

Optical investigation of samarium (III) complex doped polymer film

HAO LIANG^{a,*}, FANG XIE^a, BIAO CHEN^b, JIE XU^c

^aDepartment of Chemical Engineering, Huizhou University, Guangdong 516007, China

^bDepartment of History of Science and Technology and Archaeometry, University of Science and Technology of China, Anhui 230026, China

^cKey Lab of Green Processing & Functional Textiles of New Textile Materials, Ministry of Education, Wuhan University of Science and Engineering, Hubei 430073, China

A lanthanide doped poly(methyl methacrylate) (PMMA) film has been prepared using a Sm³⁺ complex, composed of 4,4,5,5,6,6,6-heptafluoro-1-(2-thienyl)-1,3-hexanedione, and 1,10-phenanthroline. From absorption and fluorescence spectra, the radiative properties of Sm(HTH)₃Phen doped PMMA has been evaluated using the Judd-Ofelt theory. The properties of its planar waveguide have been studied by m-line method and near-field scanning optical microscopy (NSOM).

(Received August 20, 2008; accepted June 15, 2009)

Keywords: Samarium complex; Polymer; Film; Judd-Ofelt theory

1. Introduction

Polymer matrix incorporating lanthanide complexes have received much attention for their potential applications in photonic technologies [1,2]. The main advantage of lanthanide complexes doped polymer is that they can be fabricated by inexpensive techniques such as spin coating, photolithography, low-temperature fiber drawing, and micromolding. With the development of broadband communications and optics, the polymer optical waveguide technology is growing rapidly and thin film integrated optical devices based on polymers become more important [3,4].

Polymethyl methacrylate (PMMA) is well suited as polymer-matrix due to its high transparency in the visible range, and it is robust against laser radiation [5]. These characteristics make it suitable as a host material for rare earth ions and organic dye doping. It has been known that the $^4G_{5/2} \rightarrow ^6H_{9/2}$ transition of Sm³⁺ is close to the low-loss transmission windows of PMMA. Lanthanide β -diketonate complexes have long been known to give intense emission lines upon UV light irradiation due to the effective intramolecular energy transfer from the coordinating ligands to the central lanthanide ions. In this paper, we present the studies of Sm(HTH)₃Phen [HTH: 4,4,5,5,6,6,6-heptafluoro-1-(2-thienyl)-1,3-hexanedione, Phen: 1,10-Phenanthroline] doped PMMA film and properties of its planar waveguide [6]. The HTH was chosen as the β -diketonate ligand because the fluorinated substituent in ligand increases the volatility of the complex, thus facilitating thin-film fabrication, and leads to improved thermal and oxidative stability and reduced concentration quenching of the luminescence [7-10]. In

addition to that, fluorination can improve the PL and EL efficiency and enhance luminescence intensity [8,10].

2. Experimental

2.1 Sample preparation

Sm(HTH)₃Phen and doped PMMA (the content of Sm(HTH)₃Phen in PMMA is 1%-wt) was prepared according to the procedure reported before [6,11]. The central Sm³⁺ ion is bound to three HTH 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 [12]. This encapsulated structure can protect the lanthanide ions from vibrational coupling and increase light absorption cross section by "antenna effects".

Sm(HTH)₃Phen doped PMMA film was deposited on a substrate of fused silica (3cm×2cm) using spin coating. The refractive index of the fused silica at 650nm is 1.459. The coating solution was prepared by dissolving Sm(HTH)₃Phen doped PMMA in cyclopentanone. The sample was prepared at spin speed of 1600 revolution per minutes and baked by an infrared lamp for about 20 minutes. After that, the Sm(HTH)₃Phen doped PMMA film was obtained. The thickness of the film was controlled by the concentration of the polymer solution.

2.2 Measurement of the absorption and fluorescence spectra

The absorption spectra of Sm(HTH)₃Phen doped PMMA (1cm thick slice) were measured by a PerkinElmer Lambda 900 UV-VIS-NIR spectrophotometer. The fluorescence of Sm(HTH)₃Phen doped PMMA was excited

with the 476.5 nm line of an Ar⁺ laser and recorded using a Jobin Yvon HRD monochromator in the spectral region 500–700 nm.

2.3 Measurement of the properties of Sm(HTH)₃Phen doped PMMA planar waveguide

The refractive index n_1 and the thickness h of the film were obtained by the m-line method [13]. A commercial near-field scanning optical microscopy (NSOM) from RHK Technology (USA) is used to detect the surface of the film. The light from the Ar⁺ ion laser (457.9 nm) is coupled into a very small aluminum-coated quartz single-mode glass fiber tip with a 50 nm aperture. The tip illustrates the sample and scans near the sample surface of interest. Typical pixel dwell time in our images was 10ms. Images were acquired and processed by using the software SPM32 5.06 version (RHK, USA).

