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Lead fluoroborate glasses doped with Nd^{3+}

L.C. Courrol[a,*], L.R.P. Kassab[a], V.D.D. Cacho[a], S.H. Tatumi[a], N.U. Wetter[b]

[a] *Laboratório de Vidros e Datação, Faculdade de Tecnologia de São Paulo (FATEC-SP), Centro Estadual de Educação Tecnológica Paula Souza, Praça Coronel Fernando Prestes 30, CEP 01124-060 São Paulo, SP, Brazil*

[b] *Centro de Lasers e Aplicações, IPEN-CNEN, São Paulo, SP, Brazil*

Abstract

Results of absorption, emission and fluorescence lifetime (for the $^4F_{3/2} \rightarrow {}^4I_{11/2}$ transition) are presented for a new lead fluoroborate glass doped with different concentrations of Nd_2O_3 varying from 0.04 up to 3.49 wt%. The calculated Judd–Ofelt parameters are: $(1.7 \pm 0.1) \times 10^{-20}\,cm^2$, $(3.4 \pm 0.3) \times 10^{-20}\,cm^2$, $(3.6 \pm 0.3) \times 10^{-20}\,cm^2$. Branching ratios calculations show that the $^4F_{3/2} \rightarrow {}^4I_{11/2}$ transition has the most potential for laser applications. The best spectroscopic performance was obtained for the sample doped with 1.75 wt% of Nd_2O_3: emission cross-section of $3.6 \times 10^{-20}\,cm^2$ at 1060 nm, fluorescence lifetime of 0.06 ms and effective fluorescence bandwidth of 30.43 nm. The samples have high refractive index of 2.2 and a density of about $6.9\,g/cm^3$. Concentration quenching was observed at 3.49 wt%. The results obtained suggest that this new material can be considered as an interesting candidate for laser applications with similar properties when compared to other known glasses used as laser media.

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Keywords: Laser; Glasses; Neodymium; Cross-section

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1. Introduction

In this work we report for the first time the spectroscopic properties of Nd^{3+}-doped lead fluoroborate glasses ($PbO–PbF_2–B_2O_3$) produced at the Laboratory of Glasses and Datation at the Faculty of Technology of São Paulo. The study of lead fluoroborate glasses doped with rare earth for laser applications is missing in the literature. Recently, the use of Sm^{+3}, Dy^{3+} and Nd^{3+} in lead oxyfluoride (PbO-PbF_2) [1] and lead borate (PbO-B_2O_3) glasses was published [2]. We reported spectroscopic studies of lead fluoroborate glasses doped with Yb^{3+} [3] and codoped with Yb^{3+} and Er^{3+} [4] whose results showed that the samples are good candidates for laser applications at 1022 and 1543 nm, respectively. The motivations for the study of this 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) [3].

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*Corresponding author. Centro de Lasers e Aplicações, IPEN/CNEN-SP, Cidade Universitaria, Travessa R400, 05508-900 São Paulo, SP, Brazil. Tel.: +55-11-38169314; fax: +55-11-8169315.

E-mail address: lcourrol@net.ipen.br (L.C. Courrol).

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2. Experiment

The samples with different concentrations of Nd_2O_3 (varying from 0.04 up to 3.49 wt%) were prepared using the following glass matrix: (wt%) 15.8 B_2O_3, 35.3 PbO and 48.9 PbF_2. The reagents were melted in air at 1000°C for one hour and a half using Pt crucible, and annealed for 12 h at 400°C (measured transition temperature is 480°C). Transparent and homogeneous glasses (all samples were examined using optical microscopy) stable against crystallization were produced. The refractive index (2.2) was measured with the "apparent depth method" (that relates the physical thickness to its optical thickness or apparent thickness) and the density (6.9 g/cm^3) was determined using the Archimedes method. Absorption spectra at room temperature were obtained with a spectrophotometer (Cary 17 D/OLIS). The infrared pumping was performed using an excitation beam of 800 nm from an InGaAs laser diode (Optopower A020), a Germanium detector, a 0.5 m monochometer (Spex) and a EG&G7220 lock-in amplifier. The fluorescence lifetime was measured using a pulsed laser excitation (4 ns) from an OPO pumped by a frequency-doubled Nd:YAG laser (Quantel), an InSb detector and a signal-processing Box-Car averager (PAR 4402).

