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In situ synthesis and fluorescence characterization of 2,2′-dipyridyl–Eu(III) complex in silica xerogel prepared by the sol–gel process

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Abstract

The complex of Eu(III) with 2,2′-dipyridyl is decomposed by water, and thus cannot be doped in gel glasses prepared by the sol–gel process. This paper presents a novel technique of homogeneous doping of the 2,2′-dipyridyl–Eu(III) complex in silica gel glass. By co-doping of 2,2′-dipyridyl and Eu(III) in silica xerogel, an in situ complex of Eu(III) with 2,2′-dipyridyl is synthesized in the transparent monolithic gel glass by suitable heat treatment. Compared with a sample undergoing no heat treatment, the fluorescence intensity of Eu(III) in the xerogel heated at 100 °C for 24 h increases by a factor of about ten due to the formation of the in situ 2,2′-dipyridyl–Eu(III) complex. From the fluorescence spectrum, it is suggested that the in situ complex may be $Eu(C_{10}H_8N_2)Cl_3 \cdot 4H_2O$. © 1997 Elsevier Science S.A.

Keywords: 2,2′-Dipyridyl–Eu(III) complex; Fluorescence; Silica xerogel; Synthesis

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1. Introduction

The crystal structures and luminescence properties of organometallic rare earth complexes have been widely investigated [1,2]. These complexes have desirable properties since UV excitation produces efficient intramolecular energy transfer from ligand excited states to central metal ion emissive levels and yields a characteristic narrow-band emission of the rare earth ions. A number of rare earth complex solutions display laser action. However, for many complexes dissolved in organic solvents, laser action is only observed at low temperatures and high pump energies, which limits their usefulness as laser media [2]. One of the key problems in the application of rare earth complexes is the identification of suitable host materials. The nature of the matrix may affect the optical properties of the complexes, such as the photochemical stability, thermal stability, quenching concentration and non-radiative deactivation. Inorganic matrices possess extremely good optical, thermal and chemical stability. Unfortunately, conventional melt glasses require high processing temperatures which cause rapid decomposition of most complexes. Recent developments in the low-temperature sol–gel process of oxide glass preparation have revealed the possibility of using these superior materials as hosts for organic fluorescent substances. Doping of organic dyes in sol–gel-derived silica hosts for the development of a new generation of advanced tunable solid state lasers has been widely reported [3]. However, many rare earth complexes exhibit low solubilities in the sol–gel precursor solutions [4]. Moreover, some complexes are unstable or precipitate the rare earths as hydroxides from the precursor solutions under the process conditions of gel glasses. For example, the 2,2′-dipyridyl complexes and β-diketone chelates of rare earths are decomposed by water and a few drops of HCl respectively [4,5].

In this work, we present a novel technique of homogeneous doping of the 2,2′-dipyridyl–Eu(III) complex in silica gel glass, called in situ synthesis. The in situ complex is characterized by fluorescence spectroscopy.

2. Experimental details

2.1. Preparation of doped silica xerogels

The doped silica xerogels were prepared by the acidic (HCl) hydrolysis of tetraethoxysilane (TEOS) in ethanol as reported previously [6]. Europium chloride was prepared from Eu_2O_3 (99.99% purity) by dissolution in hydrochloric acid, and 2,2′-dipyridyl was dissolved in ethanol. The starting solutions contained 11.2 ml of TEOS, 11.6 ml of ethanol and 3.6 ml of deionized water. 2,2′-Dipyridyl and/or $EuCl_3$, in

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ethanol and water respectively, were introduced into these solutions. The mixed solutions were adjusted to pH≈2 by the addition of HCl and stirred vigorously for 1 h at room temperature; they were then placed in sealed plastic containers. The precursor solutions converted to wet gels after several days of gelation at 40 °C. The containers should be perforated at the top to allow further gelation to take place at ambient temperature. The wet gels were continuously dried to obtain xerogels at room temperature.

2.2. Synthesis of 2,2′-dipyridyl–Eu(III) complex

The synthesis of the Eu(III) complex with 2,2′-dipyridyl has been reported previously [4]. Eu_2O_3 was dissolved in concentrated HCl. The solution was evaporated almost to dryness to obtain hydrated europium chloride. Solid 2,2′-dipyridyl (2 mmol) was added to a warm solution of 1 mmol of hydrated europium chloride dissolved in 5 ml of absolute ethanol. The mixture was heated to 60 °C and kept at this temperature for about 30 min. The resulting precipitates were filtered, washed with small portions of cold ethanol several times and dried to constant weight in vacuo. The type of 2,2′-dipyridyl–Eu(III) complex was $Eu(C_{10}H_8N_2)_2Cl_3 \cdot 2H_2O$. This stoichiometry was confirmed by IR spectroscopy and elemental analysis (found: C, 39.69%; H, 3.68%; N, 9.31%; calculated: C, 39.59%; H, 3.32%; N, 9.24%).

