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Fluorescence and attenuation properties of Er^{3+}-doped phosphate-glass fibers and efficient infrared-to-visible up-conversion

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Abstract. Fluorescence spectra of phosphate glasses with different erbium doping have been measured. The flouresence intensity reaches its maximum at an Er^{3+}-doping concentration of 0.75 mol%. When the Er^{3+} doping exceeds 0.75 mol%, the fluorescence intensity decreases due to concentration quenching. The attenuation at 1.53 μm of the fiber is 12.8 db/m. The fluorescence up-conversion of 1.064 μm Nd:YAG laser pulses into intense green 547 and 667 nm light in the fiber has been measured. The fluorescence output power of green (547 nm) and red (667 nm) light is 178 and 42 μW, respectively with an excitation power of 1 W. The two signals are referred to as $^4S_{3/2} \rightarrow {}^4I_{15/2}$ and $^4F_{9/2} \rightarrow {}^4I_{15/2}$ transitions through two-photon absorption fluorescence.

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It has been recognized for more than 30 years that certain lanthanide-containing materials under photoexcitation emit light at wavelengths significantly shorter than that of the exciting radiation [1–3]. This up-conversion luminescence can arise from photoexcited pairs and triads as well as multiphoton absorption at a single ion [3]. Efficient visible-light generation by infrared-light excitation in optical fiber was first reported in 1978 [4]. Since then there has been widespread interest in frequency up-conversion of infrared radiation into visible light in glass fiber owing to its simple experimental configuration and practicality [5]. Materials exhibiting efficient infrared-to-visible up-conversion have many important applications, such as display, data storage, optical communication, and ultrashort pulse generation in the visible and violet regions [6, 7]. The up-conversion properties of various lanthanide ions in a wide range of glassy and crystalline hosts, such as silica glass [8, 9] and heavy metal fluoride and chloride glasses [10–14], have been extensively examined. But the infrared-to-visible up-conversion in phosphate host glass received little attention [15]. In this paper, phosphate host glasses doped with various Er^{3+} ion concentrations have been prepared. Absorption spectra in the wavelength range of 300–1600 nm and fluorescence spectra near 1.53 μm of the Er^{3+}-doped phosphate glass with different doping concentrations have been recorded. The relationship between fluorescence intensity and the doped Er^{3+} ion concentration has been given. Fibers have been drawn from the 0.75 mol% Er^{3+}-doped phosphate glass. Attenuation of the fiber in the wavelength band ranging from 1200 to 1600 nm has been measured and the results indicate that the fiber we used for up-conversion experiments is of good optical quality. Efficient up-conversion from a wavelength of 1.064 μm of a pulsed Nd:YAG laser into visible (green and red) radiation has been performed in this phosphate fiber.

1 Experiments

The basic glass composition was determined according to the P_2O_5–BaO–R_2O (R = Li, Na and K) phase diagram. The addition of Al_2O_3 is expected to alter the glass's ability for fiber-drawing, and the addition of PbO is expected to improve the glass's optical properties. Thus, the composition P_2O_5 (56.0 mol%), BaO (15.5 mol%), Li_2O (7.5 mol%), Na_2O (3.0 mol%), K_2O (10.0 mol%), Al_2O_3 (7.0 mol%) and PbO (1.0 mol%) has been chosen for fiber cladding glass. Glasses with a further doping of erbium in the above composition have been used for the required fiber core glass. The doped Er^{3+} ion concentrations are from 0.05 to 1.25 mol% at a concentration interval of 0.3 mol%. To prepare these phosphate glasses with five Er^{3+}, the mixtures of starting oxide materials were melted in a quartz crucible at about 1150°C. O_2 gas was passed into the furnace during melting to eliminate any water impurities. Under such conditions, the loss due to

volatilization can be reduced to its minimal value, and the reaction can be completed without contamination by water impurity.

