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RESEARCH ARTICLE

Synthesis and optical properties of europium pentafluoropropionate 1,10-phenanthroline complex and its silica glass

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Abstract Europium pentafluoropropionate 1,10-phenanthroline complex, $Eu(C_2F_5COO)_3 \cdot Phen$ (Phen = 1,10-phenanthroline), were synthesized and characterized by elemental analysis, Fourier transform infrared spectroscopy (FT-IR), photoluminescence (PL) spectroscopy and thermogravimetric analysis (TA). At the same time, its silica glass was synthesized by *in situ* processes. The excitation spectra of the complex demonstrate that the energy collected by "antenna ligands" was transferred to Eu^{3+} ions efficiently. The room-temperature PL spectra of the complexes are composed of the typical Eu^{3+} ions red emission, due to transitions between $^5D_0 \rightarrow {}^7F_{J(J\,=\,0\,\rightarrow\,4)}$. The decomposition temperature of the complex was 290°C, which indicates the host complex is quite stable to heat. Then the affection of anneal temperatures on PL properties of SiO_2 glass were studied. The PL intensity of the SiO_2 glass annealed at 160°C was higher than other annealed temperatures for 24 h in air.

Keywords organometallic complex, silica glass, luminescent property

1 Introduction

The design and synthesis of luminescence complexes have attracted considerable attention due to their potential application as molecular photonic devices [1], fluorescent sensors [2,3], and luminescent chemical probes [4,5].

Silica glasses obtained by the sol-gel method have been intensely investigated during the last decade [6,7]. Compared with conventional glasses technique, this method has many advantages, such as low temperature process, high concentration of rare-earth doped, pure host matrix and organic molecule easily introduced. But the sol-gel method can produce a lot of hydroxyl groups in silica gel, which cause the radiationless transition process of rare-earth ions. In order to decrease the nonradiative energy loss and obtain high luminescence, organic ligands have been used. In the silica glasses, the organic ligand absorbs energy and then transfers efficiently to the metal ion [8]. Moreover, these ligands can also be acted as the second assistant ligands to replace water or other small molecules in coordination sphere [9]. It has been reported in my previous study that pentafluoropropionate as the first liagnd not only can increase the luminescence properties, but also reduce the radiationless transition process via vibrational absorption of C–H and O–H bonds [10,11]. In this study, we presented *in situ* preparation processes and luminescence behaviors of europium pentafluoropropionate 1,10-phenanthroline complex in the sol-gel derived host material. It was found that the decomposition temperature of the complex was 290°C, which indicates the host complex is quite stable to heat. According to the optical spectrum, $Eu(C_2F_5COO)_3 \cdot Phen$ encapsulated in the SiO_2 glass will be a promising inorganic–organic hybridized material.

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2 Experiments

2.1 Materials and measurement

All analytical reagents were obtained from commercial sources and used directly without further purification. Elemental analysis (C, H, N) was determined with a German Vario EL III instrument. The infrared spectra were recorded as KBr pellet on a Nicolet 170SX FT-IR

spectrometer. Excitation and emission spectra were obtained at room temperature using a spectrofluorometer FL900 (Edinburgh Instruments) with a Xe lamp as a light source fitted with a Hamamatsu photomultiplier. The TG-DTG measurements were done with a Thermoanalyzer Systems Q1000DSC + LNCS + FACS Q600SDT of TA company.

2.2 Sythesis of $Eu(C_2F_5COO)_3 \cdot Phen$ complex

First, 2.11 g (6 mmol) Eu_2O_3 was dissolved in 4.10 g (36 mmol) C_2F_5COOH with 20 mL H_2O. The solution was refluxed for 4 h under stirring. Then, it was concentrated by vacuum rotary evaporation. A white precipitate, $Eu(C_2F_5COO)_3 \cdot 2H_2O$, was obtained. 1,10-Phenanthroline $\cdot H_2O$ 0.594 g (3 mmol) and $Eu(C_2F_5COO)_3 \cdot 2H_2O$ 2.031 g (3 mmol) were mixed in 40 mL tetrahydrofuran and stirred for 2 h at room temperature. The products, $Eu(C_2F_5COO)_3 \cdot Phen$ was achieved after dried in vacuum under 120°C for 12 h. Elemental analysis calcd. for $Eu(C_2F_5COO)_3 \cdot Phen$: C 30.7, H 0.98, N 3.41; found: C 30.80, H 1.04, N 3.39%. IR (KBr, cm^{-1}): 1728(s, $\nu_{as(COO)}$), 1664(vs, $\nu_{as(COO)}$), 1523(m, $\nu_{(C=N)}$), 1435(m, $\nu_{s(COO)}$), 1327(m, $\nu_{s(COO)}$), 1219(vs, $\nu_{(C\text{-}F)}$), 844(s, $\nu_{(C\text{-}H)}$), 729(vs, $\nu_{(C\text{-}F)}$).

