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Lead fluoroborate glass doped with ytterbium

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Abstract

Absorption and luminescence spectra were measured in a new ytterbium-doped lead fluoroborate glass. The best spectroscopic performance was obtained for the concentration of 1.153×10^{20} ions/cm^3 of Yb^{3+}: emission cross-section of 1.07×10^{-20} cm^2 at 1022 nm, fluorescence lifetime of 0.81 ms, and high absorption cross-section (2.57×10^{-20} cm^2) at the absorption peak wavelength (976 nm). The lifetime is shortened with the increase of the Yb^{3+} concentration and decreases to 0.09 ms for 10.6×10^{20} ions/cm^3. The results suggest that this material can be considered an interesting candidate for laser applications as it has very similar properties when compared to other known glasses used as laser media.

Keywords: Amorphous materials; Luminescence

1. Introduction

It is known that knowledge of the spectroscopic properties of Yb^{3+} ions is of fundamental importance for efficient laser action. Yb:glass is a promising material with numerous attractive properties [1]: the broad fluorescence spectrum (compared with Nd^{3+}) provides sufficient bandwidth to generate and amplify ultrashort laser pulses, the millisecond upper-state lifetime enables free-running lasers and laser diodes for pump sources. It is also particularly advantageous for Q-switched lasers and high-power ultrashort pulse amplification. The simple electronic energy level structure ($^2F_{5/2}\rightarrow{}^2F_{7/2}$) results in a small quantum defect and the location of the absorption band (900–1000 nm) is suited for pumping with InGaAs laser diodes. Besides, glasses with a relatively high linear refractive index, doped with Yb^{3+}, usually show also a high nonlinear refractive index, which is a desirable effect for ultrashort pulse generation [2].

Recently, the literature reported the use of Sm^{3+}, Dy^{3+}, and Nd^{3+} in lead oxyfluoride ($PbO–PbF_2$) [3] and lead borate ($PbO–B_2O_3$) [4] glasses. The aim of this work is to characterize laser transitions of Yb^{3+} in a new lead fluoroborate glass ($PbO–PbF_2–B_2O_3$) by emission cross-section and fluorescence lifetime.

In order to increase the laser efficiency of a particular transition, the emission cross-section and the fluorescence lifetime should be made as large as possible. So we present in this work the lead fluoroborate sample doped with Yb^{3+} that presents the best spectroscopic properties which are comparable to the known Yb:phosphate and Yb:tellurite laser glasses [5,6].

The motivations for this new glass matrix are: high refractive index (2.2) that is normally responsible for the high spontaneous emission probability, very good glass forming region, good physical and chemical stability, transmission from the visible region (0.4 μm) up to the long infrared (4 μm) [7]. A wide infrared transmission window normally indicates that the vibrational phonon energy is small. This reduced phonon energy normally provides opportunities towards the realization of more efficient lasers.

2. Experimental

The glass presented in this work was prepared by melting for 1.5 h the appropriate quantities (~11 g) of the glass matrix compounds, $43.5H_3BO_3–22.5PbCO_3–$

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$34.0PbF_2$ (mol.%) and $0.5Yb_2O_3$ (mol.%), inside an alumina crucible at 1000 °C in air. This is the first time that this new composition has been tested. The obtained glass was annealed at 400 °C onto a pre-heated brass mold, cut in slabs of 3 mm and polished for optical measurements. Yellow colored transparent and homogeneous samples, in the system $PbO–PbF_2–B_2O_3$, were produced.

The concentration of the Yb^{3+} ions (1.153×10^{20} ions/cm^3) was determined by X-ray fluorescent spectrometry with wavelength dispersion (resolution of ±0.01 wt.%).

The refractive index of 2.2 was determined by means of the 'apparent depth method' [8] that relates the physical thickness of a transparent specimen to its optical or apparent thickness and measured with a 10× objective lens of a Carl Zeiss microscope.

The absorption spectrum was measured using a Carry spectrometer in the range 920–1120 nm, at room temperature. The emission spectrum was obtained by optically pumping the samples with a GaAlAs laser diode and analyzing the signal with a 0.5 m (Spex) monochromator, using a Ge detector. The estimated errors in these emission measurements are ±5%. The lifetime of the excited Yb^{3+} ions was measured using a pulsed laser excitation (4 ns) from an OPO pumped by a frequency doubled Nd:YAG laser and detecting the signal with a fast S-20 extended type photomultiplier detector connected to a signal processing Box-Car (PAR 4402) in average operation mode.