3. Results and discussion

The absorption spectra of the Nd^{3+} occur due to the transition from the ground state $^4I_{9/2}$ to various excited states. Fig. 1 presents the absorption spectrum at room temperature for the sample doped with 1.75 wt%. The emission spectra are shown in Fig. 2. At larger neodymium concentrations, concentration quenching by ion–ion interaction becomes important. We can observe in Fig. 2 that there is a quenching for the sample containing 3.49 wt% of Nd_2O_3.

The Judd–Ofelt parameters (Ω_t) were calculated with the expression below (using the absorption bands shown in Fig. 1) that equates the experimental to the calculated oscillator strength for an induced electric dipole transition [5]:

$$\frac{mc^2}{\pi e^2 \rho \lambda_p^2} \int k(\lambda)\, d\lambda = \frac{8\pi^2 mc}{3h(2J+1)\lambda_p} \left(\frac{(n^2+2)^2 S_{ed}}{9n} \right), \tag{1}$$

where c represents the velocity of light, n the refractive index, ρ the concentration of Nd^{3+} ions, λ_p the absorption peak wavelength, m and e the mass and the electron charge, $k(\lambda)$ the absorption coefficient, S_{ed} represents the line strengths for the induced electric dipole transition. The line strength

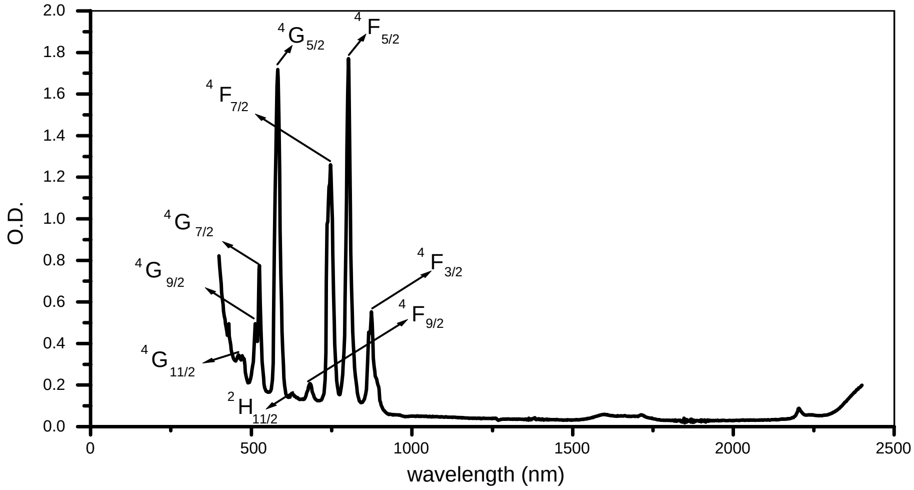

Fig. 1. Absorption spectrum at room temperature for the lead fluoroborate glass doped with 1.75 wt% of Nd_2O_3 (excitation at 797 nm).

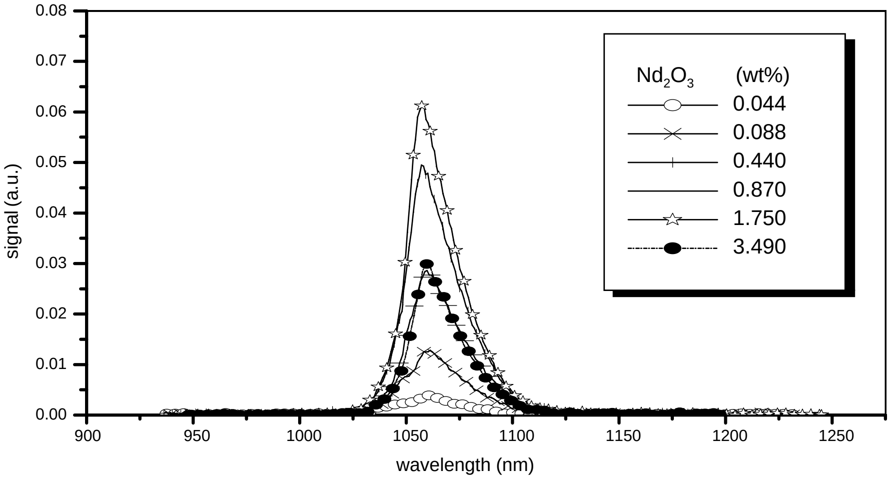

Fig. 2. Emission spectra for the lead fluoroborate glasses doped with different concentrations of Nd_2O_3 ($^4F_{3/2} \rightarrow {}^4I_{11/2}$ transition).