Fiber preforms were prepared from the above composition by the rotational casting method [16]. The high-temperature cladding glass melt (1000°C) was poured into a 15 cm long cylindrical iron mould which was preheated at around 400°C, and was then rotated at speeds $\geqslant$ 3000 rot./min. A highly concentric phosphate cladding glass tube whose inner diameter was precisely controlled by the initial volume of injected glass melt was thus obtained. There was no detectable variation in wall thickness along the entire length of the glass tube, and no bubbles were observed. The core phosphate glass was next transferred into the tube by pouring at high temperature the core glass melt down a phosphate glass rod in order to avoid bubble formation. The as-prepared fiber preforms were drawn into fibers using a resistance ring furnace with a localized heat zone of about 8 mm long. The fiber-drawing temperature was set at 650 $\pm$ 5°C. Fibers with an outer diameter of about 100 μm in which the core diameter is about 68 μm have been drawn. The Numerical Aperture (NA) of these fibers is about 0.155.

Fluorescence spectra of these glasses were measured by a grating monochromator. A xenon lamp was used as the light source. Its output light passed though a filter, and was then directly focused onto the glass sample. A GDB-240 photomultiplier tube was used as the detector. The fluorescence spectra were recorded by an X–Y recorder. The absorption spectrum of the phosphate glass in the range of 300–1600 nm was measured with a Perkin-Elmer model Lamda-9 full spectral spectrophotometer. Attenuation spectra of the phosophate-glass fiber were measured through a conventional fiber-cutting method. Light from a 30 W WBr lamp was focused into a monochromator, and was then injected into the glass fiber by a light-injector. The light power signal from the other end of the fiber was collected by a short-wavelength low-temperature infrared TeCdHg detector. The measured results were processed with a computer. A light-amplification system was used to raise the signal/noise ratio due to the weak light signal emanating from the fiber.

Up-conversion experiments were performed in a 45 cm long 0.75 mol% Er^{3+}-doped phosphate-glass fiber. A Q-switched and mode-locked Nd : YAG laser was used as an excitation source. The laser delivered about 100 ps mode-locked pulses at a 100 MHz repetition rate, modulated by a 1.2 kHz frequency Q-switching. The laser's maximal average output powers were 2 W at 1.064 μm. The output light of the laser was first beam-split. One beam of the light was used for power monitoring. The other beam was focused by a 10 × objective lens directly into the fiber. The output light from the other end of the fiber was then focused into a monochromator. The emission spectra were recorded with the monochromator.

2 Results and discussion

The fluorescence spectra near 1.53 μm of the above five as-prepared phosphate glasses with Er^{3+}-doping concentrations from 0.05 to 1.25 mol% are shown in Fig. 1. The relationship between the peak value of fluorescence intensity and Er^{3+} concentration is shown in Fig. 2. The fluorescence intensity first increases as the doped erbium ion concentration increases. Then the fluorescence intensity reaches a maximum at an Er^{3+} concentration of about 0.75 mol%, according to the experimental curve shown in Fig. 2. Over this doping concentration, the fluorescence intensity decreases as the doped erbium ion concentration decreases, due to the doped solute concentration quenching. From Fig. 2, the phosphate glass with a doping concentration of 0.75 mol% Er^{3+} ions was chosen as the composition for core glass, which was used in the following experiments. Figure 3 shows the absorption spectrum of the 0.75 mol% Er^{3+}-doped phosphate glass. This absorption spectrum was recorded from 300 to 1600 nm and was measured at 300 K. The electronic levels reached from the $^4I_{15/2}$ ground level can be identified from the recorded absorption spectrum and are listed in Table 1. From the absorption spectrum, three important absorption bands, $^4I_{15/2} \rightarrow {}^4I_{13/2}$ (1.53 μm), $^4I_{15/2} \rightarrow {}^4I_{11/2}$ (977 nm), and $^4I_{15/2} \rightarrow {}^4I_{9/2}$ (797 nm), evidently exist. The largest absorption band is the $^4I_{15/2} \rightarrow {}^4I_{13/2}$ (1.53 μm) band. In the following up-conversion experiments, the absorption band at a wavelength of 977 nm was used to decide the excitation wavelength. In this absorption, the maximal absorption occurred at a wavelength of 977 nm with an

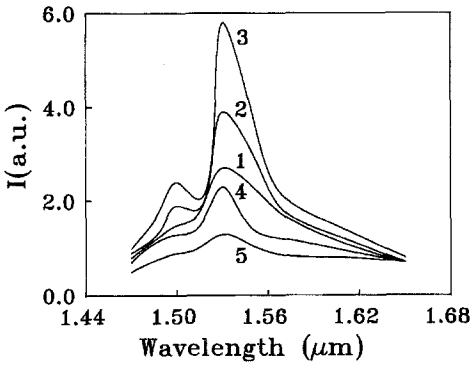

Fig. 1. Fluorescence spectra of the Er^{3+}-doped phosphate glasses measured at room temperature (*1*, 0.05 mol%; *2*, 0.35 mol%; *3*, 0.65 mol%; *4*, 0.95 mol%; *5*, 1.25 mol%)

