SPECTROSCOPIC PROPERTIES OF LEAD FLUOROBORATE GLASSES DOPED WITH YTTERBIUM

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Abstract

A new lead fluoroborate glass (PbO-PbF_2-B_2O_3) doped with ytterbium (Yb:PbFB) is presented. Samples with different concentrations of Yb^{3+} were produced and had their emission cross-sections, fluorescence lifetimes and minimum pump intensities determined. They have high refractive index of 2.2 and a density of 4.4 g/cm^3. For a doping level of $1.153x10^{20}$ $ions/cm^3$, the fluorescence lifetime, after excitation at 968 nm, is 0.81 ms, which is comparable to Yb:tellurite laser glass. Also, an emission band at 1022 nm is measured with emission cross-section of approximately $1.07x10^{-20}$ cm^2 and fluorescence effective linewidth of 60 nm, which is comparable to Yb:phosphate laser glass.

OCIS codes: (300.6360) Spectroscopy, laser; (140.3380) Laser materials

Introduction

The increasing importance of glasses doped with rare-earth ions as possible lasing materials has created considerable interest in the study of their optical properties. Materials doped with trivalent ytterbium ions exhibit highly efficient emission using InGaAs laser diodes as pump source. As there are only two manifolds in the Yb^{3+} energy level scheme, the $^2F_{7/2}$ ground state and $^2F_{5/2}$ excitation state, it is commonly believed that concentration quenching and multiphonon relaxation should not affect the excitation wavelength. The lack of intermediate levels and the large separation between the excited state and the ground state manifolds reduces non-radiative decay. The Yb^{3+} ions are of interest for the next generation of high field lasers and also as a sensitizer of energy transfer for infrared to visible upconversion and infrared lasers [1,2]. It is known that knowledge of the spectroscopic properties of Yb^{3+} ions is of fundamental importance for laser action. These properties include emission cross-section, peak wavelengths, fluorescence lifetime and fluorescence quenching processes. Laser glasses are usually evaluated by means of emission cross-section and fluorescence lifetime. These properties are calculated using intensity parameters based on the Judd-Ofelt theory [3,4]. Since there is only the $^2F_{5/2} \rightarrow {}^2F_{7/2}$ transition for Yb^{3+}, it is impossible to calculate directly the Judd-Ofelt parameters. For this reason, the compositional dependence of the spectroscopic properties of Yb^{3+} doped glasses are not well established. Up to now, there are only a few papers involving the effect of composition on the emission cross-section of Yb^{3+} in simple systems as borate, phosphate, silicate and telluride glasses [5,6,7,8].

Only recently, studies of lead oxyfluoride (PbO-PbF_2) [9] and lead borate glasses (PbO-B_2O_3) [10] doped with rare-earth were reported. In this paper, we present optical and physical properties of a new lead fluoroborate glass (PbO-PbF_2-B_2O_3), doped with different concentrations of ytterbium (Yb:PbFB), produced at the Laboratory of Glasses and Datation of the Faculty of Technology of São Paulo. The optical and physical properties were determined by means of absorption, luminescence and its associated lifetime, refractive index and density measurements. Calculations of spontaneous emission probability and emission cross-sections were performed.