2.3 Sythesis of the complex in silica matrix

The solution used to prepare the silica xerogel consisted of 1 mol tetraethyl orthosilicate (TEOS), 4 mol ethanol and 4 mol distilled water. A small amount of HCl was added to the solution to promote hydrolysis. 0.01 mol Phen and 0.01 mol $Eu(C_2F_5COO)_3 \cdot 2H_2O$ were added. The pH value was controlled within the acid region (about 2–3). The mixed solution was vigorously stirred at room temperature for 1 h. The resulting sol was subsequently kept in a sealed container at 40°C until the onset of gelation. Aging and drying were allowed to proceed under ambient conditions over a period of several weeks.

3 Results and discussion

3.1 Thermogravimetric analyses of the complex

Thermogravimetric analysis (TGA) curve recorded in N_2 atmosphere from 30°C to 600°C for $Eu(C_2F_5COO)_3 \cdot Phen$ was shown in Fig. 1. It indicates that the decomposition processes of $Eu(C_2F_5COO)_3 \cdot Phen$ can be divided into two stages. The decomposition temperature of the complex $Eu(C_2F_5COO)_3 \cdot Phen$ was found to be 290°C. For the complex $Eu(C_2F_5COO)_3 \cdot Phen$, the first stage is 290°C–338°C, which was corresponded to the loss of 1 mol Phen and 2 mol pentafluoropropionate anions. This degradation can be explained that the Eu–N bonds are less stable and easy to be broken down. The second stage of temperature

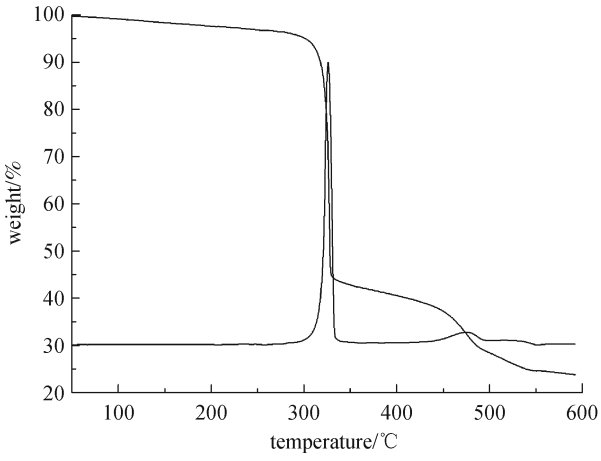

Fig. 1 TGA and DTA curves of the complex

was 335°C–550°C corresponded to the loss of 1 mol pentafluoropropionate anions. The decomposed stage has 75.5% mass loss, and the mass of the residue is 24.5% according with the theoretical mass summation (25.6%) of EuF_3. The result of powder X-ray diffraction experiment proved that the major ingredient of the residue was EuF_3. The thermal analysis indicates that the complex is quite stable to heat.

3.2 Photoluminescence (PL) spectroscopy

Excitation and emission spectra of the complex were recorded at room temperature. It emitted intense red fluorescence when exposed under ultraviolet light. The excitation spectrum of $Eu(C_2F_5COO)_3 \cdot Phen$ and $Eu(C_2F_5COO)_3 \cdot Phen$ in silica glass was shown in Fig. 2, which were recorded by monitoring the $^5D_0 \rightarrow {}^7F_2$ emission band at 612 nm. Each of the excitation spectra consists of a very broad band instead of a characteristic narrow band of Eu^{3+} (395 nm), which indicates that the europium complex has been synthesized by an *in situ* technique via silica gel process. Compared to that of pure complex, the maximum excitation wavelength of the complex in silica gel shows a small red-shift changing from 332 to 344 nm, which implies that different compositions may exist in the two samples. For pure complex, the surrounding environment of the Eu^{3+} is homogeneous, so the excitation spectrum consists of asymmetric and broad band ranging from 250 to 400 nm. However, silica gel is a non-crystalline substance with a porous microstructure, so the excitation spectrum becomes an asymmetric band. The bands at 395, 415 and 465 nm are sharp f–f transitions characteristic of the Eu^{3+} ion, corresponding to those from the ground $^7F_0$ level to the $^5L_6$, $^5D_3$ and $^5D_2$ multiplet terms, respectively.

