

# Plastic Optical Fiber Lasers and Amplifiers Containing Lanthanide Complexes

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## 1. Introduction

Organic dye-doped polymers have been widely investigated as gain media in solid-state dye lasers. Dye molecules which have large absorption and induced emission cross sections due to allowed  $\pi-\pi$  transitions are ideal active dopants for the generation and amplification of intense light pulses. However, continuous wave operation is not feasible with organic dyes because of the triplet losses. On the other hand, lanthanide ions that have long metastable state lifetimes are widely used in silica glass-based fiber amplifiers and for both continuous and pulsed lasers.

It has been more than 30 years since the first lanthanide lasers were reported.<sup>1–3</sup> During this period a wide variety of lanthanide lasers and amplifiers have been investigated, and extensive progress has been made by many researchers. Many reviews have been written concentrating primarily on the physical and chemical properties of lanthanides in many matrices for laser action.<sup>4–8</sup> Recently, several books have focused on lanthanide-doped fiber amplifiers for optical communications.<sup>9–11</sup> The success of lanthanide-doped fiber amplifiers has inspired thousands of publications and continues to motivate research on the many diverse components that are required in these systems. Optical links are now used primarily in applications such as telecommunications with single-mode silica optical fibers, which have the ability to provide high-bandwidth and long-distance communications. However, as the demand for bandwidth increases in the office and home, it has become increasingly important to develop very low cost optical links that can be readily installed by users.

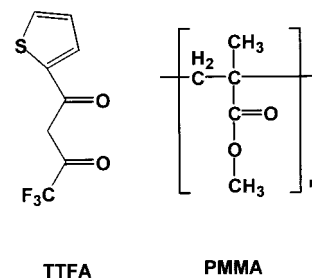
Plastic optical fibers (POF) have received increasing attention because of their clear technical advantages over glass fibers, such as flexibility and a large

core diameter, which enables efficient connection and coupling resulting in a low-cost system for a local area network. Recently a low-loss (100 db/km), high-bandwidth 5.12 GHz for 100 m transmission graded index plastic optical fiber (GI-POF) has been developed.<sup>12</sup> Also, an all fluorinated POF, whose low loss region is extended to the visible and near-infrared, has been successfully prepared.<sup>13</sup> Plastic optical fiber amplifiers (POFA) that generate signal light in the visible and near-infrared are potentially important because of their adaptability for POF-based short span optical local distribution networks.

This review describes recent progress on plastic optical fiber lasers and amplifiers with lanthanides. We focus especially on the design and selection of plastic optical fiber and chelate materials.

## 2. Systems Containing $\text{Eu}^{3+}$ , $\text{Tb}^{3+}$ , and $\text{Sm}^{3+}$

The possible utilization of lanthanide-ion metal chelates for laser materials was suggested by Whan, Crosby,<sup>14</sup> and Shimischek. Lempick<sup>15</sup> and co-workers observed the laser action of Eu-chelates in organic solutions at around  $-140\text{ }^\circ\text{C}$  by pumping with a high-power xenon flash lamp. An attempt to utilize a plastic as a matrix was reported by Wolff and Pressley.<sup>16</sup> They found that a solid solution of Eu tris-(4,4,4-trifluoro-1-(2 thenoyl)-1, 3-butenedione) ( $\text{Eu}(\text{TTFA})_3$ ) in poly(methyl methacrylate) (PMMA) exhibited laser action. Figure 1 shows the ligand and



**Figure 1.** Chemical structures of 4,4,4-trifluoro-1-(2-thenoyl)-1,3-butenedione; TTFA and poly(methyl methacrylate); PMMA.

plastic matrix structures. When a clear plastic fiber containing the chelate was excited at 340 nm using a xenon lamp at liquid nitrogen temperature, stimulated emission was observed at around 613 nm.



Ken Kuriki was born in Tokyo, Japan, in 1973. He received his B.S. degree in Applied Chemistry from Keio University, Japan, in 1996. In 1996 he was an associate as a visiting scientist in Y. Okamoto's group at Polytechnic University, Brooklyn, NY. He obtained his Ph.D. degree in Material Science in 2002 under the direction of Yasuhiro Koike: thesis title On the Design of Plastic Optical Fiber Lasers and Amplifiers with Organic Dyes and also Lanthanide Chelates.



Yasuhiro Koike was born in Tokyo, Japan, in 1954. He received his B.S., M.S., and Ph.D. degrees from Keio University, Japan, in 1977, 1979, and 1982, respectively. From 1997 to present, he has served as Professor of Faculty of Science and Technology of Keio University. From 2000 to present, he has served as Director of the "Koike Photonics Polymer Project" of Exploratory Research for Advanced Technology, financed by Japan Science and Technology Corporation. From 1989 to 1990, he worked as a visiting researcher at AT&T Bell Laboratories. His research interests are fundamentals of photonics polymer materials and their applications, high-speed polymer optical fiber, graded-index polymer, light-scattering, optical amplifier and polymer fiber laser, birefringence-free polymer, etc. In 1994 he received the Society of Plastic Engineers (SPE), International Technology Award-Fred O. Conley. He has presented numerous invited talks in international conferences and published two books and over 100 articles in the field of photonic chemistry.

The stimulated emission of  $\text{Tb}(\text{TFFA})_3$  in PMMA was also reported by Huffman.<sup>17</sup> He prepared a fiber approximately 0.75 mm in diameter by 60 mm in length. Both ends of the fiber were polished, and one end was silvered. The fluorescence at 545 nm was recorded with excitation at 335 nm at 77 K. A threshold for stimulated emission was detected with 225 J input. In addition to PMMA, polystyrene and epoxy resins were also used as organic polymer matrices.

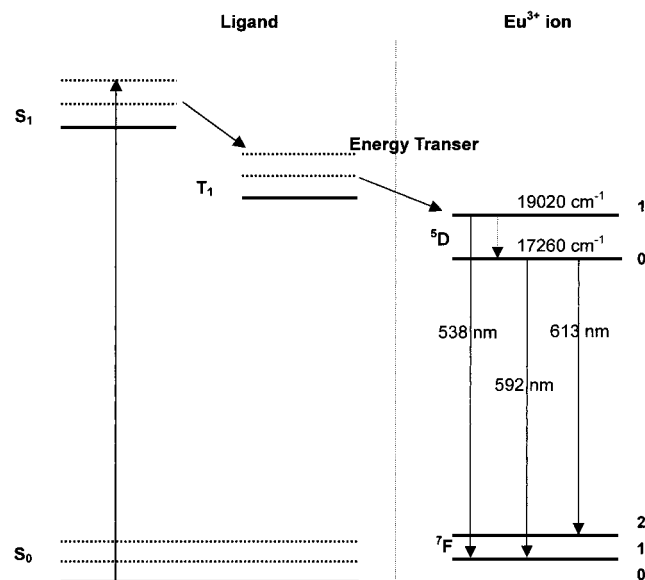
The utilization of lanthanide (Eu, Tb, Sm, Nd, Er, and Tm) chelates as lasers and amplifiers has two major advantages: lanthanide ion salts have very limited solubility in organic media and the salts tend to aggregate in these media, resulting in concentra-



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tion quenching at relatively low concentrations. Encapsulating lanthanide ions with organic ligands makes it possible to incorporate them in organic hosts with higher concentrations. Another feature is that lanthanide ions in chelate systems are pumped more effectively than in the conventional crystal and glass systems because of energy transfer processes in the chelate complexes (Scheme 1). There are several

