1 March 1995

OPTICS COMMUNICATIONS

ELSEVIER

Optics Communications 115 (1995) 110–114

Upconversion of 1.064 μm Nd:YAG laser pulses into intense visible light in erbium-doped phosphate fibers

Ya-lin Lu, Yan-qing Lu, Hui Fang, Nai-ben Ming

Laboratory of Solid State Microstructures, Nanjing University, Nanjing 210008, China

Received 14 April 1994; revised version 28 November 1994

Abstract

Absorption spectra and fluorescence spectra in Er^{3+}-doped phosphate glasses have been measured. Some emission parameters, such as emission cross section, spontaneous emission probability, and fluorescence linewidth of the Er^{3+}-doped phosphate glass, have been calculated. Upconversion of 1.064 μm Nd:YAG laser pulses into intense green 547 nm and red 667 nm light in a Er^{3+}-doped phosphate glass fiber has been achieved. Fluorescence efficiencies of the two signals, green 547 nm and red 667 nm fluorescences, are 1.78×10^{-2}% and 4.2×10^{-3}%, respectively. The two signals are refered to ${}^4S_{3/2}\rightarrow{}^4I_{15/2}$ and ${}^4F_{9/2}\rightarrow{}^4I_{15/2}$ radiative transitions by two-photon absorption fluorescence.

1. Introduction

Efficient visible light generation by infrared light excitation in optical fibers was first reported in 1978 [1]. Since then there have been widespread interest in frequency upconversion of infrared radiation into visible wavelength light in glass fiber owing to its simple experimental configuration and practicality [2]. Recent demonstrations [3–6] of room-temperature upconversion lasers have also stirred interest in their potential as practical sources of short wavelength radiation for display and data storage applications, as well as for communications and ultrashort pulse generation at visible and ultraviolet wavelengths [7,8]. Upconversion is a process which converts long-wavelength radiation into short-wavelength radiation by a multiphoton mechanism. Excited state absorption (ESA), addition of photons by energy transfer, and photon avalanche absorption (PAA) [9] are three main processes of upconversion [10]. Materials exhibiting efficient infrared to visible upconversion have many important applications. The upconversion properties of various lanthanide ions in a wide range of glassy and crystalline hosts, such as silica glass [11,12] and heavy metal fluoride glasses [13–17], have been extensively examined over the past 25 years. Other materials such as some oxides, sulfides, fluorides and oxyhalides doped with various Er^{3+} concentrations have also been extensively studied in the past years [10]. But the infrared to visible upconversion in phosphate host glass has received little attention [18]. In this letter, phosphate glass doped with 0.75 mol% Er^{3+} have been prepared. Some optical properties of the glass, such as absorption spectrum of in the range of 300 nm to 1600 nm and fluorescence spectrum near 1.53 μm were measured. According to these optical properties, some emission characteristic parameters, such as spontaneous emission probability, emission cross section and effective fluorescence linewidth, have been calculated. A fiber drawn from the 0.75 mol% Er^{3+}-doped phosphate glass has been used to measure infrared to visible upconversion when excited by a 1064 nm Nd:YAG laser. Efficient red 667 nm and

0030-4018/95/$09.50
SSDI 0030-4018(94)00679-2

green 547 nm upconversion luminescences have been measured.

2. Experimental arrangement

Phosphate glass used for fiber cladding composed of 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%) in molar amounts. Glass with further doping of 0.75 mol% Erbium in above composition has been used for required fiber core glass. This Erbium molar concentration corresponds to Er^{3+} ion concentration of about 0.69×10^{20} ions/cm^3. To prepare the Phosphate glass, the mixtures of starting materials were melted in quartz crucible at about 1150 °C. O_2 gas was passed into the furnace during melting to eliminate any water impurities. Fibers were drawn from these as-prepared glass. In our experiments below, a 45 cm long fiber with outer diameter of about 100 μm and the core diameter of about 68 μm has been used. The numerical aperture (N.A.) of the fiber is about 0.155.

Absorption spectra of the glass were recorded with a PERKIN ELMER model LAMDA-9 full-spectra spectrophotometer in the range of 300 nm to 1600 nm. Fluorescence spectra of the glass were measured by a grating monochromator. Xenon lamp was used as a light source. Its output light passed through a filter, then was directly focused onto the glass sample. The generated fluorescence light was collected by a grating monochromator. A GDB-240 photomultiplier tube was used as a detector. The fluorescence spectra were recorded by a X–Y recorder.