3. Results and discussion

3.1 Absorption and fluorescence spectra

The absorption spectrum of Sm(HTH)₃Phen doped PMMA are shown in Fig. 1. The ground state of the Sm ion is ⁶H_{5/2} and the absorption bands arise due to transitions from this ⁶H_{5/2} level to various excited levels. The spectral lines observed and assigned as transitions of different excited states are ⁴I_{9/2}, ⁴F_{3/2}, ⁶F_{11/2}, ⁶F_{9/2}, ⁶F_{7/2}, ⁶F_{5/2}, ⁶F_{3/2}, ⁶F_{1/2} and ⁶H_{5/2} [14]. The assignment of the bands for Sm(HTH)₃Phen doped PMMA are given in the figure.

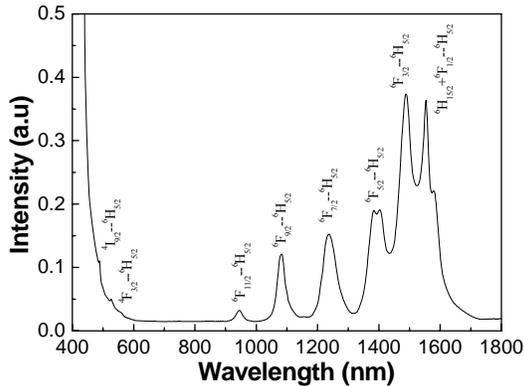


Fig.1. Absorption spectrum of Sm(HTH)₃Phen doped PMMA.

The fluorescence emission spectrum of Sm(HTH)₃Phen doped PMMA film is shown in Fig.2. It can be observed that the emission spectrum consists of the characteristic emission lines of Sm³⁺: three emission peaks are centered at 564, 608, 648 nm and can be assigned to the ⁴G_{5/2}→⁶H_{5/2}, ⁴G_{5/2}→⁶H_{7/2}, ⁴G_{5/2}→⁶H_{9/2}, respectively. The peak corresponds to ⁴G_{5/2}→⁶H_{9/2} transition has the largest intensity.

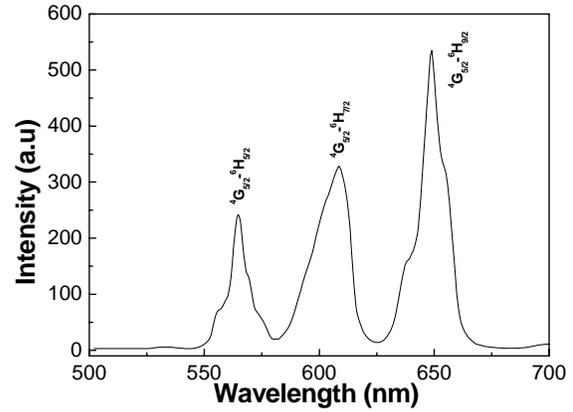


Fig.2. Fluorescence emission spectrum of Sm(HTH)₃Phen doped PMMA film.

3.2 Radiative Properties of Sm(HTH)₃Phen doped PMMA

Judd-Ofelt theory is widely used and remarkably successful for quantitatively characterizing optical 4f transitions in rare earth doped system. The observed absorption spectrum has been used to determine the oscillator strength of the different transitions. Judd-Ofelt intensity parameters, transition probability, total transition probability, branching ratio, radiative lifetime etc. have been calculated using well known relations [15,16]. These values are given in Tables 1 and 2.

Table 1. Experimental oscillator strength (f_{exp}), calculated oscillator strength (f_{calc}), and Judd-Ofelt intensity parameters (Ω_i) for Sm(HTH)₃Phen doped PMMA.

Transition	$f_{exp} \times 10^{-6}$	$f_{calc} \times 10^{-6}$
⁶ F _{1/2} + ⁶ H _{15/2} + ⁶ F _{3/2} ← ⁶ H _{5/2}	11.863	12.051
⁶ F _{5/2} ← ⁶ H _{5/2}	3.718	3.803
⁶ F _{7/2} ← ⁶ H _{5/2}	4.372	4.791
⁶ F _{9/2} ← ⁶ H _{5/2}	2.124	2.403
⁶ F _{11/2} ← ⁶ H _{5/2}	0.701	0.452
⁴ F _{3/2} ← ⁶ H _{5/2}	0.048	0.019
⁴ I _{9/2} ← ⁶ H _{5/2}	0.065	0.159
$\Omega_2 \times 10^{-20} \text{ cm}^2$	$\Omega_4 \times 10^{-20} \text{ cm}^2$	$\Omega_6 \times 10^{-20} \text{ cm}^2$
33.73	4.92	5.31

Table 2. Transition probability (A), total transition probability (A_T), radiative lifetime (τ_R) and branching ratio (β) for the emission transitions of $\text{Sm}(\text{HTH})_3\text{Phen}$ doped PMMA.

