts of lanthanide complex dopants while they simultaneously provide considerable homogeneity. In this regard, the inorganic composite matrices $\text{SiO}_2\text{-M}_x\text{O}_y$ derived from TEOS and other metal alkoxides via the sol-gel method are especially attractive because of their highly tunable refraction indices, relatively low lattice vibration energy compared with the silica counterparts, and good optical properties as well according to previous reports.^{23,24)} It is expected that such host media are probably promising for the preparation of high-performance organometallic complex-dispersed composites, such as organically modified ceramics (ORMOCER).

In the present paper, the $[\text{Tb}(\text{bpy})_2]\text{Cl}_3$ complex was incorporated into the inorganic matrices derived from TEOS and metal alkoxides, $\text{Zr}(\text{O}(\text{CH}_2)_3\text{CH}_3)_4$ and $\text{Ta}(\text{OC}_2\text{H}_5)_5$, as starting materials via the sol-gel method. Luminescence properties of the resultant composite samples were investigated, and the variation of the emission intensity was interpreted from the viewpoint of the matrix

absorbance, lattice vibration of the matrix and concentration quenching of the complex.

2. Experimental

The $[\text{Tb}(\text{bpy})_2]\text{Cl}_3$ complex was synthesized according to the procedures described elsewhere.¹⁸⁾ Mixtures of TEOS (99.9% in purity), ethanol (EtOH), and H_2O with a molar ratio of 1 : 10 : 1 were refluxed for 1 h after adding a few drops of diluted HCl solution ($\text{pH} \approx 6$) as a catalyst. Then, appropriate amounts of zirconium tetra-*n*-butoxide ($\text{Zr}(\text{O}(\text{CH}_2)_3\text{CH}_3)_4$, 85.0–90.0% in purity) or tantalum pentaethoxide ($\text{Ta}(\text{OC}_2\text{H}_5)_5$, 99.9% in purity) were added to the resultant sols as obtained above and refluxed together for another 1 h to give transparent homogeneous precursor solutions. $[\text{Tb}(\text{bpy})_2]\text{Cl}_3$, H_2O and dimethylformamide (DMF, 99.9% in purity) were mixed with molar ratios of $(\text{Si} + \text{M}) : [\text{Tb}(\text{bpy})_2]\text{Cl}_3 : \text{H}_2\text{O} : \text{DMF} = 1 : y : 4 : 1$ ($y = 0.01\text{--}0.2$), and the resultant solutions were subsequently stirred together with the above precursor sols until the mixtures became homogeneous. The complex-dispersed solutions as obtained were casted into polystyrene cups and cured at 50°C in air for several days to give solidified hybrid composites.

The resultant solid phosphor samples were characterized by luminescence, transmittance, IR spectra and XRD measurements. The luminescence spectra were recorded and corrected on a Hitachi fluorescence spectrophotometer Model 4500 equipped with xenon lamp as a light resource, using the "front face" orientation. The relative emission intensity values were normalized to that of the lamp phosphor $\text{LaPO}_4 : \text{Ce}$, Tb (Nichia Chemical Ind., Ltd.). The transmittance spectra were recorded on a Shimadzu UV 2200 double beam spectrophotometer and the FT-IR spectra on a FT/IR-430 spectrophotometer (JAS Co.) by the KBr method.

3. Results and discussion

Since transition metal alkoxides are generally far more reactive compared with silicon alkoxides, for the preparation of metal oxides or $\text{SiO}_2\text{-M}_x\text{O}_y$ composites via the sol-gel method, chelating agents such as β -diketones are usually added into the systems in order to depress their reactivity and secure the steady proceeding of the hydrolysis and subsequent polycondensation of the metal alkoxides.²⁵⁾ However, it was found that the introduction of the common chelating agents in the present systems often resulted in a significant decrease in the emission intensity of the obtained lanthanide complex-dispersed composites, owing to the coordination of the added ligands to Tb^{3+} ions through ligand exchange reaction and the consequential deterioration of the luminescence. Consequently, the activation of the metal alkoxides by adding chelating agents was not employed for the present system, and other efforts were made to establish appropriate preparation procedures to obtain transparent $(\text{SiO}_2\text{-M}_x\text{O}_y) : \text{Tb}(\text{bpy})_2^{3+}$ composite phosphors. The results demonstrated that the $\text{SiO}_2\text{-M}_x\text{O}_y$ matrices with good transparency were obtained within certain Si : M ratio range (molar ratio of $\text{Si} : \text{M} \geq 3 : 7$) by controlling the amount of the water, that is, the proceeding of the hydrolysis and the subsequent polycondensation of both silicon and metal alkoxides.