for the induced electric dipole (S_{ed}) transition is given by

$$S_{ed} = \sum_{t=2,4,6} \Omega_t \left| \langle SLJ \leq \| U^t \| S'L'J' \rangle \right|^2, \tag{2}$$

where $|\langle SLJ \| U^t \| S'L'J' \rangle|^2$ is the square of the matrix elements of the tensorial operator U^t which connects SLJ to $S'L'J'$ states. The matrix elements in the fitting procedure were those given by Carnall et al. for Nd^{3+} in aqueous solution [6]. In the case of overlapping transitions, the matrix elements were summed [7]. The three Judd–Ofelt parameters were determined by a least-squares fitting routine that compares the measured oscillator strengths for different Nd^{3+} absorption bands with the theoretical oscillator strengths using the matrix elements tabulated in Ref. [7]. The values obtained are: $\Omega_2 = (1.7 \pm 0.1) \times 10^{-20}\,\text{cm}^2$, $\Omega_4 = (3.4 \pm 0.3) \times 10^{-20}\,\text{cm}^2$, $\Omega_6 = (3.6 \pm 0.3) \times 10^{-20}\,\text{cm}^2$. The small value of Ω_2 may be associated with the micro-structural homogeneity around the Nd^{3+} ions [5]. The fact that $\Omega_2 < 2.0$ indicates covalence in bonding. The Judd–Ofelt parameters show the general tendency $\Omega_2 < \Omega_4 < \Omega_6$ observed for Nd^{3+} ion in all glasses and crystals [8]. The spontaneous emission probability [5] of $3186.0\,\text{s}^{-1}$ was determined with the following equation with λ representing the emission peak wavelength:

$$A_R = \frac{64\pi^4 e^2}{3h(2J+1)\lambda^3} \left(\frac{n(n^2+2)^2 S_{ed}}{9} \right). \tag{3}$$

The peak emission cross-section for the Nd^{3+}, $^4F_{3/2} \rightarrow {}^4I_{11/2}$ transition is expressed as

$$\sigma_{em} = \frac{\lambda^4 A_R}{8\pi n^2 c\, \Delta\lambda_{EFF}}, \tag{4}$$

where $\Delta\lambda_{EFF}$ is the effective fluorescence bandwidth. Fig. 3 presents the results of the emission cross-section for the sample doped with 1.75 wt%. Peak cross-section is dependent on the intensity parameters, Ω_t, and the bandwidth, $\Delta\lambda_{EFF}$. Both are affected by composition changes. The intensity of the $^4F_{3/2} \rightarrow {}^4I_{11/2}$ laser transition depends only on the Ω_4 and Ω_6 parameters because of the triangle rule $|J'-J| \leqslant \lambda \leqslant |J'+J|$ [9]. So Ω_2 will not have any affect on the stimulated emission and the $^4F_{3/2}$ fluorescence can then be expressed by the ratio $Q = \Omega_4/\Omega_6 = 0.94$ which is usually considered as the spectroscopic quality factor [10].

Table 1 summarizes all the results obtained and the sample doped with 3.49 wt% is not included in this table (fluorescence lifetime of 0.3 ms because of the concentration quenching). The results show that the optimum sample for laser operation at 1060 nm is the one with 1.75 wt% of Nd_2O_3. Table 2 shows the results of radiative transition