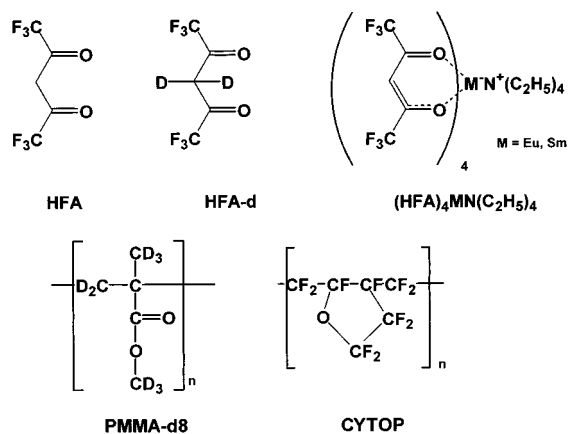
#### Scheme 1. Schematic Energy-Level Diagram for a $\text{Eu}^{3+}$ Chelate



stages in this transfer. First, absorption of energy produces an excited singlet from the ground singlet state in the ligand. Second, intersystem crossing to a triplet state takes place by a radiationless process. Competing with this are organic fluorescence and radiationless deactivation of the excited singlet as

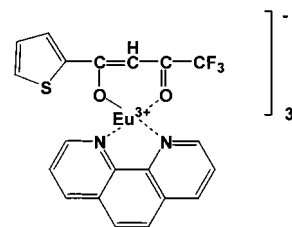
thermal energy. Third, radiationless transfer of energy occurs from the triplet state to one or more low-lying 4f levels in the lanthanide ion; the requirement for effective transfer is that the triplet state be close in energy to or above the 4f levels concerned. Fourth, emission of energy follows if one of the 4f levels excited by the transfer has an allowed transition to a lower 4f level.

The fluorescence efficiency of lanthanide chelates is an important parameter with regard to their potential use as lasers and amplifiers. However, the fluorescence yield of most of these tris chelates is relatively low because of the deactivation by the C–H bond vibrations of ligands and also the host matrix. Ligands consisting of low-frequency vibrational C–D and C–F bonds such as hexafluoroacetylacetone (HFA) and deuterated hexafluoroacetylacetone (HFA-*d*) were tested. Deuterated or fluorinated polymer matrices, such as deuterated PMMA and Cytop (Asahi Glass fluorinated polymer), were also recently investigated (Figure 2).<sup>18</sup> Recently Garito et al.<sup>19,20</sup>



**Figure 2.** Chemical structures of hexafluoro acetylacetone (HFA), deuterated hexafluoro acetylacetone (HFA-*d*), tetrakis-Eu or Sm hexafluoro acetylacetone tetra ethylammonium complex (HFA)<sub>4</sub>MN(C<sub>2</sub>H<sub>5</sub>)<sub>4</sub>, deuterated PMMA (PMMA-*d*<sub>8</sub>), and perfluorinated polymer (CYTOP).

investigated the optical properties of Sm and Eu chelates for plastic optical fiber amplifiers. They used tetrakis chelates such as Eu hexafluoroacetylacetone (Eu(HFA)<sub>4</sub>N(C<sub>2</sub>H<sub>5</sub>)<sub>4</sub>) which has four β-diketone ligand anions coordinated to the lanthanide ion and tetraethylammonium cation to balance the charge. Sm(HFA)<sub>4</sub>N(C<sub>2</sub>H<sub>5</sub>)<sub>4</sub> has a fluorescence peak of Sm<sup>3+</sup> (<sup>4</sup>G<sub>5/2</sub> → <sup>6</sup>G<sub>9/2</sub>) at 645 nm in a deuterated PMMA (PMMA-*d*<sub>8</sub>) optical fiber. Figure 2 shows these chelates and the plastic matrix. The lifetime of the metastable <sup>4</sup>G<sub>5/2</sub> state and the emission cross section were found to be 194 μs and 4.5 × 10<sup>-21</sup> cm<sup>2</sup>, respectively. With these measured optical properties, the optical gains were theoretically calculated for a waveguide of a few micrometers thickness, a length of several centimeters, and an optimized doping concentration. The numerical calculations indicate that the PMMA-*d*<sub>8</sub> waveguide amplifier doped with the Sm chelate achieves a 20 dB gain at 650 nm with a pump power of 50 mW. Similarly Kim and co-workers synthesized a tetrakis Eu complex, tris(2-thenoyl trifluoro acetate)-1,10-phenanthroline (Eu-

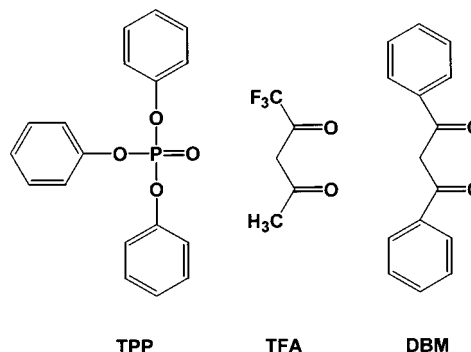


**Figure 3.** Chemical structure of europium tris(2-thenoyl trifluoro acetate)-1,10-phenanthroline.

(TTA)<sub>3</sub>phen; Figure 3), as the amplification dopant in PMMA fiber. They measured the optical loss of the fiber and estimated the optical gain more than 30 dB with 5 m long fiber at 300 mW pump power.<sup>21</sup>

Another reason for the low efficiency of these tris chelates is the formation of hydrates. Several water molecules tend to hydrate a lanthanide ion, and the OH vibration of the water molecules acts as an effective quencher to the metastable state of the lanthanide ion. Ohleman and Charles<sup>22</sup> found that both the lifetimes and the fluorescence intensity of chelates at room temperature are markedly dependent upon the nature of the Lewis base present in the system. This observation was corroborated by Kleinerlam et al.,<sup>23</sup> who found that the addition of a Lewis base increases the fluorescence yield substantially. The fluorescence enhancement was observed in solutions of trivalent Tb, Eu, and Sm chelates by addition of a Lewis base such as acetone, dimethyl sulfoxide (DMSO), tri-*n*-butyl phosphate, and various amines. The enhancement by the addition of a Lewis base may be due to the replacement of the water molecules coordinated to the lanthanide ion in the chelate.

Recently, Kobayashi et al.<sup>24</sup> observed that triphenylphosphate (TPP) increases the fluorescence yields and lifetimes in PMMA doped with various Eu chelates: Eu(TFA)<sub>3</sub>, Eu(TFA)<sub>4</sub>, Eu(HFA)<sub>3</sub>, Eu(HFA)<sub>3</sub>, Eu(TTFA)<sub>3</sub>, Eu(TTFA)<sub>3</sub>, Eu(DBM)<sub>3</sub>, and Eu(DBM)<sub>3</sub> (Figure 4). The fluorescence intensity of Eu(TFAA)<sub>3</sub>



**Figure 4.** Chemical structures of triphenyl phosphate (TPP) and various ligands: trifluoro acetylacetone (TFA) and dibenzoyl methane (DBM).

in PMMA doped with TPP was twice as high as that without TPP. Similarly, the fluorescence lifetime of Eu(TFAA)<sub>3</sub> in PMMA was found to be less than 300 μs, while in PMMA doped with TPP, Eu(TTFA)<sub>3</sub> showed a fluorescence lifetime as long as 450 μs. Eu(HFAA)<sub>3</sub>-doped GI-POF (described in below) was fabricated with 20 wt % of TPP (Tables 1 and 2). The