Emission transition	Energy (cm^{-1})	A (s^{-1})	β (%)
${}^4\text{G}_{5/2} \rightarrow {}^6\text{F}_{11/2}$	7225.3	0.31	0.04
${}^4\text{G}_{5/2} \rightarrow {}^6\text{F}_{9/2}$	8447.8	10.46	1.46
${}^4\text{G}_{5/2} \rightarrow {}^6\text{F}_{7/2}$	9615.2	3.78	0.53
${}^4\text{G}_{5/2} \rightarrow {}^6\text{F}_{5/2}$	10491.6	91.45	12.81
${}^4\text{G}_{5/2} \rightarrow {}^6\text{F}_{3/2}$	11034.1	12.52	1.76
${}^4\text{G}_{5/2} \rightarrow {}^6\text{H}_{15/2}$	11321.2	0.73	0.10
${}^4\text{G}_{5/2} \rightarrow {}^6\text{F}_{1/2}$	11438.7	12.36	1.73
${}^4\text{G}_{5/2} \rightarrow {}^6\text{H}_{13/2}$	12562.4	8.21	1.15
${}^4\text{G}_{5/2} \rightarrow {}^6\text{H}_{11/2}$	14168.9	41.03	5.75
${}^4\text{G}_{5/2} \rightarrow {}^6\text{H}_{9/2}$	15486.2	355.81	49.85
${}^4\text{G}_{5/2} \rightarrow {}^6\text{H}_{7/2}$	16673.1	149.31	20.92
${}^4\text{G}_{5/2} \rightarrow {}^6\text{H}_{5/2}$	17701.5	27.82	3.90
A_T (s^{-1})		713.79	
radiative lifetime $\tau_R = 1.401$ ms			

The parameter Ω_2 is associated to the covalence and the symmetry of the ligand field in the rare-earth site [17,18]. In Table 1, $\text{Sm}(\text{HTH})_3\text{Phen}$ doped PMMA shows a relatively larger Ω_2 . Generally, the large values obtained for Ω_2 parameters indicates a highly covalent character to the bonds between the central Sm^{3+} ions and the surrounding ligands in the $\text{Sm}(\text{HTH})_3\text{Phen}$ complex [17]. In Table 2, the transition ${}^4\text{G}_{5/2} \rightarrow {}^6\text{H}_{9/2}$ showed the largest radiative transition probability and the highest β value which indicate favorable laser action [19]. The calculated radiative lifetime of ${}^4\text{G}_{5/2} \rightarrow {}^6\text{H}_{9/2}$ is about 1.401ms. It is of the same order of magnitude as that for Sm^{3+} doped silica-glass systems that laser phenomena has been reported [20].

The fluorescence spectrum has been used to derive radiative properties such as the stimulated emission cross-section etc. The stimulated emission cross section of the transitions can be determined by [21]:

$$\sigma(\lambda_p) = \frac{\lambda_p^4}{8\pi c n^2 \Delta\lambda_{\text{eff}}} A_{J,J'}$$

where $A_{J,J'}$ is the transition probability, λ_p is the peak position of the emission line, $\Delta\lambda_{\text{eff}}$ is the effective band width of the emission transition and defined as:

$$\Delta\lambda_{\text{eff}} = \int \frac{I(\lambda) d\lambda}{I_{\text{max}}}$$

where I is the fluorescence intensity and I_{max} is the intensity at the band maximum. Calculated effective band width and stimulated emission cross section are given in Table 3.

Table 3 Fluorescence lines wavelength, effective band width ($\Delta\lambda_{\text{eff}}$) and stimulated emission cross section (δ) for different transitions of $\text{Sm}(\text{HTH})_3\text{Phen}$ doped PMMA on excitation with 476.5 nm line of Ar^+ laser.