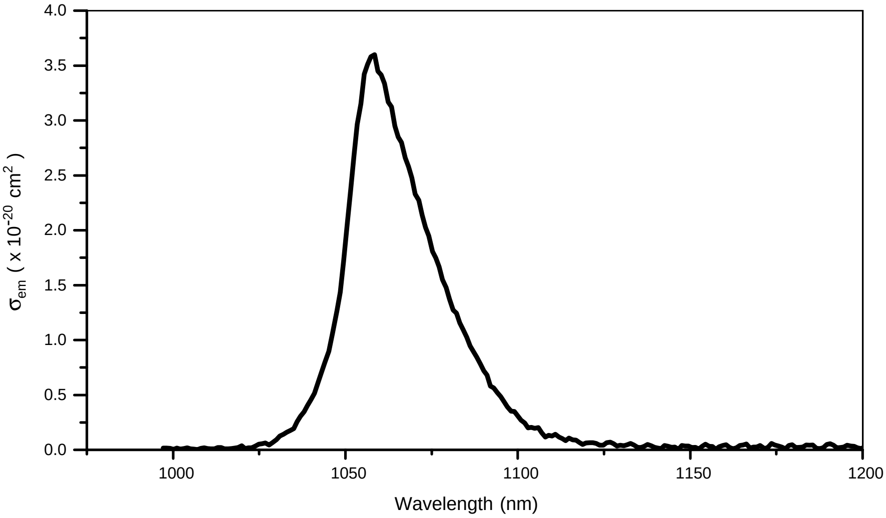

Fig. 3. Emission cross-section spectrum at 1060 nm for the lead fluoroborate glass doped with 1.75 wt% of Nd_2O_3 (peak emission cross-section of $3.6 \times 10^{-20}\,cm^2$).

Table 1
Spectroscopic results of the lead fluoroborate glasses produced with different concentrations of Nd_2O_3

Concentration of Nd_2O_3 (wt%)	Fluorescence lifetime (ms)	σ_{em} ($\times 10^{-20}\,cm^2$)	$\Delta\lambda_{EFF}$ (nm)
0.044	0.08±0.01	2.3±0.2	47.60
0.088	0.08±0.01	2.9±0.2	38.02
0.440	0.08±0.01	3.1±0.2	35.14
0.870	0.07±0.01	3.4±0.2	32.53
1.750	0.06±0.01	3.6±0.2	30.43

Table 2
Radiative transition probability and branching ratios for the lead fluoroborate glasses doped with Nd^{3+}

		λ (nm)	A_R (s^{-1})	β (%)
$^4F_{3/2} \rightarrow$				
	$^4I_{15/2}$	1869	32.2	0.5
	$^4I_{13/2}$	1382	576.9	8.5
	$^4I_{11/2}$	1060	3186.0	47.2
	$^4I_{9/2}$	879	2459.9	43.8

Table 3
Laser emission characteristics for some glasses for comparison with the sample of 1.75 wt% studied in this work ($\tau_R = 1/A_R$ is the radiative lifetime of the $^4F_{3/2} \rightarrow {}^4I_{11/2}$ transition)

Glass composition	σ_{em} ($\times 10^{-20}\,cm^2$)	λ_P (nm)	τ_R (μs)	$\Delta\lambda_{EFF}$ (nm)
Fluorozirconate [12]	3.0	1049	450	26.4
P107 [5]	3.9	1054	322	26.5
L-223 [5]	3.5	1054	371	27.2
ZBAN [11]	3.2	1048	360	27.8
Our glass	3.6	1060	313	30.4

probabilites (A_R) and branching ratios (β) calculated by [5] $\beta = A_R/\Sigma_{J'} A_R$. The branching ratios can be used to predict the relative intensities of all emission originating from a given excited state. The results in Table 2 show that $^4F_{3/2} \rightarrow {}^4I_{11/2}$ transition has the most potential for laser application with fluorescence peak at 1060 nm. Table 3 shows spectroscopic properties for some glasses including the one presented in this work (with 1.75 wt% of Nd_2O_3): P107, a commercially available laser phosphate glass [5]; L223, a fluorophosphate glass; ZBAN, a heavy metal fluoride glass [11] and a fluorozirconate glass [12].

4. Conclusion

Laser transitions were studied, for the first time, in lead fluoroborate glasses doped with Nd^{3+}. The sample with the best spectroscopic performance (1.75 wt% of Nd_2O_3) presents emission cross-section of $3.6 \times 10^{-20}\,cm^2$ at 1060 nm, fluorescence lifetime of 60 ms and effective fluorescence bandwidth of 30.43 nm. Considering the similar properties to other known glasses used as laser media (ZBAN, phosphate, fluorophosphate and fluorozirconate glasses) we suggest the use of this new material for laser application at 1060 nm.

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