**Table 1. Wavelengths and Intensities of Fluorescence Spectrum Peaks and Lifetimes for Europium Chelates in PMMA. The Chelate Concentration Was 800 ppm-wt**

	fluorescence wavelength $\lambda_{\max}$ (nm)	fluorescence intensity $I_{\max}$ (a.u.) <sup>a</sup>	lifetime $\tau$ (ms)
Eu (TFA) <sub>3</sub>	613	22	0.31
Eu (HFA) <sub>3</sub>	614	128	0.39
Eu (TTFA) <sub>3</sub>	614	51	0.31
Eu (DBM) <sub>3</sub>	614	89	0.37

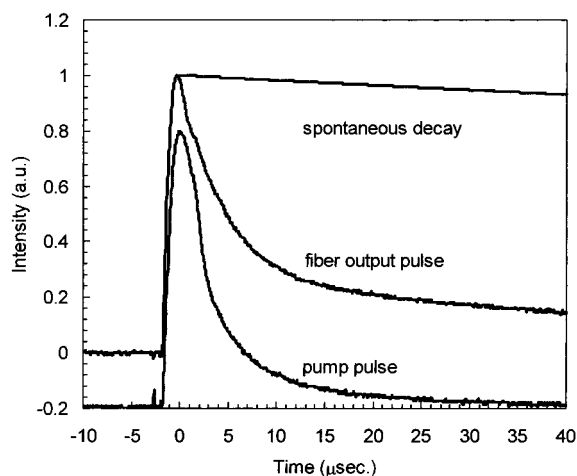
<sup>a</sup> Arbitrary units.

**Table 2. Wavelengths and Intensities of Fluorescence Spectrum Peaks and Lifetimes for Europium Chelates in PMMA Doped with 20 wt % of TPP. The Chelate Concentration Was 800 ppm-wt**

	fluorescence wavelength $\lambda_{\max}$ (nm)	fluorescence intensity $I_{\max}$ (a.u.) <sup>a</sup>	lifetime $\tau$ (ms)
Eu (TFA) <sub>3</sub>	614	43	0.39
Eu (HFA) <sub>3</sub>	615	615	0.61
Eu (TTFA) <sub>3</sub>	614	67	0.40
Eu (DBM) <sub>3</sub>	613	195	0.55

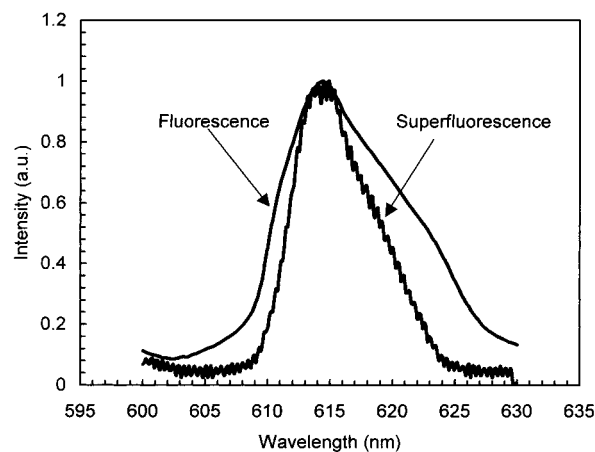
<sup>a</sup> Arbitrary units.

attenuation loss was measured to be 0.4 dB/m at 650 nm for the fiber doped with 1 wt % of the Eu chelate. Lifetime shortening and spectral narrowing verified the occurrence of superfluorescence (shortening fluorescence lifetime) at 614 nm in the 70 cm fiber,<sup>25</sup> as shown in Figures 5 and 6. The fiber was pumped in

**Figure 5.** Temporal profiles of pump and GI-POF containing Eu(HFA)<sub>3</sub>, 1 wt %, output pulses at 300 J and spontaneous decay.

a close-coupled multiple coaxial geometry with xenon flashlamps. The results showed that GI-POFs containing lanthanide chelates are promising as optical amplifiers and laser sources for a variety of communications and sensor applications.

POFs can be classified in two types: step index (SI) and graded index (GI). In the case of the SI-POF, there is a core region and a cladding as shown in Figure 7. The higher refractive index of the core compared to the cladding causes total internal reflection at the core-cladding interface. Commonly, poly(methyl methacrylate) is used as the core mate-

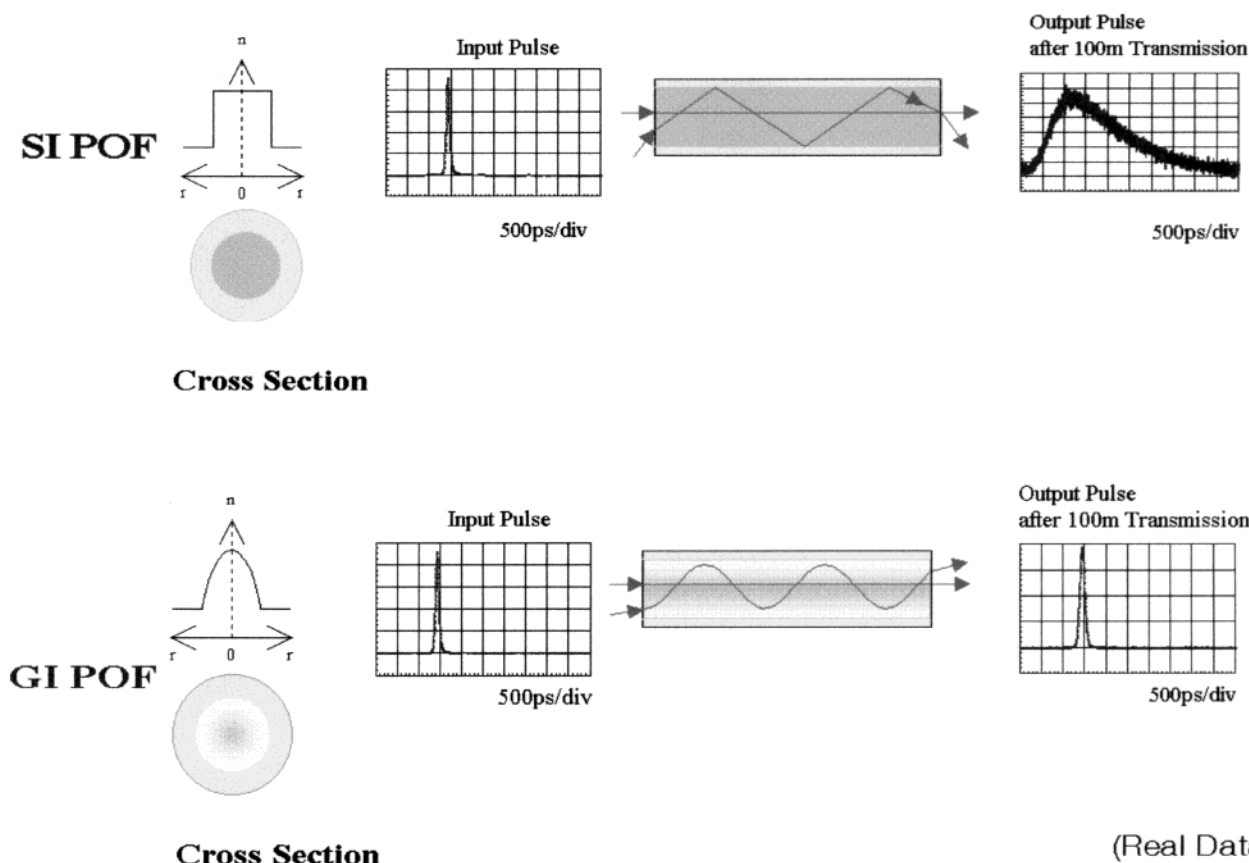
**Figure 6.** Fluorescence and superfluorescence spectra of an Eu(HFA)<sub>3</sub>-doped POF.

rial and a fluoroplastic is used as the cladding material. In this case, the refractive index difference between core and cladding is about 0.1. On the other hand, in the case of GI-POF a refractive index distribution of the fiber core is in a parabolic form. Thus, if the index profile is optimum, all modes propagate at the same velocity without spreading an impulse, which affords a remarkable increase in the bandwidth.

