EVALUATION OF THE MOST SUITABLE NEW GLASS LASER MEDIUM TO INCORPORATE YTTERBIUM: ALKALI NIOBIUM TELLURITE, LEAD FLUORBORATE OR HEAVY METAL OXIDE

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Abstract

The most important advantage of Ytterbium compared to others dopants such as Neodymium is its broadband emission nature, which is very suitable for both tunable and ultrafast lasers.

In this paper we present the study and characterization of three different glass families: Alkali Niobium Tellurite, Lead Fluoroborate and of Heavy Metal Oxides, all prepared containing Ytterbium.

The Ytterbium (Yb) emission spectrum in Tellurite glass samples was obtained by excitation into the absorption peak at 975 nm. The Yb peak emission cross-section was calculated using the fluorescence lineshape, the radiative lifetime (0.59 ms) and the refractive index 2.09. With these values we found the emission cross-section of Yb in Tellurite glass doped.

Lead Fluorborate glasses have high refractive index of 2.2, and an absorption band centered at 968nm. The spontaneous emission probability was calculated and we determined that it decreases with the increase of Yb concentration. The same applies for the fluorescence lifetime and to the emission cross-section. We measured the fluorescence lifetime of 0.81ms, and an emission band at 1022nm with an effective emission linewidth of 60nm.

Heavy metal oxide glass also has high refractive index (2.5) and transmission cutoff of about 8μm. In this glass the fluorescence effective linewidth was 86nm and radiative lifetime 300 μs.

Calculations of the minimum pump intensity are also presented. A comparison of laser properties of these three different glasses and their importance is shown and analyzed.

I. Introduction

Developments in high-field lasers for next generation nuclear fusion has indicated that the Yb-doped materials, particularly glasses, are the best host materials to efficient energy storage in the excited state [1]. Since Yb^{3+} has the [Xe] $4f^{13}$ electron configuration, it offers the advantage of a small number of 4f states. Materials doped with Yb^{3+} ions have efficient emission when pumped by diode lasers without the possibility of excited state absorption[2]. The Yb^{3+} ions are of interest also as a sensitizer of energy transfer for infrared to visible up conversion and infrared lasers [2].

Since there are only two manifolds in the Yb^{3+} energy level scheme, the $^2F_{7/2}$ ground state and $^2F_{5/2}$ excited 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.

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].

It was shown recently that Yb doped Tellurite glasses have more advantages over some other excellent laser glasses, being comparable to laser crystals like Yb:YAG and Yb:YAP, showing high emission cross-section and long luminescence lifetime [6 9]. In this paper we present the study and characterization of three different families:

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Alkali Niobium Tellurite (TeO_2-Nb_2O_5-K_2O-Li_2O), Lead Fluoroborate (PbO-PbF_2-B_2O_3) and of Heavy Metal Oxide (Bi_2O_3-PbO-Ga_2O_3), stable against crystallization, were prepared containing Yb^{3+}.

The Yb emission spectrum in Tellurite glass samples was obtained by excitation into the absorption peak of Yb^{3+} at 968nm. The Yb emission cross-section at the peak of $^2F_{5/2}$à $^2F_{7/2}$ transition was calculated using the fluorescence lineshape, the radiative lifetime ($_R$ =0.59 ms) and the refractive index n equal to 2.09. With these values we found that the emission cross-section of Yb in Tellurite glass corresponds to 1.10x $10^{-20}cm^{-2}$ at 1028nm.

Lead Fluorborate glass has high refractive index (2.2), density of about 4.4g/cm^3, and an absorption band at 976nm associated to the $^2F_{5/2} \rightarrow {}^2F_{7/2}$ transition of Yb^{3+}. The spontaneous emission probability is calculated and decreases with the increase of Yb^{3+} concentration. The same applies for the fluorescence lifetime and to the emission cross-section. For 1.15 $x10^{20}$ ions/cm^3 doping level the fluorescence lifetime measured is of 0.81ms (for Yb: Tellurite laser glass it is 0.9ms), for excitation of 968nm; an emission band at 1022nm is measured with emission cross-section of approximately $1.07x10^{-20}cm^2$ (comparable to Yb:Phosphate laser glass), and fluorescence effective linewidth of 60nm.

Heavy metal oxides have high refractive index (2.5) and transmission cutoff of about 8μm. In this glass the absorption cross-section measured was $2.20x10^{-20}cm^2$ at 968 nm, the emission cross-section was $0.23x10^{-20}cm^2$, at the extraction wavelength (1012 nm), the fluorescence effective lifetime was 86 nm and the fluorescence lifetime of 0.4 ms.

A comparison of laser properties of these three different glasses and their importance is shown and analyzed in the following section.

