**ARTICLE**

**Optical Properties of Nd$^{3+}$ in Nd(DBM)$_3$Phen-doped Poly(methyl methacrylate)**

Zhi-qiang Zheng$^a$, Hao Liang$^c$, Hai Ming$^b$, Qi-jin Zhang$^c$, Jian-ping Xie$^b$

a. Department of Physics, Fujian Normal University, Fuzhou 350007, China; b. Department of Physics, University of Science and Technology of China, Hefei 230026, China; c. Department of Polymer Science and Engineering, University of Science and Technology of China, Hefei 230026, China

(Dated: Received on June 10, 2005; Accepted on December 2, 2005)

Nd(DBM)$_3$Phen-doped (DBM is dibenzoylmethane and Phen is phenanthroline) polymethyl methacrylate (PMMA) is prepared. Optical absorption, excitation and emission spectra were analyzed for Nd$^{3+}$ in Nd(DBM)$_3$Phen-doped PMMA. Using the Judd-Ofelt theory, the absorption spectrum was analyzed. The Judd-Ofelt (J-O) intensity parameters of Nd(DBM)$_3$Phen-doped polymethyl methacrylate were calculated to be $\Omega_2 = 20.97 \times 10^{-20}$ cm$^2$, $\Omega_4 = 3.42 \times 10^{-20}$ cm$^2$, $\Omega_6 = 2.90 \times 10^{-20}$ cm$^2$. The radiative lifetime ($631 \mu$s) of the excited $^4F_{3/2}$ level is given. The stimulated emission cross-sections and the fluorescence branch ratios for the $^4F_{3/2} \rightarrow ^4I_{15/2}$ transitions are also evaluated. Analysis reveals that Nd(DBM)$_3$Phen-doped PMMA is promising for application in polymer optical fibers and planar waveguides.

**Key words:** Radiative properties, Judd-Ofelt analysis, Nd(DBM)$_3$Phen, Polymer

I. INTRODUCTION

In recent years, there has been more interest in polymer optical fibers and polymer planar waveguides for their applications in optical communication systems and optical sensors, especially in local networks and data communications. Rare-earth-doped polymer systems are also of interest. Nd$^{3+}$, Eu$^{3+}$, Sm$^{3+}$ and Er$^{3+}$ have been doped into POF and PMMA [1-5]. Super-fluorescence is found in Eu$^{3+}$-doped GI POF [6] and additionally heated at 75 $^\circ$C for 48 h under 608 kPa nitrogen and additionally heated at 75 $^\circ$C until solidification was completed. The samples were cut and polished for optical measurements.

II. EXPERIMENTAL METHODS

Nd(DBM)$_3$Phen was synthesized according to a previously reported procedure [13]. The central Nd$^{3+}$ is bound to three dibenzoylmethane (DBM) ligands and one phenanthroline (Phen) ligand. 1,10-phenanthroline acts as a synergic shielding ligand, which strongly enhances the fluorescent intensity of the complex. We used a thermal polymerization technique to make Nd(DBM)$_3$Phen-doped PMMA. First, 15 mL purified methyl methacrylate (MMA), 0.02 g 2,2-azoisobutyronitrile (AIBN) as an initiator, and a specified amount of Nd(DBM)$_3$Phen were mixed in a vessel. This solution was filtrated through a microporous filter (d=0.20 $\mu$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 $^\circ$C for 48 h under 608 kPa nitrogen and additionally heated at 75 $^\circ$C until solidification was completed. The samples were cut and polished for optical measurements.

Optical absorption measurements were made using a spectrophotometer (Perkin-Elmer Lambda 900). Excitation and fluorescence spectra of Nd(DBM)$_3$Phen-doped PMMA were recorded on a fluorescence spectrophotometer (an Edinburgh FL/FS 920).

III. RESULTS AND DISCUSSION

A. Absorption, excitation and emission spectra

Figure 1 shows the absorption spectrum of Nd(DBM)$_3$Phen-doped PMMA (1-cm-thick slice). The
concentration of Nd$^{3+}$ in Nd(DBM)$_3$Phen-doped PMMA is 0.5wt%. All the absorption bands originate from the ground $^4I_{9/2}$ level. The band positions along with assignments in the absorption spectrum are shown in Table I. Excitation and fluorescence spectra of Nd(DBM)$_3$Phen-doped PMMA are shown in Fig.2 and Fig.3, respectively. Figure 2 shows the excitation spectrum of Nd(DBM)$_3$Phen-doped PMMA monitored at 1068 nm for the transition $^4F_{3/2} \rightarrow ^4I_{11/2}$. From Fig.2 we can see that the broad excitation maximum around the 412 nm wavelength is assigned to absorption of a DBM ligand, and the transitions of excitation spectrum (450-900 nm) are assigned (starting from $^4I_{9/2}$) based on the Nd$^{3+}$ free ion energy level structure.

