

Amplified Spontaneous Emission of Eu(DBM)₃Phen Doped Step-Index Polymer Optical Fiber by End-Pumping with a YAG

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ABSTRACT: Eu(DBM)₃Phen doped poly(methyl methacrylate) core step-index polymer optical fiber (SI POF) has been fabricated and related properties of the doping material were discussed. Amplified spontaneous emission (ASE) at 613 nm of a SI POF with 40 cm length has been observed at ambient temperature by end-pumping with a YAG at 355

nm. The threshold of the absorbed pump power for the onset of ASE is about 0.01 mJ. © 2005 Wiley Periodicals, Inc. *J Appl Polym Sci* 98: 912–916, 2005

Key words: polymer optical fiber; Eu; luminescence; amplified spontaneous emission

INTRODUCTION

Polymer optical fibers (POFs) have attracted much attention in past decades because they have some unique characteristics, such as flexibility, ease of handling, and relatively low cost in coupling due to their large core diameter.^{1,2} These characteristics make them especially suitable as a transmission medium in local area networks and short-haul optical communications. With the development of POF, increasing research activities have been also carried out in the field of polymer optical fiber amplifiers or lasers.^{2–7}

Luminescent rare earth organic complexes are promising active dopants used in polymer-based optical components.^{2,3} As a luminescent material, Eu(DBM)₃Phen shows excellent solubility in organic polymer host and high fluorescence intensity. In addition, the emission of Eu³⁺ at 613 nm (⁵D₀ → ⁷F₂) is around the low-loss windows of poly(methyl methacrylate) (PMMA)-made POF (650 nm). It has been chosen as the active dopant of POF in our work.

In this paper, a step-index polymer optical fiber (SI POF) doped with Eu(DBM)₃Phen was prepared by a preform technique. Related properties of the doped material were discussed. Amplified spontaneous emission (ASE) at 613 nm of the doped SI POF was observed at ambient temperature by end-pumping with a YAG at 355 nm. The Eu³⁺ content of the SI POF is 4000 ppm wt and fiber length is 40 cm.

EXPERIMENTAL

Materials

Eu₂O₃ (99.99%) was purchased from Shanghai Yaolong Non-Ferrous Co. Ltd. and used without further purification. Methyl methacrylate (MMA) was purified according to standard procedures. 2,2-Azoisobutyronitrile (AIBN) and dibenzoylmethane (DBM) were recrystallized from methanol before use. Other chemicals were analytical grade. Eu(DBM)₃Phen was synthesized using the method described in Ref.⁸

Fabrication of Eu(DBM)₃Phen doped PMMA SI POF

To fabricate Eu(DBM)₃Phen doped SI POF preforms, a thermal polymerization technique was used. First, 15 mL purified MMA, 0.02 g AIBN as an initiator, 35 μL *n*-butylmercaptane as a chain-transfer agent, and a specified amount of Eu(DBM)₃Phen were mixed in a vessel. The above solution was filtrated through a

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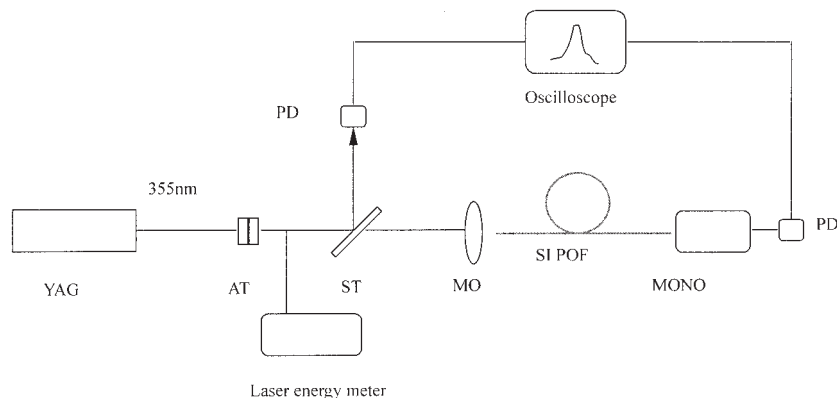


Figure 1 Experimental arrangement for ASE. AT, optical attenuator; MO, microscope objective; ST, sheet glass; PD, photodiode; MONO, monochromator.

microporous filter ($d = 0.20 \mu\text{m}$) before being injected into a Teflon tube. The solution was degassed under vacuum, and then the thermal polymerization of the filled tube was carried out in a water bath at 50°C for 48 h under 6 atm nitrogen and additionally heated at 75°C until solidification was fulfilled. After solidification, the tube was placed into a vacuum oven at 110°C for 4 h to complete polymerization and remove the remaining volatiles.

