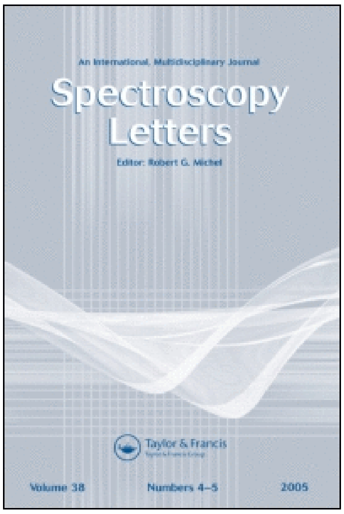

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Optical Properties of Polymethyl Methacrylate Doped with Neodymium Chelates

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Optical Properties of Polymethyl Methacrylate Doped with Neodymium Chelates

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Abstract: The luminescence of $Nd(DBM)_3(H_2O)_2$-, $Nd(DBM)_3Phen$-, and $Nd(DBM)_3(TOPO)_2$-doped polymethyl methacrylate (PMMA) was investigated under excitation at

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17,100 cm^{-1} ($^4I_{9/2} \rightarrow {}^4G_{7/2}$). The $^4F_{3/2} \rightarrow {}^4I_{11/2}$ transition of the Nd(DBM)$_3$(TPPO)$_2$-doped PMMA showed the strongest intensity. In order to predict the radiative properties of Nd(DBM)$_3$(TOPO)$_2$-doped PMMA, its absorption spectrum was measured and Judd-Ofelt parameters ($\Omega_2, \Omega_4, \Omega_6$) were calculated. The values of the radiative lifetime and the emission cross-section of $^4F_{3/2} \rightarrow {}^4I_{11/2}$ transition are comparable with those shown by glasses used in solid state laser applications. It can be concluded that Nd(DBM)$_3$(TOPO)$_2$-doped PMMA is an efficient luminescent material.

Keywords: Chelate, Judd-Ofelt theory, luminescent material, polymer

INTRODUCTION

In recent years, rare-earth-doped polymer systems are of interest for their potential applications for laser systems, polymer optical fiber amplifier, and integrated waveguides.[1–6] In these doped systems, rare-earth β-diketonates are often adopted because they show good compatibility with the polymer matrix.[5–10]

Trivalent neodymium has been well studied for its laser characteristics of $^4F_{3/2} \rightarrow {}^4I_{11/2}$ transition.[7] In this paper, Nd β-diketonate chelate–doped polymer luminescent material was fabricated by incorporating Nd(DBM)$_3$(H$_2$O)$_2$, Nd(DBM)$_3$Phen, and Nd(DBM)$_3$(TOPO)$_2$ into polymethyl methacrylate (PMMA). PMMA was selected as the matrix for its low optical absorption, simple synthesis, and low cost. The fluorescence spectra measurement showed that the $^4F_{3/2} \rightarrow {}^4I_{11/2}$ transition intensity of Nd(DBM)$_3$(TPPO)$_2$-doped PMMA is the strongest. According to the absorption spectrum, the Judd-Ofelt parameters of Nd(DBM)$_3$(TOPO)$_2$-doped PMMA were calculated, and its radiative properties were predicted. The result showed that it is a promising luminescent material for $^4F_{3/2} \rightarrow {}^4I_{11/2}$ transition.

MATERIALS AND METHODS

Nd(DBM)$_3$(H$_2$O)$_2$ and Nd(DBM)$_3$Phen were synthesized according to the literature.[11] To synthesize Nd(DBM)$_3$(TOPO)$_2$, the chloroform containing Nd(DBM)$_3$(H$_2$O)$_2$ and trioctylphosphine oxide (TOPO) was refluxed under stirring for 7 hr. The molar ratio of Nd(DBM)$_3$(H$_2$O)$_2$ and TOPO is 1:2. After volatilization of the chloroform, the products were recrystallized from acetone/petroleum ether and dried under vacuum.

Nd chelates–doped PMMA was prepared by bulk polymerization. First, the methyl methacrylate (MMA) solution (0.03 mol · dm^{-3}) of Nd chelates is obtained by dissolving Nd chelates in purified MMA. Then, 30 mg 2,2-azoisobutyronitrile (AIBN) as initiator was added to 20 mL of the above solution. The prepolymerization was carried out at 85°C for 30 min. After that, the pre-polymerized solution was poured into a model. The polymerization of the model was carried out at 50°C for 24 hr and additionally heated at 90°C until solidification was fulfilled. The samples were cut and polished for optical measurements.

The fluorescence spectra were measured by an Edinburgh Instruments FLS920 spectrophotometer. The absorption spectrum was recorded with a UV-VIS-NIR spectrophotometer (Perkin Elmer Lambda 900) at room temperature. The refractive index of Nd-doped PMMA is $n = 1.495$ and was measured using an Abbe refractometer (Shanghai Optical Instrument Factory).