II. Experimental Procedure

II.1 Lead Fluoroborate Glasses

The glasses used in this work were prepared with 99.99% pure elements (all products from Fluka and Aldrich). Concentration of 0.5 mol% of Yb_2O_3 were added to the following glass matrix of: (mol%) 43.5H_3BO_3 - 22.5$PbCO_3$ - 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.

II.1 Heavy Metal Oxide Glasses

The oxide glass presented in this work, with 0.5mol% of Yb_2O_3 were prepared, respectively with (mol%)25.0Bi_2O_3 -57.0PbO-18.0 Ga_2O_3. After melting the starting powders in Pt crucibles at 1000°C for one hour and a half they are poured onto preheated mold and further annealed for 3h, at 400° C and then cooled inside the furnace.

II.3 Niobium Tellurite Glasses

Appropriate mixtures of reagent-grade TeO_2; Nb_2O_5; Li_2CO_3; K_2CO_3 were melted in gold crucibles for 30 min at 830^{0}C, in air. The liquids were quenched at room temperature in steel molds and, annealing treatments were performed at temperature near Tg (glass transition temperature) for 30 min. Samples with compositions of : 80TeO_2-10Nb_2O_5-5K_2O-5Li_2O, stable against crystallization, were also prepared containing rare earth ions with the concentrations specified shown in Table 1.

Glass samples with two polished faces and 3 mm thickness were used for refractive index, absorption, emission and lifetime measurements. Specimen surfaces were polished flat and parallel. We used a Carl Zeiss microscope with a 10x objective lens to measure the refractive index. The refractive index was determined by means of the "apparent depth method" [10]. This method relates the physical thickness of a transparent specimen to its optical thickness (apparent thickness).

The absorption spectra in the range 920-1120 nm were measured using a Cary Spectrometer 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 968 nm. The diode laser beam is treated with a beamshaper [11] 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 emissions from the sample were analyzed with a 0.5 m monochromator (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 were measured using pulsed laser excitation (4 ns) from an OPO pumped by a frequency doubled Nd:YAG laser (Quantel). The signal was detected by a fast S-20 extended type photomultiplier detector and analyzed using a signal processing Box-Car averager (PAR 4402). The densities were measured with the

Archimedes method, and the X ray Fluorescent Spectrometry with wavelength dispersion determined the concentrations of Yb^{3+}.

Table 1. Concentrations, densities and refractive index of studied glasses.

Host	*Density (g/cm³)*	*Refractive index*	*Yb(Mol %) (ions/cm³)*
Lead fluoroborate	4.40	2.20	0.5 ($1.15x10^{20}$)
Heavy metal oxides	4.63	2.52	0.5 ($0.64x10^{20}$)
Niobium Tellurite	5.50	2.09	5 ($4.21x10^{20}$)

III. Results

Absorption and emission cross-sections spectra, are shown in figures 1, 2 and 3 for the three hosts doped with Yb^3. Table 2 presents some of the spectroscopic properties as the fluorescence lifetimes measured ($_f$), fluorescence effective linewidth (Δ_{eff}), as well as the spontaneous emission probabilities (A_R) and the emission cross-sections (σ_{em}) that were calculated using the following equations[5]:

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

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

where c represents the velocity of light, n the refractive index, λ_p the absorption peak wavelength (968nm), 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 (λ) the normalized line shape function of the fluorescence transition of Yb^{3+}. In Table 2 $\sigma_{abs}(\lambda_0)$ and $\sigma_{em}(\lambda_0)$ represent the absorption and the emission cross-sections at the extraction wavelength (λ_0) and $\sigma_{abs}(\lambda_p)$ the absorption cross-section at the laser pump wavelength (λ_p).

Table 3 presents the minimum pump intensity (I_{min}), which is a measure for the ease of pumping the laser material. I_{min} describes the minimum absorbed pump intensity that is required for transparency to be achieved at the extraction wavelength (λ_0) and is calculated by the following equation[9]:

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

where:

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

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

In the equations above I_{sat} is the pump saturation intensity and $_{min}$ is defined as the minimum fraction of Yb ions that must be excited to balance the gain exactly with the ground-state absorption at λ_0. ($_{min}$=0.17 and I_{sat}=9.9kW/cm² for the lead fluoroborate glass, $_{min}$=0.30, I_{sat}=23.0kW/cm² for the heavy metal oxide one and $_{min}$=0.20, I_{sat}=8.0kW/cm² for the niobium tellurite.)

Table 2: Spectroscopic properties of Yb^{3+} doped Lead Fluoroborate , Heavy Metal Oxide and niobium Tellurite glasses.