The emission spectra of $Eu(C_2F_5COO)_3 \cdot Phen$ was shown in Fig. 3, which composed of narrow and well-resolved characteristic emission peaks of Eu^{3+} arising from

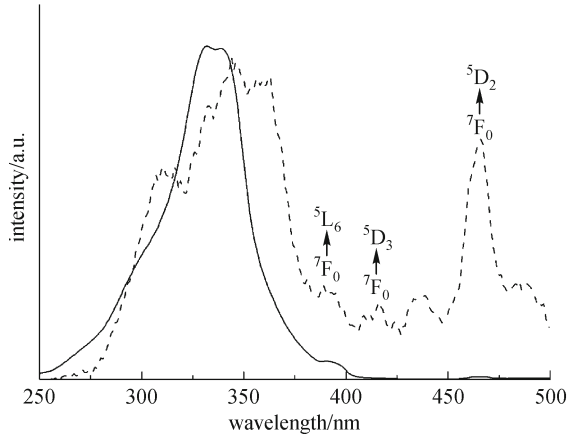

Fig. 2 Room temperature excitation spectra (λ_{em} = 612 nm) of the complex (solid line) and the silica glass (dash line)

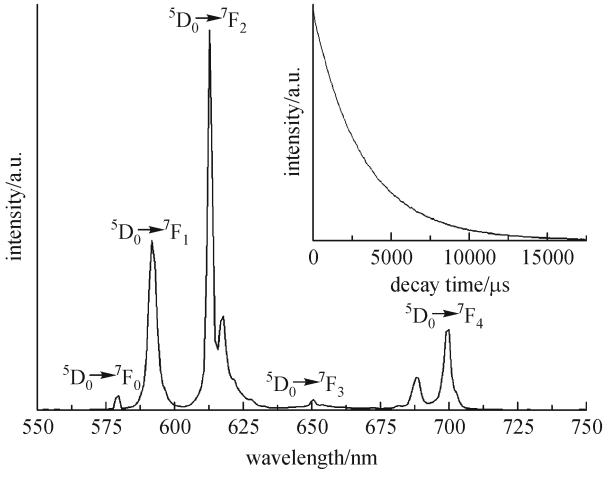

Fig. 3 Room temperature emission spectra (λ_{em} = 329 nm) of $Eu(C_2F_5COO)_3 \cdot Phen$. Inset is the decay curve monitored at 612 nm

the transition $^5D_0 \rightarrow {}^7F_0$ (580 nm), $^5D_0 \rightarrow {}^7F_1$ (592 nm), $^5D_0 \rightarrow {}^7F_2$ (613 and 619 nm), respectively. A relevant feature that may be noted for the complex is the high intensity of the $^5D_0 \rightarrow {}^7F_2$ transition, relative to the $^5D_0 \rightarrow {}^7F_1$ lines, indicating that the Eu^{3+} ion coordinated in a local site without an inversion center. Further, the emission spectra of the complex was chacterized only one peak for $^5D_0 \rightarrow {}^7F_0$ transition, suggesting the presence of a single chemical environment around the Eu^{3+} ion and also showing that the Eu^{3+} ion occupies a low-symmetry site. The lifetime value (τ_{obs}) of the $^5D_0$ level was determined from the luminescence decay profile for $Eu(C_2F_5COO)_3 \cdot Phen$ at room temperature. And the lifetime value of the complex was fitting by bi-exponential function with the fast and slow decay lifetimes 2970 and 820 μs. The data presented suggested that two kind of symmetrical sites of Eu^{3+} ions exist in this composite. The lifetime value is longer than many fluorinated europium complexes [12,13]. Considering the long lifetime, the multiphonon relaxation by coupling to O–H and C–H vibrations are reduced.

But the emission intensity of the silica glass was weaker than that of the complex. Synthesis of the complex by an *in situ* technique via silica gel process can introduce some of H_2O molecules or OH groups to the europium ion, thus the emission intensity was quenched. In addition, the emission intensity of silica glass increased with the annealing temperatures and approached its maximum at 160°C, and then it decreased with the annealing temperature increase successively. The changes of the emission intensity can be explained as follows: as the annealing temperature increases, the concentration of hydroxyl groups (OH) presented in the glasses will decrease. Therefore the multiphonon relaxation of the $^5D_0$ level is less effective and the higher emission intensity is expected. On the other hand, the decrease of intensity observed in samples annealed at higher temperatures is likely to be due to a lower interaction between the europium and the organic ligand, which can not protect the metal ion from interactions with –OH groups. The overall efficiency of this energy transfer process decreases as the temperature increases, due to the decrease of the stability of the complex.

