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Abstract

Spectroscopic properties of heavy metal oxide glasses (Bi₂O₃-PbO-Ga₂O₃) doped with Er³⁺ are presented. The literature published the use of Pr^{3+} , Dy^{3+} and Tm^{3+} in this host [1,2]. We reported, last year [3, 4], the use of Nd³⁺ and Yb³⁺. In the case of Er^{3+} the literature presented the study of the 2700nm emission and this work deals with the 1532nm one [5]. The glasses have high refractive index (of 2.52), transmission cutoff in the far infrared (at 9µm) knoop hardness of 321kg/mm^2 density and of 7.0g/cm^3 . Measurements of absorption, emission and fluorescence lifetime are shown. Measured lifetimes showed a maximum value of 3.94ms for the glass with 0.5wt% of Er₂O₃. The lifetime increase at low Er₂O₃ concentration was attributed to radiation trapping [6] whereas the subsequent decrease to concentration quenching.

Introduction

Er³⁺ doped glasses as laser material for microchip lasers and waveguide amplifiers at 1500nm have recived great attention in the past years. It offers the possibility of very significant the areas of optical applications in communications, fibre lasers, laser radar and range finding. The aim of this work is to present spectroscopic properties (at 1500nm) in glasses of heavy metal oxide (Bi₂O₃-PbO-Ga₂O₃) doped with different concentrations of Er₂O₃. This host of heavy metal oxides, discovered [7] in 1985, is of great interest in optoelectronic devices due to its properties, namely extended infrared transmission (up to 9µm), high refractive index (of about 2.5) and nonlinear optical behavior. It is known that the low vibrational frequencies of the cation-anion bonds, such as Pb-O and Bi-O allow good infrared transmission and low non radiative decay rate. Besides the high refractive index increases the radiative decay, provides large transiion crosssection and large optical nonlinearity. These properties can give rise to new laser transitions and can increase the efficiency of those already used in other glass hosts. We present the results of heavy metal oxide glasses doped with concentrations of Er_2O_3 that varies from 0.05wt% up to 2.0wt%. In the calculation of the Judd-Ofelt parameters the magnetic dipole oscillator strength of the 1500nm emission was considered because it exerts a considerable effect to the total radiative transition.

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Materials and Methods

The samples were prepared (Figure 1) adding 0.05, 0.1, 0.5, 1.0 and 2.0wt% of Er_2O_3 to the glass matrix: $42.12Bi_2O_3 - 45.91PbO - 11.98Ga_2O_3$ (wt%). After melting the powders in Pt crucibles at 1000°C, for one hour and a half, they are poured into pre-heated brass molds, annealed for 3 hours at 300° C and then cooled inside the furnace up to room temperature.



Fig. 1 – The process for the production of the samples.

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 was measured with a 10 x 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 7.0g/cm³ was measured with the Archimedes method.

Emission spectrum was determined using an excitation beam of 968 nm from a GaAlAs laser diode (Optopower A020). The emission was analyzed with a 0.5 m monochrometer (Spex) and detected by a Ge detector, intensified with a EG&G7220 lock-in amplifier (Figure 2).



Fig.2 –*Experimental procedure for the emission measurements*

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The lifetime of the excited Er^{3+} ions was measured (Figure 3) using a pulsed laser excitation (4 ns) from an OPO pumped by a frequency doubled Nd:YAG laser (Quantel) with a fast S-20 extended type photomultiplier and analyzed using a signal processing Box-Car averager (PAR 4402).



Fig. 3 – Experimental procedure for the fluorescence lifetime measurements

Results

For the absorption measurements we obtained the following spectrum (Figure 4).



Fig. 4 - Absorption spectrum for the heavy metal oxide glass (PbO- Bi_2O_3 - Ga_2O_3) doped with 0.1wt% of Er_2O_3 .

In this spectrum we can observe four picks related to the absorption of Er^{3+} : 652 nm, 798 nm, 977 nm and 1532 nm regarding the ${}^{4}\mathrm{F}_{9/2}$, ${}^{4}\mathrm{I}_{9/2}$, ${}^{4}\mathrm{I}_{11/2}$ and ${}^{4}\mathrm{I}_{13/2}$ transitions, respectively. The pick of approximately 2250 nm refers to the OH band. The emission spectra are shown in Figure 5. We can observe that there is a quenching for concentrations higher than 1.0wt%.

The results of the fluorescence lifetime measurements are presented in Figure 6.

We can observe that from 0.05wt% up to 0.5wt% of Er_2O_3 there is an increase of the fluorescence lifetime, and from 0.5wt% up to 2.0wt% there is a decrease. This increase at low Er_2O_3 concentration was attributed to radiation trapping, whereas the subsequent decrease to concentration quenching.



