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Optical-transition probabilities of Nd^{3+} ions in polymer optical fibers

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Abstract

The optical properties of Nd^{3+}-doped polymethyl methacrylate (PMMA) have been studied because of its possible application to polymer optical fibers. Neodymium octanoate (NOCA) is doped into PMMA and its radiative properties are evaluated by Judd–Ofelt theory. Analyses reveal that NOCA-doped PMMA is promising for use in rare-earth-doped polymer devices. © 2001 Published by Elsevier Science B.V.

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1. Introduction

With the increasing interest in polymer optical fiber (POF), research to find efficient new materials for POF device becomes more important. Rare-earth ion-doped glass fiber amplifiers and fiber lasers have been very successful. In recent years, much work has been done on rare-earth ion-doped POF. Nd^{3+}, Eu^{3+}, Er^{3+}, Pr^{3+} and Sm^{3+} ions were doped into POF [1–3], and some of the work is exciting. For example, amplified spontaneous emission (ASE) was found in Nd-doped POF [4], and super-fluorescence was found in Eu-doped POF [5]. This indicates that a rare-earth doped POF has the possibility to make a POF amplifier or POF laser. There is much work worth doing. It is essential to understand the radiative properties of the rare-earth complexes. The property of a rare-earth ion transition that is most influenced by the surrounding environment is the observed metastable-state lifetime, which should be maximized for efficient laser properties. In this paper, we analyzed the absorption spectrum of Nd^{3+}-doped polymethyl methacrylate (PMMA), which was first developed in our lab [1], with Judd–Ofelt theory [6,7]. We obtained the oscillator strength and optical intensity parameters as calculated by Judd–Ofelt theory using values of the absorption spectrum. Using these calculated values, we derived the radiative lifetime of the $^4F_{3/2}$ excited J manifold and the branching relations of the fluo-

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rescence transitions to the lower lying ^4I_J manifold.

2. Theory

The rare-earth ion transition is mainly electric dipole. In the free rare-earth ion, parity would forbid any electric dipole transitions within $4f^N$ states. However, if those states mix with high-lying opposite-parity states, such as 5d, such transitions are possible and, may be dominant. In fact, magnetic-dipole oscillator strengths are roughly two orders of magnitude smaller than electric dipole, and thus the magnetic-dipole transition can be neglected.

From Judd and Ofelt theory, the electric dipole oscillator strength can be expressed by:

$$P = \frac{8\pi^2 mc}{3h}\frac{(n^2+2)^2}{9n}v\sum_{\lambda=2,4,6}\frac{\Omega_\lambda}{(2J+1)} \times \left|\left\langle f^N\psi_J\|U^{(\lambda)}\|f^N\psi'_{J'}\right\rangle\right|^2 \quad (1)$$

where n is the refractive index, which is 1.49 for PMMA. m, c, and h are the electronic quality, velocity of light and Planck's constant respectively. v is the frequency in inverse centimeters, $U^{(\lambda)}$ are the doubly reduced unit tensor operators, which can be derived from Ref. [8]. Ω_λ are the optical intensity parameters, $f^N\psi_J$ are wave function of the states with N electrons in the 4f shell having total angular momentum J. All the parameters are in CGS units.

The experimental line oscillator strength P_{exp} can be calculated from the following formula:

$$P_{exp} = 4.318\times10^{-9}\int \alpha(v)\,dv \quad (2)$$

where $\alpha(v)$ is the molar extinction coefficient (per molar concentration per centimeter) as a function of frequency v (per centimeter). Using the experimental oscillator strength P_{exp} for the dipole transition as obtained from Eq. (2), the oscillator strength parameters Ω_λ can be obtained by a least squares fitting of Eq. (1). We can see from Eq. (1) that, by use of the determined Ω_λ parameters and the reduced matrix elements $\langle\|U^{(\lambda)}\|\rangle$, the oscillator strengths for any transition can be calculated.

