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Enhanced Luminescence in (Dy_x, Tm_y) ComplexesLI Wen-xian, SHI Xiao-yan, SUN Xiao-jun,
SUN Xue-lian, CHAI Wen-juan, REN Tie, ZHAO Lei

(College of Chemistry and Chemical Engineering, Inner Mongolia University, Hohhot 010021, China)

Abstract: Complexes of $(\text{Dy}_x, \text{Tm}_y)\text{L}_5(\text{ClO}_4)_3 \cdot 3\text{H}_2\text{O}$ ($x:y = 1.000:0.000, 0.995:0.005, 0.990:0.010, 0.950:0.050, 0.900:0.100, 0.800:0.200$; $\text{L} = \text{C}_6\text{H}_5\text{COCH}_2\text{SOCH}_2\text{COC}_6\text{H}_5$) were synthesized. The properties of the complexes were characterized with elemental analysis, infrared spectra (IR) and ultraviolet absorption spectra. The fluorescence spectra of these complexes were discussed in detail, indicating that the fluorescence intensity of Dy (III) is enhanced by Tm (III). This phenomenon may be due to the intra-molecular energy transfer. The complex shows the best luminescence properties when the ratio of Dy (III) to Tm (III) is 0.950:0.050. As a result, the complexes can emit white fluorescence under the ultraviolet excitation. It is predicted the complexes will become a class of luminescence materials that emit white fluorescence.

Key words: (Dy_x, Tm_y) complex; luminescence enhancement; energy transfer

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1 Introduction

In the last decades many rare earth complexes have attracted much attention^[1~3] due to their long luminescence lifetimes and high emissions efficiency. These complexes have been used in many areas, such as fluorescence materials^[4~6], electroluminescence devices^[7~10], fluorescence probes and labels in a variety of biological systems^[11~14]. Based on the different ligands and the central RE ions, many light-emitting complexes have been synthesized. The main ligands include aromatic carboxylic acid, 1, 10-phenanthroline (phen), pyridine and β -diketon^[15~17]. Because of good coordination abilities and solubility, many sulfoxide complexes were intensely studied in the past several decades^[18,19]. Then, they also become one important group for strong sensitized luminescence of RE ions. Generally speaking, the organic ligands are considered as the efficient sensitizer for the luminescence of rare earth

ions^[20]. The ligands that present this property were called as “antenna” by Lehn^[21]. In the RE (III) complexes, the organic ligands can absorb and transfer energy efficiently to the metal ion (intra-molecular energy transfer) and efficiently makes the luminescence intensity of RE complexes enhanced. At the same time, some studies indicated that the addition of certain nonluminous lanthanide ions such as Gd (III) and La (III) ions can also change the fluorescence property of the rare earth complexes^[22, 23]. So, studying the effect of different rare earth ions on luminous rare earth complexes is helpful to find potential application of luminous rare-earth complexes.

In this paper, a series of $(\text{Dy}_x, \text{Tm}_y)\text{L}_5(\text{ClO}_4)_3 \cdot 3\text{H}_2\text{O}$ ($\text{L} = \text{C}_6\text{H}_5\text{COCH}_2\text{SOCH}_2\text{COC}_6\text{H}_5$) were synthesized to improve dysprosium emission. The second rare earth Tm (III) ions were incorporated. A series of highly luminescent complexes were synthesized and characterized. Then, we studied the

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Biography: LI Wen-xian, born in 1961, female, Baotou, Inner Mongolia, Professor. Her work focuses on rare earth luminescence materials.
E-mail: nmglwx@163.com, Tel: (0471)4990061-60311

luminescence properties of the complexes in the solid state. When the ratio of Dy (Ⅲ) to Tm (Ⅲ) is 0.950: 0.050, the complex showed the strongest fluorescence. In addition, the intensity of the ⁴F_{9/2}→⁶H_{13/2} radiation transition of Dy (Ⅲ) at 577.4 nm was obviously enhanced comparing with one of the ⁴F_{9/2}→⁶H_{15/2} at 487 nm. The fluorescence intensity of the ⁴F_{9/2}→⁶H_{15/2} can be increased to 212%, and the fluorescence intensity of the ⁴F_{9/2}→⁶H_{13/2} can be increased to 264%. As a result, the intensity difference of the two emission peaks are getting smaller and smaller. And then, the complexes can emit white light under the ultraviolet excitation. So, the complexes synthesized by us will become a class of luminescence materials that emit white light.