The Teflon tube was used in the fabrication for the following reasons: its nonstick property allowed the preform to be easily separated from it; it has excellent chemical and thermal stability; it has a smooth finish of its inner surface.

The preform with a diameter of 10 mm prepared by this process was then heat-drawn into an optical fiber at 180°C by a take-up spool. The preform moved down with a constant velocity V_1 and was heat-drawn by a drive roll with velocity V_2 . By controlling the ratio of V_2 to V_1 , the $\text{Eu}(\text{DBM})_3\text{Phen}$ doped SI POF with a requested diameter can be obtained. The cladding (a resin containing fluorine with refractive index of 1.393) was coated during the drawing process.

Thermal gravimetric analysis

Thermal stability of the materials was studied by thermal gravimetric analysis (TGA) using a TGA-50H Shimadzu thermogravimetric analyzer, under nitrogen atmosphere, at a heating rate of $10^\circ\text{C min}^{-1}$.

Spectra measurement

The absorption spectra of DBM, Phen, and $\text{Eu}(\text{DBM})_3\text{Phen}$ MMA monomer solution were recorded on a Shimadzu UV-2401 UV-vis spectrophotometer by use of 1-cm cell at room temperature. The fluorescence emission spectrum of $\text{Eu}(\text{DBM})_3\text{Phen}$ doped PMMA was recorded on

a Shimadzu RF-5301PC spectrofluorophotometer (the sample was cut to 2 mm thickness and polished).

Measurement of the fluorescence decay curves

The measurement of the fluorescence decay curves was performed at room temperature. The third harmonic (355 nm) of a YAG laser was used as a pump source. The emission at 613 nm (the $^5\text{D}_0 \rightarrow ^7\text{F}_2$ transition in Eu^{3+}) was monitored and recorded as a function of time. Data were acquired using a Tektronix TDS 5000 digital oscilloscope and analyzed using the computational program Origin.

Experimental arrangement for ASE of $\text{Eu}(\text{DBM})_3\text{Phen}$ doped SI POF

The experimental arrangement for optical measurements of ASE is shown in Figure 1.

The pump beam from a YAG operating at 355-nm wavelength was launched into the doped polymer optical fiber by a microscope objective. The full width at half maximum of the pump pulse is about 5 ns and the repetition rate is 10 Hz. An optical attenuator was used to adjust the incident intensity. The input power of the laser beam was measured by a laser energy meter. The output power of fluorescence was detected by a photodiode connected with a dual-channel oscilloscope. The trigger is another photodiode that accepted 8% reflective light from the sheet glass.

The diameter of the fiber sample used in this work was $400 \mu\text{m}$ and the length was 40 cm. The Eu^{3+} content of the doped SI POF was 4000 ppm wt. The refractive index of the core was 1.468. The index difference between the core and cladding region was 0.075. Therefore, the numerical aperture of POF was 0.46. The POF ends were mounted in a special clamp and polished mechanically.

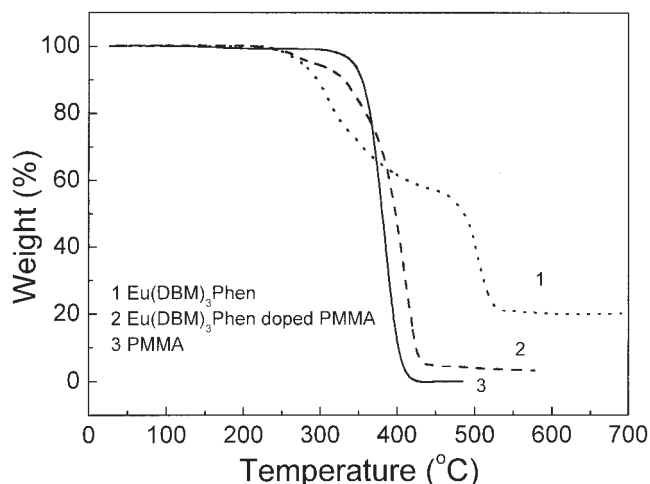


Figure 2 Thermal gravimetric analysis curves of $\text{Eu}(\text{DBM})_3\text{Phen}$, PMMA, and $\text{Eu}(\text{DBM})_3\text{Phen}$ doped PMMA.

RESULTS AND DISCUSSION

Thermal gravimetric analysis

TGA was carried out to measure the thermal stability of $\text{Eu}(\text{DBM})_3\text{Phen}$ doped PMMA. Figure 2 shows the TGA curves of $\text{Eu}(\text{DBM})_3\text{Phen}$, PMMA, and $\text{Eu}(\text{DBM})_3\text{Phen}$ doped PMMA (the concentration of the Eu ion is 5000 ppm wt).

