

Optical properties of Er(DBM)₃Phen-doped polymer and fabrication of ridge waveguide

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Abstract

Er(DBM)₃Phen (DBM = dibenzoylmethane; phen = 1,10-phenanthroline)-doped PMMA-GMA (poly-methyl-methacrylate-glycidyl-methacrylate) copolymer is prepared, the absorption spectrum and photoluminescence spectrum are analyzed. The full width at half maximum (FWHM) of the photoluminescence spectrum is about 85 nm. The Judd–Ofelt theory is used to analyse the absorption spectrum of Er³⁺ and obtain the intensity parameters: $\Omega_2 = 4.08 \times 10^{-20} \text{ cm}^2$, $\Omega_4 = 0.77 \times 10^{-20} \text{ cm}^2$ and $\Omega_6 = 0.70 \times 10^{-20} \text{ cm}^2$. The line strengths, predicted spontaneous transition probabilities and the radiative lifetime are calculated with the J–O intensity parameters. The calculated radiative lifetime of excited ⁴I_{13/2} state of Er³⁺ is 12.4 ms. Ridge waveguide is fabricated using reactive ion etching. Based on the parameters we calculated, Er(DBM)₃Phen-doped PMMA-GMA is a potential material for polymeric optical waveguide amplifiers.

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1. Introduction

In recent years, much attention has been attracted to the development of polymeric optical waveguide devices [1–3]. Polymeric materials have excellent properties: high bandwidth, simple processing steps, low cost and compatible with silicon substrate. According to these advantages, polymers are promised host candidates for optical waveguide devices. In optical communication networks, erbium doped waveguide amplifiers (EDWA) play a key role in achieving signal amplification and reducing various losses. Many factors, such as absorption cross-section, metastable state life-

time, and spontaneous transition probability, affect the performance of waveguide amplifiers. So it is valuable to evaluate these parameters of Er³⁺ in polymeric materials.

In this work, Er(DBM)₃Phen-doped PMMA-GMA copolymer is synthesized. The lower glass transition temperature of linear MMA (78 °C) will lead to dissolve with each layer of waveguide devices and limit the fabrication of optical waveguide devices. However, the PMMA-GMA copolymer system could solve this problem because its higher T_g (125 °C). Based on this advantage, a multi-layer waveguide is designed. PMMA (Polymethylmethacrylate) is used as the bottom and top cladding layers, and the Er(DBM)₃Phen-doped PMMA-GMA is used as the core material. Ridge waveguide is fabricated using reactive ion-beam etching. The optical absorption properties of Er(DBM)₃Phen-doped PMMA-GMA are investigated. Using Judd–Ofelt theory [4,5], the phenomenological

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intensity parameters Ω_t ($t = 2, 4, 6$), spontaneous transition probability and radiative lifetime are calculated.

2. Experimental Details

The monomers of methyl methacrylate and methyl acrylic propyl epoxy are prepared respectively. Two percent hydroquinone is added as inhibitor. Then the fresh distilled monomers are commixed to accomplish copolymerize reaction. Butyl acetate is impregnant and 2, 2'-azo bis iso butire nitrile (AIBN) is initiator. The copolymerization reaction is accomplished at 70–75 °C under agitation during 4 h. The copolymer solution is diluted and filtrated through a 0.45 μm filter. The content of solid can be controlled from 18% to 21% after distilling part impregnant. Finally, Imidazole is added as curing agent. The $\text{Er}(\text{DBM})_3\text{phen}$ is prepared according to the method of the literature [6]. The $\text{Er}(\text{DBM})_3\text{phen}$ is dissolved in dimethyl formamide, and mixed into copolymer solution under agitation. The corresponding concentration of Er^{3+} is $0.16 \times 10^{20} \text{ cm}^{-3}$. The compound solution is gradually heated from 70 °C to 125 °C under nitrogen atmosphere during 10 h and the cross-linking occurs at 125 °C. Finally, a small transparent disc with a 0.66 mm thickness is obtained.