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Experimental Procedure

The glasses presented in this work are prepared with 99.99% pure elements (all products from Fluka and Aldrich). Different concentrations of Yb_2O_3 (0.5 to 2.0 mol%) were added to the following glass matrix: (mol%) $43.5H_3BO_3$ - $22.5PbCO_3$ - $34.0PbF_2$. They are melted in air at 1000 °C for approximately one hour and a half, using alumina crucibles. Next, the melt is poured into pre-heated brass molds for a quick solidification and then annealed at 400 °C (below the glass transition temperature) for 12 h. Yellow colored, transparent and homogeneous samples were obtained. Glass samples with two polished faces and 3 mm thickness are used for refractive index, absorption, emission and lifetime measurements. Specimen surfaces must be polished, flat and parallel. We used a Carl Zeiss microscope with a 10x objective lens to measure the refractive index. The refractive index of 2.2 was determined by means of the "apparent depth method" [11]. This method relates the physical thickness of a transparent specimen to its optical thickness (apparent thickness). The absorption spectra were measured using a Carry Spectrometer in the range 920-1120 nm at room temperature. The emission spectra were obtained by exciting the samples with a GaAlAs laser diode (Optopower A020) at 968 nm. This diode system contains a broad area semiconductor laser with a maximum of 20 W of continuous output power operating at 964 nm. The diode laser beam is treated with a beamshaper [12] and focused by a single f = 5 cm lens. Close to the focus, and for a depth of focus of 2 mm, the beam has a rectangular profile, with transverse dimensions of approximately 260 x 260 μm. During the emission measurements, the sample is pumped by the diode laser beam, chopped at 40 Hz with 7.5 W, of diode output power, and focused onto the sample with a lens of 5 cm focal length. The emission from the sample is analyzed with a 0.5 m monochrometer (Spex) and a Germanium detector. The signal was intensified with an EG&G7220 lock-in amplifier and processed by a computer. The lifetimes of excited Yb^{3+} ions are measured using a pulsed laser excitation (4 ns) from an OPO pumped by a frequency doubled Nd:YAG laser (Quantel). The signal is detected by a fast S-20 extended type photomultiplier detector and analyzed using a signal processing Box-Car averager (PAR 4402). The density, of 4.4 g/cm^3 was measured with the Archimedes method. The concentration of Yb^{3+} ions (as well as the other compounds of the glass) were determined by the X-ray Fluorescent Spectrometry with wavelength dispersion (resolution of ± 0.01) and used to determine the absorption cross-section.

Results

Figure 1 presents the absorption spectrum for the sample doped with 1.153×10^{20} ions/cm^3 of Yb^{3+}, with 3 mm thickness, in order to show the optical transparency. Figure 2 shows absorption and emission cross-section spectra of all the samples produced.

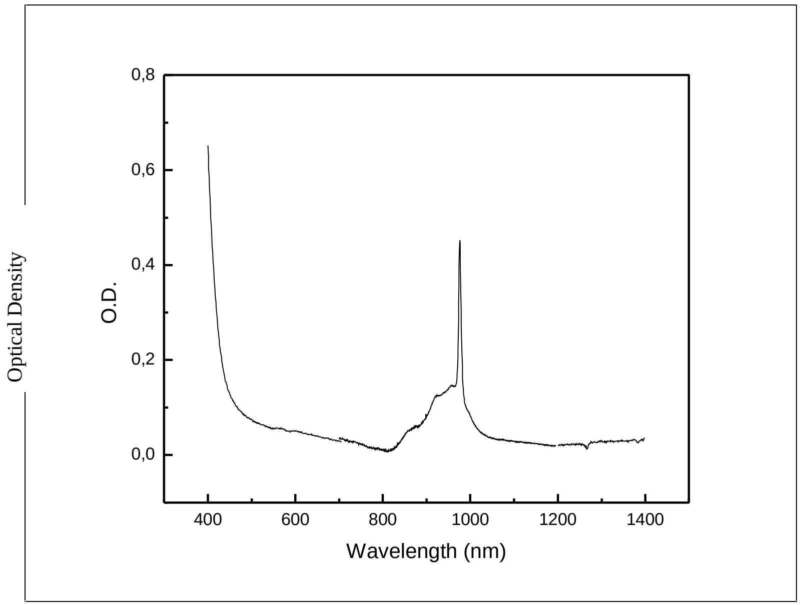

Figura 1: Absorption spectrum for the lead fluoroborate glass (3 mm thickness) doped with 1.153×10^{20} ions/cm^3 of Yb^{3+}.

The fluorescence lifetimes measured ($_f$) are shown in Table 1. The highest value is 0.81 ms for the sample doped with 1.153×10^{20} ions/cm^3 of Yb^{3+} and, as the concentration increases, the lifetime shortens gradually. The spontaneous emission probability (A_R), presented in Table 1, and the emission cross-section (σ_{em}), shown in Figure 2, are calculated using the equations [5] that follow:

$$A_R = \frac{8\pi c n^2 (2J'+1)}{\lambda_p^4 (2J+1)} \int k(\lambda) d\lambda \qquad (1)$$

$$\sigma_{em}(\lambda) = \frac{\lambda^4 A_R g(\lambda)}{8\pi n^2 c} \qquad (2)$$

where c represents the velocity of light, n the refractive index, λ_p the absorption peak wavelength, the concentration of Yb^{3+} ions, $k(\lambda)$ the absorption coefficient, J' and J the total momentum for the upper and lower levels and $g(\lambda)$ the normalized line shape function of the fluorescence transition of Yb^{3+}. Also seen in Table 1 is $\Delta\lambda_{eff}$, the fluorescence effective-linewidth.

