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Journal of Non-Crystalline Solids 304 (2002) 233–237

JOURNAL OF NON-CRYSTALLINE SOLIDS

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Spectroscopic properties of lead fluoroborate and heavy metal oxide glasses doped with Yb^{3+}

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Abstract

A new glass of heavy metal oxide ($25.0Bi_2O_3$–57.0PbO–$18.0Ga_2O_3$ (mol%)) doped with Yb^{3+} is presented and compared with lead fluoroborate glass ($43.5H_3BO_3$–$22.5PbCO_3$–$34.0PbF_2$ (mol%)), also doped with ytterbium. The interest in Yb^{3+} for laser action and short pulse generation under diode pumping has been reported in the literature. Spectroscopic properties were studied for both glasses doped with 0.5 mol% of Yb_2O_3. The absorption cross-section of the heavy metal oxide glass is $(2.20 \pm 0.15) \times 10^{-20}$ cm^2 at the absorption peak wavelength of 968 nm and its emission cross-section is $(0.75 \pm 0.05) \times 10^{-20}$ cm^2 at the extraction wavelength of 1012 nm. A fluorescence effective linewidth of 86 nm and a fluorescence lifetime of 0.40 ms were measured. In the case of the lead fluoroborate glass used for comparison, these values change to $(2.56 \pm 0.18) \times 10^{-20}$ cm^2 (absorption cross-section), $(1.07 \pm 0.08) \times 10^{-20}$ cm^2 (emission cross-section at 1022 nm), 60 nm (fluorescence effective linewidth) and 0.81 ms (fluorescence lifetime). Calculations of the minimum pump intensity are also presented. Both have spectroscopic properties for laser applications that are similar to those of other known glasses (phosphate and tellurite laser glasses) used as active laser media. The large emission bandwidth measured for the heavy metal oxide is of interest for tunable lasers.

PACS: 42.70.-a

1. Introduction

The aim of this work is to present new spectroscopic properties of ytterbium doped heavy metal oxide glass (Bi_2O_3–PbO–Ga_2O_3) and compare these results with those of lead fluoroborate glass (PbO–PbF_2–B_2O_3). Both glasses are doped with 0.5 mol% of Yb_2O_3. Recently, optical studies of lead oxyfluoride (PbO–PbF_2) and lead borate glasses (PbO–B_2O_3) doped with rare earth for laser applications were published [1,2]. For these glasses the literature reported studies with Sm^{3+}, Nd^{3+} and Dy^{3+}. Spectroscopic properties of lead fluoroborate glasses (PbO–PbF_2–B_2O_3) doped with different concentrations of Yb^{3+} ions were published in an earlier work [3]. In that paper we

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0022-3093/02/$ - see front matter
PII: S0022-3093(02)01028-1

presented the results of emission and absorption cross-sections, fluorescence lifetimes and minimum pump intensity. For comparison we use in the present work the results of the fluoroborate glass sample with the best spectroscopic performance (doped with 0.5 mol% of Yb_2O_3), as stated in that Ref. [3].

Since 1995, the literature has presented the use of Er^{3+}, Tm^{3+}, Dy^{3+}, and Pr^{3+} [4–6] in the heavy metal oxide host for laser applications. We reported [7] the use of Nd^{3+} in this host and, now, the use of Yb^{3+} reported for the first in this host, to our knowledge. This host of heavy metal oxide, discovered [8] in 1985, is of interest in optoelectronic devices due to its properties, namely extended infrared transmission (up to 9 μm), refractive index of about 2.5 and nonlinear optical properties. Its wide infrared transmission window indicates that vibrational phonon energy is small compared to other oxide glasses. This reduced phonon energy of approximately 500 cm^{-1} [4,6,9] provides opportunities towards the realization of more efficient lasers and fiber optic amplifiers.

Finally we can add the motivation for these hosts: high refractive index, good physical and chemical stability and wide transmission window [3,7].