2.3. Measurements

The fluorescence spectra and differential thermal analysis (DTA) curves were measured with a Hitachi 850 spectrofluorometer and a Lcp-1 differential thermal analyser respectively. The elemental analysis data were obtained with a Carlo—Erba 1106 elemental analyser.

3. Results and discussion

3.1. In situ synthesis of Eu(III) complex with 2,2′-dipyridyl

The derived silica xerogels were heat treated as follows: heated to 100 °C at a rate of 20 °C h^{-1} and kept at this temperature for 24 h in air, followed by cooling in the furnace to obtain transparent monolithic gel glasses for measurement of the fluorescence spectra.

Fig. 1 shows the emission spectra of Eu(III) in 2,2′-dipyridyl and Eu(III) co-doped sample measured at room temperature. On heating at 100 °C, the two emission bands of Eu(III) arising from the $^5D_0 \rightarrow {}^7F_1$ and $^5D_0 \rightarrow {}^7F_2$ transitions split into two main bands each. Meanwhile, the fluorescence intensity increases by a factor of approximately ten and the relative intensity ratio of $^5D_0 \rightarrow {}^7F_2 / {}^5D_0 \rightarrow {}^7F_1$ increases with respect to that in the samples with no heat treatment. In Eu(III)-doped silica xerogel with the same Eu(III) concentration as in the co-doped sample, the emission spectrum shows no changes, but the fluorescence intensity increases slightly after being heated at 100 °C compared with the sample with no heat treatment. Fig. 2 shows the excitation spectra for the $^5D_0 \rightarrow {}^7F_2$ emission of Eu(III) in co-doped silica xerogel measured at room temperature. The sharp bands between 320 and 450 nm in the excitation spectrum of the xerogel with no heat treatment represent the f–f* transitions of Eu(III). On heating at 100 °C, the excitation spectrum exhibits remarkable changes. Two broad bands centred at 250 and 300 nm respectively are substituted for the sharp bands.

The changes in the fluorescence spectrum of 2,2′-dipyridyl in silica xerogel during heat treatment have been studied. Details of this work will be presented elsewhere. With increasing heat treatment temperature, the Si–O network is gradually formed and strengthened, and the 2,2′-dipyridyl molecules are isolated and adsorbed onto the pore wall of the silica network. Owing to the shielding of the Si–O network,

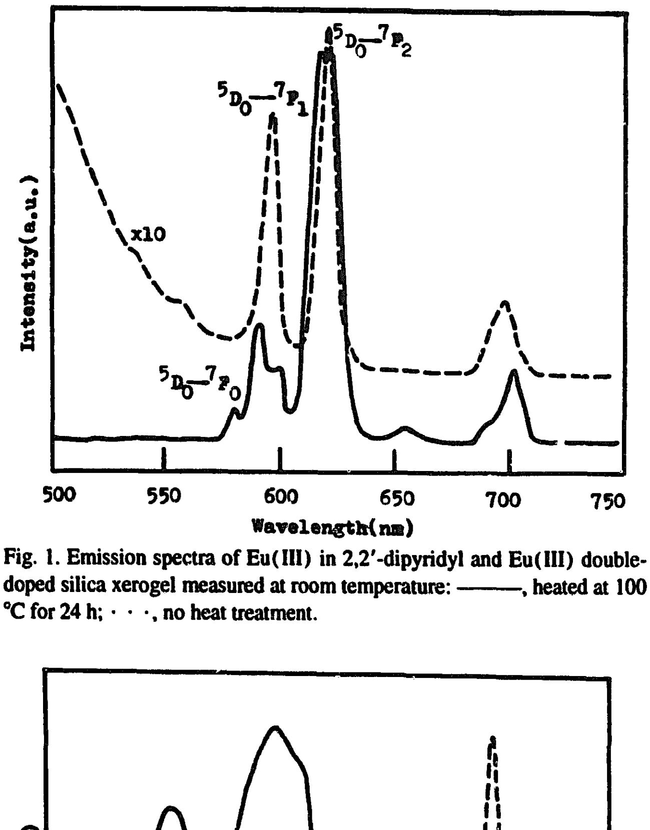

Fig. 1. Emission spectra of Eu(III) in 2,2′-dipyridyl and Eu(III) double-doped silica xerogel measured at room temperature: ———, heated at 100 °C for 24 h; · · ·, no heat treatment.