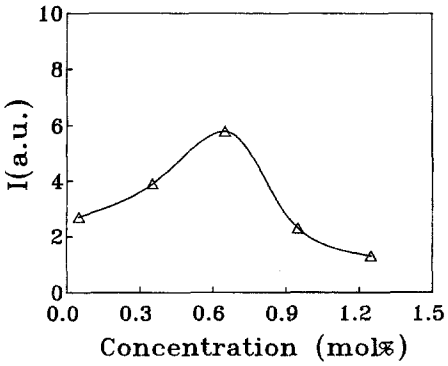

Fig. 2. The relationship between fluorescence intensity and Er^{3+} ion concentration

absorption coefficient of about 27%. But the band extends to low frequencies over a wavelength of 1.1 μm. At a wavelength of 1.064 μm, which is the output wavelength of our excitation source of a Q-switched and mode-locked Nd:YAG laser, the absorption coefficient is about 13%. The results show that the 1.064 μm excitation is less beneficial. The attenuation spectrum in the wavelength range of 1200–1600 nm of a 45 cm length of fiber (NA = 0.155) is shown is Fig. 4. The attenuation curve is similar to the results of erbium-doped silica fiber in [17]. The attenuation of our fiber is at the same order as their results. At a wavelength of 1.53 μm, the attenuation of our fiber is about 12.8 db/m, which is only slightly higher than the result of about 10.2 db/m in [17]. The result of attenuation shows that this 0.75 mol% Er^{3+}-doped phosphate fiber drawn with the above procedure is of good optical quality for further up-conversion experiments.

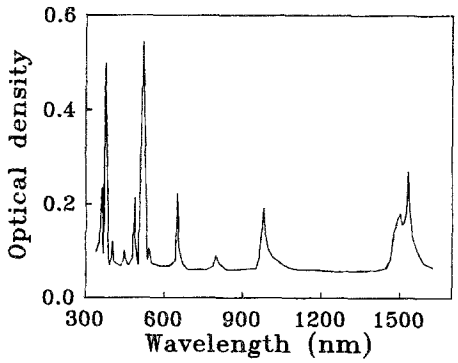

Fig. 3. Absorption spectrum of the 0.75 mol% Er^{3+}-doped phosphate glass

Table 1. Electronic levels reached from the $^4I_{15/2}$ ground-state level in 0.75 mol% Er^{3+}-doped phosphate glass

E [cm^{-1}]	Level	E [cm^{-1}]	Level
27501	$^2G_{9/2}$	19275	$^2H_{11/2}$
26525	$^4G_{11/2}$	18437	$^4S_{3/2}$
24667	$^2H_{9/2}$	15394	$^4F_{9/2}$
22625	$^4F_{3/2}$	12547	$^4I_{9/2}$
22242	$^4F_{5/2}$	10235	$^4I_{11/2}$
20559	$^4F_{7/2}$	6524	$^4I_{13/2}$

The up-conversion luminescence spectrum of the 45 cm long Er^{3+}-doped phosphate fiber in the range of 450–700 nm was measured with a 1.064 μm, laser excitation, as shown in Fig. 5. The laser's average output power used is about 1 W. In the visible region there are two signal bands emanating from the fiber. One is a red light signal peaking at 667 nm with a nearly 8 nm bandwidth spectrum. The other is a green light signal peaking at 547 nm with a 5.5 nm bandwidth spectrum and asymmetric toward high frequencies. The 667 nm red signal was relatively weak, whereas the 547 nm green light was very intense. The 547 nm fluorescence band is wider than the 667 nm band, and has an observable fluorescence output at 532 nm. It might be due to some other nonlinear optical processes such as Second Harmonic Generation (SHG) in fiber, which might influence up-conversion fluorescence measurements. The weak 532 nm fluorescence output is probably due to the short length of the fiber we used (45 cm long, in most published experiments of SHG in fibers, the lengths of fibers were several to tens of meters). In our experiments, when the average infrared excitation power is 1 W, the output powers of the two 547 and 667 nm visible bands are 178 and 42 μW, respectively. Thus, the fluorescence up-conversion efficiencies of the two bands are 1.78×10^{-2}% and 4.2×10^{-3}%, respectively. They are higher than that obtained in Er^{3+}-doped silica fiber [9]. In their experiments, three fluorescence bands, 467, 546 and 667 nm, were obtained in a 40 cm long fiber with 1.064 μm excitation. Their corresponding up-conversion efficiencies were 4×10^{-4}%, 1×10^{-2}% and 3×10^{-3}%, respectively. In our experiments no 467 nm blue signal was measured.

