A Novel Unclad Nd^{3+}-Doped Polymer Optical Fiber

QIJIN ZHANG,[1,*] HAI MING,[2] and YAN ZHAI[1]

[1]Department of Materials Science and Engineering, University of Science and Technology of China, Hefei, Anhui 230026, People's Republic of China; [2]Department of Physics, University of Science and Technology of China, Hefei, Anhui 230026, People's Republic of China

SYNOPSIS

Neodymium octanoate was synthesized from neodymium oxides and dissolved in poly(methyl methacrylate) (PMMA), forming a solid solution. The investigation of the absorption spectrum of Nd^{3+}-doped PMMA showed that the spectrum was similar to that of Nd^{3+}-doped silica glasses. The Nd^{3+}-doped PMMA was used to draw a fiber and an unclad Nd^{3+}-doped PMMA optical fiber was made. The emission output of the fiber at about 585 nm was observed under green source pumping at 532 nm by optimization of the Nd^{3+} concentration and the length of the fiber. Under 1 W pumping radiation, a 60 μW output was obtained for the fiber with a Nd^{3+} concentration of 70 ppm and the length of 15 cm. © 1996 John Wiley & Sons, Inc.

INTRODUCTION

Polymer optical fibers (POF), especially poly(methyl methacrylate) (PMMA) core ones, are now expected to be of general use. POF, which can be used to transmit optical signals along plastic fibers, are in many ways superior to their counterpart glass: They are easier to handle because of their good ductility and light weight, easier to splice together and to use for light sources because of their large core diameter and high numerical aperture, and easier to manufacture because of low melting temperature and low cost of polymer materials from which POF can be made. Presently, POF are often used in local area networks, datalinks, and optical sensors.[1,2]

By introduction of appropriate additives into the core, we can obtain POF with special functional features. Recently, a few groups have investigated organic-doped POF. The results showed that the spectrum of future applications of such fibers was very broad—from logic and storage elements for full-optical computers[3,4] to sensitive detectors which can be used for medical equipment designation.[5]

A polymer optical fiber amplifier (POFA) was previously prepared, the core of which was made of rhodamine B (RB)-doped PMMA.[6] A dye used in the POFA must satisfy some critical properties, such as photochemical stability, adequate solubility in the polymer bulk, and a minimal overlap between the dye fluorescence and its absorption spectra. Although rare earth-doped glass fiber has been successfully used in silica optical fiber amplifiers,[7] work on rare earth-doped polymer optical fiber amplifiers has not been found. The reason may be that the rare earth metals are not compatible with organic polymers. In this article, the preparation of neodymium octanoate (NdOA) was made, and organic salt was doped into PMMA and the UV-vis absorption spectra of Nd^{3+}-doped PMMA (Nd–PMMA) were examined. Fluorescence features of Nd^{3+}-doped POF made from Nd–PMMA (to our knowledge, this kind of fiber is presented for the first time) was measured and compared with that of RB-doped POF.

EXPERIMENT

Reagent

Starting from Nd_2O_3 (>99.9%, purchased from Shanghai and used without further purification),

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neodymium octanoate was synthesized according to the procedure reported before.[8] Yield: about 60% NdOA; IR (KBr): $\nu_{(C=O)}$, 1720 cm^{-1} disappeared, $\delta_{(OCO)}$, 684–712 cm^{-1}, $\nu_{(OCO)}$, 1540 cm^{-1} newly produced.

ANAL: C, 49.59% (cald: 50.24%); H, 7.21% (cald: 7.85%).

RB is a commercial analytical reagent and was used as another dye without further purification.

Preparation of Doped POF

Nd^{3+} (or RB)-doped PMMA fiber was fabricated as follows:

1. Inhibitors contained in commercial methyl methacrylate (MMA) were eliminated by rinsing with a 5% alkali solution to negate the influence of ultraviolet absorption due to inhibitors. Afterward, residual alkali was washed away with pure water and the monomer was dried by adding Na$_2$SO$_4$. The dried monomer was distilled under reduced pressure and a middle fraction was collected.

2. Purified MMA was poured into a reaction vessel with 0.01 mol/L of 2,2-azoisobutyron-itrile (AIBN) as an initiator, 0.03 mol/L n-butyl mercaptan as a chain-transfer agent, and the specified amount of NdOA (or RB). The vessel was heated in an electric furnace at 135°C for 12 h to polymerize the monomer. The temperature was gradually increased to 180°C and then the vessel was kept at that temperature for 12 h to complete the polymerization.

3. The temperature of the vessel was increased to a fiber drawing temperature and the melted polymer was extruded by dry nitrogen gas from the upper end of the vessel. The NdOA (or RB)-doped PMMA fibers were drawn out from the nozzle at a controlled diameter by regulating the temperature, drawing velocity, and gas pressure.

