The Possibility of Graded-Index Plastic Optical Fibers Containing Lanthanide Chelates for Amplifiers and Lasers

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Summary: Absorption spectra of lanthanide ions in perfluorinated (PF) plastic solution were measured, and Judd-Ofelt parameters (Ω_2, Ω_4, Ω_6) were determined by the absorption measurements. Fluorescence spectrum of Nd^{3+} in PF plastic solution from 900 nm to 1350 nm, pumped at 580 nm, were measured for the first time.

1. Introduction

Glasses doped with lanthanide ions have a long history of use for optical devices, for example in the incorporation of neodymium (Nd) ions in glasses for lasers and amplifiers. Currently, the most widely used optical amplifiers in optical communications are erbium (Er) -doped fiber amplifiers (EDFAs), which have high gain, low noise, and lack of polarization sensitivity [1]. Pumping with diode lasers emitting at 980 or 1480 nm, the generating gain has a broad range of wavelengths from 1520 to 1630 nm. Praseodymium (Pr) doped low phonon hosts have been employed for a practical and efficient 1.3-μm amplifier for telecommunication system. Low phonon energies of hosts are an essential requirement for efficient luminescence from Pr ions due to the distance between energy levels ($^1G_4 \rightarrow {}^3H_5$). Initial interest in fluoride glass optical fiber doped with Pr ions was generated in 1991 with the demonstration of a 1.3-μm amplifier operating [2]. Recently, the high fluorescence efficiency of Pr-doped sulfide glass has been demonstrated experimentally [3]. Unlike EDFAs, Pr-doped fiber amplifiers (PDFAs) have remained laboratory devices.

Fluorinated plastics are generating a great deal of interest because of their potential use in the growing optical fiber communications industries owing to high optical transparency. One promising candidate is poly(perfluoro-butenylvinylether) (PF plastic)

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[4], which is highly transparent from 500 to 1300 nm, and relatively easier to prepare than fluorinated glasses, such as fluorozirconate and sulfide glasses. Graded-index plastic optical fibers (GI-POF) with PF plastic have generated growing interest in low-loss high-speed plastic links in the home, the car and the airplane [4]. The PF plastic allows GI-POF to operate in the conventional communications wavelengths that are used by glass fiber. GI-POFs have several advantages over traditional glass fibers. The large diameter (up to 1 mm) allows easy connections and results in cheap devices [5].

In this work, absorption spectra of lanthanide ions in PF plastic solution were measured, and Judd-Ofelt parameters [6,7] to calculate radiative properties of lanthanide ions were determined by the absorption measurements. Understanding of the Judd-Ofelt parameters (Ω_2, Ω_4, Ω_6) and the radiative properties leads naturally to an overall understanding of the properties of PF plastic with a low-phonon energy for applications in telecommunications. Fluorescence spectrum of Nd^{3+} in PF plastic solution from 900 nm to 1350 nm pumped at 580 nm were measured for the first time.

2. Experiments with doped PF plastic solutions

Deuterated-tris(1,1,1,5,5,6,6,7,7,7-decafluoro-2,4-heptanedione)Nd;Nd(DFA-D)$_3$, Pr(DFA-D)$_3$, Er(DFA-D)$_3$, Eu(DFA-D)$_3$ were prepared in our laboratory by the method described in the literature [8]. The PF plastic solution consists of perfluorocarbon liquid (3M™ PF-5080) plus PF plastic (9:1). Absorption measurements of solutions doped with the chelates were made using a spectrophotometer (Hitachi, U-2000). Fluorescence measurements were made using a spectrum analyzer (ANDO).

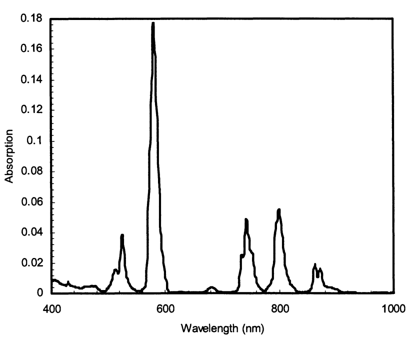

Figure 1 Absorption spectrum of Nd(DFA-d)$_3$-doped PF plastic solution. The chelate concentration is 0.010 M.

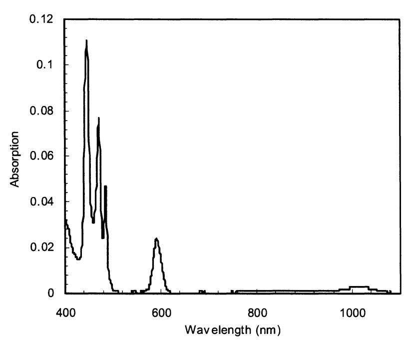

Figure 2 Absorption spectrum of Pr(DFA-d)$_3$-doped PF plastic solution. The chelate concentration is 0.010 M.