2 Experiments

2.1 Reagents and Apparatus

The purity of lanthanide oxides exceeds 99.99%, the rare earth perchlorates were prepared by dissolving the oxides (99.99%) in HClO₄ (2 mol/L). All the other chemicals were of analytical reagent grade. Carbon, hydrogen analysis was determined by PE-2400 elemental analysis instrument. Rare earth contents of the complexes were determined by Ethylene-diamine tetracetic acid (EDTA) titration using Xylenol-orange as an indicator. Conductivity measurements were made using a 10⁻³ mol · L⁻¹ solution in acetone on a DDS-11D conductivity meter at room temperature. IR spectra were recorded on KBr disk using NEXUS-670 FT spectrometer in 400 ~ 4 000 cm⁻¹ region. The ultraviolet spectra (190 ~ 400 nm) of the ligand and its complexes were recorded on a Shimadzu UV-265 spectrophotometer and dimethylsulfoxide (DMSO) was used as a reference

and solvent (concentrations: 5 × 10⁻⁵ mol · L⁻¹). The fluorescence spectra were determined by Hitachi F-3010 fluorescence photometer. The phosphorescence spectra were measured by using SPEX1934D phosphorescence photometer at room temperature.

2.2 Synthesis of Ligand

Bis (benzoylmethyl) sulfide was dissolved in acetic acid, then 30% hydrogen peroxide was added to it at once. The mixture was stirred continuously at room temperature for 2 h. After the reaction stopped, the mixture was extracted with ether until the pH of mixture is 7. Then, a white solid was precipitated, filtered and dried in vacuum. Yield: 95%. mp:110 ~ 111 °C.

Element anal. for C₁₆H₁₄SO₃, Calcul. : C, 67.1%; H, 4.90%; Found: C, 66.6%; H, 4.68% .

2.3 Preparation of the Complexes

1 mmol rare earth perchlorate was weighed in the ratios of Dy (Ⅲ) to Tm (Ⅲ) [Dy (Ⅲ): Tm (Ⅲ)] = 1.000: 0.000, 0.995: 0.005, 0.990: 0.010, 0.950: 0.050, 0.900: 0.100, 0.800: 0.200 and dissolved in the ethanol. 5 mmol ligand was weighed and also dissolved in the ethanol. Then, the mixed rare earth perchlorates were added dropwise in the solution of ligand to give the complexes as a precipitate. The mixture was stirred for 0.5 h and precipitate was filtered. The products were washed with ether for several times, and then dried in vacuum to give the complexes as white powder (yield > 90%).

3 Results and Discussion

Analytical data for the complexes were presented in Table 1. The composition of the complexes was conformed to the formula of (Dy_x, Tm_y) L₅-

Table 1 Elemental analyses values for the complexes %

Complexes	Anal. calcd. (found)		
	C	H	RE
Dy _{1.000} Tm _{0.000} L ₅ (ClO ₄) ₃ · 3H ₂ O	49.12(49.36)	3.71(3.91)	8.34(8.36)
Dy _{0.995} Tm _{0.005} L ₅ (ClO ₄) ₃ · 3H ₂ O	49.09(49.36)	3.72(3.91)	8.13(8.36)
Dy _{0.990} Tm _{0.010} L ₅ (ClO ₄) ₃ · 3H ₂ O	49.21(49.36)	3.71 (3.91)	8.53(8.36)
Dy _{0.950} Tm _{0.050} L ₅ (ClO ₄) ₃ · 3H ₂ O	49.52(49.35)	3.71(3.91)	8.59(8.38)
Dy _{0.900} Tm _{0.100} L ₅ (ClO ₄) ₃ · 3H ₂ O	49.43(49.34)	3.75(3.91)	8.30(8.39)
Dy _{0.800} Tm _{0.200} L ₅ (ClO ₄) ₃ · 3H ₂ O	49.51(49.32)	3.72(3.91)	8.21(8.42)