3.3 Judd-Ofelt analysisof $Eu(C_2F_5COO)_3 \cdot Phen$

Judd-Ofelt analysis is one of the most successful theories for evaluating the potential radiative properties of rare-earth-doped materials [14]. Interaction parameters of ligand fields are given by the Judd-Ofelt parameters, $\Omega_{t\,(t\,=\,2,4,6)}$. To estimate the strength of crystal field in the complex, we calculated the Judd–Ofelt parameter Ω_2 which is more sensitive to the symmetry and sequence of ligand fields. According to the Judd-Ofelt theory [15], the spontaneous emission probability of an electric dipole transition between initial J manifold $|(S, L)\, J>$ to terminal manifold $|(S', L')\, J'>$ is given by

$$A_{\mathrm{ed}} = A[(S,L)J;(S',L')J'] = \frac{64\pi^4 e^2 \nu^3}{3h(2J+1)} \frac{n(n^2+2)^2}{9} S_{\mathrm{ed}},$$

$$S_{\mathrm{ed}} = \sum_{\lambda=2,4,6} \Omega_\lambda \left| \left\langle (S,L)J \left\| U^{(\lambda)} \right\| (S',L')J' \right\rangle \right|^2, \qquad (1)$$

where h is the Plank's constant, m is the mass of electron, c is the velocity of light, n is the refractive index of medium, v is the wavenumber of the transition, J is the total angular momentum of ground state, and the $\|U^{(\lambda)}\|^2$ are the squared reduced matrix elements of the rank $\lambda = 2,4,6$. The squared reduced matrix elements $\left\langle {}^5D_0 \left\| U^{(2)} \right\| {}^7F_2 \right\rangle = 0.0032$ and

$\left\langle {}^5\mathrm{D}_0 \middle\| U^{(4)} \middle\| {}^7\mathrm{F}_4 \right\rangle = 0.0023$ in Eq. (1) were taken from Ref. [16].

It is well-known that the ${}^5\mathrm{D}_0 \rightarrow {}^7\mathrm{F}_1$ of Eu^{3+} ion is a magnetic dipole transition. This transition is independent of the environment and can be used as a reference. The experimental radiative rate of the spontaneous emission, A_{rad}, can be determined by summing of the all spontaneous contributions. For this purpose, each spontaneous emission coefficient A_{0J} for each ${}^5\mathrm{D}_0$–${}^7\mathrm{F}_J$ transition is obtained from [17]:

$$A_{0J} = A_{01}\frac{I_{0J}}{I_{01}}\frac{\nu_{01}}{\nu_{0J}}, \tag{2}$$

where I_{01} and I_{0J} are the integrated intensities of the ${}^5\mathrm{D}_0 \rightarrow {}^7\mathrm{F}_1$ and ${}^5\mathrm{D}_0 \rightarrow {}^7\mathrm{F}_J$ transitions ($J = 2$ and 4) with ν_{01} and ν_{0J} being the respective energy barycenters of these transitions.

The experimental intensity parameters, Ω_2 and Ω_4, can be estimated from the emission spectra (Fig. 3) based on the ${}^5\mathrm{D}_0 \rightarrow {}^7\mathrm{F}_2$ and ${}^5\mathrm{D}_0 \rightarrow {}^7\mathrm{F}_4$ electronic transitions of Eu^{3+} ion according to the following equation [18]:

$$\frac{\int I_J(\upsilon)\mathrm{d}\upsilon}{\int I_{\mathrm{md}}(\upsilon)\mathrm{d}\upsilon} = \frac{A_J}{A_{\mathrm{md}}} = \frac{e^2}{S_{\mathrm{md}}}\frac{\upsilon_J^3}{\upsilon_{\mathrm{md}}^3}\frac{(n^2+2)^2}{9n^2}\Omega_t\left\|U^{(t)}\right\|^2. \tag{3}$$