One of the novel preparation techniques for a GI-POF is based on the interfacial gel polymerization, which was developed by Koike et al. at Keio University.<sup>26</sup> For example, in the case of the preparation of a GI-POF fiber based on PMMA, a cylindrical tube with 6 mm i.d. and 10 mm o.d. was prepared and then a monomer, (MMA) solution containing an initiator, chain transfer agent, and a low molecular weight organic compound that has higher refractive index than PMMA was added into the tube. The polymerization was carried out, and the resulting rod was heated and drawn into a fiber. Thus, for the preparation of plastic fiber lasers and amplifiers using a lanthanide chelate as a laser material, a lanthanide chelate was also added into the above-mentioned monomer solution. The resulting fiber has a quadratic profile distribution both of a high refractive index material and a lanthanide chelate, because the low molecular weight agent and the chelate are progressively confined to the center region of the polymer formed during the interfacial gel polymerization process. In the case of a SI-POF, the chelate is uniformly distributed in the fiber.

### 3. Systems Containing Nd<sup>3+</sup>

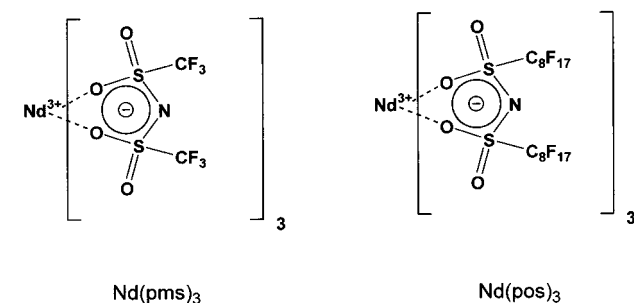
Solid systems containing the neodymium ion, Nd<sup>3+</sup>, have been regarded as the most popular fluorescent materials for laser system applications.<sup>27,28</sup> Since high-power Nd lasers with an output wavelength at around 1060 nm are of interest in laser inertial confinement experiments, Nd-containing matrices such as oxide, fluoride, phosphate, and mixed glass matrices have been investigated for the capability of high-power laser operation.<sup>29-31</sup> However, a Nd glass laser would have an intrinsic problem of heat degradation under conditions of high-power laser emis-



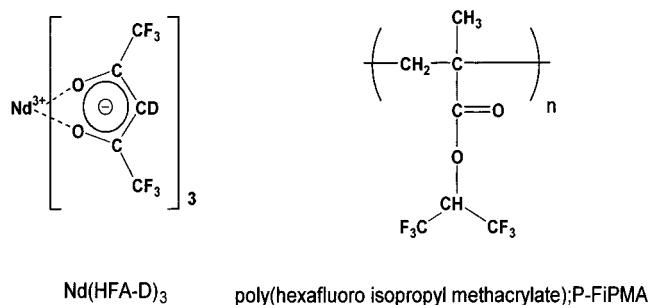
**Figure 7.** Structures of step index (SI) and graded index (GI) plastic optical fibers (POFs) and schematic representation of light through SI and GI POFs.

sion with repetition rate; repeated operation causes accumulation of heat, resulting in degradation of solid matrices. Thus, a liquid Nd-containing fluorescent media has been considered because the system can be cooled by circulation, which enables the laser system to work with high power and high repetition rate.

The radiative transition in the Nd ion occurs the level  ${}^4F_{3/2}$ . The energy gap of an important radiative transition in the Nd ion ( ${}^4F_{3/2} \rightarrow {}^4I_{15/2}$ ,  $5400\text{ cm}^{-1}$ ) matches well the vibrational energies of C–H and O–H bonds ( $5900$  and  $6900\text{ cm}^{-1}$ , respectively) with vibrational quanta  $\nu = 2$ , and vibrational excitation leads to effective quenching of the excited state of Nd. In conventional organic solvents containing many C–H bonds, de-excitation via vibrational excitation prevails. Thus, Heller et al.<sup>32,33</sup> dissolved Nd oxide or chloride in a liquid which contained no atoms lighter than oxygen such as  $\text{SeOCl}_2$  and  $\text{POCl}_3$  for enhanced fluorescence of Nd ion in a liquid matrix, and eventually laser emission was observed. However, such unconventional solvents are not appropriate for practical applications. Yanagida and co-workers<sup>34–37</sup> synthesized the Nd complexes with various deuterated and fluorinated chelates such as deuterated hexafluoroacetylacetonate (HFA-*d*), perfluoromethylsulfonylaminates (PMS), and perfluorooctylsulfonylaminates (POS) (Figure 8). These Nd chelates were dissolved in deuterated solvents and also incorporated in polymer matrices such as PMMA and polyhexafluoroisopropyl methacrylate (P-FiPMA) (Figure 9). The typical emission spectra of the plastic

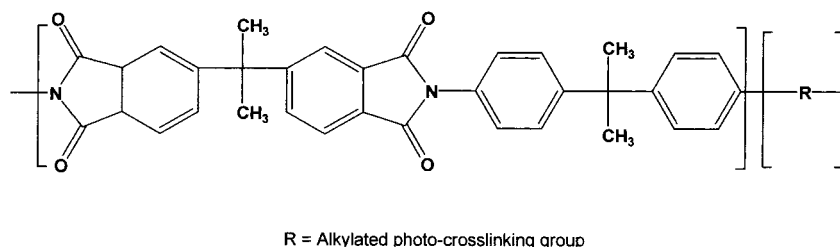


**Figure 8.**  $\text{Nd}^{3+}$  complexes with bis(perfluoroalkylsulfonyl)aminates.



**Figure 9.** Chemical structures of deuterated Nd chelate and P-FiPMA.

systems were obtained by exciting at  $585\text{ nm}$ , and infrared fluorescence at  $870$ ,  $1060$ , and  $1350\text{ nm}$  was observed. Some of the complexes exhibited a quantum efficiency as high as 3% in deuterated solvents. These results are summarized in Table 3.



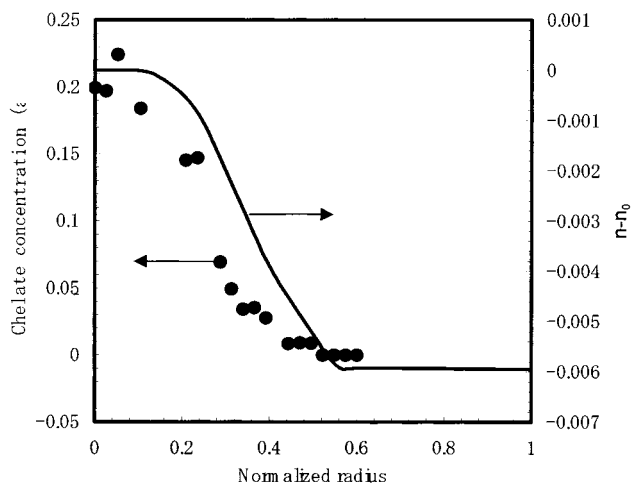
**Figure 10.** Generic molecular formula for Ultradel9000 polyimides.