Figure 6 shows the variation of fluorescence intensities of the two bands as the excitation power. A typical logarithmic linear relationship between fluorescence intensity and excitation power is obtained. For the line corresponding to 547 nm green light, its slope is 1.96, which nearly equals 2 (power dependence). This power dependence indicates that the generation of 547 nm green light is due to two-photon absorption at a single ion. In fact, in the

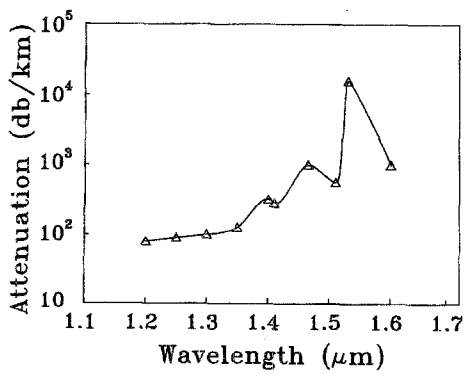

Fig. 4. Attenuation spectrum of the 0.75 mol% Er^{3+}-doped phosphate-glass fiber

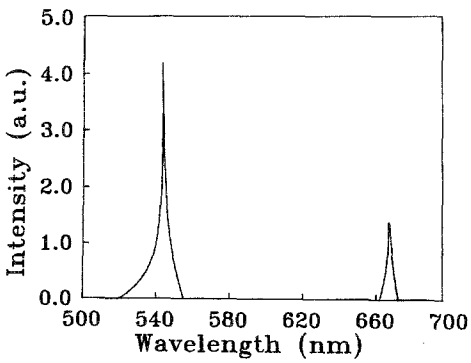

Fig. 5. Up-conversion luminescence spectra of the Er^{3+}-doped phosphate-glass fiber

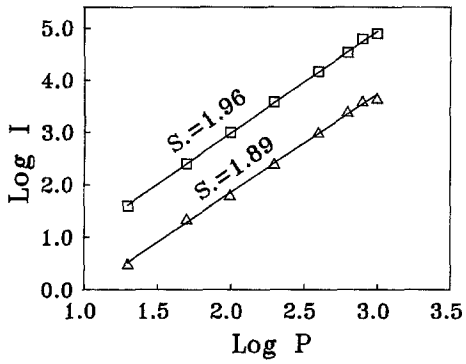

Fig. 6. Logarithmic linear relationship between fluorescence intensity and excitation power

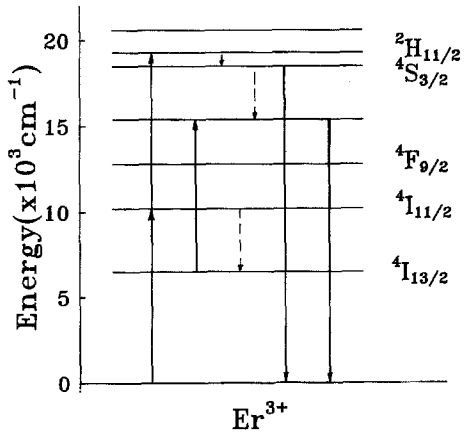

Fig. 7. Er^{3+} energy-level diagram in the Er^{3+}-doped phosphate glass

0.75 mol% Er^{3+}-doped phosphate-glass fiber, a low level of doped Er^{3+} ion concentration indicates that it is impossible that the Er^{3+} ions tend to form pairs or aggregates in this glassy sample, whereas a mechanism of a two-photon absorption at a single ion is far more compatible with our observed fluorescence emission results. The process of the two-photon absorption at a single ion is sequential as shown below;

