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Journal of Luminescence 102–103 (2003) 91–95

JOURNAL OF LUMINESCENCE

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Spectroscopic properties of heavy metal oxide glasses doped with erbium

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Abstract

Glasses of heavy metal oxide (Bi_2O_3–PbO–Ga_2O_3) doped with different concentrations of Er^{3+} are presented. Measurements of absorption, emission and fluorescence lifetime at 1532 nm are shown. Measured lifetimes showed a maximum value of 3.94 ms for the glass with 0.50 wt% of Er_2O_3. The increase of lifetimes at low Er_2O_3 concentration was attributed to radiation trapping whereas the subsequent decrease to concentration quenching. Interesting spectroscopic properties for laser action at 1532 nm were observed for the sample with 0.1 wt% of Er_2O_3: fluorescence lifetime of 3.76 ms, emission cross-section of $0.69 \times 10^{-20}\,cm^2$ and effective line width of 68.7 nm.

PACS: 42.70. –a

Keywords: Laser; Glasses; Erbium; Fluorescence

1. Introduction

The aim of this work is to present spectroscopic properties in a heavy metal oxide glass (Bi_2O_3–PbO–Ga_2O_3) doped with different concentrations of Er_2O_3. This host of heavy metal oxides, discovered [1] in 1985, is of great interest in optoelectronic devices due to its properties, namely extended infrared transmission (up to 8 μm), high refractive index (of about 2.5) and nonlinear optical behavior. The literature published the use of Pr^{3+}, Dy^{3+} and Tm^{3+} in this host [2,3]. We reported the use of Nd^{3+} and Yb^{3+} [4,5]. In the case of Er^{3+} the literature reported the study of the 2700 nm emission [6] and this work deals with the 1532 nm one. This last emission coincides with the third optical communication window (being of interest in the area of telecommunication). This is the transition that provides amplification near 1540 nm in erbium doped fiber amplifiers and radiation for eye safe remote sensing applications.

2. Experiment

The samples were prepared adding 0.05, 0.10, 0.50, 1.00 and 2.00 wt% of Er_2O_3 to the following

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PII: S0022-2313(02)00497-0

glass matrix: 42.12Bi_2O_3–45.91PbO–11.98Ga_2O_3 (wt%). After melting the powders in Pt crucibles at 1000°C, for 1 h and a half, they are poured into pre-heated brass molds, annealed for 3 h at 300°C and then cooled inside the furnace up to room temperature. The refractive index of 2.52 was determined by means of the "apparent depth method", that relates the physical thickness to its optical thickness (apparent thickness). The optical thickness is measured with a 10 × objective lens of a Carl Zeiss microscope. Absorption spectrum at room temperature was recorded with a Cary Spectrometer in the 920–1120 nm range. The density of 7.0 g/cm^3 was measured with the Archimedes method. Emission spectrum was measured using an excitation beam of 968 nm from a AlGaAs laser diode (Optopower A020). The emission was analyzed with a 0.5 m monochrometer (Spex), detected by a Ge detector and intensified with a EG&G7220 lock-in amplifier. The lifetime of the excited Er^{3+} ions was measured using a pulsed laser excitation (4 ns) at 800 nm from an OPO pumped by a frequency doubled Nd:YAG laser (Quantel) with an InSb detector with specific line filters using a signal processing Box-Car averager (PAR 4402).

3. Results and discussion

For the absorption measurements we obtained the spectrum shown in Fig. 1. In this spectrum we can observe four peaks related to the absorption of Er^{3+}: 652, 798, 977 and 1532 nm regarding the $^4F_{9/2}$, $^4I_{9/2}$, $^4I_{11/2}$ and $^4I_{13/2}$ transitions, respectively. The peak of approximately 2250 nm refers to the OH band. The emission spectra are demonstrated in Fig. 2. We can observe that there is a quenching for concentrations higher than 1.00 wt%. Besides the peak at 1532 nm related to the samples doped with 0.05 and 0.10 wt% has a different shape when compared to those of the other samples whose peaks are broadened as the concentration increases and this may be attributed to the presence of trapps. Decay curves from $^4I_{13/2} \rightarrow {}^4I_{15/2}$ transition were almost exponential. So the nonradiative transition from the $^4I_{13/2}$ level is mainly due to the fast energy migration among donors that results in fast energy transfer to the quenching acceptors. The fluorescence lifetime measured were fitted to exponential decay and the results are shown in Fig. 3. We can observe in this figure that from 0.05 wt% up to 0.50 wt% of Er_2O_3, there is an increase of the fluorescence lifetime, and from 0.50 wt% up to 2.00 wt% there is a decrease. The increase of the lifetimes at low Er_2O_3 concentration was attributed to radiation