**Table 3. Quantum Yield of Nd Chelates in Organic Matrices**

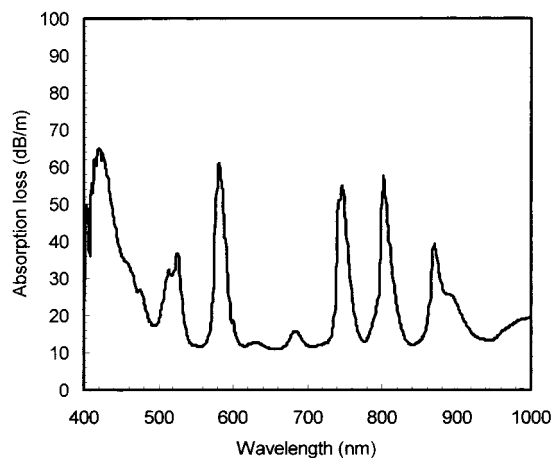
complex	matrix	transmittance (%)	quantum yield (%)
Nd(HFA-H) <sub>3</sub>	PMMA	79	<0.01
Nd(HFA-D) <sub>3</sub>	PMMA	79	0.1
Nd(HFA-D) <sub>3</sub>	PMMA/DMSO- <i>d</i> <sub>6</sub>	83	0.5
Nd(HFA-D) <sub>3</sub>	P-FiPMA/DMSO- <i>d</i> <sub>6</sub>	83	0.7
Nd(HFA-D) <sub>3</sub>	DMSO- <i>d</i> <sub>6</sub>	90	1.1
Nd(POS) <sub>3</sub>	DMSO- <i>d</i> <sub>6</sub>	-	3.3

Lin et al.<sup>38</sup> also reported that the optical properties of Nd chelates in various polymeric systems. Among polymeric materials, they selected polyimides which have mechanical strength as well as a high glass transition temperature,  $T_g \sim 400$  °C. They claimed that the best material among Nd–chelate–polymeric systems investigated was the fluorinated chelate complex Nd(HFA)<sub>3</sub> in a fluorinated polyimide (Ultradel 9000 series, Amoco Chemical Company) (Figure 10). They fabricated a waveguide using these materials and observed photoluminescence (PL) at 880, 1060, and 1330 nm. However, the PL signal was weak and the lifetime was short compared with the PL of Nd-doped inorganic host materials.

Guided wave optical elements, including thin film waveguides and optical fibers, are the most important building blocks for point to point optical interconnects. Chen and co-workers<sup>39</sup> fabricated various optical waveguides based on Nd<sup>3+</sup>-doped systems. Recently they reported Nd-doped polyamide waveguides and achieved an optical gain of 8 dB at 1060 nm. NdCl<sub>3</sub>·6H<sub>2</sub>O was dissolved into a partially fluorinated polyamide, Ultradel9120. Thin film waveguides were fabricated by spin coating of the  $\gamma$ -butyrolactone solution of the doped polymer onto the substrate. Slott et al.<sup>40</sup> synthesized lissamine functionalized Nd complexes that were incorporated in partially fluorinated polycarbonate. Good quality optical waveguides were prepared by spin coating, but the fluorescence lifetime of Nd<sup>3+</sup> in the waveguide was relatively short (0.8  $\mu$ s) due to coupling with O–H and C–H vibrations of the complexes. Besides Nd-doped plastic waveguides, other plastic devices containing Nd have been recently investigated. Zhang and co-workers developed a POF containing Nd octanate, Nd(OOC(CH<sub>2</sub>)<sub>6</sub>CH<sub>3</sub>)<sub>3</sub>. The salt was incorporated into PMMA, and then the fiber was drawn into a diameter 0.6 mm and a length of 250 mm. The Nd content in the fiber was 200 ppm, and the cladding material was a silica resin. An argon laser at 514 nm was coupled into the fiber end with the face slanted in order to prevent feedback. The 25 cm long POF was coiled into a 4 cm diameter loop, and the output fiber end was connected to an optical



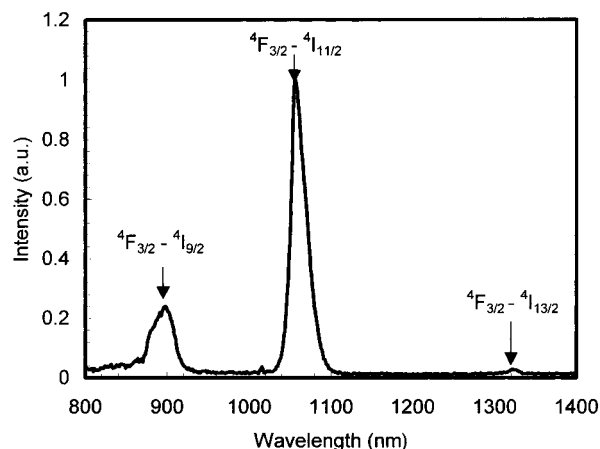
**Figure 11.** Refractive index and chelate concentration distributions of the Nd(HFA-*d*)<sub>3</sub>-doped POF perform rod. The chelate concentration in the POF was 1 wt %.



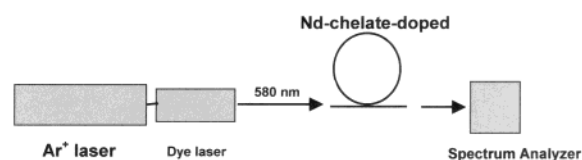
**Figure 12.** Absorption spectrum of Nd(HFA-*d*)<sub>3</sub>-doped PMMA-*d*<sub>8</sub> optical fiber.

spectrum analyzer. They observed fluorescence of the fiber from the transition of <sup>4</sup>G<sub>5/2</sub> to <sup>4</sup>I<sub>9/2</sub> and detected the optical amplification.

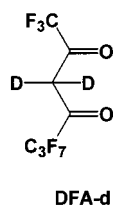
Recently Kuriki et al. reported a GI–POF containing a Nd–chelate, Nd(HFA-*d*)<sub>3</sub>, using PMMA-*d*<sub>8</sub> as the plastic matrix.<sup>41</sup> A typical graded index distribution of the refractive index and the chelate concentration of the fiber is shown in Figure 11. The absorption spectrum of the fiber exhibited several strong bands in the visible and infrared regions (Figure 12). Infrared fluorescence (900, 1060, and 1300 nm) of the Nd ion was observed at room temperature when it was pumped with an Ar-pumped dye laser at 580 nm. The spectrum and the experimental arrangement are shown in Figures 13



**Figure 13.** Fluorescence spectrum of the Nd-chelate-doped POF pumped by a dye laser at 580 nm.



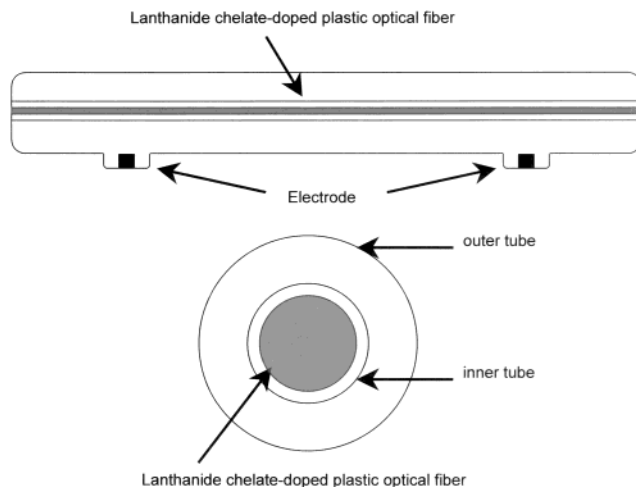
**Figure 14.** Experimental arrangement for dye-laser-pumped Nd-chelate-doped POF.