$(\text{ClO}_4)_3 \cdot 3\text{H}_2\text{O}$ ($x:y = 1.000:0.000, 0.995:0.005, 0.990:0.010, 0.950:0.050, 0.900:0.100, 0.800:0.200$; $L = \text{C}_6\text{H}_5\text{COCH}_2\text{SOCH}_2\text{COC}_6\text{H}_5$). All the complexes are white powder, stable in atmospheric condition and soluble in acetone, dimethylformamide (DMF) and DMSO. The molar conductivity values in acetone indicated that the complexes were the type of 1:1 electrolytes^[24].

3.1 Infrared Spectrum

The most important IR assignments in the spectra of the ligand and the mixed complexes can be seen in Fig. 1 ~2 and Table 2.

Compared with IR spectrum of the ligand (Fig. 1), some absorption bands in the IR spectrum of mixed complexes (Fig. 2) have shifted. This phenomenon showed that rare earth ions are bonded with the ligand. As shown in IR spectra of the ligand, the $\text{S}=\text{O}$ group stretching modes appears at $1\,033\text{ cm}^{-1}$. However, the $\text{S}=\text{O}$ stretching frequency of the mixed complexes shift to a lower wave number by $42 \sim 44\text{ cm}^{-1}$, it suggests that rare earth ions are bonded with oxygen atom in sulfinyl group. The $\text{C}=\text{O}$ stretching frequency of the ligand appears at $1\,676\text{ cm}^{-1}$ as the strongest absorption in IR spectra, the absorptions of phenyl group appear at $3\,060\text{ cm}^{-1}$ ($\nu_{\text{C-H}}$), 755 cm^{-1} ($\delta_{\text{C-H}}$), 685 cm^{-1} ($\delta_{\text{C-H}}$). After coordination, there are no significant shifts, which suggest that the oxygen atoms in carbonyl group and phenyl are not coordinated to rare earth ions. In addition, there are three additional peaks

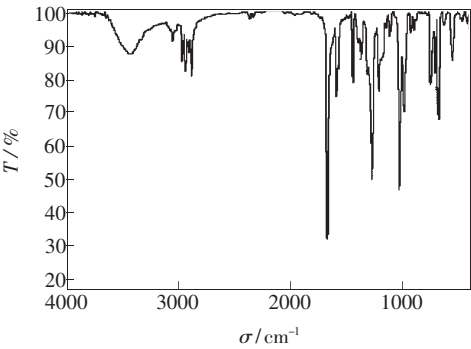


Fig. 1 IR absorption spectrum of ligand $\text{C}_6\text{H}_5\text{COCH}_2\text{SOCH}_2\text{COC}_6\text{H}_5$

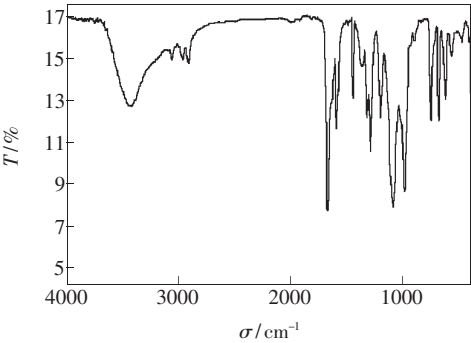


Fig. 2 IR absorption spectrum of $\text{Tb}_{0.990}\text{Tm}_{0.010}\text{L}_5(\text{ClO}_4)_3 \cdot 3\text{H}_2\text{O}$, $(\text{Dy}_{0.950}\text{Tm}_{0.050})\text{L}_5(\text{ClO}_4)_3 \cdot 3\text{H}_2\text{O}$