RESULTS AND DISCUSSION

Fluorescence Properties

Figure 1 shows the fluorescence spectra of Nd(DBM)$_3$Phen- and Nd(DBM)$_3$(TOPO)$_2$-doped PMMA from 6500 to 12,000 cm^{-1} under the excitation at 17,100 cm^{-1} ($^4I_{9/2} \rightarrow {}^4G_{7/2}$). The fluorescence spectra consisted of three bands, which were assigned to the transition of $^4F_{3/2} \rightarrow {}^4I_{9/2}$, $^4F_{3/2} \rightarrow {}^4I_{11/2}$, and $^4F_{3/2} \rightarrow {}^4I_{13/2}$, respectively. The emission of the $^4F_{3/2} \rightarrow {}^4I_{11/2}$ is the strongest.

Under the same condition, luminescence of Nd(DBM)$_3$(H$_2$O)$_2$-doped PMMA was not observed. The quenching via vibrational excitation of H_2O should be responsible for this phenomenon of Nd(DBM)$_3$(H$_2$O)$_2$-doped PMMA, because the probability of energy transfer to the H_2O (3450 cm^{-1}) vibration is much higher. Accordingly, it should be possible to observe fluorescence by replacing H_2O in the vicinity of Nd(DBM)$_3$ with ligands having

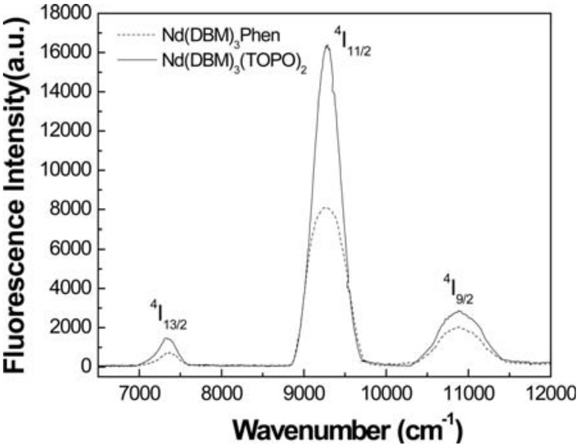

Figure 1. Fluorescence spectra of Nd(DBM)$_3$Phen- and Nd(DBM)$_3$(TOPO)$_2$ -doped PMMA under the excitation at 17,100 cm^{-1} ($^4I_{9/2} \rightarrow {}^4G_{7/2}$).

lower vibrational modes. Both Nd(DBM)$_3$Phen and Nd(DBM)$_3$(TOPO)$_2$ showed fluorescence in PMMA. In Fig. 1, $^4F_{3/2} \rightarrow {}^4I_{11/2}$ transition intensity of Nd(DBM)$_3$(TOPO)$_2$ -doped PMMA is larger than that of Nd(DBM)$_3$Phen. The enhanced fluorescence of Nd(DBM)$_3$(TOPO)$_2$ is ascribed to its lower vibrational structure of TOPO ($P = O$: 1125 cm^{-1}) than that of the Phen ($C = N$: 1630 cm^{-1}).

The fluorescence spectra measurement result showed that the $^4F_{3/2} \rightarrow {}^4I_{11/2}$ transition intensity of Nd(DBM)$_3$(TPPO)$_2$ -doped PMMA is the strongest. In order to evaluate the radiative properties of Nd(DBM)$_3$(TOPO)$_2$-doped PMMA, the Judd-Ofelt analysis[12,13] was carried out according to its absorption spectrum.

Judd-Ofelt Analysis

Figure 2 shows the absorption spectrum of Nd(DBM)$_3$(TOPO)$_2$ -doped PMMA at room temperature in the range 10,500–21,000 cm^{-1}. Absorption bands are observed at $\nu = 11{,}000$–11,800, 12,000–13,000, 13,000–14,000, 14,300–16,400, 16,400–17,900, 17,900–19,200, and 19,200–20,400 cm^{-1}. They are attributed to the Nd^{3+} transitions from the ground state, $^4I_{9/2}$, to various excited states. One of the important characteristics of the spectrum is the stark splitting of the absorption peak around $\nu = 11{,}300$–11,600 cm^{-1}, which is attributed to the $^4I_{9/2} \rightarrow {}^4F_{3/2}$. Slight splitting of the $^4F_{3/2}$ degenerate levels should be induced by changed in the ligand field around Nd^{3+} and it proved that there is an asymmetric coordination environment of Nd(DBM)$_3$(TOPO)$_2$-doped PMMA.