Measurement

The X-ray diffraction spectra were conducted on a Grigerflex D/MAX-γ A rotating X-ray diffraction spectroscope with a copper target at an operating voltage of 40 kV and an electric current of 100 mA. UV-vis spectra were recorded on a UV-240 spectro-photometer with a blank sample as a reference stan-dard and the elemental analysis was performed on a Perkin-Elmer 240 elemental analyzer.

The second harmonic radiation at wavelength λ = 532 nm from the ORC-1000 Nd : YAG laser (Clark-MXR) was used as a pump source for fluorescence measurements. The laser was operated for the present experiments in the cw mode. The coupling of laser radiation into the fiber was achieved by a 10× microscope objective lens. Emission radiation from the other end of the fiber was directed to a 0.22 m spectrometer and detected by a photomultiplier. To increase the signal-to-noise ratio, the phase-sensitive detection scheme (lock-in) was employed by chopping the pumping beam. To cut residual fundamental radiation, appropriate color filters were placed before the entrance slit of the spectrometer.

RESULTS AND DISCUSSION

UV-vis Absorption Spectra of Nd^{3+} in PMMA

As rare earth ions are compatible with an inorganic matrix, rare earth ion-doped silica glass can be made and the study of the photoluminescence of these materials began several decades ago.[9] Especially after the laser properties of Nd^{3+}-doped silica glass were found, the spectroscopic properties of rare earth ion-doped amorphous glass received more and more interest around the world.[10] However, due to poor solubility in an organic matrix, the study of rare earth ion-doped polymer has been carried out widely only in recent years.[11,12] To change the situation mentioned above, two methods have often been adopted: First, the chelate of rare earths was made and then mixed with the polymers[13]; second, the rare earth ion-containing monomers were synthesized and then polymerized.[14] In this work, another method, developed in our laboratory, was used. Neodymium octanoate (NdOA) instead of chelates was synthesized according to the method reported before.[8] Light blue–purple crystal particles were obtained and the wide-angle X-ray diffraction of them is shown in Figure 1(a). NdOA can be dissolved in MMA. The solution obtained was solidified by polymerization of MMA and the Nd^{3+}-doped PMMA (Nd-PMMA) was made. Figure 1(b) shows that the diffraction of NdOA has disappeared in the X-ray diffraction of Nd-PMMA made by bulk polymerization. This can be explained by the formation of a solid solution of NdOA in PMMA because NdOA is a long-chain aliphatic ester.
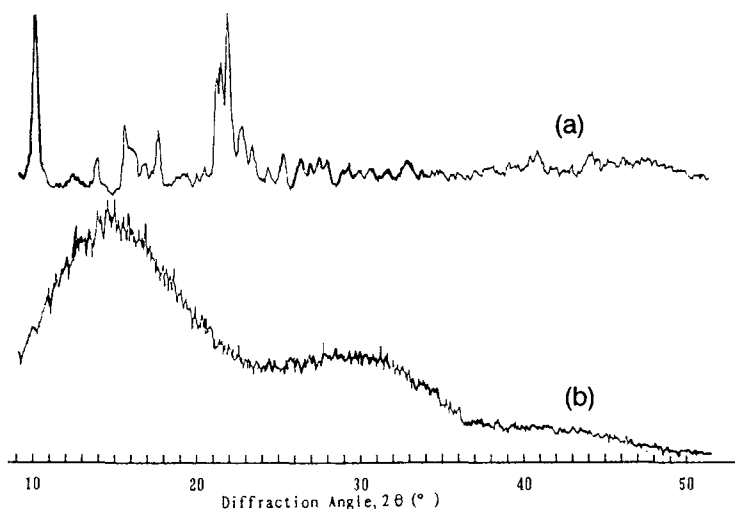
Figure 1 X-ray diffraction of (a) neodymium octanoate and (b) Nd^{3+}-doped PMMA; Nd^{3+} content: 700 ppm; thickness of sample plate: 1 mm.

