Radiative properties of a europium (III) ternary complex containing electro-transporting group ligands doped polymer

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A europium ternary complex containing electro-transporting group ligands has been synthesized and doped into silicone rubber. Its luminescence properties have been investigated by fluorescence emission spectrum and lifetime measurements. According to the fluorescence emission spectrum, the Judd-Ofelt parameters Ω_2, Ω_4 of europium complex doped silicone rubber have been calculated and the radiative properties were presented and analyzed also.

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Keywords: Europium complex, Polymer, Judd-Ofelt theory

1. Introduction

The lanthanides complexes are well known to be efficient emitters under UV/VIS excitation [1]. From all lanthanides complexes, europium *β*-diketone complexes are famous for their luminescence properties. As red-emitting material, they have high fluorescent quantum efficiency, pure luminescent color and good stability [2].

Polymers are promising host candidates in lanthanides complexes doped materials for applications in photonics, optoelectronics and integrated optics, because of their excellent properties such as high transparency, low cost, and easy fabrication [3~6]. Silicone based polymers possess a unique set of properties that makes them highly suitable for optical applications. In addition to their excellent thermal stability and mechanical properties, they are highly transparent in the ultra-violet, visible, and selected bands of the near-IR spectra.

In this article, a europium ternary complex with an electro-transporting group (*biphenyl* group), $Eu(MBPTFA)_3Phen$, has been synthesized, in which the central ligand is *1-(4'-meothoxybiphenyl-4-yl)-4,4,4-trifluorobutane-1,3-dione* (MBPTFA), and the neutral ligand is *1,10-phenanthroline* (Phen). A silicone based polymer, methyl vinyl silicone rubber has been chosen as the matrix to prepare $Eu(MBPTFA)_3Phen$ doped polymer. According to its fluorescence spectra and lifetime measurement, the Judd-Ofelt parameters, the radiative decay rate A_{rad}, the non-radiative rates A_{nrad} and the emission quantum efficiency η were calculated and analyzed.

2. Experimental

The europium (III) ternary complex containing electro-transporting group ligands, *1,10-phenanthroline-tris[1-(4'-meothoxybiphenyl-4-yl)-4,4,4-trifluorobutane-1,3-dione]-europium*, $Eu(MBPTFA)_3Phen$, was synthesized according to the procedure reported before [7]. The molecular structure of $Eu(MBPTFA)_3Phen$ is shown in Fig. 1. The central Eu^{3+} ion is bound to three MBPTFA ligands, Phen acts as a synergic shielding ligand, which can reduce the rate of nonradiative decays and enhance the fluorescence intensity of the complex strongly [8].

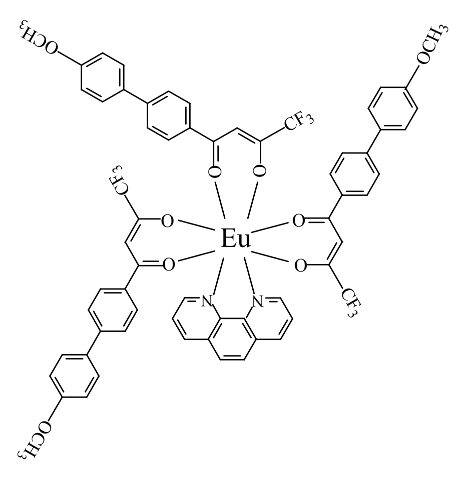

Fig. 1. Chemical structure of $Eu(MBPTFA)_3Phen$.

Methyl vinyl silicone rubber (brand 110) was supplied by Dongjue Silicone Group Company Limited. Eu(MBPTFA)$_3$Phen doped silicone rubber fluorescence material was prepared by mixing 100 g of the silicone rubber, 2 g of *2,5-dimethyl-2,5-di(tert-butylperoxy)hexane* (DHBP) and 5 g of Eu(MBPTFA)$_3$Phen in a Haake rheomix 600 mixer at 50℃ and at 80 rpm for 15 min. Then, the achieved compound was put into a mould of 10 mm thickness and vulcanized under the pressure of 20 MPa for 20 min at 180℃ to obtain the cured Eu(MBPTFA)$_3$Phen doped silicone rubber material.