2. Experimental procedure

The samples were prepared adding 0.5 mol% of Yb_2O_3 to the following glasses matrix: $43.5H_3BO_3$–$22.5PbCO_3$–$34.0PbF_2$ (mol%) and $25.0Bi_2O_3$–57.0PbO–$18.0Ga_2O_3$ (mol%). After melting the powders in alumina (for the lead fluoroborate glass) and Pt crucibles (for the heavy metal oxide glass) at 1000 °C for one hour and a half, they are poured into heated molds and annealed for 12 h (to avoid internal stress) at 400 °C (lead fluoroborate glass) and at 300 °C (heavy metal oxide glass) and then cooled inside the furnace. The temperatures used for the annealing are based on the transition temperatures of each host (330 °C for the heavy metal oxide and 450 °C for the lead fluoroborate glass). The samples produced are transparent, homogeneous, stable against crystallization, since their preparation 12 months ago, and have red (heavy metal oxides glass) and yellow colorations (lead fluoroborate glass).

The refractive index (2.52 ± 0.03 for the heavy metal oxide and 2.20 ± 0.02 for the lead fluoroborate glass) were determined by means of the 'apparent depth method' [10] that relates the physical thickness to its optical thickness (apparent thickness). Absorption spectra (with error of ±2%) at room temperature were recorded with a spectrometer (Cary) in the 920–1120 nm range. Emission spectra were measured using an excitation beam of 968 nm from a InGaAs laser diode (Optopower A020). The emission was analyzed with a 0.5 m monochrometer (Spex) and detected by a Ge detector, intensified with a lock-in amplifier (EG&G7220). Errors in these measurements are estimated in ±5%, based on the signal to noise ratio. The lifetimes of the excited Yb^{3+} ions were measured using pulsed laser excitation (4 ns) from an OPO pumped by a frequency doubled Nd:YAG laser (Quantel) and a Judson InSb detector with appropriated emission filter and then analyzed using a signal processing Tektronix digital oscilloscope in average mode connected to a computer with a GPIB interface (with error of ±5%). The concentrations of Yb^{3+}(1.15×10^{20} ions/cm^3 for the lead fluoroborate glass and of 6.44×10^{19} ions/cm^3 for the heavy metal oxide one) were determined by X-ray fluorescent spectrometry with wavelength dispersion (resolution of ±0.01 wt%). All the equipments used in the measurements were calibrated with reference to secondary standards prior to their use. Therefore the systematic errors, we expect, are smaller than the random errors.

3. Results

Figs. 1 and 2 show spectra of the absorption and emission cross-sections for the two hosts doped with Yb^{3+}. Table 1 presents some of the spectroscopic properties, mainly the fluorescence lifetimes (τ_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 [11]:

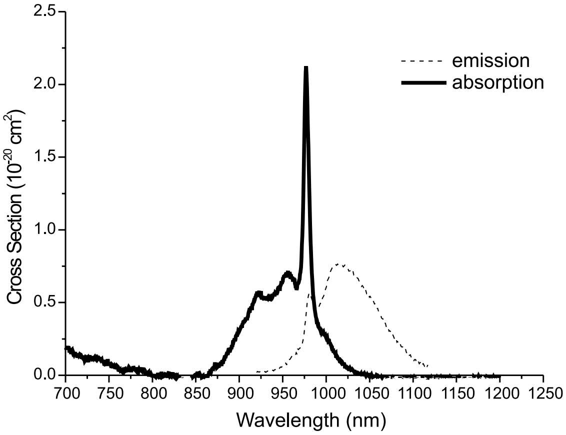

Fig. 1. Absorption and emission cross-sections spectra for the heavy metal oxide glass with 0.5 mol% of Yb_2O_3.

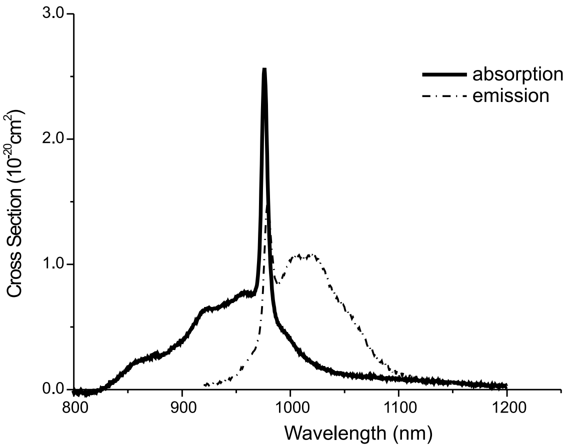

Fig. 2. Absorption and emission cross-sections spectra for the lead fluoroborate glass with 0.5 mol% of Yb_2O_3.