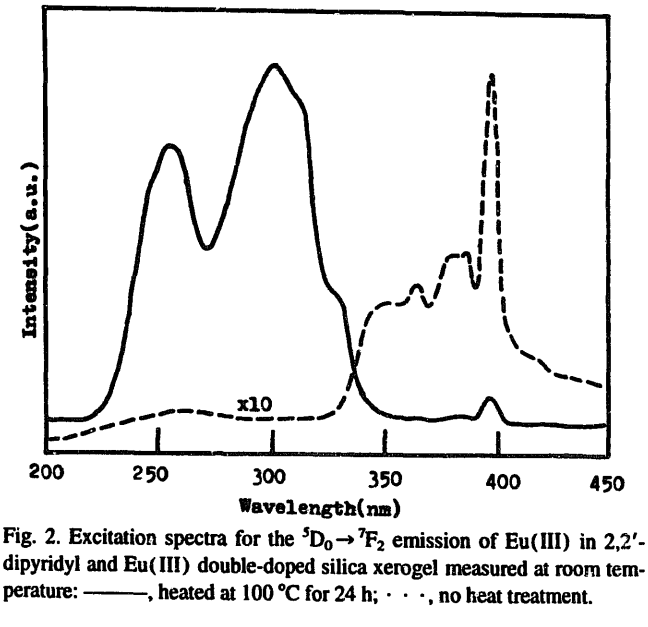

Fig. 2. Excitation spectra for the $^5D_0 \rightarrow {}^7F_2$ emission of Eu(III) in 2,2′-dipyridyl and Eu(III) double-doped silica xerogel measured at room temperature: ———, heated at 100 °C for 24 h; · · ·, no heat treatment.

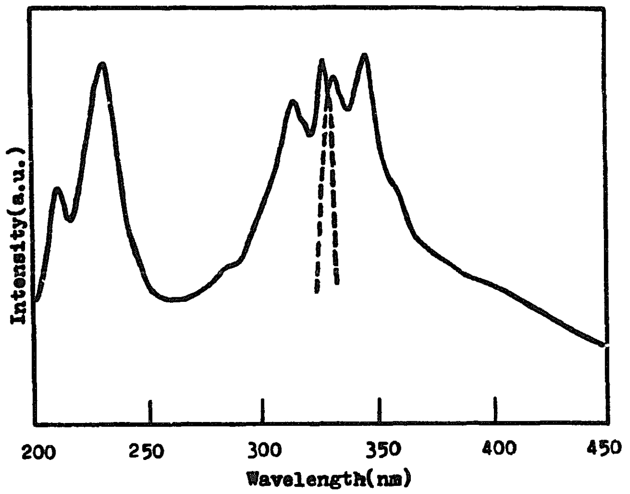

Fig. 3. Excitation (left) and emission (right) spectra of 2,2′-dipyridyl in silica xerogel heated at 550 °C for 24 h, measured at room temperature.

2,2′-dipyridyl molecules are stable in the xerogel when heated to high temperatures, even above the boiling temperature of 2,2′-dipyridyl (approximately 248 °C). The fluorescence spectra of 2,2′-dipyridyl in the silica xerogel heated at 550 °C for 24 h are shown in Fig. 3. The excitation spectrum for 393.3 nm emission of 2,2′-dipyridyl is similar to that observed for 613.3 nm emission of Eu(III) in 2,2′-dipyridyl and Eu(III) co-doped silica xerogel heated at 100 °C (see Fig. 2), but the two broad bands of the former are split into several sharp bands and exhibit a slight shift with respect to the bands of the latter. Thus it is suggested that the two broad bands shown in Fig. 2 correspond to the absorption of 2,2′-dipyridyl resulting from the synthesis of a complex of Eu(III) with 2,2′-dipyridyl. The melting point of 2,2′-dipyridyl is about 77 °C. When the co-doped xerogel is heated at 100 °C, the molten activated 2,2′-dipyridyl molecules diffuse and collide with Eu(III), leading to the formation of the 2,2′-dipyridyl–Eu(III) complex. On UV excitation, the pump energy absorbed by 2,2′-dipyridyl is intramolecularly transferred to Eu(III) emissive levels, and the complex gives the intense characteristic line emission of Eu(III). In the sol–gel precursor solutions and the xerogels without heat treatment, the 2,2′-dipyridyl–Eu(III) complex could not be synthesized because of the possible limitations of excess water, the presence of hydrochloric acid and the dynamic and/or thermodynamic conditions. In this work, the 2,2′-dipyridyl–Eu(III) complex is formed in a solid matrix (silica xerogel) by suitable treatment; therefore the technique is called in situ synthesis and the complex an in situ complex.