Figure 1 shows the transmittance spectra of the typical resultant transparent $\text{SiO}_2\text{-ZrO}_2$ and $\text{SiO}_2\text{-Ta}_2\text{O}_5$ composite matrices, together with that of the silica matrix derived by the sol-gel method. Although the transparency of the $\text{SiO}_2\text{-M}_x\text{O}_y$ composite matrices is pretty good in the region above 500 nm, the edge of the absorption spectrum shifts to the long wavelength side as SiO_2 is partially substituted by metal oxide units in the matrix network. As a result, the

Fig. 1. Transmission spectra of (a) silica matrix, (b) $\text{SiO}_2\text{-ZrO}_2$ ($\text{Si} : \text{Zr} = 3 : 7$) and (c) $\text{SiO}_2\text{-Ta}_2\text{O}_5$ ($\text{Si} : \text{Ta} = 3 : 7$). The matrices have been heat-treated at 200°C for 5 h in air.

obtained composite host materials usually take on a light yellow color.

The lanthanide complex, $[\text{Tb}(\text{bpy})_2]\text{Cl}_3$, was doped into the $\text{SiO}_2\text{-ZrO}_2$ and $\text{SiO}_2\text{-Ta}_2\text{O}_5$ composite matrices with various matrix compositions, respectively, and all of the resultant inorganic-organic hybrid phosphors were found to provide intense green emissions characteristic of Tb^{3+} ions under UV light irradiation. The emission intensity of the ORMOCER composite phosphors doped with 3 mol% of $[\text{Tb}(\text{bpy})_2]\text{Cl}_3$ as a function of the matrix composition is presented in Fig. 2. It can be seen that the emission intensity values of the $(\text{SiO}_2\text{-Ta}_2\text{O}_5) : \text{Tb}(\text{bpy})_2^{3+}$ composite phosphors are generally higher than those of the $(\text{SiO}_2\text{-ZrO}_2) : \text{Tb}(\text{bpy})_2^{3+}$ ones even though the matrix composition, i.e., the Si : M ratio, is the same for each other. It should be noted that the luminescence intensity maximizes at a matrix composition of $\text{Si} : \text{M} = 9 : 1$ in either case, indifferent to the metal oxide substitutes in the matrix networks. This observation is due to the counteraction between the influence from the absorptivity of the matrices (especially in the region below 400 nm) and that from the lattice vibration energy of the matrix network on the emission intensity. As shown in Fig. 3, the absorptivity of the $\text{SiO}_2\text{-Ta}_2\text{O}_5$ composite matrices below 400 nm gradually increases with raising the content of the metal oxide component, leading to a tendency of decrease in the emission intensity for the composite phosphors, since the UV flux for the excitation of the lanthanide complex molecules is subsequently decreased. On the other hand, apart from the absorptivity of the matrix, the multiphonon relaxation based on the lattice vibration of the matrix is also crucial to the emission intensity of the obtained composite phosphors. A series of FT-IR spectra recorded on the $(\text{SiO}_2\text{-Ta}_2\text{O}_5) : \text{Tb}(\text{bpy})_2^{3+}$ phosphors are shown in Fig. 4. As we can see, both peaks A and B, which are ascribed to the Si-O-Si and Si-O-Ta stretching mode,^{26),27)} respectively, shift to the low wavenumber side as the content of the Ta_2O_5 component in the matrices is increased. This definitely results in the tendency of an increase of the emission intensity with an elevation of the Ta_2O_5 substituents in the matrix for the composite phosphors, because the multiphonon-assisted relaxation as caused by the lattice vibration of Si-O-M is subsequently depressed. Similar results were obtained on the $(\text{SiO}_2\text{-ZrO}_2) : \text{Tb}(\text{bpy})_2^{3+}$ series. Therefore, the comprehensive influences from the above two inverse tendencies lead to the observation that maximum emission intensity is achieved at the matrix composition of $\text{Si} : \text{M} = 9 : 1$ in the intensity versus the network modifier content curves.