The UV-vis spectrum of Nd–PMMA was recorded with a nondoped PMMA sample as a reference. The absorption of Nd^{3+} can be observed with the same number of absorption peaks as that of Nd^{3+} in silica glass.[15] However, a blue shift of about 5 nm was found by comparison with the absorption of Nd^{3+} in inorganic glasses[16] (see Table I). The blue shift may result from interactions (which is characteristic of covalent bonds) between Nd^{3+} and the ester group in Nd–PMMA. Neodymium belongs to the rare earth group and is located in the first part of the group series, so the spectral absorption of Nd^{3+} is more sensitive to the change of the properties of ligands than are other rare earths.[15] It was reported that Nd^{3+} in oxide glasses might have seven to nine ligand anions of around O^{2-} as the ion-size ratio ($R_{Nd^{3+}}/R_{O^{2-}}$) is equal to 0.743.[17] The results of the elementary and IR analyses showed that the structure of neodymium octanoate was one of coordination compounds with six ligand bonds from three carboxylic anions. It is easily deduced that there are still unoccupied positions around Nd^{3+}. Being different from silica glasses, PMMA as a matrix contains many ester groups. According to the ligand field theory,[18] the properties of chemical bonds between ions and ligands would influence the absorption and emission of the ions and π-bonds in ester groups of PMMA and could make the interaction of covalent bonds in Nd–PMMA weaker than those in Nd^{3+}-doped silica glasses in which no π-bond exists because the bond is an electron donor and Nd^{3+} is an electron acceptor. This phenomenon is called the nephelauxetic effect and was also observed in different inorganic glasses.[19]

Preparation of Unclad Nd-PMMA Optical Fiber

POF are often divided into two types: graded index POF and step index POF, in terms of the refractive-index distribution of core materials along the radial direction of the POF. No matter what type POF is made, a high transparency is required for a core polymer. PMMA is most often used as a core material because it is easily purified at the monomer

Table I   Absorption of Nd^{3+} in Organic and Inorganic Matrices

	Energy Level									
	^4D	$^2P_{1/2}$	$^4G_{9/2}$	$^2K_{13/2}$	$^2G_{7/2}$	$^2G_{5/2}$	$^4F_{9/2}$	$^4F_{7/2}$	$^4F_{5/2}$	$^4F_{3/2}$
Silica glass[a] (nm)	350	433	517	537	575	588	692	744	813	885
PMMA (nm)[b]	347	428	510	524	574	582	680	740	798	870

[a] Data from Gan et al.[16]
[b] Nd^{3+} concentration: 700 ppm; thickness of sample plates: 1 mm; T: room temperature.

level and has highly amorphous characteristics which result in its high transparency. Nd–PMMA can be obtained by bulk polymerization. For preparation of unclad Nd–PMMA optical fiber, Nd–PMMA was obtained in the vessel as a light blue-purple color cylinder with a radius of 0.5 mm and a homogeneously distributed refractive-index before being drawn. When the concentration of NdOA was low, such as dozens of ppm, the color was hard to observe visually. In prior work,[20] with a plate sample of Nd–PMMA NdOA doped into PMMA as an additive, a similar color change was observed and the fluorescence intensity and the thermal stability of Nd–PMMA both increased with Nd content, increasing from 25 to 377 ppm.

Unclad Nd^{3+} (or RB)-doped POFs were made according to the fiber-drawing method reported previously[21] with only a small technical change. The diameter of fibers was found to be dependent on three factors: pressure of dry nitrogen gas, the rate of fiber drawing, and the temperature of the melted polymer inside the vessel. For example, the fiber diameter could be controlled by regulating the relative values of them and some data are listed in Table II. The results show that the drawing rate is the main factor affecting the diameter of the fiber. This would result from the large viscosity of the melted Nd–PMMA. The data in Table II do not show a significant difference between PMMA and Nd–PMMA because the Nd contents of all Nd–PMMA samples are very low.

Fluorescence of Unclad Nd^{3+}-doped PMMA Fiber

From Table I, it can be seen that no matter what matrix Nd^{3+} is doped into there are absorption peaks at about 532 and 585 nm. Figure 2 shows the emission of unclad Nd^{3+}-doped PMMA fiber excited by green light at 532 nm under different conditions. The maximum emission takes place at about 585
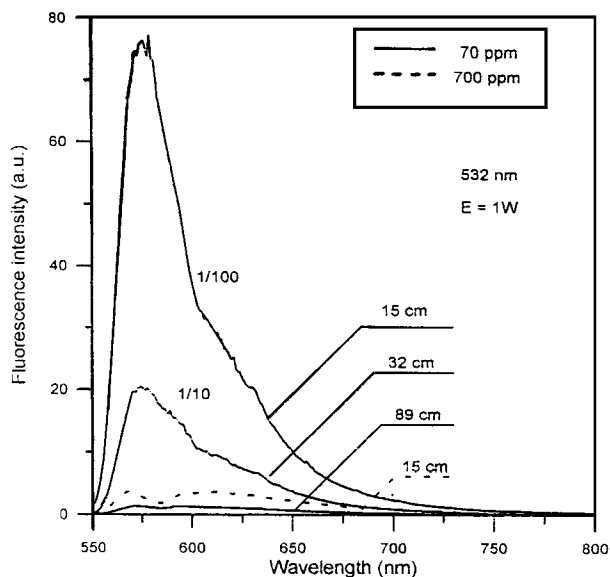