The formation of an in situ complex of Eu(III) with 2,2′-dipyridyl modifies the local environment of Eu(III). Eu(III) is substantially shielded from the immediate local surroundings by the 2,2′-dipyridyl shell, which reduces the non-radiative transition probabilities from the excited state of Eu(III) to the surroundings, such as water, and thus also intensifies the fluorescence emission of Eu(III). Furthermore, the fluorescence intensity ratio of the $^5D_0 \rightarrow {}^7F_2$ transition to the $^5D_0 \rightarrow {}^7F_1$ transition is assumed to be an indication of the degree of asymmetry in the surroundings of Eu(III) [7]. The local field symmetry of Eu(III) is reduced on formation of the in situ 2,2′-dipyridyl–Eu(III) complex. Therefore the intensity of the $^5D_0 \rightarrow {}^7F_2$ emission of the forced electric dipole transition relative to the $^5D_0 \rightarrow {}^7F_1$ emission increases greatly after the co-doped xerogel is heated at 100 °C, as shown in Fig. 1.

3.2. Fluorescence characterization of the in situ 2,2′-dipyridyl–Eu(III) complex

In order to characterize the in situ complex, we compared its fluorescence spectrum with that of a pure 2,2′-dipyridyl–Eu(III) complex. The DTA curves of 2,2′-dipyridyl and $Eu(C_{10}H_8N_2)_2Cl_3 \cdot 2H_2O$ are shown in Fig. 4. The endothermic bands peaking at 77 °C and 248 °C in the curve of 2,2′-dipyridyl are attributed to the melting and boiling of 2,2′-dipyridyl respectively. The $Eu(C_{10}H_8N_2)_2Cl_3 \cdot 2H_2O$ powder was heated at 250 °C for 30 min in air. The treated powder was confirmed to be $Eu(C_{10}H_8N_2)Cl_3 \cdot 4H_2O$ by elemental analysis (found: C, 24.41%; H, 3.31%; N, 5.71%; calculated: C, 24.68%; H, 3.05%; N, 5.76%). It seems that $Eu(C_{10}H_8N_2)_2Cl_3 \cdot 2H_2O$ loses one 2,2′-dipyridyl molecule at around 154 °C to yield $Eu(C_{10}H_8N_2)Cl_3 \cdot 4H_2O$. $Eu(C_{10}H_8N_2)Cl_3 \cdot 4H_2O$ decomposes in the range 270–420 °C, and the combustion of the residual organics can be observed at elevated temperature in the DTA curve of $Eu(C_{10}H_8N_2)_2Cl_3 \cdot 2H_2O$. Fig. 5 shows the emission spectra of $Eu(C_{10}H_8N_2)_2Cl_3 \cdot 2H_2O$ and $Eu(C_{10}H_8N_2)Cl_3 \cdot 4H_2O$. The emission bands arising from the $^5D_0 \rightarrow {}^7F_J$ ($J = 1, 2, 3, 4$) transitions are split into several components each. In general, a spherical symmetry exists for free Eu(III), and each level is $(2J+1)$-fold degenerate. The spherical symmetry is destroyed by placing Eu(III) in a crystal, and each level splits under the influence of the electric field produced by the environment. The hamiltonian for Eu(III) in a crystal is the sum of the free-ion hamiltonian and the potential *V* provided by the crystal environment about the ion. *V* can be regarded as a perturbation. By comparing the field splitting of the $^5D_0 \rightarrow {}^7F_1$ and $^5D_0 \rightarrow {}^7F_2$ transitions in the co-doped xerogel heated at 100 °C, as shown in Fig. 1, with that of these tran-

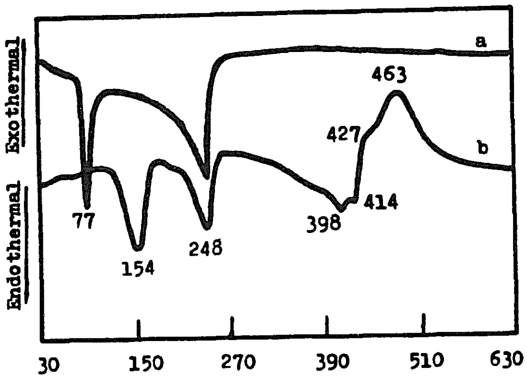

Fig. 4. DTA curves of 2,2′-dipyridyl (a) and complex $Eu(C_{10}H_8N_2)_2$-$Cl_3 \cdot 2H_2O$ (b).