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

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

where c represents the velocity of light; n, the refractive index; λ_p, the absorption peak wavelength (968 nm); ρ, 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+}. In Table 1 $\sigma_{abs}(\lambda_0)$ and $\sigma_{em}(\lambda_0)$ represent the absorption and the emission cross-sections at the extraction wavelength (λ_0), $\sigma_{abs}(\lambda_p)$ the absorption cross-section at the absorption peak wavelength (λ_p) and (τ_f) the fluorescence lifetimes obtained fitting the measured values to single exponentials. Table 2 presents the minimum pump intensity (I_{min}) which is a measure for the ease of pumping the laser material to get laser action. 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 [12]:

$$I_{min} = \beta_{min} I_{sat}, \tag{3}$$

where

$$\beta_{min} = \frac{\sigma_{abs}(\lambda_0)}{\sigma_{em}(\lambda_0)+\sigma_{abs}(\lambda_0)} \quad \text{and} \quad I_{sat} = \frac{hc}{\lambda_p \tau_f \sigma_{abs}(\lambda_p)}.$$

In the equations above I_{sat} is the pump saturation intensity and 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

Table 1
Spectroscopic properties of Yb^{3+} doped lead fluoroborate and heavy metal oxide glasses

Host	Concentration (10^{20} ion/cm^3)	$\sigma_{em}(\lambda_0)$ (10^{-20} cm^2)	$\sigma_{abs}(\lambda_p)$ (10^{-20} cm^2)	$\sigma_{abs}(\lambda_0)$ (10^{-20} cm^2)	λ_0 (nm)	A_R (s^{-1})	$\Delta\lambda_{eff}$ (nm)	τ_f (ms)	$\sigma_{em}\tau_f$ (10^{-20} cm^2 ms)
Lead fluoroborate	1.15 ± 0.06	1.07 ± 0.08	2.56 ± 0.18	0.22 ± 0.02	1022	3515.2	60.70	0.81 ± 0.04	0.86
Heavy metal oxide	0.64 ± 0.03	0.75 ± 0.05	2.20 ± 0.15	0.13 ± 0.01	1012	3000.0	86.00	0.40 ± 0.02	0.10

Table 2
Spectroscopic properties of some laser glasses and the YAG laser crystal doped with Yb^{3+}

Materials	σ_{em} (10^{-20} cm^2)	λ_0 (nm)	I_{min} (kW/cm^2)	τ_f (ms)	$\sigma_{em}\tau_f$ (10^{-20} cm^2 ms)
QX[a]	0.70	1018	1.80	2.00	1.40
ADY[a]	1.03	1020	1.12	1.58	1.63
LY[a]	0.80	1028	1.95	1.68	1.35
PN[a]	1.35	1035	0.59	1.36	1.83
PNK[a]	1.08	1016	1.29	2.00	2.16
FP[a]	0.50	1020	0.80	1.20	0.60
YTG[a]	2.35	1024	0.81	0.90	2.12
YAG crystal[b]	2.00	1031	1.53	1.08	2.16
Lead fluoroborate	1.07 ± 0.08	1022	1.69 ± 0.15	0.81 ± 0.04	0.86
Heavy metal	0.75 ± 0.05	1012	3.40 ± 0.31	0.40 ± 0.02	0.10

[a] Data from Refs. [13–16] where the relative errors in the emission measurements are estimated to be <5%, errors in the lifetime measurements are <10% and errors for I_{min} are not presented.
[b] Data from Ref. [12] where the errors are not presented.

at $\lambda_0(\beta_{min} = 0.171$ and $I_{sat} = 9.9$ kW/cm^2 for the lead fluoroborate glass and $\beta_{min} = 0.148$, $I_{sat} = 23.0$ kW/cm^2 for the heavy metal oxide glass).