3. Results and discussion

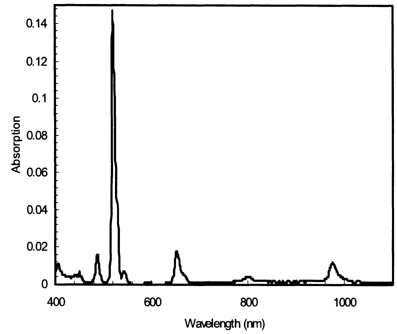

Figure 3 Absorption spectrum of $Er(DFA\text{-}d)_3$-doped PF plastic solution. The chelate concentration is 0.010 M.

Figures 1-3 show absorption spectra of Nd, Pr and Er-chelate-doped PF plastic solutions, respectively. 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, respectively. It has been reported by Hasegawa et. al. that in organic solutions, Nd-chelates with asymmetric ligands exhibited high absorption for $^4I_{9/2} \rightarrow {}^4G_{5/2} + {}^2G_{7/2}$ transitions (580 nm) [9]. The asymmetric chelate, $Nd(DFA\text{-}d)_3$, shows similar behavior in the fluorinated polymer solution; i.e. Nd ions are affected by the coordination structure around them resulting in high absorption at 580 nm. Pr ion absorption bands can be seen at 450, 600 nm, and 1020 nm in Figure 2. Er ion absorption bands can be seen at 490 nm, 520, 650, 800, and 980 nm in Figure 3. The Judd-Ofelt theory is a widely used and remarkably successful theory for quantitatively characterizing optical *4f* transitions in lanthanide doped glasses and crystals. In the theory, three Judd-Ofelt parameters (Ω_2, Ω_4, Ω_6) are determined by measuring the absorption oscillator strengths for a number of ground-state transitions. From these parameters, radiative lifetimes for the lanthanide chelates in PF plastic solution were obtained. Listed in Table 1 are Judd-Ofelt parameters for Nd and Er ions obtained in this work along with the Judd-Ofelt parameters found in previous studies in typical glasses and a deuterated plastic. They can then be used to calculate the emission or absorption oscillator strength between any pair of excited states, which allows a quantitative estimate of stimulated emission or excited-state absorption cross sections.

Table 1 Judd-Ofelt parameters (Ω_λ) and radiative lifetimes (τ_R) for $Nd(DFA\text{-}d)_3$ and $Er(DFA\text{-}d)_3$in PF plastic solution

Host	$\Omega_2(10^{-20}\,cm^2)$	$\Omega_4(10^{-20}\,cm^2)$	$\Omega_6(10^{-20}\,cm^2)$	τ_R (msec.)
Nd^{3+} in PF plastic solution	10.6	6.51	4.72	0.548
Nd^{3+} in PMMA-d8 [10]	9.45	2.70	5.27	0.187
Nd^{3+} in ZBAN [11]	3.1	3.7	5.7	0.419
Er^{3+} in PF plastic solution	12.4	1.32	1.67	12.0
Er^{3+} in ZBAN [12]	2.54	1.39	0.97	9.24

1,1,1,5,5,6,6,7,7,7-decafluoro-2,4-heptanedione : DFA poly(deuterated methyl methacrylate) : PMMA-d8

It is interesting to compare the Judd-Ofelt parameters and the radiative properties found in this study with those in previous studies. The radiative lifetime for Nd^{3+} in PF plastic solution is almost same as that in ZBLA (ZrF^4-BaF^2-LaF^2-AlF^3). In this study, a Nd ion in a chelate is coordinated with 6 oxygen atoms of organic ligands as a kind of covalent bond. The values of Ω_2 found in this study are higher than those in ZBLA. There is a general trend in glass hosts that an Ω_2 is proportional to the covalency of the hosts. Our results show the same phenomena in the deuterated plastic and PF plastic solution.

Figure 4 provides the fluorescence spectra of Nd^{3+} in PF plastic solution by pumping at 580 nm at room temperature. There are several peaks at 0.90, 1.06, and 1.3 μm. The spectrum of a lanthanide ion depends on the host. 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.

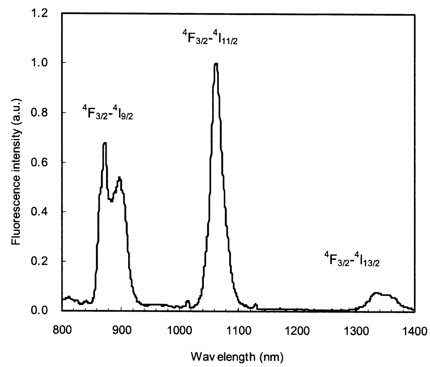

Figure 4 Fluorescence spectrum of Nd^{3+} in PF plastic solution pumped at 580 nm.

4. Conclusions

We have successfully incorporated lanthanide-chelates into PF plastic solutions and have measured the absorption spectra. Judd-Ofelt parameters (Ω_2, Ω_4, Ω_6) were determined by the absorption measurements. Lanthanide ion-doped PF plastic waveguides and optical fibers may find many applications in lasers, amplifiers, and switches.

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