**Figure 15.** Chemical structure of deuterated (1,1,1,5,5,6,6,6,7,7,7-decafluoro 2,4-heptanedione; DFA-*d*).

and 14, respectively. They also prepared a GI-POF using deuterated tris(1,1,1,5,5,6,6,6,7,7,7-decafluoro 2,4-heptanedione) (Figure 15) as the Nd ligand, Nd-(DFA-*d*)<sub>3</sub>. The GI-POF was pumped with a frequency-doubled Q-switched Nd:YAG laser at 530 nm, and a fluorescence decay curve at 1060 nm was observed with an uncooled photodiode. The amplification properties of an organic dye-doped POF have been investigated using coaxial excitation by a high-power pulse laser. However, there have been no the experimental reports of plastic optical fiber amplifiers (POFA) pumped by CW coaxial excitation because, as mentioned previously, the organic dye is inadequate for CW excitation due to its triplet state losses. Also, for the lanthanide chelate-doped POFA, sufficient heat may be generated in the core region by the pumping to result in the melting of the fiber.

Fuji<sup>42</sup> proposed a novel structure of a Nd chelate-doped plastic optical fiber amplifier (POFA) which is pumped by CW-side excitation. The proposed POFA system and its cross section are schematically illustrated in Figure 16. From the calculation using this Nd chelate as a dopant, he showed that the maximum signal gain of 21 dB can be achieved by 20 W of pumping power for the POFA length of 20 cm. The side excitation offers very low pump power density so that the heat produced is very small, thus avoiding the melting the fiber.

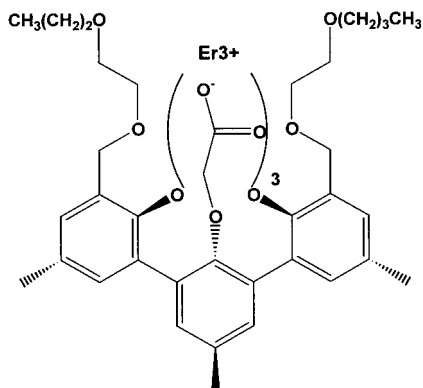


**Figure 16.** Schematic structure of the proposed POFA. The excitation tube has a double structure. The core diameter is 0.5 mm.

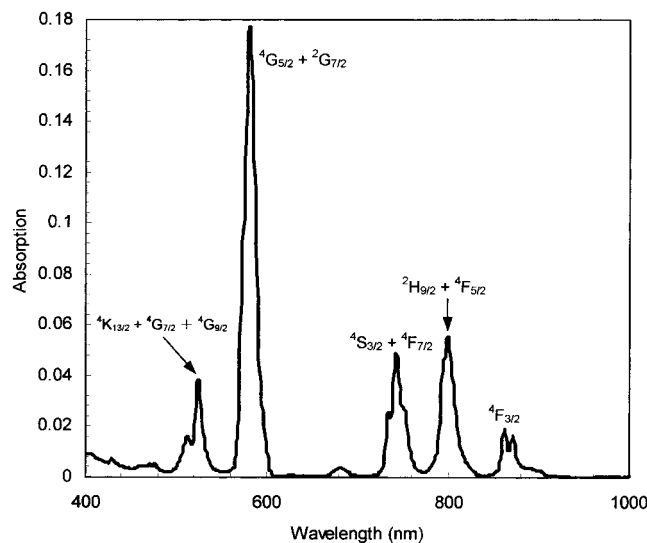
#### 4. Systems Containing Er<sup>3+</sup> and Other Lanthanide Ions

Erbium-doped materials have attracted a lot of attention because of their potential application in optoelectronics. The Er ion exhibits a 4f intrashell transition from its first excited state (<sup>4</sup>I<sub>13/2</sub>) to the ground state (<sup>4</sup>I<sub>15/2</sub>), which occurs at a wavelength of 1540 nm. In the free Er ion the optical 4f intrashell transitions are partially forbidden. Incorporated in solid host, however, the crystal field of the host induces the mixing of states, which makes some of the transitions allowed. The luminescence lifetime of the first excited state can be as long as several milliseconds. These features make Er-doped materials very attractive for laser and optical amplifiers operating at 1540 nm, one of the standard telecommunications wavelengths. Er-doped planar optical amplifiers have been demonstrated using silica,<sup>43</sup> Al<sub>2</sub>O<sub>3</sub>,<sup>44</sup> and LiNbO<sub>3</sub><sup>45</sup> hosts. However, as plastic waveguides are becoming more important both as fibers and in thin film configurations, it is interesting to study the doping of planar plastic waveguides with Er and to investigate if optical amplification can be achieved. Such plastic amplifiers could then be integrated in existing optical polymer devices such as splitters, switches, and multiplexers with low coupling losses.

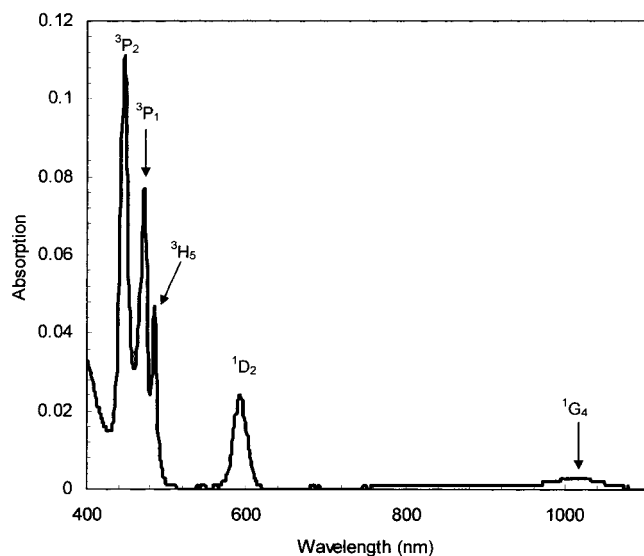
Slott et al.<sup>46</sup> investigated the optical properties of Er, which was encapsulated by cage-like organic ligands (polydentate hemispherand organic cage compound, see Figure 17). These complexes were incorporated in KBr or dissolved in organic solvents such as dimethyl formamide and deuterated butanol. Room temperature photoluminescence at 1540 nm was observed due to a 4f intrashell transition in the Er ion, excited directly at the 4f manifolds (at 488 nm) or indirectly (at 287 nm) via the aromatic parts of the ligands. A broad luminescence spectrum of 70 nm (full-width at half-maximum) was obtained. The result showed that this system may yield a high-gain bandwidth for optical amplification. The absorption cross section at 1540 nm was  $1.1 \times 10^{-20}$  cm<sup>2</sup>, which was higher than that in most other Er-doped materi-



**Figure 17.** Er in a complex of polydentate hemispherand ligand.

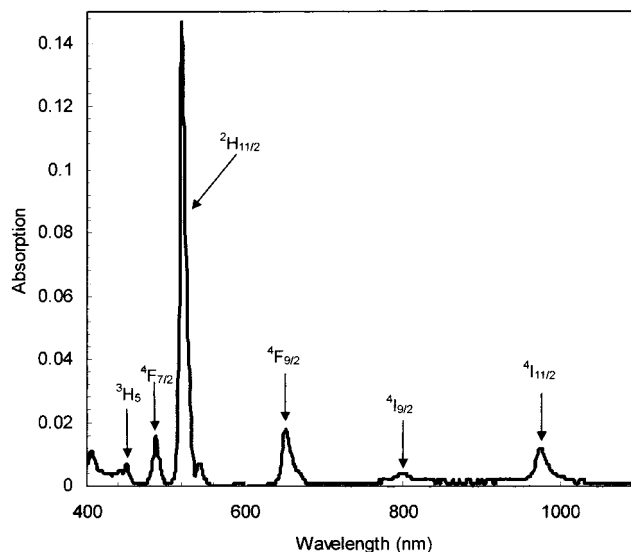


**Figure 18.** Absorption spectrum of Nd(DFA-*d*)<sub>3</sub>-doped PF plastic solution. The chelate concentration is 0.010 M.