about $1\,091 \sim 1\,094\text{ cm}^{-1}$, $1\,021\text{ cm}^{-1}$, $623 \sim 624\text{ cm}^{-1}$, all of them are attributed to the ClO_4^- group. When ClO_4^- isn't coordinated, it is T_d symmetry and there are two absorption bands. When ClO_4^- is coordinated, it is C_{3v} symmetry and there are five absorption bands^[25, 26]. In the IR spectra of the complexes, three absorption bands can be seen clearly. So, ClO_4^- isn't all with the T_d symmetry and some

Table 2 Major IR spectra data of ligand and coordination compounds

Assignment (cm^{-1})	Ligand	$n(\text{Dy}):n(\text{Tm})$ 1.000:0.000	$n(\text{Dy}):n(\text{Tm})$ 0.995:0.005	$n(\text{Dy}):n(\text{Tm})$ 0.990:0.010	$n(\text{Dy}):n(\text{Tm})$ 0.950:0.050	$n(\text{Dy}):n(\text{Tm})$ 0.900:0.100	$n(\text{Dy}):n(\text{Tm})$ 0.800:0.200
$\nu_{\text{O-H}}(\text{H}_2\text{O})$	3 425	3 447	3 445	3 445	3 445	3 445	3 446
$\nu_{\text{C-H}}(\text{C}_6\text{H}_5)$	3 060	3 063	3 064	3 064	3 064	3 064	3 064
$\delta_{\text{C-H}}(\text{C}_6\text{H}_5)$	755	755	755	755	756	756	755
	685	685	686	686	686	686	686
$\nu_{\text{S=O}}$	1 033	989	991	990	990	990	990
$\nu_{\text{C=O}}$	1 676	1 675	1 675	1 676	1 676	1 676	1 676
$\delta_{\text{Cl-O}}(\text{ClO}_4^-)$	—	623	625	624	625	625	625
$\nu_{\text{Cl-O}}(\text{ClO}_4^-)$	—	1 094	1 091	1 092	1 092	1 091	1 093
		1 021	1 021	1 021	1 021	1 021	1 021

of them should have C_{3v} symmetry. In terms with the molar conductivities, it can be induced that two ClO_4^- are bonded with RE (Ⅲ) through oxygen atom, respectively.

3.2 UV Spectra

Fig. 3 and Fig. 4 exhibit the UV spectrum of the free ligand and Dy(Ⅲ) complexes in DMSO solution. From the spectra, the free ligand exhibits one absorption band at 258.4 nm, which is attributed to $\pi \rightarrow \pi^*$ transition. In the spectrum of the mixed complexes the band is shifted to 268.4 nm. This indicates that the complexes are formed and the conjugated system is increased after coordinating with the RE (Ⅲ) ions^[27].

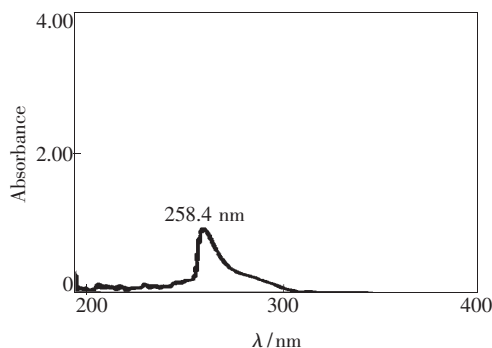


Fig. 3 UV absorption spectrum of $\text{C}_6\text{H}_5\text{COCH}_2\text{SOCH}_2\text{COC}_6\text{H}_5$