3. Experiment

Different from silica glass, organic polymers are not compatible with rare-earth ions. To remedy this situation, two methods have often been adopted: First, the chelate of rare-earth ions was made and then mixed with the polymer. Second, the rare-earth ion-containing monomers were synthesized and then polymerized. In this paper, we used another method to prepare the Nd^{3+}-doped PMMA materials: neodymium octanoate (NOCA) instead of chelate was synthesized. After purification and drying, the methyl methacrylate (MMA) was distilled under reduced pressure. The purified MMA was poured into a reaction vessel to mix with 0.01 mol/l, 2,2-azoisobutyronitrile, 0.03 mol/l *n*-butyl mercapian (chain transfer agent) and a proper amount of synthesized NOCA. The vessel was heated at 95 °C for 12 h and additionally heated at 60 °C for 24 h to polymerize the monomer. By regulating the drawing velocity of fiber, the feeding velocity of preform stick, and the temperature of the melted polymer, the Nd^{3+}-doped PMMA fibers were drawn.

A typical absorption spectrum of the Nd^{3+} ions doped PMMA, measured by a model UV240 Shimadzu spectrophotometer, is shown in Fig. 1. Compared with the absorption of Nd^{3+}-doped silica glasses, a blue shift can be found. This shows that the covalence of Nd–O in silicate is weaker than in PMMA. We can see that the 583-nm absorption band (attributed to $^4I_{9/2}\rightarrow{}^4G_{5/2}$) is hypersensitive. In the following calculation, I assume the Nd^{3+} concentration is 1×10^{20} cm^{-3}, which is high enough to obtain lasing in the material and low enough to exclude concentration quenching. It is the same value that C. Koeppen used to simulate the Sm^{3+}-doped polymer fiber amplifier [3].

4. Results and discussion

The oscillator parameters Ω_λ, which are independent of the electronic quantum numbers within

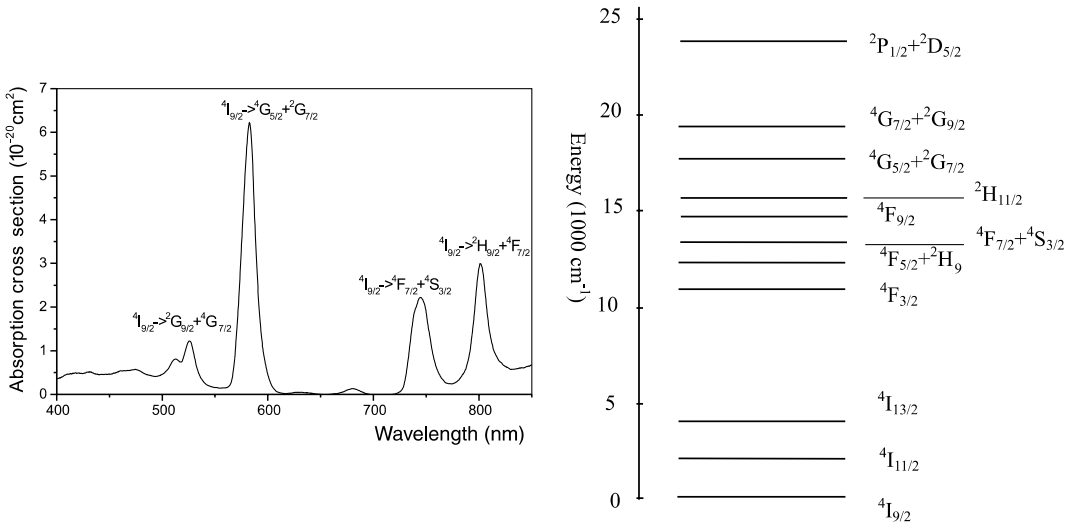

Fig. 1. The absorption cross-section spectrum of Nd^{3+}-doped PMMA and $4f^3$ electronic-energy level of Nd^{3+} ions in PMMA. Energy levels are labeled according to the values of absorption spectrum.