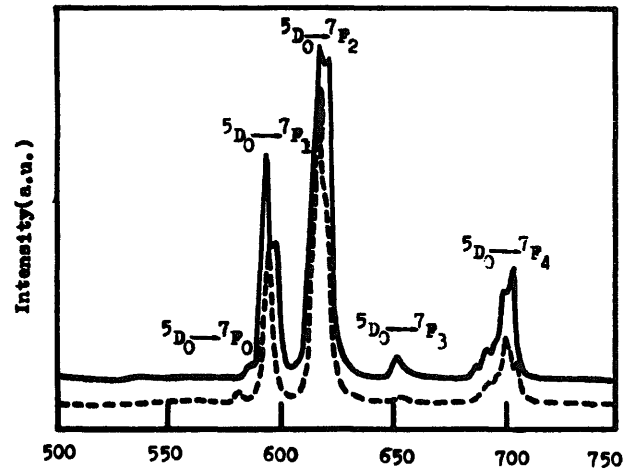

Fig. 5. Emission spectra of Eu(III) in $Eu(C_{10}H_8N_2)_2Cl_3 \cdot 2H_2O$ (· · ·) and $Eu(C_{10}H_8N_2)Cl_3 \cdot 4H_2O$ (———).

sitions in $Eu(C_{10}H_8N_2)Cl_3 \cdot 4H_2O$, it is concluded that the surroundings of Eu(III) in the in situ 2,2′-dipyridyl–Eu(III) complex are similar to those in $Eu(C_{10}H_8N_2)Cl_3 \cdot 4H_2O$, which indicates that the in situ 2,2′-dipyridyl–Eu(III) complex may be $Eu(C_{10}H_8N_2)Cl_3 \cdot 4H_2O$. The molar ratio of Eu(III) to 2,2′-dipyridyl is 10 : 1 in the silica xerogel. Owing to the deficient 2,2′-dipyridyl and excess physically adsorbed water in the xerogel, compared with the preparation conditions of complex $Eu(C_{10}H_8N_2)_2Cl_3 \cdot 2H_2O$ described above, $Eu(C_{10}H_8N_2)Cl_3 \cdot 4H_2O$ will be formed in the xerogel on heating at 100 °C.

Moreover, there may be an additional interaction between the in situ complex and the host, such as the Si–O network, adsorbed water and residual organics, which may introduce new perturbing effects and may possibly modify slightly the regular arrangement of the nearest neighbours of Eu(III) in the in situ complex. This results in a further reduction in the local symmetry of Eu(III). Therefore the fluorescence intensity ratio of the $^5D_0 \rightarrow {}^7F_2$ transition to the $^5D_0 \rightarrow {}^7F_1$ transition in the in situ complex is larger than that in the pure complex $Eu(C_{10}H_8N_2)Cl_3 \cdot 4H_2O$ (see Figs. 1 and 4).

More precise work should be performed on the characterization of the in situ complex of Eu(III) with 2,2′-dipyridyl. Further studies are in progress in our laboratory and will be published shortly.

In the same type of experiment, an in situ 2,2′-dipyridyl–Tb(III) complex is formed in silica gel glass on heating at 100 °C for 24 h.

4. Conclusions

The excitation spectrum of free rare earth ions can be attributed to transitions from the ground state to higher levels of the f orbital giving rise to sharp bands due to f–f* transitions. However, intra-f-orbital transitions are parity forbidden in the free ion. Therefore the intensities of the absorption bands induced by f–f* transitions are weak. Organic ligands usually have high UV molar absorptivity. If complexes of rare earths with appropriate organic ligands are synthesized, the fluorescence intensity of the rare earth ions can be increased significantly as a result of indirect excitation of the rare earth ions through efficient intramolecular energy transfer within the complexes. By co-doping Eu(III) and 2,2′-dipyridyl in silica xerogel, a 2,2′-dipyridyl–Eu(III) complex can be synthesized in situ in the transparent monolithic gel glass by a suitable heat treatment; the in situ complex is characterized as $Eu(C_{10}H_8N_2)Cl_3 \cdot 4H_2O$ by fluorescence spectroscopy. In situ synthesis of rare earth complexes in gel-based media appears to be promising for potential applications in new bulk lasers and integrated optical device sources.

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