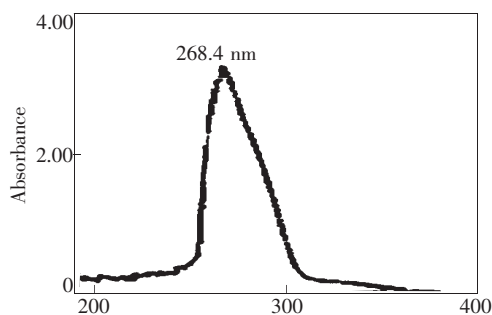


Fig. 4 UV absorption spectra of $\text{Dy}_{0.950}\text{Tm}_{0.050}\text{L}_5(\text{ClO}_4)_3 \cdot 3\text{H}_2\text{O}$

3.3 Fluorescence Spectra

The excitation and emission spectrum of (Dy_x, Tm_y) $\text{L}_5(\text{ClO}_4)_3 \cdot 3\text{H}_2\text{O}$ ($x:y = 1.000:0.000, 0.995:0.005, 0.990:0.010, 0.950:0.050, 0.900:0.100, 0.800:0.200$; $\text{L} = \text{C}_6\text{H}_5\text{COCH}_2\text{SOCH}_2\text{COC}_6\text{H}_5$) complexes are measured in solid state at room temperature. The spectrum of Dy (Ⅲ) complex and mixed complexes is reported in Fig. 5, Fig. 6 and Fig. 7. The excitation spectra were obtained

by monitoring the emission of the Dy (Ⅲ) at 487 nm, and all the complexes have the similar excitation spectrum that are dominated by a broad band from 250 to 450 nm with the maximum peak at about 330 nm, which is attributed to the f-f transition of Dy (Ⅲ) ion. The strong emission intensities indicate that the ligand is a good organic ligand to absorb energy and transfer it to Dy (Ⅲ) ion, emitting the characteristic fluorescence of Dy (Ⅲ) ion.

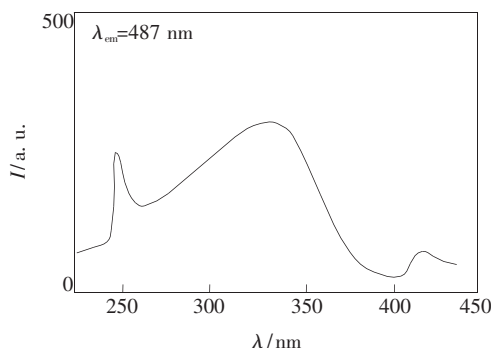


Fig. 5 Fluorescent EX spectrum of $\text{DyL}_5(\text{ClO}_4)_3 \cdot 3\text{H}_2\text{O}$

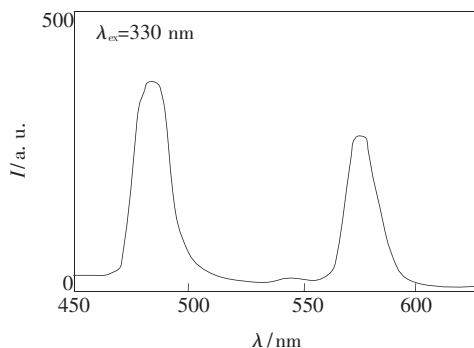


Fig. 6 Fluorescent EM spectrum of $\text{DyL}_5(\text{ClO}_4)_3 \cdot 3\text{H}_2\text{O}$

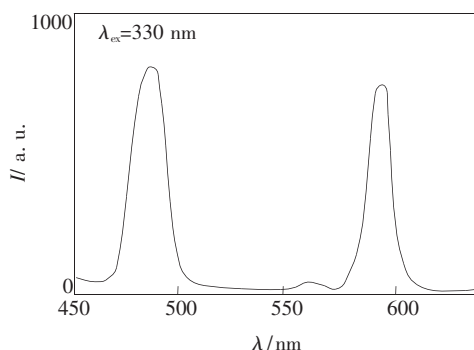


Fig. 7 Fluorescent EM spectrum of $\text{Dy}_{0.950}\text{Tm}_{0.050}\text{L}_5(\text{ClO}_4)_3 \cdot 3\text{H}_2\text{O}$