It can be seen in Figure 2 that the degradation temperature for $\text{Eu}(\text{DBM})_3\text{Phen}$ doped PMMA is about 210°C, while pure PMMA has a degradation temperature of 290°C. The decrease of thermal stability is due to the relatively lower degradation temperature of $\text{Eu}(\text{DBM})_3\text{Phen}$, which is about 210°C. The degradation temperature of $\text{Eu}(\text{DBM})_3\text{Phen}$ and $\text{Eu}(\text{DBM})_3\text{Phen}$ doped PMMA is far above the fiber heating drawing temperature (180°C), so the preform fabricated in this way shows good thermostability during the processing and fiber drawing.

Absorption spectra of $\text{Eu}(\text{DBM})_3\text{Phen}$ and its ligands

Absorption spectra of $\text{Eu}(\text{DBM})_3\text{Phen}$, DBM, and Phen in MMA solution are shown in Figure 3. The concentration of the solution is 10 ppm. The DBM solution showed a strong absorption band around 250–380 nm, while the absorption of the Phen is negligible. $\text{Eu}(\text{DBM})_3\text{Phen}$ showed an absorption band around 300–400 nm. The shift of the absorption band of $\text{Eu}(\text{DBM})_3\text{Phen}$ solution is the indication of the formation of a coordination bond between DBM ligands and the Eu ion. The sharper absorption peak around 300 nm of $\text{Eu}(\text{DBM})_3\text{Phen}$ also indicated the formation of coordination bond between Phen and the Eu ion.

The DBM ligand absorption band is much stronger than that of the Eu^{3+} ion, and the peak extinction coefficient of $\text{Eu}(\text{DBM})_3\text{Phen}$ is about $\epsilon = 3.01 \times 10^4 \text{ M}^{-1} \text{ cm}^{-1}$ at 342 nm (in MMA solvent), being several orders of magnitude larger than that of a primary Eu pump band, in which $\epsilon = 4.3 \text{ M}^{-1} \text{ cm}^{-1}$ at 466 nm (in MMA solvent). Through an intramolecular ligand to rare earth ion energy transfer process, the metastable state of the rare earth ion can be populated by pumping ligand absorption bands, which are much stronger than that of the rare earth ion. It also has been shown that in chelates of europium, inversion can be attained by using as a pump band of the intense absorption of the ligand, from which the energy absorbed is transferred intramolecularly to the Eu^{3+} ion.⁹ Accordingly, the laser wavelength around the DBM absorption bands can be used as a pump source light. In this paper, 355 nm of YAG laser was used in the ASE experiment.

Fluorescence of $\text{Eu}(\text{DBM})_3\text{Phen}$ doped PMMA

The fluorescence emission spectrum recorded from 550 to 750 nm under excitation at 355 nm of $\text{Eu}(\text{DBM})_3\text{Phen}$ doped PMMA is shown in Figure 4 (the thickness of the polished doped PMMA is 2 mm and the concentration of the Eu ion is 4000 ppm wt). Four emission peaks are centered at 579, 591, 613, and 652 nm and can be assigned to the $^5\text{D}_0 \rightarrow ^7\text{F}_0$, $^5\text{D}_0 \rightarrow ^7\text{F}_1$, $^5\text{D}_0 \rightarrow ^7\text{F}_2$, and $^5\text{D}_0 \rightarrow ^7\text{F}_3$, respectively. The presence of only one $^5\text{D}_0 \rightarrow ^7\text{F}_0$ line indicates that the Eu^{3+} ion occupies only a single site and a single chemical environment exists around it.¹⁰ The $^5\text{D}_0 \rightarrow ^7\text{F}_2$ transition at 613 nm dominates all other transitions; the emission intensity of this transition is strongly dependent on the chemical environment in which the Eu ion is located. The much stronger intensity of $^5\text{D}_0 \rightarrow ^7\text{F}_2$ indicates that the ligand field surrounding the Eu ion is highly polarizable.¹¹ This also indicates that

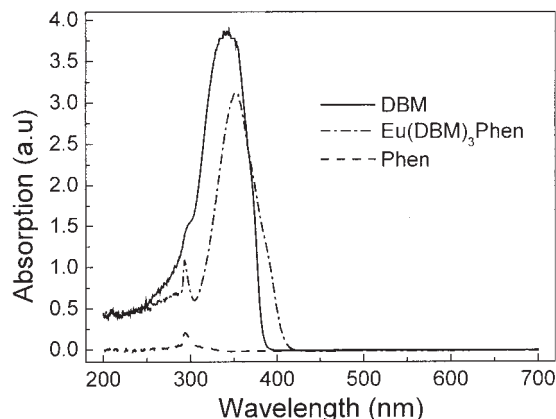


Figure 3 Absorption spectra of $\text{Eu}(\text{DBM})_3\text{Phen}$, DBM, and Phen in MMA monomer solution.

