Judd-Ofelt Analysis of Nd(TTA)$_3$Phen-doped 6-FDA/Epoxy Planar Waveguides

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The fluorescent complex Nd(TTA)$_3$Phen (TTA = thenoyltrifluoroacetone, Phen = 1, 10-phenanthroline), was doped into the host material 6-FDA epoxy (6-fluorinated-dianhydride cured epoxy). The room-temperature absorption spectrum of Nd^{3+} transitions was experimentally obtained, with which the Judd-Ofelt model was applied to determine the Judd-Ofelt parameters. These parameters are used to calculate the emission probabilities of transitions and branching ratios of the Nd^{3+} from the excited-state $^4F_{3/2}$ to lower-lying manifolds. The radiative lifetime of $^4F_{3/2}$ was obtained from the emission probabilities. The results of the analysis indicate this Nd (III) complex doped polymer material is promising to be used in planar waveguide lasers and amplifers.

Introduction

There has been much interest in rare-earth-doped polymer planar optical waveguide for applications in amplifiers and lasers. Polymers are promising host candidates for these applications because of their excellent properties such as high transparency, low cost, and easy fabrication. One way to incorporate rare-earth ions into a polymer is to encapsulate the ions in organic chelates and dope these complexes directly. Recently, work has been done on rare-earth-doped polymer planar waveguides [1, 2]. In our work, Nd(TTA)$_3$Phen was synthesized and doped in to the fluorinated host 6-FDA epoxy. The ligands with fluorine and the fluorination of the host material can improve the luminescent quenching from C-H and water.

Knowledge of the transition intensities of 4f-4f transitions and of the absorption and emission cross sections is the first step in investigating the performance of the rare-earth-doped waveguides. In this paper, we used the Judd-Ofelt method [3, 4] to analyse the measured absorption spectrum of Nd^{3+} transitions. This method is successfully applied for the calculation and characterization of the optical transitions in rare-earth doped materials [5~8]. The results of the analysis indicate this Nd (III) complex doped polymer material is promising to be used in planar waveguide lasers and amplifers.

Experimental procedure

The Nd(TTA)$_3$Phen was synthesized according to the procedure as described in [9]. A film of Nd(TTA)$_3$Phen doped 6-FDA epoxy was spin-coated on an thermally oxidized wafer. The refractive index and the thickness as determined with a prism coupler were 1.53 (at 632.5nm) and 4.3 μm, respectively. The concentration was 1.1×10^{19} Nd/cm^3.

White light was coupled into the film and coupled out after propagating a certain distance through the film using a prismcoupler. Varying the propagation distance and collecting the light from the outcoupling prism by a spectrum analyzer Spectro320, the room-temperature loss spectrum of Nd^{3+} in 6-FDA epoxy was recorded. After subtraction of the background loss, the absorption spectrum of Nd^{3+} in 6-FDA epoxy was obtained from the recorded spectrum (Fig. 1).

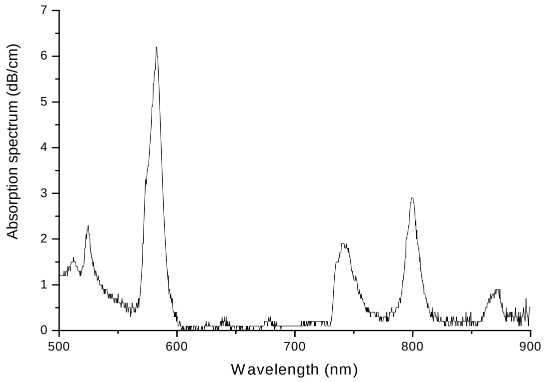

Fig. 1. Room temperature absorption spectrum of Nd^{3+} in 6-FDA epoxy from 450nm to 900nm.

Data analysis

The electric dipole line strength S is adopted to describe the transition between two of the eigenstates of the ion in the Judd-Ofelt theory. The line strength S between initial state J characterized by (S, L, J) and the final state J' given by (S', L', J') can be written as [5~8]:

$$S_{calc}(J \to J^{'}) = \sum_{t=2,4,6} \Omega_t \left| \left\langle (S,L)J \left\| U^{(t)} \right\| (S^{'},L^{'})J^{'} \right\rangle \right|^2 = \Omega_2 \cdot \left[U^{(2)}\right]^2 + \Omega_4 \cdot \left[U^{(4)}\right]^2 + \Omega_6 \cdot \left[U^{(6)}\right]^2 \quad (1)$$

where Ω_t (t=2,4,6) are the Judd-Ofelt parameters, and $U^{(t)}$ (t=2,4,6) are the doubly reduced matrix elements depend only on angular momentum. As $U^{(t)}$ (t=2,4,6) are independent of the host, the values can be obtained from some former papers. [5, 10]

The parameters Ω_t (t=2,4,6) are determined by measuring the line strength for a number of ground-state transition. Four absorption peaks can be observed from Fig 1 and the four peak wavelengths of the Nd^{3+} bands are given in Table 1.

The measured line strengths $S_{meas}(J \to J')$ of the bands are determined using following expression:

$$S_{meas}(J \to J^{'}) = \frac{3ch(2J+1)n}{8\pi^3 \lambda e^2 N_0}\left[\frac{9}{(n^2+2)^2}\right]\Gamma \quad (2)$$

where *c* is the velocity of light, *h* is the Planck's constant, *e* is the elementary charge, *J* is the angular momentum, N_0 is the density of ion, λ is the mean wavelength of the absorption bands, *n* is the wavelength-dependent refractive index which is determined from Sellmeier's dispersion equation, and $\Gamma = \int \alpha(\lambda) d\lambda$ is the integrated absorption coefficient. The results

Table 1. Values of reduced matrix elements for the absorption transitions of Nd^{3+} in 6-FDA epoxy at 300K.