The fluorescence emission spectrum of Eu(MBPTFA)$_3$Phen doped silicone rubber were recorded on a Shimadzu RF-5301PC spectrofluorophotometer. The measurement of the fluorescence decay curves was performed at room temperature. The third harmonic (355 nm) of a Nd:YAG laser was used as a pump source. The emission at the $^5D_0 \rightarrow {}^7F_2$ transition of Eu^{3+} was monitored and recorded as a function of time. Data were acquired using a Tektronix TDS 5000 digital oscilloscope and analyzed using a computational program ORIGIN®6.1.

3. Results and discussion

3.1 Fluorescence emission spectrum Eu(MBPTFA)$_3$Phen doped silicone rubber

The fluorescence emission spectrum of Eu(MBPTFA)$_3$Phen doped silicone rubber is shown in Fig. 2.

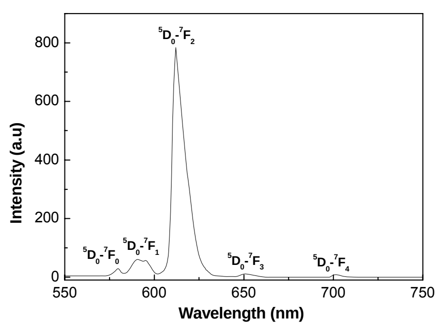

Fig. 2. Fluorescence emission spectrum of Eu(MBPTFA)$_3$Phen doped silicone rubber.

The emission spectrum was recorded form 550 nm to 750 nm under the excitation at 396 nm. It can be found five emission peaks corresponding to $^5D_0 \rightarrow {}^7F_{0,1,2,3,4}$ can be clearly distinguished for Eu(MBPTFA)$_3$Phen doped silicone rubber. The presence of only one $^5D_0 \rightarrow {}^7F_0$ line indicates that the Eu^{3+} ion occupies only a single site and a single chemical environment exists around it. The $^5D_0 \rightarrow {}^7F_2$ transition dominates all other transitions and emission intensity of this transition strongly depends on the chemical environment where the Eu^{3+} ion is located. The much stronger intensity of $^5D_0 \rightarrow {}^7F_2$ than those of other transitions indicates the ligand field surrounding the Eu^{3+} ion is highly polarizable [9]. It also indicated that Eu(MBPTFA)$_3$Phen doped silicone rubber has good color purity and the Eu^{3+} ion is in a site without a center of inversion.

3.2 Judd-Ofelt analysis of Eu(MBPTFA)$_3$Phen doped silicone rubber

It is well known that due to selection rules, the $^5D_0 \rightarrow {}^7F_{2,4,6}$ transitions of Eu^{3+} are allowed by induced electric dipole mechanisms. According to the Judd-Ofelt theory, the spontaneous emission probability of an electric dipole transition between initial J manifold $\left|(S,L)J\right\rangle$ to terminal manifold $\left|(S',L')J'\right\rangle$ is given by [10,11]:

$$A_{ed} = A\left[(S,L)J;(S',L')J'\right] = \frac{64\pi^4 e^2 \nu^3}{3h(2J+1)} \frac{n(n^2+2)^2}{9} S_{ed}$$
$$= \frac{64\pi^4 e^2 \nu^3}{3h(2J+1)} \frac{n(n^2+2)^2}{9} \sum_{t=2,4,6} \Omega_t \left|\left\langle (S,L)J \left\| U^{(t)} \right\| (S',L')J' \right\rangle\right|^2$$

where h is Plank's constant, m is the mass of the electron, c is the velocity of light, n is the refractive index of the medium, v is the wavenumber of the transition and J is the total angular momentum of the ground state, the $\left\|U^{(t)}\right\|^2$ are the squared reduced matrix elements of the rank t=2, 4, 6 and their values are not change with the host for Ln^{3+} ions. The three coefficients Ω_2, Ω_4, Ω_6 contain implicitly the odd-symmetry crystal field terms, radial integrals and perturbation denominators.