A Q-switched and mode-locked Nd:YAG laser was used as a excitation source in upconversion experiments. 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 maximum average output power as 2 W at 1.064 μm. The output light of the laser was firstly beam splitted. One beam of the light was used for power monitoring. The other beam was directly coupled into the fiber by a 10× objective lens. The output light from the fiber's other end was then focused into a monochromator. Thus the emission spectra were recorded with the monochromator.

3. Results and discussions

Fig. 1 shows the 0.75 mol% Er^{3+}-phosphate glass's absorption spectrum in the wavelength range of 300 nm to 1600 nm measured at 300 K. The electronic levels reached from $^4I_{15/2}$ ground state level can be identified from the recorded absorption spectrum and are listed in Table 1. The Er^{3+} fluorescence spectrum of the phosphate glass of $^4I_{13/2} \to {}^4I_{15/2}$ transition is shown in Fig. 2. The central wavelength λ_p of the fluorescence spectrum is 1.536 μm. The energy of Er^{3+} $^4I_{13/2} \to {}^4I_{15/2}$ emission band measured at room temperature is 6510 cm^{-1} which is slightly different from absorption transition energy $^4I_{15/2} \to {}^4I_{13/2}$, as listed in Table 1.

According to Judd-Ofelt theory [19], the expression for absorption line strength of absorption transition $J \to J'$ is

$$S(JJ') = \sum_t \Omega_t \, U^{(t)}(JJ')^2 . \tag{1}$$

Here $t=2$, 4, 6. $U^{(t)}(JJ')$ is a reduced matrix element of the irreducible tensor operator of rank t. For

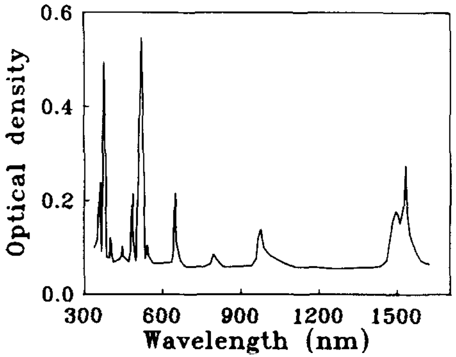

Fig. 1. Absorption spectrum in 0.75 mol% Er^{3+}-doped phosphate glass measured at temperature of 300K.

Table 1
Electronic levels reached from $^4I_{15/2}$ 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	$^4I_{13/2}$

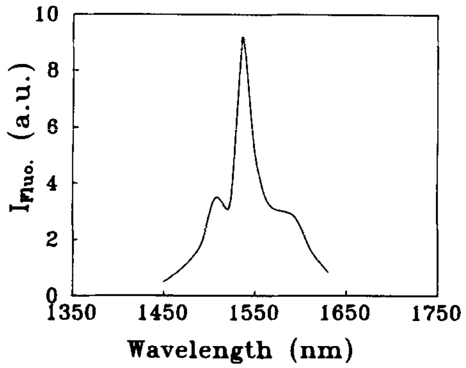

Fig. 2. Fluorescence spectrum near 1.53 μm of the Er^{3+}-doped phosphate glass measured at room temperature.

a given Er^{3+} ion, $U^{(t)}(JJ')$ varies only slightly from medium to medium, it can be considered unchanged. $U^{(t)}(JJ')$ for absorption transitions from the ground state of Er^{3+} ion or for transitions from excited states can be found in reference 20. Ω_t ($t=2, 4, 6$) are the intensity parameters which is only dependent on the properties of used host material. The absorption line strength $S(JJ')$ is associated with the integrated absorption coefficient $K(\lambda)$, which can be calculated from absorption spectrum, by the formula

$$K(\lambda)=S(JJ')8\pi^3e^2N_0\lambda_a(n^2+2)^2/(27cnh(2J+1)) . \quad (2)$$

The emission line strength of emission transition $J'\to J$, which is also determined by Eq. (1), is associated with the spontaneous emission probability $A(J'J)$ by

$$A(J'J)=S(J'J)64\pi^4e^2n(n^2+2)^2/(27(2J+1)\lambda_a^2) . \quad (3)$$

In Eqs. (2) and (3), h, e, and c are Plank's constant, the electronic charge and the light velocity, respectively. J and n are angular momentum and the material's refractive index. N_0 is the number of Er^{3+} ions per unit volume. λ_a is the mean wavelength that corresponding to the $J\to J'$ transition.