Fig. 2. Emission intensity of ORMOCER phosphors incorporating 3 mol% of $[\text{Tb}(\text{bpy})_2]\text{Cl}_3$ in (a) $\text{SiO}_2\text{-ZrO}_2$ and (b) $\text{SiO}_2\text{-Ta}_2\text{O}_5$ matrices of various compositions. The samples have been heat-treated at 200°C for 5 h in air.

Fig. 3. Absorption spectra of $\text{SiO}_2\text{-Ta}_2\text{O}_5$ matrices: (a) $\text{Si}:\text{Ta}=10:0$, (b) $\text{Si}:\text{Ta}=9:1$, (c) $\text{Si}:\text{Ta}=7:3$ and (d) $\text{Si}:\text{Ta}=3:7$. The samples have been heat-treated at 200°C for 5 h in air.

Since the transparent ORMOCER phosphors incorporating 3 mol% of $[\text{Tb}(\text{bpy})_2]\text{Cl}_3$ provided the highest emission intensity at the matrix composition of $\text{Si}:\text{Ta}=9:1$, subsequently a series of $(\text{SiO}_2\text{-Ta}_2\text{O}_5):\text{Tb}(\text{bpy})_2^{3+}$ ($\text{Si}:\text{Ta}=9:1$) composite phosphors doped with various amounts of $[\text{Tb}(\text{bpy})_2]\text{Cl}_3$ complex were prepared. The FT-IR spectra of the resultant samples were recorded, and the spectrum profiles are shown in Fig. 5. Obviously, the absorption peaks (denoted as A and B) assigned to the $[\text{Tb}(\text{bpy})_2]\text{Cl}_3$ complex steadily become more intense with elevating the complex concentration in the ORMOCER composite phosphors, suggesting that most of the complex molecules are incorporated into the composite matrices without serious modification or decomposition, in a similar manner to the case of $\text{SiO}_2:\text{Tb}(\text{bpy})_2^{3+}$ composites as previously reported.¹⁸⁾

The luminescence intensity of the resultant phosphors was measured as a function of the complex concentration and heat treatment temperature, as shown in Fig. 6. The emission intensity of the composite phosphors incorporating different amounts of the Tb(III) complex demonstrates similar dependencies on the treatment temperature, that is, it increases with the temperature at the beginning, maximizes at 150°C , and then declines with the temperature being further increased to the values above 200°C . The initial increase of the emission intensity below 150°C is

Fig. 4. FT-IR spectra of the $(\text{SiO}_2\text{-Ta}_2\text{O}_5):\text{Tb}(\text{bpy})_2^{3+}$ (3 mol%) composites with different matrix compositions: (a) $\text{Si}:\text{Ta}=9:1$, (b) $\text{Si}:\text{Ta}=7:3$ and (c) $\text{Si}:\text{Ta}=3:7$. The samples have been heat-treated at 200°C for 5 h in air.

Fig. 5. FT-IR spectra of the $(\text{SiO}_2\text{-Ta}_2\text{O}_5):\text{Tb}(\text{bpy})_2^{3+}$ ($\text{Si}:\text{Ta}=9:1$) composites incorporating various amounts of the complex: (a) 1 mol%, (b) 3 mol%, (c) 6 mol%, (d) 10 mol% and (e) 15 mol%. The samples have been heat-treated at 200°C for 5 h in air.

ascribed to the elimination of the residual solvents and condensation of the $-\text{OH}$ groups as the composite samples are heat-treated, since the non-radiative relaxation through O-H vibration which inflicts serious influence on the luminescence of the rare earth compounds²⁸⁾ will be greatly depressed after such heat treatment. However, when the heat treatment temperature is further increased, the

Fig. 6. Emission intensity of the $(\text{SiO}_2\text{-Ta}_2\text{O}_5) : \text{Tb}(\text{bpy})_2^{3+}$ ($\text{Si} : \text{Ta}=9 : 1$) composite phosphors with various $[\text{Tb}(\text{bpy})_2]\text{Cl}_3$ concentrations as a function of heat treatment temperature. Heat treatment: 5 h, in air.