the ground $4f^3$ configuration of the Nd^{3+} ion, may be regarded as phenomenological parameters that characterize the radiative transition probability [9]. Using Eqs. (1) and (2), together with the values of the absorption spectrum, Ω_λ can be calculated: $\Omega_2 = 2.11 \times 10^{-20}$ cm^2, $\Omega_4 = 3.78 \times 10^{-20}$ cm^2, $\Omega_6 = 2.61 \times 10^{-20}$ cm^2. Compared with the Ω_λ values calculated from Nd^{3+} complexes in acetone-d_6 ($\Omega_2 = 61.6 \times 10^{-20}$ cm^2, $\Omega_4 = 9.24 \times 10^{-20}$ cm^2, $\Omega_6 = 7.49 \times 10^{-20}$ cm^2 [3]), these values are smaller. Which reflects that the environment of Nd^{3+} was different. The Ω_2 parameter is most sensitive to the local structure and composition [10]. Since it reflects the asymmetry of the local environment at the Nd^{3+} site, a small value in PMMA suggests a more centrosymmetric coordination environment. Several of the Nd^{3+} laser pumping bands and several important excited-state absorption transitions depend strongly on Ω_2, such as the hypersensitivity transition ($^4I_{9/2} \rightarrow {}^4G_{5/2} + {}^2G_{7/2}$) absorption band. So this band is efficient to pump Nd^{3+} in many hosts [11]. The $^4F_{3/2}$J manifold is the only excited J manifold that is not relaxed predominately by multi-phonon process. So much attention is paid to it. One should note that none of the fluorescence transitions from the $^4F_{3/2}$ level depend on the Ω_2, but mainly depend on the parameters Ω_4, Ω_6 [12].

To justify the result, we use the calculated Ω_λ to calculate the oscillator strength of the absorption bands. The experimental and corresponding calculated oscillator strength data for Nd^{3+}-doped PMMA are displayed in Table 1. The high-absorption coefficient of the hypersensitive $^4I_{9/2} \rightarrow {}^4G_{5/2} + {}^2G_{7/2}$ transitions implies a relative high value of the oscillator strength (see Table 1), because the reduced matrix elements $\langle||U^{(\lambda)}||\rangle$ of that transition are large. The root-mean-square derivation of the experiment and calculation line strengths is calculated in the usual way:

$$\mathrm{rms} = \sum \left[\frac{P^i_{\mathrm{exp}} - P^i_{\mathrm{cal}}}{N - M} \right]^{1/2} \tag{3}$$

Table 1
Experimental and calculated line strengths of Nd^{3+} in PMMA

Transitions	Barycenter (nm)	P_{exp} ($\times 10^6$)	P_{cal} ($\times 10^6$)
$^4I_{9/2} \rightarrow {}^4F_{7/2} + {}^2H_{9/2}$	801.4	3.52	3.98
$^4I_{9/2} \rightarrow {}^4S_{3/2} + {}^4F_{7/2}$	744.5	3.99	4.43
$^4I_{9/2} \rightarrow {}^4F_{9/2}$	680	0.33	0.32
$^4I_{9/2} \rightarrow {}^4G_{5/2} + {}^2G_{7/2}$	582.6	12	12
$^4I_{9/2} \rightarrow {}^4G_{7/2}$	524	2.64	2.55
$^4I_{9/2} \rightarrow {}^4G_{11/2}$	513.2	0.85	1.05
rms deviations $= 9.78 \times 10^{-7}$			

N is the number of transitions and M is the number of parameters determined. The obtained rms value is rather large, which is due to the large oscillator strengths of the hypersensitive transitions.

To study the potential of the material for amplifying and laser applications, the lifetime of the metastable state must be analyzed, and should be as long as possible for efficient laser operation. The radiative lifetime for the excited emissions of Nd^{3+} ions can be calculated as:

$$\frac{1}{\tau_{ij}} = A_{ij}, \qquad \frac{1}{\tau_i} = \sum_j A_{ij} \tag{4}$$

where τ_{ij} is the radiative lifetimes from state i to state j, and τ_i is the total radiative lifetimes of the metastable-state $^4F_{3/2}$ manifold J.

The expression for the radiative transition rate A_{ij} from the initial $^4F_{3/2}$ manifold $|(SL)J\rangle$ (state i) to the terminal manifold $|(S'L')J'\rangle$ (state j) is:

$$A_{ij} = \frac{1}{4\pi\varepsilon_0}\frac{8\pi^2 e^2 v_{ij}^2 n^2}{mc^3} P_{ij} \tag{5}$$

P_{ij} is the corresponding oscillator strength which can be calculated by Eq. (1), where $\langle {}^4F_{3/2}\| U^{(\lambda)}\|(S'L')J'\rangle$ are given in Ref. [13]. And v_{ij} is the transition frequency in Hz (s^{-1}); c is the velocity of light. All the parameters in Eq. (5) are in MKS units.