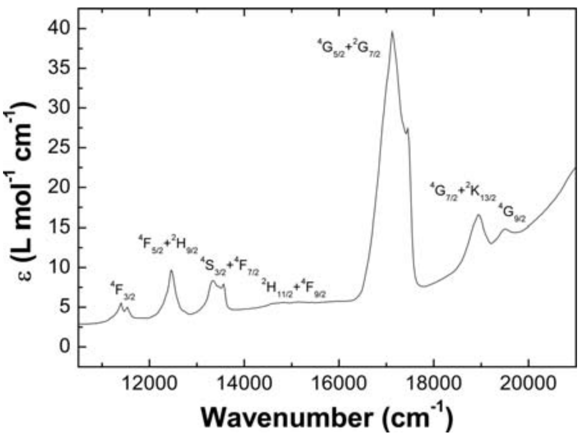

Figure 2. Absorption spectrum of Nd(DBM)$_3$(TOPO)$_2$-doped PMMA.

The oscillator strength of an absorption band is determined experimentally from the area under the absorption band and can be expressed using the following equation:[14]

$$P_{\exp} = 4.318 \times 10^{-9} \int \varepsilon(\nu) d\nu \qquad (1)$$

where $\varepsilon(\nu)$ is the molar extinction coefficient ($dm^3\ mol^{-1}\ cm^{-1}$) at the energy ν (cm^{-1}), which has been evaluated from Beer's law.

According to Judd-Ofelt theory, the oscillator strengths are giving by[14]:

$$P = \left[\frac{8\pi^2 mc\nu}{3h}\right] \times \left[\frac{(n^2+2)^2}{9n}\right] \sum_{\lambda=2,4,6} \frac{\Omega_\lambda}{(2J+1)} \times \langle f^N \Psi_J \| U^(\lambda) \| f^N \Psi'_{J'} \rangle^2 \qquad (2)$$

where m is the mass of electron, c is the velocity of light, h is the Plank constant, n is the refractive index, ν is the frequency in inverse centimeters, J is the total angular momentum of the initial state, $U^{(\lambda)}$ are tensor operators of rank λ given by Carnall et al.[14] The $f^N \Psi_J$ are wave functions of the states with N electrons in the 4f shell having total angular momentum J, and Ω_λ are Judd-Ofelt parameters.

Using the oscillator strengths, the corresponding theoretical oscillator strengths and the Judd-Ofelt parameters Ω_λ can be calculated numerically by a least-squares method.

The usual measure of the fitting quality is the root mean square deviation (*rms*) between the experimental and calculated oscillator strengths, and the *rms* deviation is calculated in the usual way:

$$rms = \left[\frac{\sum_{i=1}^{N} (P^i_{\exp} - P^i_{calc})^2}{N-3}\right]^{\frac{1}{2}} \qquad (3)$$

where N is the number of levels fitted.

The values of oscillator strengths and Judd-Ofelt parameters of $Nd(DBM)_3(TOPO)_2$-doped PMMA are listed in Table 1.

It is well-known that the oscillator strength of the hypersensitive transition $^4I_{9/2} \rightarrow {}^4G_{5/2} + {}^2G_{7/2}$ at $\nu = 16{,}400\text{–}17{,}900\,cm^{-1}$ is enhanced as the symmetry of the ligand field is reduced. From Table 1, the oscillator strength of $Nd(DBM)_3(TOPO)_2$ -doped PMMA at the hypersensitive transition is very large. The reason may be due to the fact that $Nd(DBM)_3(TPPO)_2$ have no center of symmetry in PMMA, which has been discussed above. The *rms* deviation is $\pm 0.82 \times 10^{-6}$ for $Nd(DBM)_3(TOPO)_2$-doped PMMA matrix, which is comparable with previous studies of other neodymium systems.[5,15]

Table 1. The oscillator strengths and Judd-Ofelt parameters of $Nd(DBM)_3(TOPO)_2$ -doped PMMA

		Oscillator strength $P \times 10^6$	
Wavenumber range (cm^{-1})	Excited states	P_{exp}	P_{calc}
19,200–20,400	$^4G_{9/2}$	1.97	1.44
17,900–19,200	$^4G_{7/2}$, $^2K_{13/2}$	6.99	7.91
16,400–17,900	$^4G_{5/2}$, $^2G_{7/2}$	83.77	83.71
14,300–16,400	$^2H_{11/2}$, $^4F_{9/2}$	1.44	0.68
13,000–14,000	$^4S_{3/2}$, $^4F_{7/2}$	6.87	6.43
12,000–13,000	$^4F_{5/2}$, $^2H_{9/2}$	5.72	6.31
11,000–11,800	$^4F_{3/2}$	2.21	1.53
rms deviation (10^{-6})		± 0.82	
Ω_2 (10^{-20} cm^2)		32.64	
Ω_4 (10^{-20} cm^2)		2.89	
Ω_6 (10^{-20} cm^2)		4.81	