3. Results

The absorption and emission cross-section spectra are shown in Fig. 1. The absorption peak wavelength corresponding to the energy separation of the lowest crystal field components of the ground and excited states is situated at 976 nm. The wavelength of the fluorescent peak emission, related to the $^2F_{5/2}\rightarrow^2F_{7/2}$ transition, normally varies with the host and was measured at 1022 nm. The spontaneous emission probability (A_R=3515.2 s^{-1}) and the emission cross-section spectrum, shown in Fig. 1, were calculated with the following equations [9]:

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

$$\sigma_{em}(\lambda) = \frac{\lambda_0^4 A_R g(\lambda)}{8\pi c n^2} \tag{2}$$

where c represents the velocity of light, n the refractive index, λ_p=976 nm the absorption peak wavelength, ρ the concentration of Yb^{3+} ions, $k(\lambda)$ the absorption coefficient, J' and J the total momentums for the upper and lower levels, $g(\lambda)$ the normalized line shape function. The fluorescence effective linewidth, calculated from the measured emission spectrum, is 60 nm and the emission cross-section, at $\lambda_0 = 1022$ nm, the emission peak wavelength is 1.07×10^{-20} cm^2.

The coexistence of the absorption and emission at 976 nm is responsible for the reabsorption and it is the β_{min} parameter that addresses the effect of the resonant absorption loss of Yb^{3+}. β_{min} is defined as the minimum fraction of Yb ions that must be excited to balance the gain exactly with the ground-state absorption at $\lambda_0 = 1022$ nm, the emission peak wavelength.

The value of this parameter is given by β_{min}=0.17 and is calculated with the following equation:

$$\beta_{min} = \frac{\sigma_{abs}(\lambda_0)}{\sigma_{abs}(\lambda_0)+\sigma_{em}(\lambda_0)} \tag{3}$$

where $\sigma_{abs}(\lambda_0)$ and $\sigma_{em}(\lambda_0)$ are the absorption and emission cross-sections at $\lambda_0 = 1022$ nm.

This value of 0.17, calculated for the β_{min} parameter, is comparable to the one of well-known Yb:ZBLAN glass whose β_{min} is 0.100.

The fluorescence lifetime measured was fitted to an exponential decay and the result was τ_f=0.81 ms. Fig. 2 presents the experimental data and the theoretical fit. Table 1 compares the spectroscopic properties of the ytterbium-doped lead fluoroborate glass, presented in this work, with some phosphate (QX, PNK), fluorophosphate (FP), tellurite (YTG) laser glasses and the YAG laser crystal [5,6,10–12].

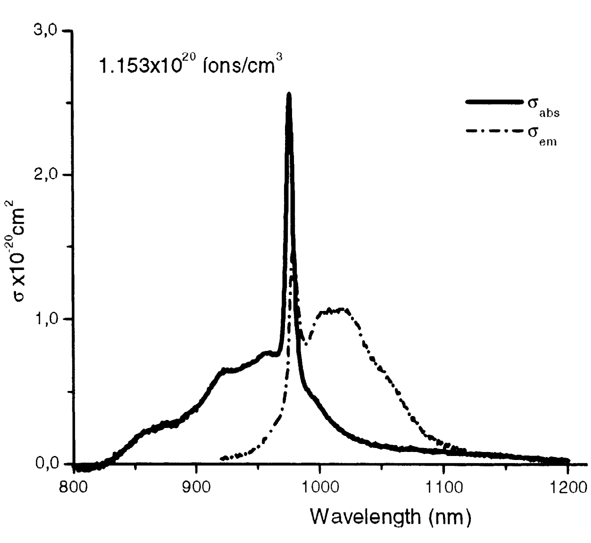

Fig. 1. Absorption and emission cross-section spectra for the lead fluoroborate glass doped with Yb^{3+} (excitation of 976 nm).

4. Discussion

An efficient host for laser operation should show a combination of the following properties: large emission cross-section to provide high gain, long fluorescence lifetime to minimize pump losses incurred from spontaneous emission, large absorption cross-section at the pump wavelength and the possibility to incorporate a high

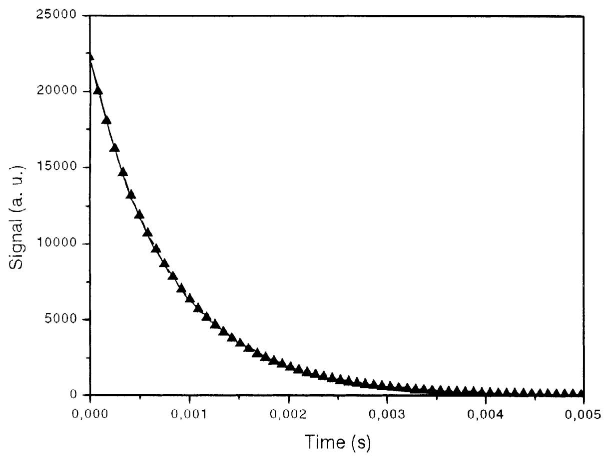

Fig. 2. Experimental decay of the fluorescence lifetime (curve with symbol) and theoretical fit (solid curve) for the lead fluoroborate glass doped with Yb^{3+}.