Fig. 7. FT-IR spectra of the $(\text{SiO}_2\text{-Ta}_2\text{O}_5) : \text{Tb}(\text{bpy})_2^{3+}$ ($\text{Si} : \text{Ta}=9 : 1$, 3 mol%) composite phosphor measured at: (a) 50°C, (b) 150°C and (c) 300°C after heat treatment at the corresponding temperature for 5 h.

decomposition of a part of the complexes takes place and accounts for the decrease of the emission intensity when the heat treatment temperature exceeds 200°C. This is well evidenced by the FT-IR spectra measurements as presented in Fig. 7. The absorption peaks assigned to O-H stretching vibration mode ($\sim 3400\text{ cm}^{-1}$), the O-H bending mode (1653 cm^{-1}), as well as the Si-OH asymmetrical stretching mode ($\sim 960\text{ cm}^{-1}$) obviously decreased after the heat treatments. On the other hand, those peaks ascribed to the complex dopant (denoted as A and B)¹⁸ inversely demonstrated gradual decreases upon heat treatment, suggesting decomposition of a part of the complexes.

The emission intensity increases with raising the complex concentration at the initial stage (10 mol%) while no further increase in the emission intensity is observed when

the dopant concentration exceeds 10 mol%. This stagnation might be due to the concentration quenching effect as caused by the aggregation of the complexes. The relative emission intensity of the inorganic-organic hybrid glass phosphors maximized at ca. 75% vs. $\text{LaPO}_4 : \text{Ce, Tb}$ for $(\text{SiO}_2\text{-Ta}_2\text{O}_5) : \text{Tb}(\text{bpy})_2^{3+}$ with the concentration of 10–15 mol% after a heat treatment at 150°C. In particular, it should be noted that large amount of the Tb(III) complex (20 mol%) was doped into the $\text{SiO}_2\text{-Ta}_2\text{O}_5$ matrix and the resultant materials still provided phosphors with good transparency, indicating that the complex molecules should have been either homogeneously dispersed in the matrix or otherwise the size of the micro-phases or fine pores within the products, if there could be any, must be below the order of 400 nm. This is a great improvement for producing high-performance light emitting materials as fabricated by the introduction of metal oxide components into the composite matrices, in comparison with the $\text{SiO}_2 : \text{Tb}(\text{bpy})_2^{3+}$ composite phosphors, in which only up to 5 mol% of the complex could be incorporated into the host matrix.

4. Conclusions

Green ORMOCER phosphors are successfully obtained by doping $[\text{Tb}(\text{bpy})_2]\text{Cl}_3$ into the $\text{SiO}_2\text{-M}_x\text{O}_y$ ($\text{M}=\text{Zr}$ or Ta) composite matrices via the sol-gel method. The lattice vibration energy of the matrices gradually decreases with increasing the contents of M_xO_y modifiers and leads to a tendency of an increase in the emission intensity as the content of metal modifiers in the matrices increases, while on the other hand, a simultaneous increase of the absorptivity of the matrices below 400 nm results in an decrease of the emission intensity. As a result, the emission intensity of the composite phosphors generally maximizes at the $\text{Si} : \text{M}$ mole ratio of 9 : 1, owing to the competition between the above two factors. In particular, transparent phosphors are obtained within wide complex dopant concentration range of 0–20 mol% for the composites with the same $\text{Si} : \text{Ta}$ ratio. Consequently, the relative emission intensity of the hybrid $(\text{SiO}_2\text{-Ta}_2\text{O}_5) : \text{Tb}(\text{bpy})_2^{3+}$ glass phosphors obtained under the optimized preparation conditions is maximized to ca. 75% vs. $\text{LaPO}_4 : \text{Ce, Tb}$ and is the highest value among the sol-gel derived $[\text{Tb}(\text{bpy})_2]\text{Cl}_3$ -containing transparent green phosphors.

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