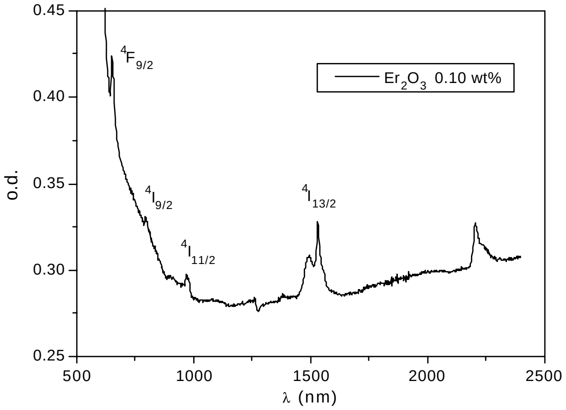

Fig. 1. Absorption spectrum at room temperature for the heavy metal oxide glass (PbO–Bi_2O_3–Ga_2O_3) doped with 0.10 wt% of Er_2O_3.

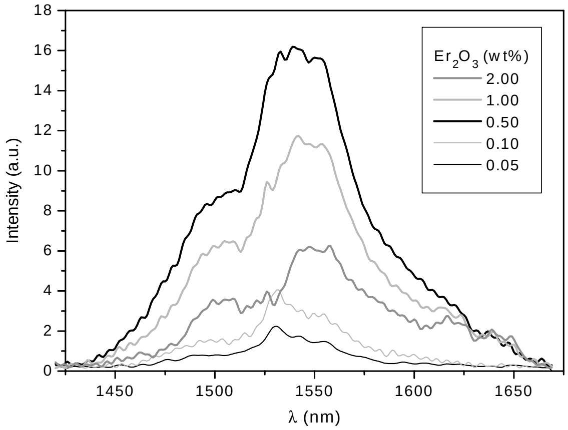

Fig. 2. Emission spectra at 1532 nm for the heavy metal oxide glass (PbO–Bi_2O_3–Ga_2O_3) doped with different concentrations of Er_2O_3.

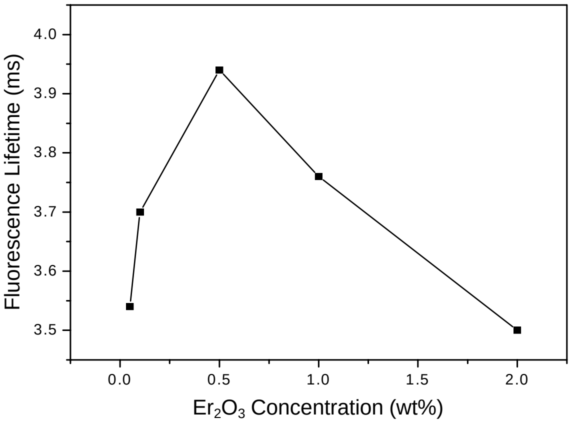

Fig. 3. Measured lifetimes of the $^4I_{13/2}$ level.

trapping [7], whereas the subsequent decrease was caused by concentration quenching.