The absorption spectrum is recorded with Cary 500 Scan UV–Vis–NIR Spectrophotometer, and the photoluminescence spectrum is measured with SPEX 934D phosphorimeter. The refractive indices of the material are measured using WVASE32 from 400 nm to 1700 nm wavelength.

3. Spectrum analysis

The absorption spectrum of the disc is shown in Figs. 1 and 2. In order to compare their shapes, the intensities of

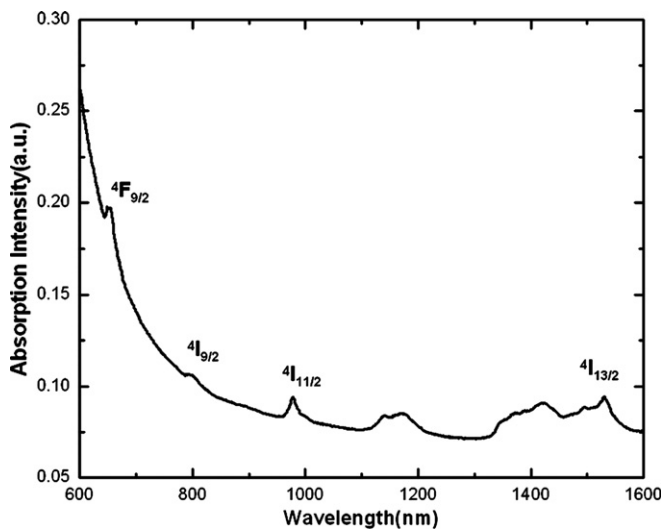


Fig. 1. Absorption spectrum of $\text{Er}(\text{DBM})_3\text{Phen}$ -doped PMMA-GMA at room temperature (from 600 nm to 1600 nm wavelength).

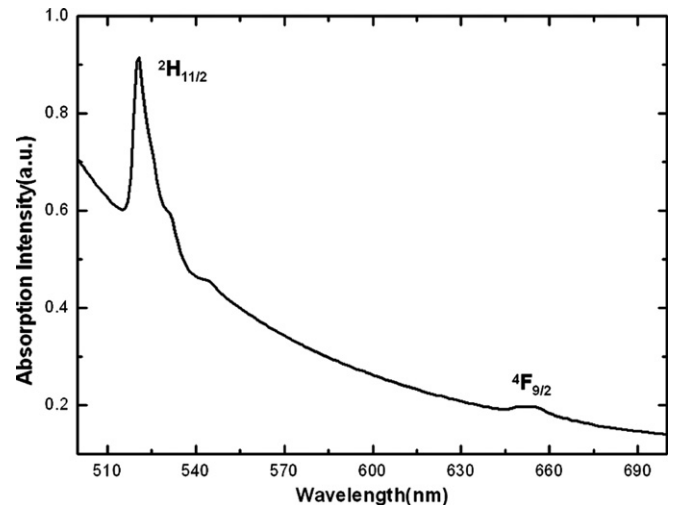


Fig. 2. Absorption spectrum of $\text{Er}(\text{DBM})_3\text{Phen}$ -doped PMMA-GMA at room temperature (from 500 nm to 700 nm wavelength).