The $^5D_0 \rightarrow {}^7F_1$ of Eu^{3+} ion is a magnetic dipole transition which is independent of the environment and can be used as a reference. The spontaneous emission probability of magnetic dipole transition A_{md} is [12]:

$$A_{md} = \frac{64\pi^4 \nu^3}{3h(2J+1)} n^3 S_{md}$$

S_{md} refers to the strength of the magnetic dipole line strength of the $^5D_0 \rightarrow {}^7F_1$ transition, which is a constant and independent of the medium.

The $\left\|U^{(t)}\right\|^2$ values of Eu^{3+} ion are taken from Carnall et al [13]. The spontaneous emission probability of an electric dipole transition A_{ed} depends on $\left\|U^{(t)}\right\|^2$. The Ω_t can be determined from the ratios of intensities of $^5D_0 \rightarrow {}^7F_{2,4,6}$ transitions to the intensity of $^5D_0 \rightarrow {}^7F_1$ transition as follows:

$$\frac{\int I_J(\nu)d\nu}{\int I_{md}(\nu)d\nu} = \frac{A_J}{A_{md}} = \frac{e^2}{S_{md}} \frac{\nu_J^3}{\nu_{md}^3} \frac{(n^2+2)^2}{9n^2} \Omega_t \left\|U^{(t)}\right\|^2$$

The obtained values for parameter Ω_2 and Ω_4 of Eu(MBPTFA)$_3$Phen doped silicone rubber are 18.4×10^{-20} cm^2 and 0.442×10^{-20} cm^2, respectively. Compared with

Eu^{3+} doped inorganic system, $Eu(MBPTFA)_3Phen$ doped silicone rubber show a relative larger Ω_2 value [12,14]. The large Ω_2 value indicates the presence of covalent bonding between the Eu^{3+} ion and the surrounding MBPTFA ligands [15]. The much stronger hypersensitive transition $^5D_0\rightarrow{}^7F_2$ accounts for such a Ω_2 value. The Ω_4 parameters have been related together to bulk properties of the lanthanide based hosts, but there is no theoretical prediction for this sensibility to macroscopic properties [16]. The Ω_6 intensity parameter was not determined because the $^5D_0\rightarrow{}^7F_6$ transition could not be experimentally detected. This indicated that the Ω_6 is not important here.

3.3 Radiative properties of $Eu(MBPTFA)_3Phen$ doped silicone rubber

Once the intensity parameters Ω_t are determined, they can be used to calculate the radiative properties of $Eu(MBPTFA)_3Phen$ doped silicone rubber. The total transition emission probability A_T is calculated using [10,11]:

$$A_T = \sum_{S,L,J} A\left[(S,L)J;(S',L')J'\right]$$

where $A\left[(S,L)J;(S',L')J'\right]$ is the spontaneous emission probability of a transition between initial J manifold $\left|(S,L)J\right\rangle$ to terminal manifold $\left|(S',L')J'\right\rangle$.

The fluorescence branching ratio is obtained from [10,11]:

$$\beta\left[(S,L)J;(S',L')J'\right] = \frac{A\left[(S,L)J;(S',L')J'\right]}{\sum_{S,L,J} A\left[(S,L)J;(S',L')J'\right]}$$

The radiative lifetime of the transition involved is an important parameter in consideration of the pumping requirement for the threshold of laser action and can be calculated as [10,11]:

$$\tau_{rad}\left[(S,L)J\right] = \frac{1}{\sum_{S,L,J} A\left[(S,L)J;(S',L')J'\right]}$$

Another important radiative property is the stimulated emission cross section of the measured fluorescence [10,11]:

$$\sigma\left[(S,L)J;(S',L')J'\right] = \frac{\lambda_p^4}{8\pi c n^2 \Delta\lambda_{eff}} A\left[(S,L)J;(S',L')J'\right]$$

where λ_p is the peak position of the emission line, $\Delta\lambda_{eff}$ is the effective band width of the emission transition.

The obtained spontaneous transition probability of electric dipole transition A_{ed} and magnetic dipole transition A_{md}, the total transition probability A_T, the fluorescence branching ratio β, the stimulated emission cross section σ and the radiative lifetime τ_{rad} are presented in Table 1.