4. Discussion

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 to permit greater pulsed power, and for the absorption cross-section at the pump wavelength to be as large as possible to allow for efficient diode pumping. The optimum host is the one that fulfils these requirements. Therefore, the lead fluoroborate glass doped with Yb^{3+} has more favorable spectroscopic properties than the heavy metal oxide glass. These properties are shown in Table 2, which presents some phosphate (QX, ADY, LY, PN, PNK), fluorophosphate (FP) and tellurite (YTG) laser glasses, doped with Yb^{3+} [13–16]. The lead fluoroborate glass has similar I_{min} as the well-known laser materials Yb:YAG [12] and Yb:QX [14], fluorescence lifetime comparable to Yb:YTG (a tellurite laser glass) and emission cross-section comparable to Yb:PNK (a phosphate laser glass). The heavy metal oxide glass has emission cross-section comparable to Yb:QX and a fluorescence effective linewidth (86.0 nm) larger than Yb:PNK (46.0 nm) [13] and than the lead fluoroborate glass (60.7 nm). It should be pointed out that such a large fluorescence effective linewidth, as is the case of the ytterbium doped heavy metal oxide glass, as well as its absorption cross-section (2.20×10^{-20} cm^2 at 968 nm) are important features for short pulse generation in diode pumped lasers or for tunable lasers. We should add that both samples had good mechanical resistance under high-brightness diode laser pumping. At 7.5 W of cw diode pump power there was no visible fracture of the samples even in the absence of cooling. Also, their high refractive index provides larger spontaneous emission probability, comparable to Yb:YTG (3739 s^{-1}) [16], as explained by Eq. (1).

5. Conclusion

The measurements show that, as the lead fluoroborate glass doped with Yb^{3+}, its absorption cross-section is larger than in other laser host glasses and its emission cross-section is comparable to a commercial phosphate laser glass (Yb:QX). Both glasses have spectroscopic properties for laser applications, as their properties are similar to other known glasses (phosphate and tellurite laser glasses) already used as active laser media. The heavy metal oxide glass has a larger emission bandwidth, which is of interest for tunable lasers.

References

[1] P. Nachimuthu, R. Jagannathan, V.N. Kumar, D.N. Rao, J. Non-Cryst. Solids 217 (1997) 215.
[2] M.B. Saisudha, J. Ramakrishna, Phys. Rev. B 53 (1995) 6186.
[3] L.R.P. Kassab, S.H. Tatumi, A.S. Morais, L.C. Courrol, N.U. Wetter, V.L.R. Salvador, Opt. Exp. 8 (2001) 585.
[4] Y.G. Choi, K.H. Kim, J. Am. Ceram. Soc. 82 (1999) 2762.
[5] J. Heo, Y.B. Shin, J.N. Jang, Appl. Opt. 21 (1995) 4284.
[6] Y.G. Choi, J. Heo, J. Non-Cryst. Solids 217 (1997) 199.
[7] L.R.P. Kassab, S.H. Tatumi, C.M.P. Mendes, L.C. Courrol, N.U. Wetter, Opt. Exp. 6 (2000) 104.
[8] W.R. Dumbaugh, Phys. Chem. Glasses 27 (1986) 119.
[9] Y.B. Shin, H.T. Lim, Y.G. Choi, Y.S. Kim, J. Heo, J. Am. Ceram. Soc. 83 (2000) 787.
[10] F. Donald Bloss, An Introduction to the Methods of Optical Crystallography, Holt, Rinehart and Winston, USA, 1961.
[11] X. Zou, H. Toratani, Phys. Rev. B 52 (1995) 15889.
[12] L.D. Deloach, S.A. Payne, L. Smith, W.L. Kway, W.F. Krupke, J. Opt. Soc. Am. B 11 (1994) 269.
[13] C. Jiang, H. Liu, Q. Zeng, X. Tang, F. Gan, J. Chem. Phys. Solids 61 (2000) 1217.
[14] R. Koch et al., Opt. Commun. 134 (1997) 175.
[15] V. Petrov, U. Griebner, D. Ehrt, W. Seeber, Opt. Lett. 22 (1997) 408.
[16] C. Jiang, F. Gan, J. Zhang, P. Deng, G. Huang, Mater. Lett. 41 (1999) 209.