Thus according to the measured integrated absorption coefficient of various absorption bands shown in Fig. 1, we can calculate the absorption line strength $S(JJ')$ of various corresponding absorption transitions $J\to J'$ by using Eq. (2). Then with the uasage of the found $U^{(t)}(JJ')$ for absorption transitions $J\to J'$ from ground state of Er^{3+} ion [20] the phosphate host glass's intensity parameters Ω_t ($t=2, 4, 6$) can be calculated by Eq. (1). Further using the found $U^{(t)}(J'J)$ for transitions from excited states ($J'\to J$) [20] *and the above calculated* Ω_t, we can thus calculate emission line strength $S(J'J)$ also by using Eq. (1), and can calculate the spontaneous emission probability $A(J'J)$ through Eq. (2).

From the recorded fluorescence spectrum shown in Fig. 2, we have

$$\Delta\lambda_{\rm eff}=\int I\,d\lambda/I_p , \quad (4)$$

where $\Delta\lambda_{\rm eff}$ is effective fluorescence linewidth. I_p is the corrected maximal experimental fluorescence intensity. λ is fluorescence wavelength. With the usage of previously calculated spontaneous emission probability $A(J'J)$, the stimulated emission cross section of the 0.75 mol% Er^{3+}-doped phosphate glass thus could be calculated according to the formula [21]

$$\sigma=\lambda_pA(J'J)/(8\pi cn^2\Delta\lambda_{\rm eff}) , \quad (5)$$

where λ_p is the central wavelength of fluorescence spectrum. Table 2 lists our calculated intensity parameters Ω_t, spontaneous emission probability $A(J'J)$, effective fluorescence linewidth $\Delta\lambda_{\rm eff}$ and the stimulated emission cross section σ, of the phosphate glass doped with 0.75 mol% erbium.

Upconversion luminescence spectra of the Er^{3+}-doped phosphate fiber in the range of 450 nm to 700 nm were measured with 1.064 μm excitation, as shown in Fig. 3. The laser's average output power is 1 W. In the visible-wavelength region there are two signal bands emanating from the tested fiber. One is red light signal peaked at 667 nm with a nearly 8 nm bandwidth spectrum. The other is green light signal peaked 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. In our experiments, when the average infrared excitation power is 1W, the out-

Table 2
Some emission characteristic parameters of the Er^{3+}-doped phosphate glass

Ω_2	Ω_4 ($\times10^{-20}$)	Ω_6	$A(J'J)$ (s^{-1})	$\Delta\lambda_{\rm eff}$ (nm)	σ ($\times10^{-21}$cm^2)
8.10	2.20	1.85	172	60.2	9.0

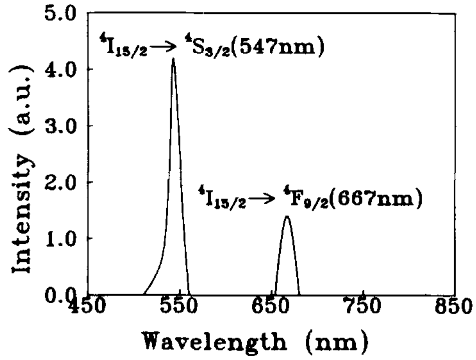

Fig. 3. Upconversion luminescence spectra of the Er^{3+}-doped phosphate glass fiber.

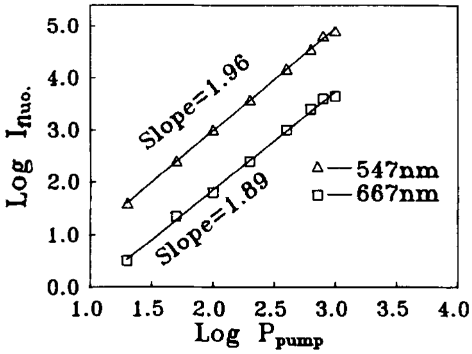

Fig. 4. Logarithmic linear relationship between fluorescence intensity and excitation power.

put power of the two 547 nm and 667 nm visible bands are 178 μW and 42 μW, respectively. Thus the upconversion efficiencies of the two bands are 1.78×10^{-2}% and 4.2×10^{-3}%, respectively. The results we obtained are slightly better than what were obtained in Er^{3+}-doped silica fibre [12]. In Ref. [12], three fluorescence bands, 467 nm, 546 nm and 667 nm, were obtained in a 40 cm long fibre also with 1064 nm excitation. Their corresponding upconversion efficiencies were 4×10^{-4}%, 1×10^{-2}% and 3×10^{-3}%, respectively. In our experiments, no 467 nm blue signal was measured.