Transition	λ (nm)	$\Delta\lambda_{\text{eff}}$ (nm)	δ (cm^2)
${}^4\text{G}_{5/2} \rightarrow {}^6\text{H}_{9/2}$	648	14.5	2.57×10^{-21}
${}^4\text{G}_{5/2} \rightarrow {}^6\text{H}_{7/2}$	608	19.2	6.31×10^{-22}
${}^4\text{G}_{5/2} \rightarrow {}^6\text{H}_{5/2}$	564	11.7	1.94×10^{-23}

In Table 3, the stimulated emission cross-section is seen to be largest for the ${}^4\text{G}_{5/2} \rightarrow {}^6\text{H}_{9/2}$ transition and the value of δ can be compared with those obtained for the same transitions in inorganic hosts [19]. The evaluation of the emission cross section, the fluorescence branching and radiative lifetime of ${}^4\text{G}_{5/2} \rightarrow {}^6\text{H}_{9/2}$ transition reveal that $\text{Sm}(\text{HTH})_3\text{Phen}$ doped PMMA is potential to be a laser material and can be used in optical amplification at 648 nm.

3.3 Properties of $\text{Sm}(\text{HTH})_3\text{Phen}$ doped PMMA planar waveguide

To investigate the feasibility of the above $\text{Sm}(\text{HTH})_3\text{Phen}$ doped PMMA film used as a planar waveguide, its mode structure was measured by the m-line method. The incident polarized light is 650 nm wavelength from a diode laser, which is at the low-loss windows of PMMA polymer matrix. Experimental m-line data acquired for $\text{Sm}(\text{HTH})_3\text{Phen}$ doped PMMA film is shown in Fig.3(a). The optical signal transmission through the waveguide obtained by CCD is shown in Fig.3(b).

In Fig.3(a), the film was found to act as multi-mode planar waveguide at the wavelengths of 650 nm. According to reference [13], the film thickness $h=1.536\mu\text{m}$ and refractive index $n_1=1.501$ can be obtained. In Fig.3(b), it can be clearly observed that the optical signal (650nm) travels through the $\text{Sm}(\text{HTH})_3\text{Phen}$ doped PMMA layer and is confined in the transverse direction as a result of total internal reflection at the interface between the PMMA layer and the air. The results indicated that the $\text{Sm}(\text{HTH})_3\text{Phen}$ doped PMMA film deposited on the fused silica can be used as a planar waveguide to transmit optical signals. The obtained optical propagation loss of the above planar waveguide is 0.42 dB/cm.

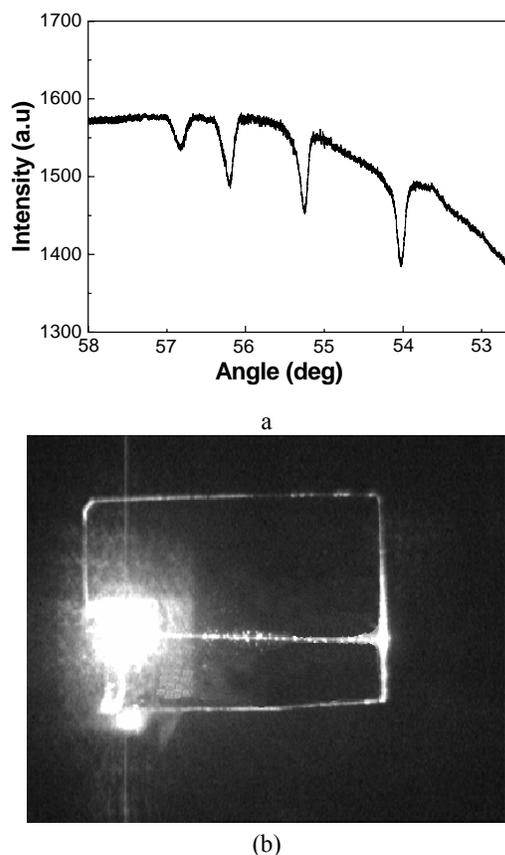


Fig.3 Experiment results of m-line method (a) and optical signal transmission through the waveguide (b).

To be used as a planar waveguide, the surface quality of the film is also important. Near-field scanning optical microscopy (NSOM) has the ability to achieve a high spatial resolution and measure the surface topography without any damage to the sample. Fig.4 is the 3D near-field topography of Sm(HTH)₃Phen doped PMMA waveguide film in an area of 10 μ m \times 10 μ m. From the figure, it can be found that the film is smooth and homogenous under the resolution of 50 nm. So the planar waveguide fabricated in this way shows good surface quality.

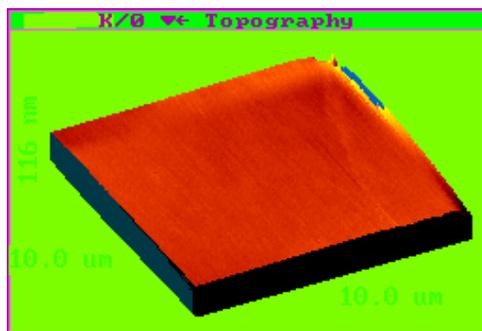


Fig. 4. 3D near-field topography of Sm(HTH)₃Phen doped PMMA waveguide film.