Radiative Properties of $Nd(DBM)_3(TOPO)_2$-doped PMMA

From the Judd-Ofelt parameters Ω_λ obtained above, the probability of $^4F_{3/2} \rightarrow {}^4I_j$ transition can be calculated using the following equation[16]:

$$A[^4F_{3/2}, (S, L)J] = \frac{64\pi^4 e^2 \nu^3}{3h(2J' + 1)} \frac{n(n^2 + 2)^2}{9} \times \sum_{\lambda=2,4,6} \Omega_\lambda |\langle ^4F_{3/2} \| U^{(\lambda)} \| (S, L)J \rangle|^2 \tag{4}$$

where $(S,L)J$ are quantum numbers of the lower state, $J' = 3/2$. Then the radiative lifetime is given by:

$$\tau_{rad} = \frac{1}{\sum_{S,L,J} A[^4F_{3/2}, (S, L)J]} \tag{5}$$

And the fluorescence branch ratio β is given by:

$$\beta[(S, L)J] = A[^4F_{3/2}, (S, L)J]\tau_{rad} \tag{6}$$

Finally the emission cross-section, σ_p, can be related to the radiative transition probability using the formula:[16]

$$\sigma_p = \frac{A_{JJ'}}{8\pi n^2 c \nu_p^2 \Delta\nu_{eff}} \quad \text{where } \Delta\nu_{eff} = \frac{\int I(\nu) d\nu}{I^{peak}} \tag{7}$$

Table 2. The transition probabilities A, fluorescence branching ratios β, emission cross-sections of $^4F_{3/2} \rightarrow {}^4I_j$ and radiative lifetime τ_{rad}

Terminal state	A (s^{-1})	β	σ $(10^{-20}\ cm^2)$
$^4I_{9/2}$	649	0.344	0.77
$^4I_{11/2}$	1022	0.542	2.63
$^4I_{13/2}$	216	0.114	1.25
ΣA	1887		
τ_{rad} (μs)	530		

where ν_p is the peak wavenumber of the transition, $I(\nu)$ is the fluorescence intensity at ν, and I^{peak} is the peak fluorescence intensity of the band.

The values of transition probabilities A, the fluorescence branching ratios β, the radiative lifetime τ_{rad} and emission cross-sections σ_p are presented in Table 2.

The radiative lifetime of the transition involved is an important parameter in consideration of the pumping requirement for the threshold of laser action. In Table 2, the calculated radiative lifetimes is 530 μs for Nd(DBM)$_3$(TOPO)$_2$ -doped PMMA. It is comparable with those radiative lifetimes of neodymium laser glasses (theoretical radiative excited state lifetime values).[16–19] However, the value of radiative lifetime obtained by Judd-Ofelt theory is not the actual value. It has only been used to estimate the radiative properties of Nd(DBM)$_3$(TOPO)$_2$-doped PMMA. The actual metastable lifetime can be measured by related instruments. The emission cross section σ_p of $^4F_{3/2} \rightarrow {}^4I_{11/2}$ fluorescence transition of Nd^{3+} is one of the most important parameters for laser design and it is dependent only on Ω_4 and Ω_6, because of the triangle rule $|J - J'| \leq \lambda \leq (J + J')$, $|U^{(t)}|^2 = 0$.[20] For a large emission cross section, the magnitude of Ω_4, Ω_6 and the fluorescence branching ratio β of $^4F_{3/2} \rightarrow {}^4I_{11/2}$ should be as high as possible. The emission cross-section σ_p of $^4F_{3/2} \rightarrow {}^4I_{11/2}$ fluorescence transition of Nd(DBM)$_3$(TOPO)$_2$-doped PMMA is 2.63×10^{-20} cm^2, which is also comparable with those shown by glasses used in the solid-state laser applications.[16–19]

From the magnitude of the radiative lifetime and the emission cross-section of $^4F_{3/2} \rightarrow {}^4I_{11/2}$ fluorescence transition, it can be concluded that Nd(DBM)$_3$(TOPO)$_2$ -doped PMMA is a promising luminescent material.

CONCLUSION

In conclusion, according to the fluorescence spectra measurement, Nd(DBM)$_3$(TPPO)$_2$-doped PMMA showed the strongest $^4F_{3/2} \rightarrow {}^4I_{11/2}$ transition intensity. Thus, its Judd-Ofelt parameters $(\Omega_2, \Omega_4, \Omega_6)$ were calculated on the basis of the absorption spectrum, and the radiative properties were also predicted according to the Judd-Ofelt theory. The values of the radiative lifetime and the emission cross-section of $^4F_{3/2} \rightarrow {}^4I_{11/2}$ fluorescence transition are comparable with those shown by glasses used in the solid-state laser applications. It can be concluded that $Nd(DBM)_3(TOPO)_2$-doped PMMA is an efficient luminescent material.

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