Table 1. Radiative properties of $Eu(MBPTFA)_3Phen$ doped silicone rubber.

Emission transition	v (cm^{-1})	A_{ed} (s^{-1})	A_{md} (s^{-1})	A (s^{-1})	β (%)	σ (10^{-21}cm^2)
$^5D_0\rightarrow{}^7F_0$	17254	0	0	0	0	0
$^5D_0\rightarrow{}^7F_1$	16931	0	51.90	51.90	7.88	0.21
$^5D_0\rightarrow{}^7F_2$	16342	601.22	0	601.22	91.32	4.99
$^5D_0\rightarrow{}^7F_3$	15364	0	0	0	0	0
$^5D_0\rightarrow{}^7F_4$	14265	5.26	0	5.26	0.80	0.027
A_T (s^{-1})				658.38		
Radiative lifetime τ_{rad} (ms)=1.519						

From Table 1, the transition $^5D_0\rightarrow{}^7F_2$ showed a high β value. It has already established that an emission level with β value near 50% becomes a potential laser emission transition [17].The emission cross section is 4.99×10^{-21} cm^2 , which is close to the typical value of Erbium in silica optical fiber (5×10^{-21} cm^2) [18]. The high fluorescence branching ratio of $^5D_0\rightarrow{}^7F_2$ transition and large emission cross section reveal that $Eu(MBPTFA)_3Phen$ doped silicone rubber is potential to be a laser material.

The metastable state lifetime of the $Eu(MBPTFA)_3Phen$ doped silicone rubber was obtained from the decay curve. The decay curve of $Eu(MBPTFA)_3Phen$ doped silicone rubber is shown in Fig. 3.

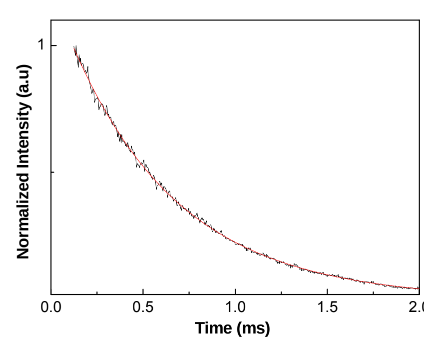

Fig. 3. Decay curve of $Eu(MBPTFA)_3Phen$ doped silicone rubber.

It can be found in Fig. 3, the decay curve can be fit with a single exponential, which is also indicating that there is only one site symmetry from the Eu^{3+} ion [8]. The metastable state lifetime of $Eu(MBPTFA)_3Phen$ doped silicone rubber is 0.589 ms, which is higher than that of $Eu(DBM)_3Phen$ doped PMMA system (0.469 ms) [6]. This indicated that the incorporation of the electro-transporting *biphenyl* group in the ligand making a more efficient energy transfer form the MBPTFA ligand to the central Eu^{3+} ion.

With the measured lifetime τ_m, together with the above calculated radiatve lifetime τ_{rad}, the luminescence quantum yield η can be calculated:

$$\eta = \frac{\tau_m}{\tau_{rad}}$$

The luminescence quantum yield η of $Eu(MBPTFA)_3Phen$ doped silicone rubber is about 38.8%, while the η of $Eu(DBM)_3Phen$ doped polymer is about 29.4% [6]. The higher luminescence quantum yield η also revealed the higher intramolecular energy transfer efficiency in $Eu(MBPTFA)_3Phen$ doped silicone rubber.

5. Conclusions

In conclusion, Eu complex with an electro-transporting group, $Eu(MBPTFA)_3Phen$, has been synthesized and has been incorporated into silicone rubber matrix and its luminescence properties has been studied. The Judd-Ofelt phenomenological parameters, Ω_2 and Ω_4 were obtained from the fluorescence emission spectrum are 18.4×10^{-20} cm^2 and 0.442×10^{-20} cm^2, respectively. Radiative properties of $Eu(MBPTFA)_3Phen$ doped silicone rubber were investigated also. The result showed that $Eu(MBPTFA)_3Phen$ doped silicone rubber can be a promising efficient luminescent material.

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