Host	*Concentration (10^{20} ion/cm³)*	$\sigma_{em}(\lambda_p)$ (10^{-20} cm²)	$\sigma_{abs}(\lambda_p)$ (10^{-20} cm²)	$\sigma_{abs}(\lambda_0)$ (10^{-20} cm²)	λ_0 (nm)	A_R (s^{-1})	$\Delta\lambda_{eff}$ (nm)	$_f$ (ms)	$\sigma_{em}\ _f$ (10^{-20}cm²ms)
Lead fluoroborate	1.15	1.07	2.56	0.13	1022	3515.2	60.7	0.81	0.86
Heavy metal oxides	0.64	0.23	2.20	0.22	1012	3000.0	86.0	0.40	0.10
Niobium Tellurite	4.21	1.10	4.09	0.28	1028	3200.0	66.1	0.59	0.65

Table 3: Spectroscopic properties of some laser glasses and crystals doped with Yb^{3+} [6 7 11 12]

Materials	σ_{em} (10^{-20} cm²)	λ_0 (nm)	I_{min} (kW/cm²)	$_f$ (ms)	$\sigma_{em}\ _f$ (10^{-20}cm²ms)
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

Heavy metal	0.23	1012	6.90	0.40	0.10
Niobium tellurite	1.10	1028	1.62	0.59	0.65

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, for the fluorescence lifetime to be long in order to permit high-pulsed power, and for the absorption cross-section at the pump wavelength to be as large as possible. So the lead fluoroborate glass doped with Yb^{3+} has more favorable spectroscopic properties than the heavy metal oxide one, which is comparable to some Yb^{3+} doped laser glasses. This can be seen in Table 3 that presents some phosphate (QX,ADY,LY,PN,PNK), fluorophosphate (FP) and tellurite (YTG) laser glasses, reported in published papers [6 7 11]. The lead fluoroborate glass has similar I_{min} as the well known laser materials YAG and QX, fluorescence lifetime comparable to Yb:YTG (a tellurite laser glass) and emission cross-section comparable to Yb:PNK (a phosphate laser glass).

However we have to remark, for the case of the heavy metal oxide glass, the high absorption cross-section, of $2.20 \times 10^{-20} cm^2$ (at 968nm), and the high fluorescence effective linewidth, of 86nm, not yet presented in the literature for ytterbium doped glasses, and an important feature for laser action in short pulse generation under diode pumping.

In conclusion, new glasses of lead fluoroborate, of heavy metal oxide and niobium tellurite doped with Yb^{3+} are reported in this paper. High absorption cross-sections (at 968nm) are measured for all of them, mainly for niobium tellurite. The lead fluoroborate glass has more favorable spectroscopic properties than the other ones; it also has very similar properties (0.81ms for the fluorescence lifetime, emission cross-section of $1.07 \times 10^{-20} cm^2$ and I =1.69kW/cm^2) when compared to other known glasses (phosphate and tellurite laser glasses) that are used as active laser media.

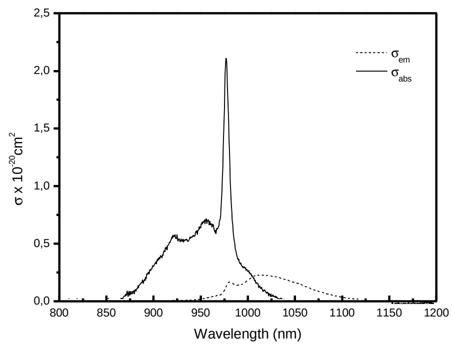

Figure 1. Absorption and emission cross-sections spectra for the heavy metal oxide glass with 0.5mol% of Yb_2O_3 .

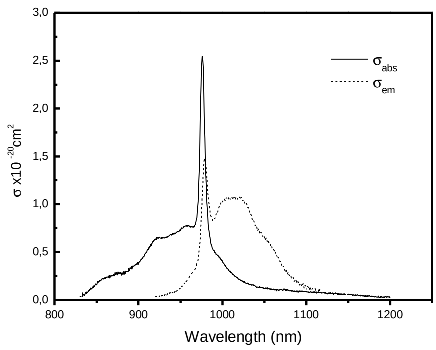

Figure 2. Absorption and emission cross-sections spectra for the lead fluoroborate glass with 0.5mol% of Yb_2O_3

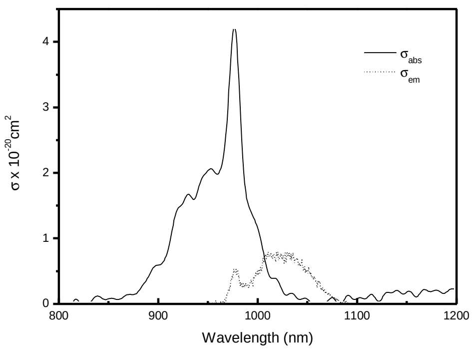

Figure 3. Absorption and emission cross-sections spectra for the niobium tellurite glass with 5mol% of Yb_2O_3

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