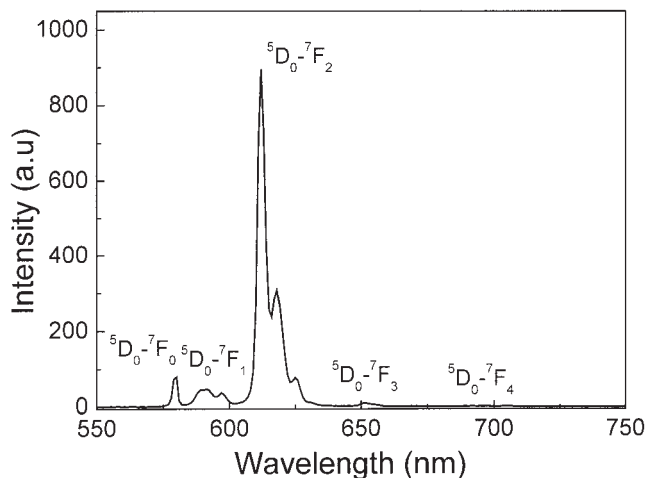


Figure 4 Fluorescence emission spectra of $\text{Eu}(\text{DBM})_3$ Phen doped PMMA excited at 355 nm

$\text{Eu}(\text{DBM})_3$ Phen doped PMMA has good color purity and that the Eu^{3+} ion is in a site without a center of inversion.¹²

Result of metastable lifetime measurement

The existence of aggregates is deleterious to the optical properties of the rare earth ion doping material. A relatively higher rare earth ion doping concentration usually induces concentration quenching, which reduces the metastable state lifetime of the doping material. To investigate the influence of the Eu ion doping concentration, the metastable state lifetime of $\text{Eu}(\text{DBM})_3$ Phen doped PMMA samples with Eu ion concentration varying from 400 to 10,000 ppm was examined.

The metastable state lifetime of the $\text{Eu}(\text{DBM})_3$ Phen doped PMMA was obtained from the decay curves. Figure 5a shows a typical decay curve and fitting curve of $\text{Eu}(\text{DBM})_3$ Phen doped PMMA (the concentration of the Eu ion is 4000 ppm wt). The decay curve can be fit with a single exponential, which also indicates that there is only one site symmetry from the Eu^{3+} ion.¹⁰ The lifetime obtained is about 0.48 ms. Figure 5b displays the lifetime dependence on doping concentration of $\text{Eu}(\text{DBM})_3$ Phen in PMMA.

From the lifetime measurement, there is no obvious decrease in metastable state lifetime up to 10,000 ppm wt. This indicates that no concentration quenching took place and the aggregates did not exist in $\text{Eu}(\text{DBM})_3$ Phen doped PMMA with the increase in doping concentration, because in rare earth containing polymers the formation of ion aggregates is always the cause of the emission concentration quenching.^{13,14} The energy transference would take place between Eu ions when they are close enough to each other within one aggregate. According to the molecular

structure of $\text{Eu}(\text{DBM})_3$ Phen, the Eu^{3+} is coordinated by four bidentate ligands: three DBM molecules and one Phen molecule. The ligands can form a sheath around the Eu^{3+} , which can act as a physical buffer between the ions and also can prevent ion aggregates from forming, and furthermore, the energy transference between ions can be avoided. In addition, rare earth ions typically prefer to coordinate with approximately eight atoms. In this case, the Eu^{3+} ion is completely coordinated by six oxygen atoms of three dibenzoylmethane ligands and two nitrogen atoms of one 1,10-phenanthroline ligand. So they do not need to cluster with each other to share coordination atoms, which is always the reason for fluorescence quenching in rare earth doped inorganic material.¹⁵ The chemical structure of $\text{Eu}(\text{DBM})_3$ Phen prevents aggregate formation.