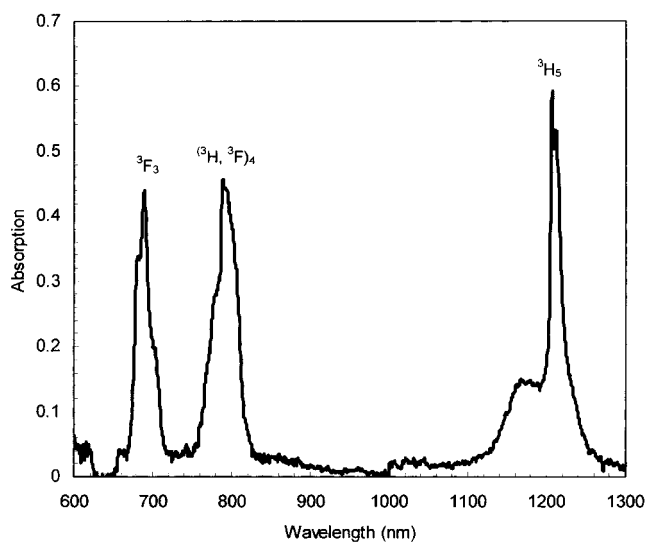


**Figure 19.** Absorption spectrum of Pr(DFA-*d*)<sub>3</sub>-doped PF plastic solution. The chelate concentration is 0.010 M.

als. Luminescence lifetimes at 1540 nm of  $<0.5 \mu\text{s}$  and  $0.8 \mu\text{s}$  in KBr and organic solvents, respectively, were observed. The short lifetime was attributed to concentration quenching or the effect of O–H groups present in the complexes. The author calculated the



**Figure 20.** Absorption spectrum of Er(DFA-*d*)<sub>3</sub>-doped PF plastic solution. The chelate concentration is 0.010 M.



**Figure 21.** Absorption spectrum of Tm(DFA-*d*)<sub>3</sub>-doped PF plastic solution. The chelate concentration is 0.010 M.

gain performance of a planar plastic waveguide amplifier based on these Er complexes and showed net optical amplification for pump powers as low as 1.4 mW reduced from 930 mW and with a typical gain of 1.7 dB/cm. These low pump powers are very interesting for practical applications.

We have also prepared thulium (Tm) and praseodymium (Pr) chelates: Tm(DFA-*d*)<sub>3</sub> and Pr(DFA-*d*)<sub>3</sub>, respectively.<sup>47,48</sup> We dissolved these Nd, Er, Pr, and Tm chelates into perfluorocarbon liquid (3M PF-5080) and also incorporated them in fluorinated plastic (FP), Cytop. The absorption spectra of these chelates in the perfluorinated liquid are shown in Figures 18–21. The location of the energy bands for Nd, Pr, Er, and Tm are similar to those recorded from other hosts. Therefore, each absorption band could be assigned with term symbols. The Nd ion has a strong absorption in the visible at around 520 and 580 nm and in the near-infrared at around 750, 800, and 870 nm. Absorption bands can be seen at 450, 600, and 1020 nm and correspond to the  $^3\text{H}_4 \rightarrow (^3\text{P}_2, ^3\text{P}_1, \text{ and } ^3\text{P}_0)$ ,  $^3\text{H}_4 \rightarrow ^1\text{D}_2$ , and  $^3\text{H}_4 \rightarrow ^1\text{G}_4$  transitions,



**Table 4. Judd–Ofelt Parameters ( $\Omega_i$ ) and Radiative Lifetimes ( $\tau_{\text{rad}}$ ) for Nd(DFA-*d*)<sub>3</sub> and Er(DFA-*d*)<sub>3</sub> in PF Plastic Solution**

host	$\Omega_2$ ( $10^{-20}$ cm <sup>2</sup> )	$\Omega_4$ ( $10^{-20}$ cm <sup>2</sup> )	$\Omega_6$ ( $10^{-20}$ cm <sup>2</sup> )	$\tau_{\text{rad}}$ (ms)
Nd <sup>3+</sup> in PF plastic solution	10.6	6.51	4.72	0.548
Nd <sup>3+</sup> in PMMA- <i>d</i> <sub>8</sub>	9.45	2.70	5.27	0.187
Nd <sup>3+</sup> in ZBAN <sup>51</sup>	3.1	3.7	5.7	0.419
Er <sup>3+</sup> in PF plastic solution	12.4	1.32	1.67	12.0
Er <sup>3+</sup> in ZBAN <sup>52</sup>	2.54	1.39	0.97	9.24

**Table 5. Calculated Radiative Transition Probabilities (*A*), Total Radiative Transition Probability (*A<sub>T</sub>*), Radiative Lifetime ( $\tau_{\text{rad}}$ ), and Branching Ratios ( $\beta$ ) for Nd<sup>3+</sup> in PF Plastic Solution**

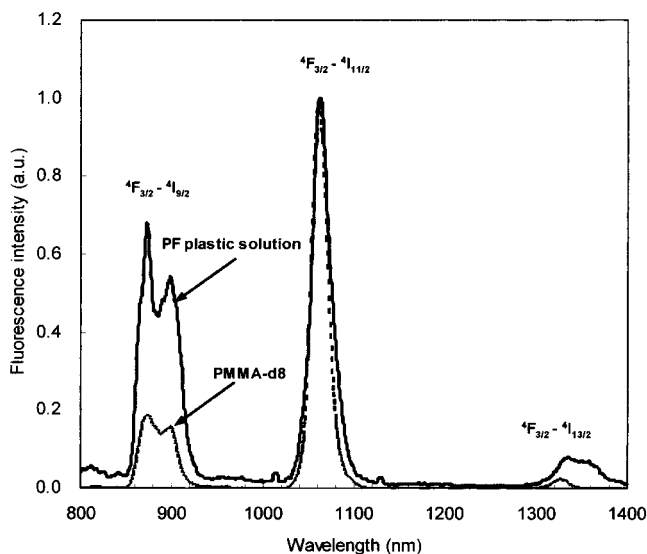
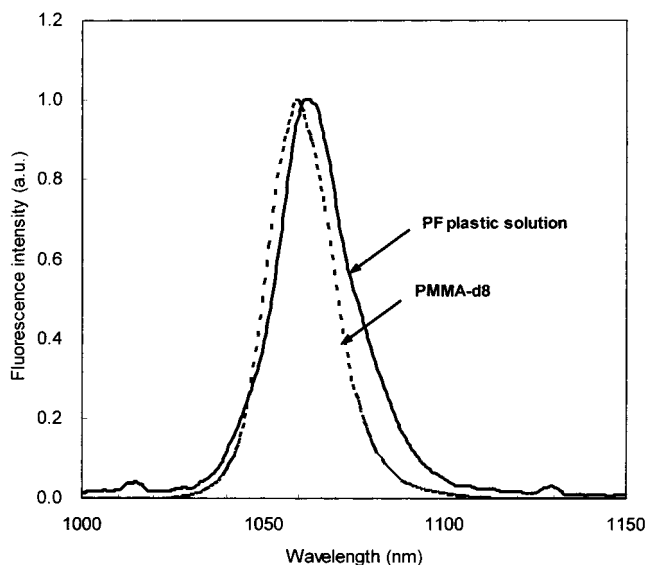
	<i>A</i> (s <sup>-1</sup> )	<i>A<sub>T</sub></i> (s <sup>-1</sup> )	$\tau_{\text{rad}}$ (ms)	$\beta$
<sup>4</sup> F <sub>3/2</sub> – <sup>4</sup> I <sub>9/2</sub>	978	2045	0.489	0.478
<sup>4</sup> F <sub>3/2</sub> – <sup>4</sup> I <sub>11/2</sub>	905			0.443
<sup>4</sup> F <sub>3/2</sub> – <sup>4</sup> I <sub>13/2</sub>	154			0.075
<sup>4</sup> F <sub>3/2</sub> – <sup>4</sup> I <sub>15/2</sub>	7.51			0.004