Fig. 4 shows the variation of fluorescence intensity of the two bands as the pumping 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 and nearly equals 2. It confirms that the generation of 547 nm green light is caused by two-photon absorption fluorescence. Fig. 5 shows the energy level

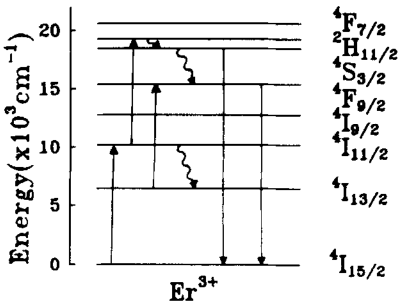

Fig. 5. Er^{3+} energy level diagram in the Er^{3+}-doped phosphate glass.

diagram of Er^{3+}-doped phosphate glass. Under the excitation of 1064 nm laser, Er^{3+} ions were excited from ground state level $^4I_{15/2}$ to $^2H_{11/2}$ through two-photon absorption. This process include the ground state absorption (GSA) ($^4I_{15/2}\rightarrow{}^4I_{11/2}$) and the excited state absorption (ESA) ($^4I_{11/2}\rightarrow{}^2H_{11/2}$). Then those Er^{3+} ions at $^2H_{11/2}$ level might rapidly nonradiatively decay to the substable level $^4S_{3/2}$ through multiphonon relaxation (MPR). Thus a radiative transition starting from the $^4S_{3/2}$ level and terminating on the ground level $^4I_{15/2}$ gives the most intense green 547 nm fluorescence, as shown in Fig. 5. In Fig. 4, the slope of the line corresponding to 667 nm red light is 1.89. It slightly smaller than 2. The slope of 1.89 confirms that the generation of 667 nm light is primarily caused by two-photon absorption fluorescence. Er^{3+} ions were firstly excited to $^2H_{11/2}$ through two-photon absorption. Then they decay to $^4S_{3/2}$ level and further decay to $^4F_{9/2}$ level through MPR. Thus the red 667 nm signal is the $^4F_{9/2}\rightarrow{}^4I_{15/2}$ upconversion fluorescence. That the deviation of slope of the line from 2 shows the complexity of the upconversion process. One of the other processes, as what was shown in Fig. 5, may contribute to the $^4F_{9/2}$ level population. The process is nonradiative decay from level $^4I_{11/2}$ to level $^4I_{13/2}$ through MPR after the excitation from the ground state level $^4I_{15/2}$, and then from $^4I_{13/2}$ to $^4F_{9/2}$ level through absorption of another infrared photon. The mechannism of energy transfer, which is the important process contributive to upconversion, was considered to be not existed in our phosphate glass fibers, due to our lower erbium doping level in the fiber (i.e. not exceeding 1 mol%). Lower doping level results in large distance between the nearest excited ions. Thus energy transfer between the two excited ions was hampered. Further works in our experiments are to use cw 980 nm laser diode as excitation source instead of using 1064 nm excitation. According to the absorption spectrum shown in Fig. 1, the wavelength of 1064 nm is on the red side of the spectrum, not at the spectrum's center. The usage of 980 nm pumping should be more practical and more efficient.

4. Conclusions

The absorption spectrum and fluorescence spectrum in 0.75 mol% erbium-doped phosphate glass have been measured. Some emission characteristic parameters of the glass such as emission cross section, spontaneous emission probability, and fluorescence linewidth have been calculated. The results shows that the phosphate glass fibers are favorable for infrared-to-visible upconversion. Under 1.064 μm excitation, the green 547 nm and the red 667 nm fluorescences have been observed in the fiber. The two fluorescence signals are refered to $^4S_{3/2}$–$^4I_{15/2}$ and $^4F_{9/2}$–$^4I_{15/2}$ two-photon upconversion fluorescence, respectively. 178 μW 547 nm green light and 42 μW 667 nm red light were obtained with average excitation power of 1W. The upconversion efficiencies are 1.78×10^{-2}% and 4.2×10^{-3}%, respectively.

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