The ${}^5\mathrm{D}_0 \rightarrow {}^7\mathrm{F}_1$ is the only transition which does not have electric dipole contribution and can be theoretically determined: $S_{\mathrm{md}} = 9.6\times10^{-42}\ \mathrm{esu}^2\cdot\mathrm{cm}^2$ [19]. Using Eq. (3), the Judd–Ofelt parameters, Ω_2 and Ω_4, can be determined. The Ω_6 intensity parameter was not determined because the ${}^5\mathrm{D}_0 \rightarrow {}^7\mathrm{F}_6$ transition could not be experimentally detected. To estimate the capability of this europium complex for being a lasing medium, the stimulated emission cross-section (σ) value was determined. The σ value is one of the most important factors for laser amplification. With the value of the radiative transition rate calculated above and the corresponding emission spectrum, the σ is calculated by [20]:

$$\sigma_{\mathrm{p}}(\lambda_{\mathrm{p}}) = \frac{\lambda_{\mathrm{p}}^4}{8\pi c n^2 \Delta\lambda_{\mathrm{eff}}}A[(S,L)J;(S',L')J'], \tag{4}$$

where c, λ_{p}, $\Delta\lambda_{\mathrm{eff}}$, n and A are the speed of light, the wavelength of the oscillation peak, the line width of fluorescence peak (FWHM), refractive index of the matrix and the radiative transition rate, respectively. With the measured lifetime τ_{obs}, together with the above calculated radiative lifetime τ_{rad}, the luminescence quantum yield η can be calculated:

$$\eta = \frac{\tau_{\mathrm{obs}}}{\tau_{\mathrm{rad}}}. \tag{5}$$

Judd–Ofelt parameters (Ω_{t}), the radiative decay rates (A_{rad}), nonradiative decay rates (A_{nr}), and measured lifetime (τ_{obs}), quantum yield (η) and the stimulated emission cross-section (σ) of ${}^5\mathrm{D}_0 \rightarrow {}^7\mathrm{F}_2$ transition are presented in Table 1. It is worth mentioning that the value for Ω_2 is relatively small ($4.42\times10^{-20}\ \mathrm{cm}^2$). This is a clear indication of a reduced degree of covalence involving the metal-ligand coordination bond and also of a slightly polarizable chemical environment for the lanthanide center. It is well known that the emission cross-section (σ) of ${}^5\mathrm{D}_0 \rightarrow {}^7\mathrm{F}_2$ fluorescence transition of Eu^{3+} is one of the most important parameters for laser design. Here, the emission cross-section (σ) of ${}^5\mathrm{D}_0 \rightarrow {}^7\mathrm{F}_2$ fluorescence transition is $20.1\times10^{-22}\ \mathrm{cm}^2$, which is larger than some europium doped materials [21,22].

4 Conclusions

In conclusion, $Eu(C_2F_5COO)_3\cdot$Phen complex and its silica glass were synthesized and investigated. The thermal analysis indicates that the complex was quite stable to heat. An intense red light emission of the composite materials was observed under ultra-violet light irradiation, indicating an efficient energy transfer between the ligand (Phen) and the Eu^{3+} ion. The ${}^5\mathrm{D}_0$ lifetime and quantum yield of the complex are 2970 μs, 820 μs and 54.8% which reflect that the multiphonon relaxations by coupling to O–H and C–H vibrations are reduced. The value of the stimulated emission cross-section obtained in this work is $20.1\times10^{-22}\ \mathrm{cm}^2$, which is larger than some europium doped materials in the literature. The emission intensities of the composites markedly depended on the annealing temperature. The highest value of the relative emission intensity was obtained for the silica glass annealed at 160°C.

Table 1 Judd–Ofelt parameters (Ω_{t}), radiative (A_{rad}) and nonradiative decay rate (A_{nr}), ${}^5\mathrm{D}_0$ lifetime (τ_{obs}), quantum yield (η) for europium doped materials

material	$\Omega_2/(10^{-20}\ \mathrm{cm}^2)$	$\Omega_4/(10^{-20}\ \mathrm{cm}^2)$	$A_{\mathrm{rad}}/\mathrm{s}^{-1}$	$A_{\mathrm{nr}}/\mathrm{s}^{-1}$	$\tau_{\mathrm{obs}}/\mu\mathrm{s}$	$\eta/\%$	$\sigma/(10^{-22}\ \mathrm{cm}^2)$	Refs.
this work	4.42	2.07	170	140	3227	54.8	20.1	–
$Eu(hfa)_3$(BIPHEPO)	48.1	–	–	–	1100	–	4.64	[21]
Eu^{3+}:L5FBE	5.64	4.44	188	–	2240	–	12.3	[22]

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