The emission spectra data for the mixed complexes are shown in Table 3. The emission bands of the complexes are assigned to the characteristic

$^4F_{9/2} \rightarrow ^6H_{15/2, \text{ or } 13/2}$, transitions of Dy at 485. 8, 577. 4 nm, respectively, and the fluorescence intensity of the $^4F_{9/2} \rightarrow ^6H_{15/2}$ radiation transition at 485. 8 nm is stronger than that of the $^4F_{9/2} \rightarrow ^6H_{13/2}$ at 577. 4 nm. As the Tm^{3+} adding, the fluorescence intensity of Dy^{3+} is enhanced, and the intensity of the $^4F_{9/2} \rightarrow ^6H_{13/2}$ emission at 577. 4 nm is obviously enhanced comparing with the $^4F_{9/2} \rightarrow ^6H_{15/2}$ emission at 487 nm. What's more, the intensity ratio of $^4F_{9/2} \rightarrow ^6H_{15/2}$ and $^4F_{9/2} \rightarrow ^6H_{13/2}$ is closed to 1 (Table 3). As a result, the intensity difference of the two peaks that belongs to Dy^{3+} is getting smaller. And then, the complexes can emit white fluorescence under the ultraviolet excitation. From the emission spectrum, when Dy (Ⅲ) : Tm (Ⅲ) = 0. 950 : 0. 050, the fluorescence

Table 3 Fluorescence emission spectra data of mixed coordination compounds

(Dy _x , Tm _y) L ₅ (ClO ₄) · 3H ₂ O	λ _{ex} /nm	λ _{em} /nm	I/a. u	Transition	Intensity ratio of
					$^4F_{9/2} \rightarrow ^6H_{15/2} / ^4F_{9/2} \rightarrow ^6H_{13/2}$
DyL ₅ (ClO ₄) · 3H ₂ O	330	485. 8	383. 9	$^4F_{9/2} \rightarrow ^6H_{15/2}$	1. 355
		577. 4	283. 4	$^4F_{9/2} \rightarrow ^6H_{13/2}$	
Dy _{0. 995} Tm _{0. 005} L ₅ (ClO ₄) · 3H ₂ O	330	485. 8	498. 0	$^4F_{9/2} \rightarrow ^6H_{15/2}$	1. 141
		577. 4	436. 4	$^4F_{9/2} \rightarrow ^6H_{13/2}$	
Dy _{0. 990} Tm _{0. 010} L ₅ (ClO ₄) · 3H ₂ O	330	485. 8	526. 0	$^4F_{9/2} \rightarrow ^6H_{15/2}$	1. 116
		577. 4	471. 4	$^4F_{9/2} \rightarrow ^6H_{13/2}$	
Dy _{0. 950} Tm _{0. 050} L ₅ (ClO ₄) · 3H ₂ O	330	485. 8	814. 7	$^4F_{9/2} \rightarrow ^6H_{15/2}$	1. 087
		577. 4	749. 2	$^4F_{9/2} \rightarrow ^6H_{13/2}$	
Dy _{0. 900} Tm _{0. 100} L ₅ (ClO ₄) · 3H ₂ O	330	485. 8	716. 2	$^4F_{9/2} \rightarrow ^6H_{15/2}$	1. 106
		577. 4	647. 5	$^4F_{9/2} \rightarrow ^6H_{13/2}$	
Dy _{0. 800} Tm _{0. 200} L ₅ (ClO ₄) · 3H ₂ O	330	485. 8	656. 1	$^4F_{9/2} \rightarrow ^6H_{15/2}$	1. 122
		577. 4	585. 0	$^4F_{9/2} \rightarrow ^6H_{13/2}$	