The results show that $\text{Eu}(\text{DBM})_3$ Phen doped PMMA promises to be an efficient luminescent material in which high doping concentration is needed, such as a short-length-amplification device. But it was found that the optical loss of POF increased dramati-

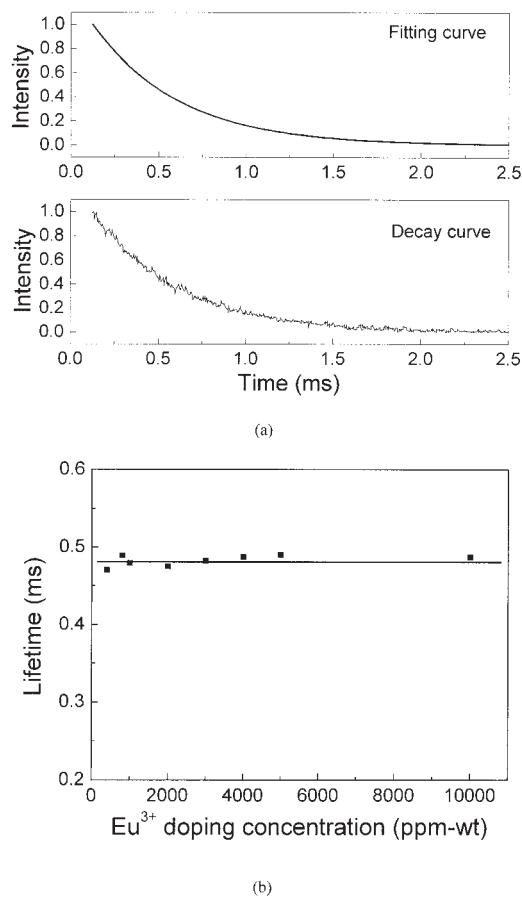


Figure 5 Metastable state lifetime of the $\text{Eu}(\text{DBM})_3$ Phen doped PMMA. (a) A typical decay curve and fitting curve of $\text{Eu}(\text{DBM})_3$ Phen doped PMMA (the concentration of the Eu ion is 4000 ppm wt); (b) lifetime dependence on doping concentration of $\text{Eu}(\text{DBM})_3$ Phen in PMMA.

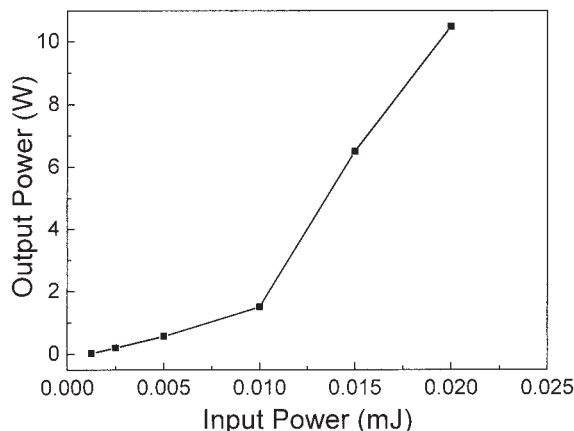


Figure 6 Output power versus absorbed pump power for a 4000 ppm wt $\text{Eu}(\text{DBM})_3\text{Phen}$ doped SI POF with a length of 40 cm.

cally while the doping concentration exceeded 4000 ppm. So the 4000-ppm $\text{Eu}(\text{DBM})_3\text{Phen}$ doped SI POF sample was selected in the ASE experiment.

ASE of $\text{Eu}(\text{DBM})_3\text{Phen}$ doped SI POF

Figure 6 shows a plot of the measured output power versus the absorbed pump power for a 4000-ppm $\text{Eu}(\text{DBM})_3\text{Phen}$ doped SI POF with a length of 40 cm, from which it can be found that a nonlinear relationship exists between input and output powers.

At low pump power, the populations of ground state are greater than that of the excitation state; the output consists mostly of spontaneous emission and the growth occurs linearly at a low rate. With the increase of pump power, the population of the excitation state would increase also. When the pump power attains a certain value that is required by the population inversion, the spontaneous emission is amplified, which is called ASE. Beyond this point, the output becomes mostly ASE and increases nonlinearly. From Figure 6, it can be found that the threshold of absorbed pump power for the onset of ASE is about 0.01 mJ. This result shows that the population inversion can

take place in the $\text{Eu}(\text{DBM})_3\text{Phen}$ doped SI POF. This character makes the doped POF usable as an amplifying medium.

CONCLUSIONS

In summary, $\text{Eu}(\text{DBM})_3\text{Phen}$ doped SI POF was fabricated by a preform technique. Thermostability and optical properties of the $\text{Eu}(\text{DBM})_3\text{Phen}$ doped PMMA were discussed. By end-pumping with a YAG laser at 355 nm, the ASE phenomenon of the doped SI POF was observed. The threshold of absorbed pump power for the onset of ASE of a 40-cm-length doped SI POF is about 0.01 mJ. The results show that $\text{Eu}(\text{DBM})_3\text{Phen}$ doped SI POF is of potential application in making polymer optical fiber amplifiers.

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