The fluorescence branching transition ratios are defined by:

$$\beta = \frac{A_{ij}}{\sum_j A_{ij}} \tag{6}$$

The sum is over all possible terminal manifolds $|(S, L)J\rangle$. This represents the total transition probability for radiative decay from the initial manifold.

The calculated radiative lifetimes, the radiative transition rate and fluorescence branching transition ratio are listed in Table 2. The $^4F_{3/2} \rightarrow {}^4I_{11/2}$ transition is most important [10], but in our work, the calculated $^4F_{3/2} \rightarrow {}^4I_{9/2}$ fluorescence branching ratio is somewhat larger than that of $^4F_{3/2} \rightarrow {}^4I_{11/2}$ transition which might be due to the large oscillator strengths rms. On the other hand, this shows that the $^4F_{3/2} \rightarrow {}^4I_{9/2}$ transition is relative stronger than that for Nd^{3+} in other hosts. The sum of the transition probabilities for the three terminal levels ($^4I_{9/2}$, $^4I_{11/2}$, $^4I_{13/2}$, see Table 2) yields a total transition probability for radiative decay of the $^4F_{3/2}$ level of $A_{tot} = 1582\ s^{-1}$, or a radiative lifetime equal to 632 μs. The fluorescence lifetime in PMMA may be less than the value as a result of competing nonradiative process, but this value is comparable with that for Nd^{3+}-doped glass systems. The $^4F_{3/2}$ metastable-state lifetime shows that it is efficient for laser pumping.

Another important optical property is the emission cross-section. Using the values for the radiative transition rates in Table 2, and the corresponding fluorescence spectrum, the stimulated emission cross-section σ_{ij} can be calculated:

$$\sigma_{ij} = \frac{A_{ij}\lambda_p^4}{8\pi^2 n^2 c\delta\lambda} \tag{7}$$

where $\delta\lambda$ is the wavelength full width at half-maximum, λ_p is the vacuum wavelength of the fluorescence peak. Using the fluorescence spectral data from Ref. [14], where is about 23.7 nm, I obtained an emission cross-section of the $^4F_{3/2} \rightarrow {}^4I_{11/2}$ transition equal to $2.27 \times 10^{-20}\ cm^2$. Similar to the spectrum in Ref. [14], the $^4F_{3/2} \rightarrow {}^4I_{11/2}$ emission band of our material will be a broad band. With this material, I think it is possible to develop a tunable laser and a broad band amplifier in the 1060 nm wavelength region.

This material has been made into a POF, and ASE has been observed [4]. With the values calculated above, along with laser theory, the ampli-

Table 2
$^4F_{3/2}$ lifetime and transition probabilities of $^4F_{3/2} \rightarrow {}^4I_J$

$^4F_{3/2} \rightarrow (S'L')J'$	λ (μm)	P_{ij} ($\times 10^6$)	A_{ij} (s^{-1})	β	τ_{ij} (ms)	τ_i (ms)
$^4F_{3/2} \rightarrow {}^4I_{9/2}$	0.90	4.40	736	0.465	1.35	
$^4F_{3/2} \rightarrow {}^4I_{11/2}$	1.06	5.91	713	0.451	1.40	0.632
$^4F_{3/2} \rightarrow {}^4I_{13/2}$	1.30	1.67	133	0.08	7.52	

fier and laser characteristics in the infrared region of Nd^{3+}-doped POF can be simulated.

5. Conclusion

In conclusion, the optical-transition probability of the Nd^{3+} ion in PMMA has been studied. The optical strength parameter was calculated using the Judd–Ofelt theory by analyzing the absorption spectrum. Through the calculated metastable-state transition lifetime and $^4F_{3/2} \rightarrow {}^4I_{11/2}$ emission cross-section, we forecast that the Nd^{3+}-doped PMMA is efficient for laser exciting, which is promising for making polymer optical device.

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