The Judd–Ofelt parameters (Ω_t) were calculated with the expression below [with the absorption bands of the electronic transitions of Er^{3+} from the initial manifold (S,L,J) to the final manifold (S', L', J')] that equates the experimental to the calculated oscillator strength for an induced electric and magnetic dipole transitions [8]:

$$\frac{mc^2}{\pi e^2 \rho \lambda_p^2}\int k(\lambda)\,\mathrm{d}\lambda = \frac{8\pi^2 mc}{3h(2J+1)\lambda_p}\left(\frac{(n^2+2)^2 S_{ed}}{9n} + nS_{md}\right), \qquad (1)$$

where c represents the velocity of light, n the refractive index, ρ the concentration of Er^{3+} ions, λ_p the absorption peak wavelength, e and m the mass and the electron charge, $k(\lambda)$ the absorption coefficient, S_{ed} and S_{md} represent the line strengths for the induced electric and magnetic dipole transition, respectively. The line strength for the induced electric dipole (S_{ed}) transition is given by

$$S_{ed} = \sum_{t=2,4,6} \Omega_t \left|\left\langle SLJ||U^t||S'L'J'\right\rangle\right|^2, \qquad (2)$$

where $|(SLJ||U^t||S'L'J')|^2$ is the square of the matrix elements of the tensional operator U^t which connects SLJ to $S'L'J'$ states (determine from the literature [9]).

Because the magnetic dipole oscillator strength of the $^4I_{15/2} \rightarrow {}^4I_{13/2}$ transition exerts a considerable effect to the total radiative transition it has to be considered in the calculation of the Judd–Ofelt parameters. In Eq. (1), the oscillator strength for the magnetic dipole transition is given by

$$f_{md} = \frac{8\pi^2 mcS_{md}n}{3h(2J+1)\lambda_p} = f' n, \qquad (3)$$

where $f = 30.82 \times 10^{-8}$ [10] for the $^4I_{15/2} \rightarrow {}^4I_{13/2}$ transition of Er^{3+}. Considering $n = 2.52$, f_{md} is 77.7×10^{-8}. The three Judd–Ofelt parameters are determined by a least-square fitting routine that compares the measured oscillator strengths for the different Er^{3+} absorption bands with the theoretical oscillator strengths using the matrix elements tabulated in Ref. [9]. The values obtained are: $\Omega_2 = (1.74 \pm 0.07) \times 10^{-20}\,cm^2$, $\Omega_4 = (0.12 \pm 0.01) \times 10^{-20}\,cm^2$ $\Omega_6 = (0.65 \pm 0.05) \times 10^{-20}\,cm^2$.

The spontaneous emission probability of $413.1\,s^{-1}$, from the initial manifold (S, L, $J = 13/2$) to the final manifold (S',L', $J' = 15/2$) was determined with the following equation [8]:

$$A_R = \frac{64\pi^4 e^2}{3h(2J+1)\lambda^3}\left(\frac{n(n^2+2)^2 S_{ed}}{9} + n^3 S_{md}\right). \qquad (4)$$

In the equation above, λ is the emission peak wavelength.

The peak emission cross-section for the Er^{3+}, $^4I_{13/2} \rightarrow {}^4I_{15/2}$ transition is expressed as

$$\sigma_{em} = \frac{\lambda^4 A_R}{8\pi n^2 c \Delta\lambda_{EFF}}, \qquad (5)$$

where $\Delta\lambda_{EFF}$ is the effective fluorescence bandwidth. Fig. 4 presents the emission cross-section spectrum of 1532 nm for the heavy metal oxide sample doped with 0.10 wt% Er_2O_3.

Table 1 summarizes the results obtained for all the samples produced. The best spectroscopic performance is measured for the sample with 0.10 wt% of Er_2O_3: emission cross-section of $0.69 \times 10^{-20}\,cm^2$ at 1532 nm, fluorescence lifetime of 3.70 ms and emission bandwidth of 68.7 nm. Although the sample with 0.50 wt% has the highest fluorescence lifetime it cannot be considered the one with the best spectroscopic performance because of its optical inhomogeneity. Besides its peak emission cross-section at