Fig. 5 - Emission spectra at 1532nm for the heavy metal oxide glass (PbO-Bi₂O₃-Ga₂O₃) doped with different concentrations of Er_2O_3 . (${}^4I_{13/2} \rightarrow {}^4I_{15/2}$ transition).

We could observe that there is a quenching for concentrations higher than 1.0wt%.

As a result of the fluorescence lifetime measurements we obtained the following graph (Figure 6).



Fig. 6 - Measured lifetimes of the ⁴I_{13/2} level.

We can observe that from 0.05wt% up to 0.5wt% of Er_2O_3 there is an increase of the fluorescence lifetime, and from 0.5wt% up to 2.0wt% there is a decrease. This increase at low Er_2O_3 concentration was attributed to radiation trapping, whereas the subsequent decrease to concentration quenching.

The spontaneous emission probability (A_R) and the emission cross-sections (σ_{em}) are calculated using the following equations:



where *n* represents the refractive index, *e* the electron charge, *m* the electron mass, *c* the velocity of light, Ω_2 , Ω_4 and Ω_6 the Judd-Ofelt parameters, *h* the Planck constant, λe the emission wavelength, *J*

the total momentum of the emission level and $\Delta \lambda_{eff}$ the effective linewidth.

For the emission cross-section we obtained the following result shown in Figure 7. Table 1 summarizes all the results obtained.



Fig. 7 - Emission cross-section spectrum at 1532nm for the heavy metal oxide glass (PbO- Bi_2O_3 - Ga_2O_3) doped with 0.1wt% of Er_2O_3 (peak emission cross-section of 0.605x10²⁰ cm²).

Table 1: Spectroscopic properties for the heavy metal oxide glass (PbO-Bi₂O₃-Ga₂O₃) doped with different concentrations of Er_2O_3 . ($\Omega_2 = 1.89 \times 10^{20}$ cm² $\Omega_4 = 0.31 \times 10^{20}$ cm² $\Omega_4 = 0.52 \times 10^{20}$ cm²)

$C_{111}, S_{24} = 0.51 \times 10^{-10} C_{111}, S_{26} = 0.52 \times 10^{-10} C_{111}$				
Concentration of Er_2O_3 (wt%)	Fluorescence Lifetime (ms) $({}^{4}I_{13/2} \rightarrow {}^{4}I_{15/2})$	$\sigma_{em} \ (x10^{-20} \text{ cm}^2) \ (^4 \text{I}_{13/2} \rightarrow {}^4 \text{I}_{15/2})$	Fluorescence Effective Linewidth (nm)	
0.05	3.54	0.589	68.0	
0.1	3.70	0.605	66.2	
0.5	3.94	0.435	92.1	
1.0	3.76	0.448	90.1	

Table 2 compares the sample with 0.1wt% of Er_2O_3 to the results of recently published papers.

Table 2: Comparison of the spectroscopicparameters.

Glass Composition	$\sigma_{em} \ (x10^{-20} \text{ cm}^2) \ (^4 \text{I}_{13/2} \rightarrow {}^4 \text{I}_{15/2})$	Fluorescence Lifetime (ms) $({}^{4}I_{13/2} \rightarrow {}^{4}I_{15/2})$	Refraction Index
Ge-Ga-S [8]	1.050	2.90	2.15
ZBLAN [9]	0.580	9.00	1.50
Ga-La-S [10]	1.570	2.30	2.40
Silicate [11]	0.440	10.20	1.46
PbO-Bi ₂ O ₃ - Ga ₂ O ₃	0.605	3.76	2.52

Conclusions

In this work Bi_2O_3 -PbO- Ga_2O_3 glasses doped with Er^{3+} are studied at about 1500nm. A good mechanical resistance under high brightness diode laser pumping (7.5 W of diode output power) was observed and a fluorescence lifetime of 0.4 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 3.94ms for the glass with 0.5wt% of Er_2O_3 . The best spectroscopic performance is measured for the sample with 0.1wt% of Er_2O_3 : emission crosssection of 0.605x10⁻²⁰ cm² at 1532nm, fluorescence lifetime of 3.7ms and emission bandwidth of 66nm. As it can be observed, the emission cross-section of the glass presented in this work is very similar to the one of ZBLAN (Table 2).

Although the sample with 0.5wt% has the highest fluorescence lifetime it can not be considered the one with the best spectroscopic performance because of its optical inhomogeneity. Besides its peak emission cross-section at 1532nm is lower (0.435×10^{-20} cm²). The glass doped with 0.1wt% of Er₂O₃ exhibits interesting spectroscopic properties for laser action at 1532nm.

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