4. Conclusion

In this work, the radiative properties of Sm(HTH)₃Phen doped PMMA has been evaluated using Judd-Ofelt theory. The result showed that the $^4G_{5/2} \rightarrow ^6H_{9/2}$ transition of the material is potential to be used in optical amplification at 648 nm. In addition to that, the feasibility of Sm(HTH)₃Phen doped PMMA film used as a planar waveguide has also been studied by the m-line method and NSOM. The film was found to act as multi-mode planar waveguide and the optical signal (650nm) transmission can be clearly observed.

Acknowledgement

This work was supported by the Natural Science Foundation of Guangdong Province, China (No. 8151601501000010), the Science and Technology Planning Project of Huizhou, China (No. 2007P48), the Key Project of Science and Technology Research of Ministry of Education (No.208089) and the Natural Science Foundation of Hubei Province (No.2008CDB261).

References

- [1] H. Liang, F. Xie, M. Liu, Z. Jin, F. Luo, Z. Zhang, *Spectrochim. Acta Part A*, **71**, 588 (2008).
- [2] H. Liang, Q. Zhang, Z. Zheng, H. Ming, Z. Li, J. Xu, B.Chen, H.Zhao, *Opt. Lett.* **29**, 477 (2004).
- [3] A. Polman, Proc. 10th European Conference on Integrated Optics (ECIO) Paderborn, Germany, April, 2001, 75 (2001).
- [4] S. Moynihan, R. Van Deun, K. Binnemans, G. Redmond, *Opt. Mat.* **29**, 1821 (2007).
- [5] L. H.Slooff, A. Polman, S. I. Klink, G. A. Hebbink, L. Grave, F. C. J. M. V. Veggel, D. N. Reinhoudt, J. W. Hofstraat, *Opt. Mat.* **14**, 101 (2000).
- [6] J. Guo, L. Fu, H. Li, Y. Zheng, F. Liu, Q. Meng, J. Wang, H. Zhang. *Chem. Lett.* **31**, 998 (2002).
- [7] M. A. Omary, M. A. Rawashdeh-Omary, H. V. K. Diyabalanage, H. V. R. Dias, *Inorg. Chem.* **42**, 8612 (2003).
- [8] V. V. Grushin, N. Herron, D. D. LeCloux, W. J. Marshall, V. A. Petrov, Y. Wang, *Chem. Commun.* **16**, 1494 (2001).
- [9] I. R. Lasker, T. -M. Chen, *Chem. Mater.* **16**, 111 (2004).
- [10] Y. X. Zheng, J. Lin, Y. J. Liang, Q. Lin, Y. N. Yu, Q. G. Meng, Y. H. Zhou, S. B. Wang, H. Y. Wang, H. J. Zhang, *J. Mater. Chem.* **11**, 2615 (2001).
- [11] B. Chen, H. Liang, J. Xu, Q. Zhang, *Spectrosc. Lett.* **39**, 63 (2006).
- [12] E. Janos, B. Andrea, K. Attila, K. Laszlo. *J. Lumines.* **72**, 570 (1997).
- [13] R. Ulrich, R. Torge, *J. Appl. Opt.* **12**, 2901 (1973).

- [14] A. Kumar, D. K. Rai, S. B. Rai, *Spectrochim. Acta Part A*, **59**, 917 (2003).
- [15] B. R. Judd, *Phys. Rev.* **127**, 750 (1962).
- [16] G. S. Ofelt, *J. Chem. Phys.* **37**, 511 (1962).
- [17] C. Koeppen, S. Yamada, G. J. Yang, A. F. Garito, Larry. R. Dalton, *J. Opt. Soc. Am. B*, **14**, 155 (1997).
- [18] A. G. Souza Filho, J. Mendes Filho, F. E. A. Melo, M. C. C. Custodio, R. Lebullenger, A. C. Hernandez, *J. Phys. Chem. Solids*, **61**, 1535 (2000).
- [19] R. R. Reddy, Y. N. Ahammed, P. A. Azeem, K. R. Gopal, T. V. R. Rao, S. Buddhudub, N. Sooraj Hussain, *J. Quant. Spectrosc. Radiat. Transfer*, **77**, 149 (2003).
- [20] M. C. Farries, P. R. Morkel, J. E. Townsend, *Electron. Lett.* **24**, 709 (1988).
- [21] W. Krupke, *IEEE J. Quantum Electron.* **7**, 153 (1971).

*Corresponding author: lianghao@ustc.edu