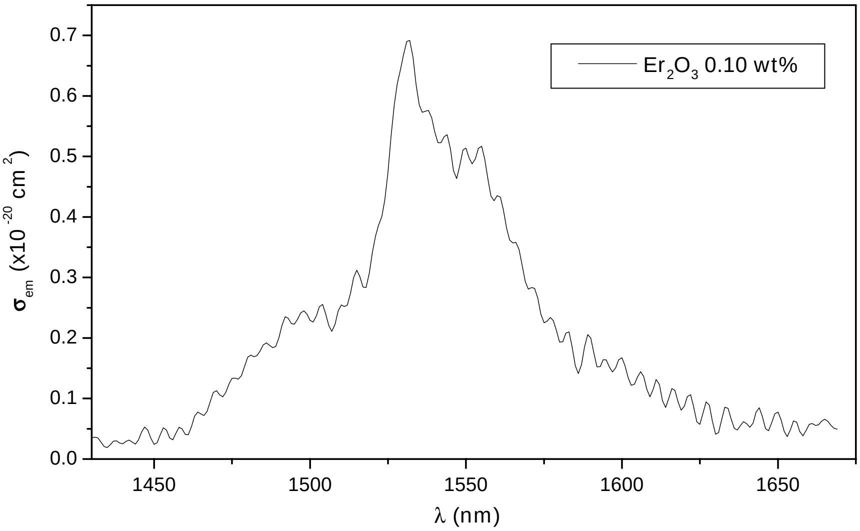

Fig. 4. Emission cross-section spectrum at 1532 nm for the heavy metal oxide glass ($PbO–Bi_2O_3–Ga_2O_3$) doped with 0.10 wt% of Er_2O_3 (peak emission cross-section of $0.69 \times 10^{-20}\,cm^2$).

Table 1
Spectroscopic properties for the heavy metal oxide glass ($PbO–Bi_2O_3–Ga_2O_3$) doped with different concentrations of Er_2O_3

Concentration of Er_2O_3 (wt%)	Fluorescence lifetime (ms) ($^4I_{13/2} \rightarrow {}^4I_{15/2}$)	σ_{em} ($\times 10^{-20}\,cm^2$) ($^4I_{13/2} \rightarrow {}^4I_{15/2}$)	Fluorescence effective line width (nm)
0.05	3.5 ± 0.2	0.67 ± 0.05	70.8
0.10	3.7 ± 0.2	0.69 ± 0.05	68.7
0.50	3.9 ± 0.2	0.52 ± 0.04	93.0
1.00	3.8 ± 0.2	0.53 ± 0.04	95.2

Table 2
Comparison of the spectroscopic parameters

Glass composition	σ_{em} ($\times 10^{-20}\,cm^2$) ($^4I_{13/2} \rightarrow {}^4I_{15/2}$)	Fluorescence lifetime (ms) ($^4I_{13/2} \rightarrow {}^4I_{15/2}$)	Refractive index
Ge–Ga–S [11]	1.05	2.9	2.15
ZBLAN [12]	0.58	9.0	1.50
Ga–La–S [13]	1.57	2.3	2.40
Silicate [14]	0.44	10.2	1.46
$PbO–Bi_2O_3–Ga_2O_3$	0.69	3.8	2.52

1532 nm is lower ($0.52 \times 10^{-20}\,cm^2$). Table 2 compares the sample doped with 0.10 wt% of Er_2O_3 with the results of recently published papers. As it can be observed, the emission cross-section of the glass presented in this work is very similar to the one of ZBLAN (a heavy metal fluoride glass) [12] and the value of the fluorescence lifetime is higher than the ones of Ge–Ga–S and Ge–La–S glasses. We remark that the refractive index has the highest value.

4. Conclusions

In this work $Bi_2O_3–PbO–Ga_2O_3$ glasses doped with Er^{3+} are studied at about 1500 nm. A good mechanical resistance under high brightness diode laser pumping (7.5 W of diode output power) was observed and a fluorescence lifetime of 0.40 ms was measured. A high refractive index of 2.52, as predicted in the literature was measured with the "apparent depth method". Measured lifetimes showed a maximum value of 3.94 ms for the glass with 0.50 wt% of Er_2O_3. The glass doped with 0.10 wt% of Er_2O_3 exhibits interesting spectroscopic properties for laser action at 1532 nm: emission cross-section of $0.69 \times 10^{-20}\,cm^2$, fluorescence lifetime of 3.76 ms and fluorescence effective line width of 68.7 nm.

Acknowledgements

We would like to thank the support from FAPESP, CAPES, Centro de Lasers e Aplicações, Laboratório de Caracterização Tecnológica—Engenharia de Minas—EPUSP and Laboratório de Sistemas Integráveis—Departamento de Engenharia Elétrica—EPUSP.

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