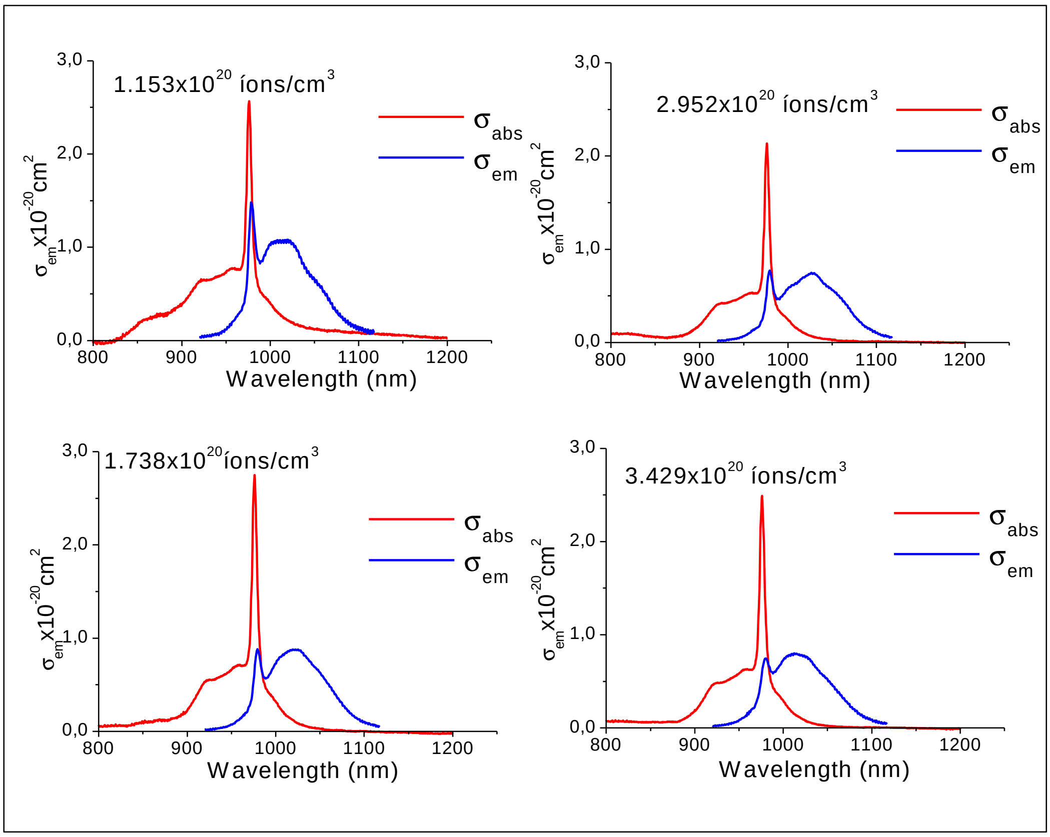

Figura 2. Absorption and emission cross-section spectra for lead fluoroborate glasses doped with Yb^{3+} for excitation at 968 nm.

Table 1: Spectroscopic properties of Yb^{3+} doped lead fluoroborate glasses.

Concentration (10^{20} ion/cm^3)	σ_{em} (10^{-20} cm^2)	A_R (s^{-1})	$\Delta\lambda_{eff}$ (nm)	$_f$ (ms)	σ_{em} $_f$ (10^{-20}cm^{2}ms)
1.153	1.07	3515.2	60.70	0.81	0.86
1.738	0.87	2703.7	81.90	0.78	0.68
2.952	0.75	2328.3	87.30	0.66	0.50
3.429	0.79	2488.5	87.20	0.59	0.47

From the point of view of laser operation, it is generally desirable for the emission cross-section to be as large as possible to provide for high gain and for the fluorescence lifetime to be long in order to permit high pulsed power.