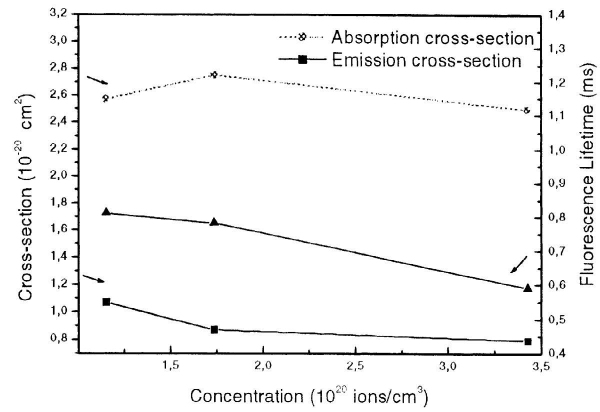

Fig. 3. Absorption and emission cross-sections and fluorescence lifetimes as a function of the doping concentrations: 1.153, 1.738 and 3.429 ions/cm^3.

concentration of Yb^{3+} ions. Table 1 shows that the ytterbium-doped lead fluoroborate glass studied in this paper has spectroscopic properties comparable to some Yb^{3+} doped laser glasses: the fluorescence lifetime of 0.81 ms compares with a tellurite laser glass lifetime (Yb:YTG) [5]. The emission cross-section of 1.07×10^{-20} cm^2 is comparable to the Yb:PNK glass (a phosphate laser glass) [6] for which this value is 1.08×10^{-20} cm^2. We remark that the QX/Yb glass [11] is already commercially available and is produced with 5 wt.% of Yb_2O_3; in the case of the glass studied in this paper, this value is 1.2 wt.%.

Concerning the other samples that were produced with different concentration of Yb^{3+}, we should add that the increase of Yb^{3+} causes the fluorescence lifetime to decrease to 0.09 ms, at 10.6 ions/cm^3. In this case the emission is very feeble and the emission cross-section was not calculated. Fig. 3 presents the data about absorption (at 976 nm) and emission (at 1022 nm) cross-sections and fluorescence lifetime as a function of the Yb^{3+} concentration. Whereas the sample with 1.153 ions/cm^3 has a slightly smaller absorption cross-section (2.57×10^{-20} cm^2) than the one with 1.738 ions/cm^3 (2.75×10^{-20} cm^2) the emission cross-section is somewhat higher (1.07×10^{-20} cm^2 for 1.153 ions/cm^3 and 0.87×10^{-20} cm^2 for 1.738 ions/cm^3). The highest fluorescence lifetime, of 0.81 ms, is measured for 1.153 ions/cm^3. For 1.738 ions/cm^3 the fluorescence lifetime (0.78 ms) changes only a little and decreases to 0.59 ms for 3.429 ions/cm^3.

We should add that the samples exhibited a very good mechanical resistance under high-brightness diode laser pumping (7.5 W of diode output power).

Table 1
Spectroscopic properties of some laser glasses and the YAG crystal doped with Yb^{3+} [5,6,10–12]

Glasses	$\sigma_{em}(\lambda_0)$ (10^{-20} cm^2)	λ_0 (nm)	τ_f (ms)	$\sigma_{em}\tau_f$ (10^{-20} cm^2 ms)
QX	0.70	1018	2.00	1.40
PNK	1.08	1016	2.00	2.16
FP	0.50	1020	1.20	0.60
YTG	2.35	1024	0.90	2.12
YAG crystal	2.00	1031	1.08	2.16
Our glass	1.07	1022	0.81	0.86

5. Conclusion

A new lead fluoroborate glass ($PbO–PbF_2–B_2O_3$) doped with 1.153×10^{20} ions/cm^3 of Yb^{3+} is presented. The fluorescence lifetime measured is 0.81 ms, the emission cross-section at the extraction peak wavelength (1022 nm) is 1.07×10^{-20} cm^2, and the absorption cross-section at the absorption peak wavelength (976 nm) is 2.57×10^{-20} cm^2. These features enable the use of this new material as an active laser media for short pulse, high power generation.

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