Figure 2 Emission spectra of Nd^{3+}-doped different length fibers with (solid line) 70 ppm concentration and (dashed line) 15 cm Nd^{3+}-doped fiber with concentration of 700 ppm on 1 W green pumping radiation; intensity of two upper curves are reduced by factors 10 and 100, correspondingly.

nm. During the experiment, Nd^{3+}-doped PMMA fiber was not very strong in absorption of the green light so that we had to use a sharp cutoff absorption yellow filter to kill the fundamental radiation. On the other hand, when Nd–PMMA was made into a fiber, the long optical path made self-absorptions very strong and the generative cut-back technique was used. For example, although a 1.5 W green source was used, an optimum fiber length should be selected. When we subsequently cut back the fiber to a concentration of 70 ppm, the emission intensity increased even faster than that of RB-doped fiber in Figure 3. It should be noticed that for the two upper curves in Figure 2 the scale was reduced by

Table II   Conditions for Drawing of Nd3+-doped PMMA Fiber

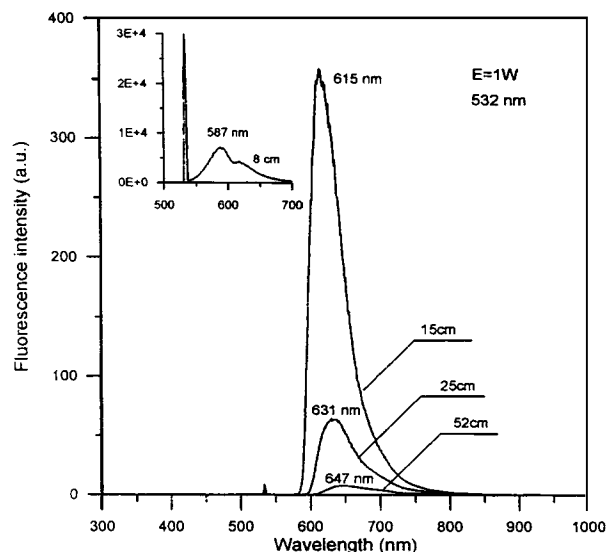| No.	Nd Contents (ppm)	Gas Pressure (atm)	Drawing Rate (mm/s)	Diameter (mm)
1	0	5	5	0.75
2	0	5	8	0.56
3	70	5	5	0.87
4	70	10	8	0.65
5	700	5	3	1.10
6	700	10	5	0.98
7	700	10	8	0.58

Temperature: viscous state.

Figure 3 Emission spectra of rhodamine-doped different length fiber on 1 W green pumping radiation. The inset shows the normalized emission spectrum from 8 cm length fiber, taken with the help of a "side-light" technique.

factors of 10 and 100, correspondingly. This may result from the C — H vibrational absorption of the matrix in the range of 600–650 nm,[21] where the emission of RB-doped PMMA fiber is located.

Nd^{3+} concentration is another factor affecting the emission intensity. Experiments with a high concentrated fiber (700 ppm) confirmed the dominant role of Nd^{3+} ions for absorption of the fluorescence. For the high concentrate 35 cm length fiber, no useful signal could be seen, and for 15 cm length fiber, the signal was more than three orders of magnitude less than that for the same length low concentrate fiber.

The absorption and fluorescence spectra of RB in PMMA bulk and doped-in PMMA fiber has been studied in detail.[6] There was a difference in the fluorescence spectrum between the fiber output and the bulk output that was caused by self-absorption of the RB. In Figure 3, a similar phenomenon is shown. An increase of emission power by a few hundred times and a blue shift of the emission peak wavelength from 647 to 587 nm can be observed when fiber length is shortened from 52 to 8 cm.

The conversion efficiency of both types of fibers was determined by measuring the absolute intensities of emission under 1 W pumping radiation. For 15 cm Nd^{3+}-doped fiber with a concentration of 70 ppm, the total average power is 60 μW, while the power for RB-doped fiber with a concentration of

16 ppm at the same length is only 5.8 μW. For the 8 cm-length RB-doped fiber, a fluorescence power of 61 μW was obtained. On the other hand, no obvious changes in the structure of the Nd^{3+}-doped fiber was observed after pumping. It is obvious that, by optimization of fiber length and impurity concentration, efficient amplification and generation of laser radiation could be made.

CONCLUSION

The absorption of Nd^{3+}-doped in PMMA is similar to that in silica glasses, although a little blue shift can be found in the former absorption spectrum. Nd–PMMA was made into unclad optical fiber and the fluorescence of the fiber is measured at 585 nm under the excitation of green light at 535 nm. The result is compared with that of rhodamine B-doped PMMA optical fiber and the potential usefulness of Nd^{3+}-doped PMMA optical fiber in optical amplifiers is tested.

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