![Absorption spectrum of Nd(DBM)$_3$Phen-doped PMMA.](image)

**FIG. 1** Absorption spectrum of Nd(DBM)$_3$Phen-doped PMMA. The inset shows the detailed profile of absorption spectrum from 615 to 715 nm wavelength.

![Excitation spectrum of Nd(DBM)$_3$Phen-doped PMMA.](image)

**FIG. 2** Excitation spectrum of Nd(DBM)$_3$Phen-doped PMMA.

Figure 3 shows the emission spectrum of Nd(DBM)$_3$Phen-doped PMMA at excitation of 412 nm using a xenon lamp. Figure 4 shows the schematic energy-level diagram for a Nd(DBM)$_3$Phen. According to sensitized emission theory, an energy transfer can occur in the Nd(DBM)$_3$Phen. There are several stages in this transfer. First, absorption of energy (412 nm light) produces an excited singlet $S_1$ state from the ground singlet $S_0$ state in the DBM ligand. Second, an intersystem crossing to a triplet $T_1$ state takes place by a radiationless process. Third, radiationless transfer of energy occurs from the triplet $T_1$ state to the $^4F_{9/2}$ of Nd$^{3+}$. Fourth, the $^4F_{9/2}$ level populates the lower level, i.e. $^4F_{3/2}$ through relaxation. Thus, the three emission peaks at 896, 1068 and 1347 nm are assigned to the transitions from $^4F_{5/2}$ level to the $^4I_{9/2}$, $^4I_{11/2}$, $^4I_{13/2}$ levels, respectively. It can be seen from Fig.1 and Fig.2 that the absorption coefficient of ligand DBM is large compared with that of Nd$^{3+}$. The sensitization lanthanide ion, on emission, is an efficient way to circumvent the low absorption coefficients of these lanthanide ions, therefore it is very interesting for practical applications.

### B. Judd-Ofelt analysis

Mathematically, the line strength of an electric-dipole transition $S_{exp}$ can be related to the absorption coefficient using the following equation [14]

$$\int k(\lambda)d\lambda = \rho \frac{8\pi^3 e^2 \hbar \lambda}{3c h(2J+1) n^2} \frac{(n^2 + 2)^2}{9} S_{exp}$$

(1)

where $k(\lambda)$ is the absorption coefficient at wavelength $\lambda$, $\rho$ is the Nd$^{3+}$ concentration, $e$, $h$ and $c$ are the electron charge, the Planck constant and velocity of light, respectively. $\hbar$ is the mean wavelength of the absorption band, $J$ is the total angular momentum of the initial level ($J=9/2$ in Nd$^{3+}$), and $n$ is refractive index, which is 1.496 for Nd(DBM)$_3$Phen-doped PMMA. All these parameters are in CGS units.

![Fluorescence spectrum of Nd(DBM)$_3$Phen-doped PMMA.](image)

**FIG. 3** Fluorescence spectrum of Nd(DBM)$_3$Phen-doped PMMA.

<table>
<thead>
<tr>
<th>Level</th>
<th>$\lambda$/nm</th>
<th>$S_{exp}$</th>
<th>$S_{calc}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$^2G_{9/2}$</td>
<td>478</td>
<td>0.0599</td>
<td>0.1711</td>
</tr>
<tr>
<td>$^2K_{15/2}$</td>
<td>528</td>
<td>3.0085</td>
<td>2.5062</td>
</tr>
<tr>
<td>$^4G_{7/2}$</td>
<td>584</td>
<td>22.607</td>
<td>22.641</td>
</tr>
<tr>
<td>$^2T_{11/2}$</td>
<td>630</td>
<td>0.0487</td>
<td>0.0415</td>
</tr>
<tr>
<td>$^4F_{9/2}$</td>
<td>681</td>
<td>0.2085</td>
<td>0.1714</td>
</tr>
<tr>
<td>$^4S_{3/2}$</td>
<td>745</td>
<td>2.078</td>
<td>2.0904</td>
</tr>
<tr>
<td>$^4F_{5/2}$</td>
<td>803</td>
<td>2.471</td>
<td>2.5393</td>
</tr>
<tr>
<td>$^4F_{3/2}$</td>
<td>877</td>
<td>0.6354</td>
<td>0.9427</td>
</tr>
</tbody>
</table>

rms$\Delta S = 27.07 \times 10^{-22}$ cm$^2$
TABLE II Calculated radiative lifetime of the metastable $^4F_{3/2}$ level, the radiative transition probabilities and fluorescence branch ratios of $^4F_{3/2} \rightarrow ^4I_{1/2}$.