**Table 6. Calculated Radiative Transition Probabilities (*A*) and Radiative Lifetime ( $\tau_{\text{rad}}$ ) for Er<sup>3+</sup> in PF Plastic Solution**

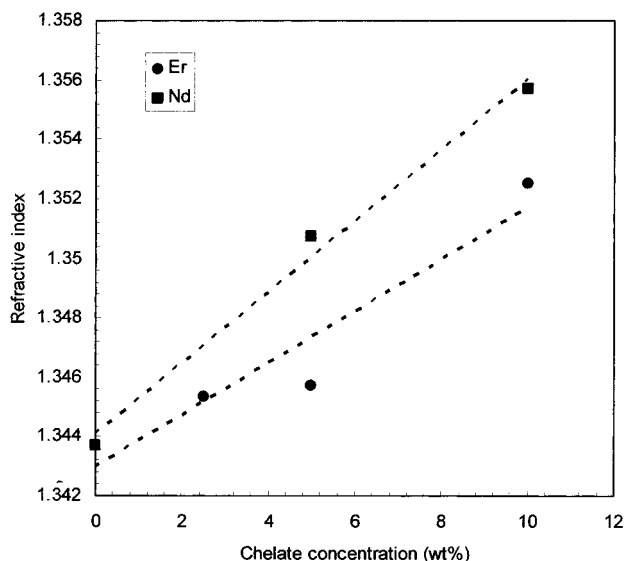
	<i>A</i> (s <sup>-1</sup> )	$\tau_{\text{rad}}$ (ms)
<sup>4</sup> I <sub>13/2</sub> – <sup>5</sup> I <sub>15/2</sub>	83.36	12.00

respectively. Er ion absorption bands can be seen at 490, 520, 650, 800, and 980 nm, and the hypersensitive <sup>4</sup>I<sub>15/2</sub> → <sup>2</sup>H<sub>11/2</sub> transition at 520 nm is an order of magnitude stronger than the other transitions. Tm ion absorption bands can be seen in the infrared region at 700, 800, and 1200 nm and correspond to the <sup>3</sup>H<sub>6</sub> → <sup>3</sup>F<sub>3</sub>, <sup>3</sup>H<sub>6</sub> → (<sup>3</sup>H, <sup>3</sup>F)<sub>4</sub>, and <sup>3</sup>H<sub>6</sub> → <sup>3</sup>H<sub>5</sub> transitions, respectively.

The Judd–Ofelt theory is widely used and remarkably successful for quantitatively characterizing optical 4f transitions in lanthanide-doped glasses and crystals.<sup>49,50</sup> In theory, the Judd–Ofelt parameters ( $\Omega_2$ ,  $\Omega_4$ ,  $\Omega_6$ ) are determined by measuring the absorption oscillator strength for a number of ground-state transitions. From these parameters, radiative lifetimes for the lanthanide chelates in the perfluorocarbon liquid were obtained. Listed in Table 4 are Judd–Ofelt parameters for Er and Nd obtained with data found by other workers in glasses. The radiative lifetime for Nd in the perfluorinated solvent is almost the same as that in ZBLA (ZrFr–BaF<sub>2</sub>–LaF<sub>2</sub>–AlF<sub>3</sub>). Tables 5 and 6 list the values of radiative transition probabilities, total radiative transition probability, radiative lifetimes, and branching ratios calculated using the Judd–Ofelt parameters for Nd and Er in the fluorinated liquid. The obtained values of branching ratios and the radiative lifetimes are very similar to those in silicate and phosphate glasses, where laser action was obtained. Figure 22 provides the fluorescence spectra of Nd<sup>3+</sup> in the fluorinated liquid pumping at 580 nm at room temperature. There are several peaks at 900, 1064, and 1300 nm corresponding to <sup>4</sup>F<sub>3/2</sub> → <sup>4</sup>I<sub>9/2</sub>, <sup>4</sup>F<sub>3/2</sub> → <sup>4</sup>I<sub>11/2</sub>, and <sup>4</sup>F<sub>3/2</sub> → <sup>4</sup>I<sub>13/2</sub> transitions, respectively. The <sup>4</sup>F<sub>3/2</sub> → <sup>4</sup>I<sub>9/2</sub> transition as dual peak character with positions at 874/900 nm. A clear difference can be seen in the 900 nm emission. The spectrum of a lanthanide ion depends on the host.

**Figure 22.** Fluorescence spectra of Nd<sup>3+</sup> in PF plastic solution and PMMA-*d*<sub>8</sub> pumped at 580 nm.**Figure 23.** <sup>4</sup>F<sub>3/2</sub>–<sup>4</sup>I<sub>11/2</sub> transition fluorescence spectra of Nd<sup>3+</sup> in PF plastic solution and PMMA-*d*<sub>8</sub> pumped at 580 nm.

The peaks and valleys in the spectra have different shapes based on the precise location of the Stark levels, the intensities of the transitions between the Stark levels, and the amount of inhomogeneous and homogeneous broadening of these levels. Figure 23 illustrates the <sup>4</sup>F<sub>3/2</sub> → <sup>4</sup>I<sub>11/2</sub> fluorescence spectra of Nd<sup>3+</sup> at 1064 nm in the fluorinated liquid and PMMA-*d*<sub>8</sub>.<sup>53</sup> Both were pumped at 580 nm. A comparison of the fluorescence curves in Figure 23 shows that for the PF solution the peak is at a longer wavelength of 1063 nm, closer to the Nd:YAG emission wavelength of 1064 nm,<sup>54</sup> and has a wide full-width at half-maximum. This observation implies a continuous tuning range of lasers and amplifiers using this material. Figure 24 shows the dependence of the refractive index on the chelate concentration for in the case of PF plastic films. The PF plastic film without chelates has a lower refractive index than the chelate-doped PF plastic films. Since the PF plastic exhibits excellent transparency over a wide



**Figure 24.** Refractive indices of Nd(DFA-*d*)<sub>3</sub>- and Er(DFA-*d*)<sub>3</sub>-doped PF plastic films at 633 nm.

wavelength range from 500 to 1300 nm, waveguide structures with doped and nondoped PF plastic films can be employed for optical applications, such as modulator arrays, lasers, amplifiers, and switches. It also indicates that PF plastics/chelates-doped PF plastics are potentially excellent structures from which to fabricate planar waveguides and optical fibers for use in communications systems.

## 5. Conclusion

Recently considerable progress has been achieved on plastic optical fiber lasers and amplifiers containing lanthanide ions. However, the ultimate limits of these systems have not yet been researched, and multidisciplinary efforts to devise new plastic optical fibers for lasers and amplifiers should be continued. Further development should be focused on obtaining lower cost, easier fabrication, better mechanical and thermal stability, and higher quantum yield of lanthanide ion fluorescence.

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