Based on the considerations above, we come to the conclusion, that the sample with the best spectroscopic properties for a laser material is the one with 1.153x10^{20} ions/cm^3 of Yb^{3+} (Table 1). The spectroscopic data of this sample are comparable to some Yb^{3+} doped laser glasses: Yb:YTG glass (a tellurite laser glass) has a fluorescence lifetime of 0.9 ms [6]; Yb:PNK glass (a phosphate laser glass) has an emission cross-section of 1.08x10^{-20} cm^2 [7]; the product of $_f$.σ_{em} is 0.60x10^{-20} cm^{2}ms in Yb:FP glass (a fluorophosphate laser glass) [13]. A complete comparison is given in Table 2 where the spectroscopic properties of some phosphate (QX,ADY,LY,PN,PNK), fluorophosphate (FP) and tellurite (YTG) laser glasses, reported in published papers [6,7,13,14], are compared with lead fluoroborate glass, doped with 1.153x10^{20} ions/cm^3 of Yb^{3+}. Table 2 also presents the minimum pump intensity (I_{min} = 1.69 kW/cm^2), which is a measure for the ease of pumping the laser material, in an otherwise lossless oscillator, calculated by the following equation [15]:

$$I_{min} = {}_{min} I_{sat} \quad (3)$$

where:

$$_{min} = \frac{\sigma_{abs}(\lambda_0)}{\sigma_{em}(\lambda_0) + \sigma_{abs}(\lambda_0)}$$

$$I_{sat} = \frac{hc}{\lambda_p \; _f \; \sigma_{abs}(\lambda_p)}$$

where $\sigma_{abs}(\lambda_0)$ = 0.22x10^{-20} cm^2 and $\sigma_{em}(\lambda_0)$ = 1.07x10^{-20} cm^2 are the absorption and the emission cross-sections, respectively, at the extraction wavelength (λ_0 = 1022 nm); $\sigma_{abs}(\lambda_p)$ = 2.56x10^{-20} cm^2 is the absorption cross-section at the laser pump wavelength (λ_p = 968 nm) and I_{sat} = 9.9 kW/cm^2 is the pump saturation intensity. The $_{min}$ = 0.1705 parameter addresses the fact that Yb^{3+} doped materials are of quasi-four-level nature and suffer from ground-state absorption.

Table 2: Spectroscopic properties of some laser glasses and the YAG crystal doped with Yb^{3+} [6,7,13,14,15].

Materials	σ_{em} (10^{-20} cm^2)	λ_o (nm)	I_{min} (kW/cm^2)	$_f$ (ms)	σ_{em} $_f$ (10^{-20}cm^{2}ms)
QX	0.70	1018	1.80	2.00	1.40
ADY	1.03	1020	1.12	1.58	1.63
LY	0.80	1028	1.95	1.68	1.35
PN	1.35	1035	0.59	1.36	1.83
PNK	1.08	1016	1.29	2.00	2.16
FP	0.50	1020	0.80	1.20	0.60
YTG	2.35	1024	0.81	0.90	2.12
YAG crystal	2.00	1031	1.53	1.08	2.16
PbFB	1.07	1022	1.69	0.81	0.86

It can be seen from above table, that PbFB has similar I_{min} as the well known laser materials YAG [15] and QX [7,14].

Conclusion

A new lead fluoroborate glass doped with different concentrations of ytterbium is presented. The samples exhibited a very good mechanical resistance under high-brightness diode laser pumping. The one with the best spectroscopic properties, doped with 1.153x10^{20} ions/cm^3 of Yb^{3+}, has fluorescence lifetime of 0.81 ms, emission cross-section of 1.07x10^{-20} cm^2 at 1022 nm, fluorescence effective linewidth of 60 nm, high absorption cross-section of 2.56x10^{-20} cm^2 at 968 nm, and I_{min} = 1.69 kW/cm^2. This new glass has very similar properties when compared to other known glasses which are also used as active laser media. These features make it a good candidate for laser action.

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