4 Conclusion

A series of highly luminescent complexes are synthesized and characterized. Composition of these complexes are revealed to be as the formula of (Dy_x, Tm_y) L₅ (ClO₄)₃ · 3H₂O (x : y = 1. 000 : 0. 000, 0. 995 : 0. 005, 0. 990 : 0. 010, 0. 950 : 0. 050, 0. 900 : 0. 100, 0. 800 : 0. 200; and L = C₆H₅COCH₂-SOCH₂COC₆H₅. The optical properties of them are studied with ultraviolet spectra, excitation and emis-

intensity of the complexes is the strongest. The change of Dy (Ⅲ) fluorescence emission intensity with the increase of Tm (Ⅲ) can be seen from Fig. 8.

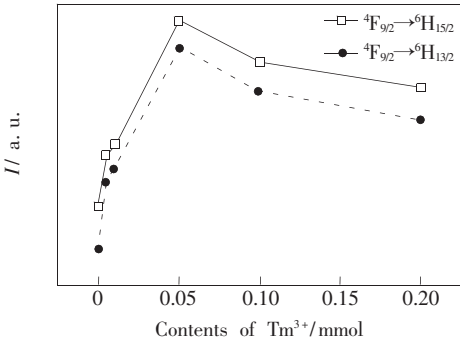


Fig. 8 Changes of Dy (Ⅲ) fluorescent emission intensity with the increase of Tm (Ⅲ) content

sion. The solid Dy complexes show characteristic emission of Dy ion. The coordination structure of the complexes and the intramolecular energy transfer process are both important factors that influence on luminescence of RE organic complexes. And then, the complexes can emit white fluorescence under the ultraviolet excitation. So, the complexes that we synthesize are likely to become a class of luminescence materials that emit white fluorescence.

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Tm³⁺ 在二苯甲酰基甲基亚砷配合物体系中 对 Dy³⁺ 的荧光增强效应

李文先, 石晓燕, 孙晓军, 孙雪莲, 柴文娟, 任 铁, 赵 磊

(内蒙古大学 化学化工学院, 内蒙古 呼和浩特 010021)

摘要: 合成了六种高氯酸掺杂稀土(Dy³⁺, Tm³⁺)与二苯甲酰基甲基亚砷的配合物。经元素分析、稀土络合滴定、摩尔电导率及差热-热重分析, 表明配合物组成为 (Dy_xTm_y)L₅(ClO₄)₃ · 3H₂O ($x:y = 1.000:0.000, 0.995:0.005, 0.990:0.010, 0.950:0.050, 0.900:0.100, 0.800:0.200$; L = C₆H₅COCH₂SOCH₂COC₆H₅)。并详细讨论了六种稀土配合物的荧光光谱。从配合物的荧光光谱图可以看出, Tm³⁺ 对 Dy³⁺ 的荧光有增强效应。这可能是因为惰性稀土离子 Tm³⁺ 与活性稀土离子 Dy³⁺ 之间有能量的传递。而且当 Dy³⁺ 与 Tm³⁺ 的量比为 0.950:0.050 时, 掺杂配合物表现出最佳的发光性质。另外, Tm³⁺ 对 577.4 nm 处 ⁴F_{9/2} → ⁶H_{13/2} 峰的荧光敏化作用的程度高于对 487 nm 处 ⁴F_{9/2} → ⁶H_{15/2} 峰的荧光敏化作用。⁴F_{9/2} → ⁶H_{15/2} 峰的荧光强度增强了 212%, 而 ⁴F_{9/2} → ⁶H_{13/2} 峰的荧光强度增强了 264%。所以, Dy³⁺ 离子的两个特征峰的发射强度比趋近于 1, 为 1.078, 使得配合物在紫外灯下发白色荧光。有可能成为一类发白色荧光的发光材料。

关键词: (Dy³⁺, Tm³⁺) 配合物; 发光增强; 能量传递

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