<table>
<thead>
<tr>
<th>SLJ</th>
<th>$^4S'$</th>
<th>$^4I_{13/2}$</th>
<th>$^4I_{11/2}$</th>
<th>$^4I_{9/2}$</th>
<th>$^4I_{7/2}$</th>
<th>$^4I_{5/2}$</th>
<th>$^4I_{3/2}$</th>
<th>$^4I_{1/2}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$^4F_{3/2}$</td>
<td>$^4I_{15/2}$</td>
<td>1835</td>
<td>0</td>
<td>0</td>
<td>0.629</td>
<td>135.67</td>
<td>0.445</td>
<td>0.413</td>
</tr>
<tr>
<td></td>
<td>$^4I_{13/2}$</td>
<td>1347</td>
<td>0</td>
<td>0</td>
<td>4.07</td>
<td>7.089</td>
<td>0.465</td>
<td>0.465</td>
</tr>
<tr>
<td></td>
<td>$^4I_{11/2}$</td>
<td>1068</td>
<td>0</td>
<td>0.142</td>
<td>4.07</td>
<td>736.89</td>
<td>0.465</td>
<td>0.465</td>
</tr>
<tr>
<td></td>
<td>$^4I_{9/2}$</td>
<td>896</td>
<td>0</td>
<td>0.229</td>
<td>0.054</td>
<td>704.80</td>
<td>0.445</td>
<td>0.445</td>
</tr>
</tbody>
</table>

$A_T(4F_{3/2})=1584$ s$^{-1}$, $\tau_R=0.631$ ms.

![FIG. 4 Schematic energy-level diagram for Nd(DBM)$_3$Phen.](image)

According to the Judd-Ofelt theory, the line strength of an electric-dipole transition between initial $J$ manifold and terminal $J'$ manifold can be expressed as [14]

$$ S = \sum_{t=2,4,6} \Omega_t \left| \langle f^N \Psi_{J'} | U^{(t)} | f^N \Psi_J \rangle \right|^2 $$

(2)

where the elements $U^{(t)}$ are the doubly reduced unit tensor operators, which have been found to be essentially independent of the ionic environment [12] and are given in Ref. [15] for the Nd$^{3+}$. $\Omega_t$ are the Judd-Ofelt(J-O) intensity parameters, which are independent of electronic quantum numbers with the ground configuration of the Nd$^{3+}$. $f^N \Psi_{J'}$ are wave functions of the states with $N$ electrons in 4f shell having total angular momentum $J$. Using Eq.(1) and the values of the absorption spectrum of Nd(DBM)$_3$Phen-doped PMMA, the experimental line strength $S_{\text{exp}}$ (units of cm$^2$) for the electric dipole transition can be obtained. After $S_{\text{exp}}$ is obtained, the J-O intensity parameter $\Omega_t$ can be derived by least-squares fitting of Eq.(2) as: $\Omega_2 = 20.97 \times 10^{-20}$ cm$^2$, $\Omega_4 = 3.42 \times 10^{-20}$ cm$^2$, $\Omega_6 = 2.90 \times 10^{-20}$ cm$^2$.

The experimental and corresponding calculated line strength data for Nd(DBM)$_3$Phen-doped PMMA are displayed in Table I. The root-mean-square deviation of the experimental and calculated line strengths is determined in the usual way

$$ \text{rms} \Delta S = \left[ \frac{\sum (S_{\text{exp}} - S_{\text{calc}})^2}{N - M} \right]^{1/2} $$

(3)

where $N$ is the number of transitions and $M$ is the number of parameters determined.