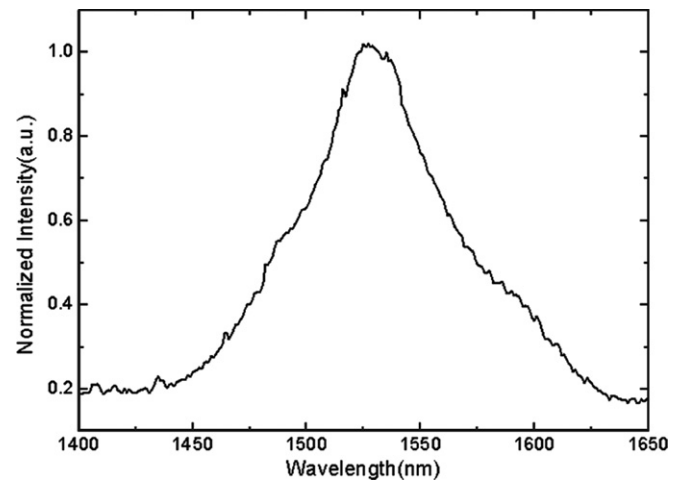


Fig. 3. Photoluminescence spectrum of Er^{3+} in $\text{Er}(\text{DBM})_3\text{Phen}$ -doped PMMA-GMA copolymer, excited at 976 nm with 50 mW pump power.

the spectrum are adjusted in size. The spectra consists of 5 absorption bands, corresponding to the transitions from the ground state $^4I_{15/2}$ to the excited states $^4I_{13/2}$, $^4I_{11/2}$, $^4I_{9/2}$, $^4F_{9/2}$ and $^4H_{11/2}$. Fig. 3 shows the room-temperature fluorescence spectrum for the $^4I_{13/2}$ to $^4I_{15/2}$ transition of Er^{3+} in $\text{Er}(\text{DBM})_3\text{Phen}$ -doped PMMA-GMA copolymer, excited at 976 nm with 50 mW pump power. The full width at half maximum (FWHM) is about 85 nm centred around 1535 nm. Broad photoluminescence spectrum can get a wide gain bandwidth. This is significant for optical amplification.

The radiative lifetime can be calculated using Judd–Ofelt theory. The measured line strengths, $S_{\text{meas}}^{\text{ed}}[(S, L)J; (S', L')J']$, for electric-dipole of the transitions from the initial state, $|(S, L)J\rangle$, to the excited state, $|(S', L')J'\rangle$, can be expressed by the following expression:

$$S_{\text{meas}}^{\text{ed}}[(S, L)J; (S', L')J'] = \frac{3ch(2J+1)}{8\pi^3 N_0 \lambda e^2} \cdot \frac{9n}{(n^2+2)^2} \cdot \Gamma, \quad (1)$$

where $\Gamma = \int \alpha(\lambda) d\lambda$ is the integrated absorbance coefficient as a function of λ , N_0 is the Er^{3+} concentration. $\bar{\lambda}$ is the mean wavelength of the absorption, c is the velocity of light, h is Planck constant, n is the refractive index. According to the Judd–Ofelt theory, the line strength, $S_{\text{calc}}^{\text{ed}}[(S, L)J; (S', L')J']$, can be expressed by the following expression:

$$S_{\text{calc}}^{\text{ed}}[(S, L)J; (S', L')J'] = \sum_{t=2,4,6} \Omega_t |(S, L)J \| U^{(t)} \| (S', L')J'|^2, \quad (2)$$

where $U^{(t)}$ are the doubly reduced matrix elements of unit tensor operators, which are independent of the host [7–9]. We use the matrix elements which were reported by Sardar et al. [10]. Ω_2, Ω_4 and Ω_6 are the Judd–Ofelt parameters, which are used to characterize the radiative transition probabilities. Once they are determined, the all transition properties can be calculated. A least-squares fitting method between $S_{\text{meas}}^{\text{ed}}$ and $S_{\text{calc}}^{\text{ed}}$ is used for calculating the J–O parameters. δ_{rms} is used to evaluate the accuracy of this method and is given by the following equation:

$$\delta_{\text{rms}} = \left[\frac{\sum (S_{\text{calc}} - S_{\text{meas}})^2}{q - p} \right]^{1/2}, \quad (3)$$

where q and p are the number of absorption bands analyzed and J–O parameters, respectively. The measured and calculated line strengths are shown in Table 1. Judd–Ofelt intensity parameters are $\Omega_2 = 4.08 \times 10^{-20} \text{ cm}^2$, $\Omega_4 = 0.77 \times 10^{-20} \text{ cm}^2$ and $\Omega_6 = 0.70 \times 10^{-20} \text{ cm}^2$, respectively. The root-mean-square (δ_{rms}) is $0.106 \times 10^{-20} \text{ cm}^2$. The spontaneous transition probability can be calculated by the J–O parameters. The expression is given by:

$$A[(S, L)J; (S', L')J'] = A_{\text{ed}} + A_{\text{md}}, \quad (4)$$

where A_{ed} and A_{md} are the transition probability for the electric-dipole and the magnetic-dipole. In some rare-earth doped materials, the effect of magnetic-dipole can be ignored compared with the electric-dipole. But for Er^{3+} , the contribution of magnetic-dipole for the ground $^4\text{I}_{15/2}$ state to the $^4\text{I}_{13/2}$ state is significant and must be taken into account. A_{ed} is expressed as

$$A_{\text{ed}}[(S, L)J; (S', L')J'] = \frac{64\pi^4 e^2}{3h(2J+1)\bar{\lambda}^3} \cdot \frac{n(n^2+2)^2}{9} \cdot S_{\text{calc}}^{\text{ed}}[(S, L)J; (S', L')J']. \quad (5)$$

Table 2

Predicted spontaneous transition probabilities and radiative lifetime of Er^{3+} in $\text{Er}(\text{DBM})_3\text{Phen}$ -doped PMMA-GMA

| Transition | λ (nm) | n | $A_{\text{ed}} (s^{-1})$ | $A_{\text{md}} (s^{-1})$ | τ_{R} (ms) |
|---|----------------|--------|--------------------------|--------------------------|------------------------|
| $^4\text{I}_{13/2} \rightarrow ^4\text{I}_{15/2}$ | 1540 | 1.4937 | 49.37 | 31.27 | 12.4 |

The values of the spontaneous transition probabilities of electric-dipole and magnetic-dipole, the radiative lifetime at 1540 nm are given in Table 2.

In this work, we use the following expression to calculate A_{md} :

$$A_{\text{md}} = \left(\frac{n}{n'}\right)^3 A'_{\text{md}}, \quad (6)$$

where n and n' are the refractive indices of Er^{3+} in copolymer and LaF_3 [11], respectively. The radiative lifetime τ_{R} is given by

$$\tau_{\text{R}} = \frac{1}{\sum_{(S', L')J'} A[(S, L)J; (S', L')J']}. \quad (7)$$

The values of the spontaneous transition probabilities of electric-dipole and magnetic-dipole, the radiative lifetime are given in Table 2. It can be seen that the contributions of magnetic-dipole for spontaneous transition probabilities of the transitions from $^4\text{I}_{13/2}$ to $^4\text{I}_{15/2}$, $^4\text{I}_{11/2}$ to $^4\text{I}_{13/2}$ and $^4\text{I}_{9/2}$ to $^4\text{I}_{11/2}$ are almost equivalent to electric-dipole's. The calculated radiative lifetime of the state $^4\text{I}_{13/2}$ to the ground state $^4\text{I}_{15/2}$ is 12.4 ms.

4. Waveguide fabrication

PMMA with a 4 μm thickness is first spin-coated onto a Si substrate to form the bottom cladding layer, followed by thermal annealing at 120 $^\circ\text{C}$ for 3 h. $\text{Er}(\text{DBM})_3\text{Phen}$ -doped PMMA-GMA copolymer with a 2.1 μm thickness is then spun as the core layer and baked at 125 $^\circ\text{C}$ to remove the solvent. The refractive indices of cladding and core are 1.483 and 1.494 at 1535 nm wavelength, respectively. An Aluminum film of 20 nm thickness is deposited onto the core layer surface by thermal evaporation. The film is taken to be a dry etching mask. A group of 12.24 μm wide waveguides are fabricated by use of a standard photolithography and reactive ion-beam etching. Finally, a 3 μm thickness PMMA is used as the top cladding, and cured at 125 $^\circ\text{C}$ for 3 h. Fig. 4 shows SEM micrograph of the waveguide without top cladding. Fig. 5 is the output