$$^4I_{15/2} \rightarrow (h\nu)^4I_{11/2} \rightarrow (h\nu)^2H_{11/2}.$$

The fluorescence emission features can be assigned to the $^2H_{11/2}$, $^4S_{3/2}$ and $^4F_{9/2}$ states as indicated in the energy-level diagram in Fig. 7. Under the excitation of a 1064 nm laser, an Er^{3+} ion was excited from the ground-state level $^4I_{15/2}$ to $^2H_{11/2}$ through two-photon absorption. Then those Er^{3+} ions at the $^2H_{11/2}$ level might rapidly non-radiatively decay to the substable level $^4S_{3/2}$ through Multi-Phonon Relaxation (MPR). Thus, a radiative transition from $^4S_{3/2}$ and terminating on the ground level $^4I_{15/2}$ gives the most intense green 547 nm fluorescence, as shown in Fig. 7. In Fig. 6, the slope of the line corresponding to 667 nm red light is 1.89, which is slightly smaller than 2. The result also confirms that the generation of the 667 nm light is primarily caused by a two-photon absorption fluorescence, but some other multi-photon absorption process may contribute to the generation of the red 667 nm light. Er^{3+} ions were first excited to $^2H_{11/2}$ through a two-photon absorption at a single Er^{3+} ion. Then these ions decay to the $^4S_{3/2}$ level and further decay to the $^4F_{9/2}$ level through MPR. Thus, the red 667 nm signal is the $^4F_{9/2} \rightarrow {}^4I_{15/2}$ up-conversion fluorescence. The deviation from power dependence of the 667 nm red light shows the complexity of the up-conversion process. One of the other possible processes, as shown in Fig. 7, may contribute to the $^4F_{9/2}$ level population. The process is that some ions at level $^4I_{11/2}$, which were excited only with the Ground-State Absorption (GSA), nonradiatively decay from the level $^4I_{11/2}$ to the level $^4I_{13/2}$ through MPR, and then transition from the $^4I_{13/2}$ to the $^4F_{9/2}$ level occurs through absorption of another infrared photon with a mechanism of the Excited-State Absorption (ESA). From Fig. 6, the up-conversion mechanism for both emission bands exhibits an average power threshold of nearly 100 mW for a 45 cm length of phosphate-glass fiber. Together with the up-conversion fluorescence efficiencies, 1.78×10^{-2}% and 4.2×10^{-3}% for the green (547 nm) and the red (667 nm) light, respectively, obtained in the fiber, we can compare our results with that obtained in [18]. In [18], a threshold of approximately 30 mW average power was obtained in a 20 m length of pure SiO_2-core fiber. The maximal conversion efficiency they obtained was 0.5% for fluorescence output. Their results are relatively better than our results. But our fiber is shorter than the fiber they used. This comparison shows that the Er^{3+}-doped phosphate-glass fiber might have some advantages for constructing a compact up-conversion fiber laser. Further works in our experiments are to use CW 980 nm laser excitation. The usage of 980 nm pumping should be more practical for constructing a compact fiber laser, and more efficient due to the fact that the $^4I_{11/2} \rightarrow {}^4I_{15/2}$ absorption transition of Er^{3+} ion is at a wavelength of about 980 nm, as shown in Fig. 3.

3 Conclusion

In conclusion, we have measured the absorption spectrum and the fluorescence spectra of phosphate glasses with different erbium doping. The decrease of fluorescence intensity when Er^{3+} concentration exceeds 0.75 mol% accounts for concentration quenching. The attenuation of the fiber drawn from 0.75 mol% Er^{3+}-doped phosphate glass at 1.53 μm is 12.8 db/m. Under 1.064 μm excitation, the green (547 nm) and the red (667 nm) fluorescences through infrared-to-visible up-conversion have been observed in the fiber. The two fluorescence signals are referred to as $^4S_{3/2} \rightarrow {}^4I_{15/2}$ and $^4F_{9/2} \rightarrow {}^4I_{15/2}$ two-photon upconversion fluorescence, respectively. 178 μW (547 nm) green and 42 μW (667 nm) red fluorescences were obtained with an average excitation power of 1 W. The up-conversion efficiencies are 1.78×10^{-2}% and 4.2×10^{-3}%, respectively.

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