C. Radiative properties

The radiative transition probability $A_{\text{rad}}$ from initial state $J$ to terminal state $J'$ is given as [14]

$$ A_{\text{rad}} = \frac{64\pi^4 \nu^3}{3h(2J+1)} \left( \sum_{t=2,4,6} \Omega_t \left| \langle f^N \Psi_{J'} | U^{(t)} | f^N \Psi_J \rangle \right|^2 \right) $$

(4)

where $\nu$ is the frequency in inverse centimeters. The total transition probability is obtained by carrying out the summation of all the final states $J'$ as

$$ A_T = \sum_{J'} A_{\text{rad}} $$

(5)

Then the fluorescence branch ratios $\beta$ are defined by

$$ \beta = \frac{A_{\text{rad}}}{A_T} $$

(6)

The radiative lifetime of the excited states can be written as

$$ \tau_R = 1/A_T $$

(7)

The stimulated emission cross-section $\sigma_p$ is given by

$$ \sigma_p = \frac{A_{\text{rad}} \lambda_p^4}{8\pi n^2 c \Delta \lambda} $$

(8)

where $\Delta \lambda$ and $\lambda_p$ are effective band width and the peak wavelength of the emission transition, respectively. The calculated radiative lifetime ($\tau_R$) of the metastable $^4F_{3/2}$ level, the radiative transition probabilities and fluorescence branch ratios of $^4F_{3/2} \rightarrow ^4I_{1/2}$ are listed in Table II. The calculated emission cross-sections for the fluorescence transitions are given in Table III. In Table II, the transition $^4F_{3/2} \rightarrow ^4I_{11/2}$ shows the largest radiative transition probability and the highest fluorescence branch ratio. The radiative lifetime of
and a broad band amplifier in the 1068 nm region. Doped PMMA has the potential to be a tunable laser that the effective linewidth of the emission transition Nd, and the emission cross-section for the 1068 nm transition is of the same order of magnitude as that for Nd\(^{3+}\)-doped glass systems [14]. From Table III, we know that the effective linewidth of the transition \(4F_{3/2} \rightarrow 4I_{11/2}\) is the largest of those of the transitions \(4F_{3/2} \rightarrow 4I_{J'}\), and the emission cross-section for the 1068 nm transition is of the same order of magnitude as that for Nd\(^{3+}\)-doped glass systems [14]. From Fig.3 we can see that the effective linewidth of the emission transition \(4F_{3/2} \rightarrow 4I_{11/2}\) is about 41 nm, which is large compared with those of the Nd\(^{3+}\)-doped glasses and Nd\(^{3+}\)-doped crystals [9,14,16]. Therefore, the Nd(DBM)\(_3\)phen-doped PMMA has the potential to be a tunable laser and a broad band amplifier in the 1068 nm region.

Some parameters of the optical properties of Nd(DBM)\(_3\)phen-doped PMMA are compared with corresponding values for other lanthanide chelates in PMMA \([3,10,17]\) in Table IV. The emission lines at 613, 648, 1534 and 1068 nm are main emission lines of Eu(DBM)\(_3\)phen, Sm(DBM)\(_3\)phen, Er(DBM)\(_3\)phen and Nd(DBM)\(_3\)phen in PMMA, respectively. The center wavelengths of the communication window of methyl methacrylate-based optical waveguides and silica-based optical waveguides are the 650 and 1550 nm, respectively. The effective linewidth of the main emission transition of Nd(DBM)\(_3\)phen-doped PMMA is large compared with those of the Eu(DBM)\(_3\)phen-doped PMMA and Sm(DBM)\(_3\)phen-doped PMMA. The large values for \(\Omega_2\) indicate the presence of covalent bonding between the rare-earth ions (Nd, Sm, Er, Eu) and the surrounding ligands (DBM, Phen) is reasonable. It reflects the large asymmetry of the local environment at the rare-earth ions.

### IV. CONCLUSIONS

In conclusion, a spectroscopic study of Nd\(^{3+}\) in Nd(DBM)\(_3\)phen-doped PMMA has been performed. The J-O intensity parameters were obtained from the absorption spectrum of Nd(DBM)\(_3\)phen-doped PMMA. The radiative lifetime of the metastable \(4F_{3/2}\) level, the stimulated emission cross-sections and the fluorescence branch ratios for the \(4F_{3/2} \rightarrow 4I_{J'}\) are also evaluated. The evaluation of the radiative properties shows that Nd(DBM)\(_3\)phen-doped PMMA has the potential to be a polymer optical active device.

### V. ACKNOWLEDGMENT

This work was supported by the National Natural Science Foundation of China (No.90201013), the Natural Science Foundation of Fujian Province of China (No.A0510014), and the Science Foundation of the Educational Department of Fujian Province of China (Nos.JB03151 and JB04246).

### REFERENCES