Transition (from $^4I_{9/2}$)	λ (nm)	n	$\left[U^{(2)}\right]^2$	$\left[U^{(4)}\right]^2$	$\left[U^{(6)}\right]^2$
$^4G_{5/2}+^2G_{7/2}$	580	1.5316	0.9710	0.5897	0.0663
$^4F_{7/2}+^4S_{3/2}$	740	1.5239	0.0010	0.0448	0.6582
$^4F_{5/2}+^2H_{9/2}$	795	1.5221	0.0100	0.2431	0.5148
$^4F_{3/2}$	865	1.5206	0	0.2296	0.0563

Table 2. Measured and calculated line strengths of Nd^{3+} in 6-FDA epoxy at 300K.

Transition (from $^4I_{9/2}$)	λ (nm)	n	Γ (nm cm^{-1})	S_{meas} (10^{-20} cm^2)	S_{calc} (10^{-20} cm^2)
$^4G_{5/2}+^2G_{7/2}$	580	1.5316	18.7295	22.1520	22.1570
$^4F_{7/2}+^4S_{3/2}$	740	1.5239	8.4009	7.8329	8.1997
$^4F_{5/2}+^2H_{9/2}$	795	1.5221	10.3377	8.9276	8.4069
$^4F_{3/2}$	865	1.5206	2.7888	2.2300	2.6969

of S_{meas} are given in Table 2.

From the least-squares fitting of S_{meas} to S_{calc}, the values of the three parameters Ω_t (t=2,4,6) can be obtained as follows:

$$\Omega_2 = 16.64\times10^{-20}cm^2, \Omega_4 = 8.85\times10^{-20}cm^2, \Omega_6 = 11.83\times10^{-20}cm^2$$

We used them to recalculate the transition line strengths of the absorption bands from Eq. (1) and the results are in Table 2.

Next, they were applied in Eq. (1) to calculate the transition line strength of the upper state transitions which are give in Table 3. Then, we obtained the corresponding radiative decay rate, radiative lifetime and fluorescence branching ratio.

The radiative decay rates $A(J \rightarrow J^{'})$, for electric dipole transitions between an excited states (*J*) and the lower-lying terminal manifolds (*J'*) were calculated from:

$$A(J \rightarrow J^{'}) = \frac{64\pi^4 e^2}{3h(2J+1)\lambda^3}\frac{n(n^2+2)^2}{9}S_{calc}(J \rightarrow J^{'}) \quad (3)$$

From the radiative decay rates, the radiative lifetime τ_r for an excited state (*J*) and the fluorescence branching ratios $\beta(J \rightarrow J^{'})$ were obtained from:

$$\tau_r = \frac{1}{\sum A(J \rightarrow J^{'})} \quad (4)$$

$$\beta(J \rightarrow J^{'}) = \frac{A(J \rightarrow J^{'})}{\sum A(J \rightarrow J^{'})} = A(J \rightarrow J^{'})\tau_r \quad (5)$$

All results are given in Table 3.

Table 3. Predicted fluorescence line strength, radiative decay rates, radiative lifetimes, and branching ratios of Nd^{3+} in 6-FDA epoxy at 300K.

Transition	S_{calc} (10^{-20} cm^2)	$A_{JJ'}$ (s^{-1})	τ_{rad} (ms)	$\beta_{JJ'}$
$^4F_{3/2} \rightarrow {}^4I_{9/2}$	2.6969	1.9491	0.18259	0.3559
$^4F_{3/2} \rightarrow {}^4I_{11/2}$	6.0710	2.9168		0.5326
$^4F_{3/2} \rightarrow {}^4I_{13/2}$	2.5080	0.5812		0.1061
$^4F_{3/2} \rightarrow {}^4I_{15/2}$	0.3313	0.0297		0.0054

Discussion of results

With the standard Judd-Ofelt method, the analysis of absorption spectrum of Nd^{3+} in 6-FDA epoxy has been performed.

It has been shown that Ω_2 is quite sensitive to the metal-ion environment [11]. A large value of Ω_2 indicate the presence of covalent bonding between the Nd^{3+} ions and the

surrounding ligands. Compared with the values of the Judd-Ofelt parameters of Nd^{3+} in other hosts as shown in Table 4, our Nd-doped material has a large Ω_2. That means the optical transition is dominated by electrical dipole transition in this system and the emission is strong.
The radiative lifetime τ_{rad} for Nd^{3+} in our material is comparable to that in deuterated (-d$_8$) PMMA, but smaller than the values in the hosts of PF (perfluorinated) plastic solution and ZBAN (ZrFr-BaF_2-LaF_2-ALF_3). The reason is that the latter two materials don't contain C-H bonds which cause quenching.

Table 4. Judd-Ofelt parameters of Nd^{3+} for different hosts.

host	$\Omega_2(10^{-20}cm^2)$	$\Omega_4(10^{-20}cm^2)$	$\Omega_6(10^{-20}cm^2)$	$\tau_{rad}(ms)$
6-FDA epoxy	16.64	8.85	11.83	0.183
PF plastic solution [6]	10.6	6.51	4.72	0.548
PMMA-d$_8$ [6]	9.45	2.70	5.27	0.187
ZBAN^{51} [6]	3.1	3.7	5.7	0.419

Conclusion

A Judd-Ofelt analysis was applied to the measured absorption spectrum of a Nd(TTA)$_3$Phen doped 6-FDA epoxy planar waveguide. The results show that Nd(TTA)$_3$Phen doped 6-FDA epoxy has good potential to be used as planar waveguide in the laser or amplifier.

Acknowledgement

The authors acknowledge the financial support of STW (TOE 6986).

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