Table 1
The measured and calculated line strengths of Er^{3+} in $\text{Er}(\text{DBM})_3\text{Phen}$ -doped PMMA-GMA

| Absorption (from $^4\text{I}_{15/2}$) | λ (nm) | n | Γ (nmcm^{-1}) | $S_{\text{meas}}^{\text{ed}} (10^{-20} \text{ cm}^2)$ | $S_{\text{calc}}^{\text{ed}} (10^{-20} \text{ cm}^2)$ |
|--|----------------|--------|---------------------------------|---|---|
| $^4\text{I}_{13/2}$ | 1530 | 1.4938 | 2.211 | 1.131 | 1.176 |
| $^4\text{I}_{11/2}$ | 978 | 1.4967 | 0.666 | 0.532 | 0.393 |
| $^4\text{I}_{9/2}$ | 798 | 1.499 | 0.119 | 0.116 | 0.140 |
| $^4\text{F}_{9/2}$ | 649 | 1.5024 | 0.630 | 0.755 | 0.735 |
| $^4\text{H}_{11/2}$ | 521 | 1.5089 | 2.210 | 3.282 | 3.287 |

The centred wavelength of 5 absorption bands, refractive indices, measured and calculated line strengths are shown in Table 1.

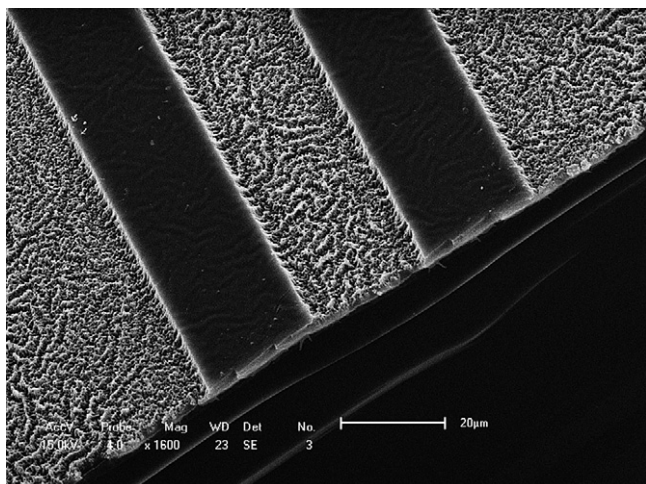


Fig. 4. SEM micrograph of the Er(DBM)₃Phen-doped PMMA-GMA waveguide without top cladding.



Fig. 5. The output near-field mode profile from a 3.0 cm long waveguide at 1535 nm wavelength.

near-field profile. The length of the device is 3.0 cm, and the input signal power is 1.0 mW.

5. Conclusions

The photoluminescence spectrum and the absorption spectrum of Er(DBM)₃Phen-doped PMMA-GMA are observed. The emission peak is 1535 nm and the FWHM is about 85 nm. The absorption spectral analysis is performed based on Judd–Ofelt theory. The J–O intensity

parameters, the line strengths, predicted spontaneous transition probabilities, and the radiative lifetime are calculated. The calculated radiative lifetime of the states ⁴I_{13/2} is 12.4 ms. Compared with Er³⁺-doped phosphate and silicate glasses [12–14], the radiative lifetime can be reached to the same level. The emission cross-section of Er(DBM)₃Phen in PMMA-GMA of 1535 nm wavelength is analogous to that of Er³⁺-doped inorganic host which is reported previously [15]. The higher glass transition temperature of PMMA-GMA copolymer satisfies the demand of optical waveguide devices' fabrication. Ridge waveguides are fabricated using the reactive ion etching. Based on the parameters we calculated and the waveguide fabricated, Er(DBM)₃Phen-doped PMMA-GMA copolymer is a potential material for polymeric optical waveguide amplifiers.

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