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Up-conversion losses in Nd^{3+} doped lead fluoroborate glasses

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Abstract

In this paper we report the determination of the ETU processes of lead fluoroborate glasses produced at Faculty of technology of São Paulo, doped with concentrations of Nd_2O_3 ranging from 0.04 wt% up to 3.49 wt%. The samples have a high refractive index of 2.2 and density of about 6.9 g/cm^3. Concentration quenching was observed at 3.49 wt% doping. The spectroscopic results suggest that these materials can be considered as candidates for laser applications when compared to other known glasses used as laser media. The best spectroscopic performance was obtained for a sample doped with 1.75 wt% of Nd_2O_3 : emission cross-section of 3.6×10^{-20} cm^2 at 1060 nm, fluorescence lifetime of 0.06 ms and effective fluorescence bandwidth of 30.43 nm. No visible emission from the $^4F_{3/2}$ level is observed when pumping with a diode laser at 797 nm. From analysis of the temporal evolution of the infrared emission from the $^4F_{3/2}$ state pumped at two excitation powers, we estimated the macroscopic energy transfer up-conversion (ETU) parameter for the studied samples. The results show ETU probability has a quadratic dependence on neodymium concentration.

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1. Introduction

Among various rare earth ions used for laser emitters, neodymium has been studied in a variety of glasses due to its potential application in the field of infrared optical amplification because of the radiative efficiency of the infrared $^4F_{3/2} \rightarrow {}^4I_{11/2}$ transition [1]. Neodymium doped glasses have a fluorescence emission line width of ~ 25 nm that potentially support sub-100 fs pulses at a wavelength of ~ 1060 μm.

When choosing a material to be used as a laser active medium, the characteristics desired for good laser performance include, gain, energy storage capacity, and optical losses among others. Gain and stored energy depend on the stimulated emission cross section, fluorescence lifetime, and coupling efficiency of the pump. Solid state Nd-laser systems pumped by high power diode lasers have high efficiencies and are now standard tools for many applications [2,3]. On the other hand, larger power and greater brightness diode lasers are efficient sources to produce non-linear effects in laser media, as up-conversion fluorescence [4]. There are a variety of systems that use this effect to convert the infrared pump radiation into visible fluorescence [5,6]. Most of these processes rely either on excited-state absorption (ESA) or energy-transfer up-conversion (ETU).

We report the up-conversion processes in Nd-doped fluoroborate glasses ($PbO–PbF_2–B_2O_3$) with different neodymium concentrations, produced at the Laboratory of Glasses and Datation at the Faculty of Technology of São Paulo. This glass material has high refractive index (2.2) [7] that is responsible for the high spontaneous

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emission probability, very good glass forming region, physical and chemical stability and transmission from the visible region (0.4 μm) up to the infrared, 4 μm [7]. Differently from other materials such as fluoride glasses [8], the lead fluoroborate glass does not produce visible emissions under continuous diode laser pumping at 797 nm, nevertheless losses in the $^4F_{3/2}$ metastable level are observed. Up-conversion processes such as energy transfer can be a loss source originating in the upper laser level [9]. These mechanisms have already been studied in Nd-doped glasses [10], showing that ETU from $^4F_{3/2}$ state constitutes an important source of loss.

2. Experiment

The samples with different concentrations of Nd_2O_3 (varying from 0.04 wt% 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, stable against crystallization, were produced. Glass samples with two polished faces and 3 mm thickness were used for refractive index, absorption, and emission and lifetime measurements. The samples surfaces were polished flat and parallel. A Carl Zeiss microscope with a 10× objective lens was used to measure the refractive index. The refractive index was determined by means of the 'apparent depth method'. The densities were measured with the Archimedes method.

The absorption spectra in the range 920–1120 nm were measured using a Varian Spectrometer Cary 17 D at room temperature. The emission spectra were obtained by exciting the samples, at 797 nm, with a laser diode (Optopower A020). This diode system contains an area semiconductor laser with a maximum of 20 W of continuous output power operating at this wavelength. The diode laser beam was treated with a beam-shaper [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 square profile, with transverse dimensions of approximately 260×260 μm. During the emission measurements, the sample was pumped with a 7.5 W of diode laser beam, modulated at 40 Hz. The emissions of the samples were analyzed with a 0.5 m monochromator (Spex) and a Germanium detector. The signal was amplified with an lock-in EG&G 7220 and processed by a computer.

A time resolved luminescence spectroscopy technique was employed to measure the Neodymium luminescence decays induced by resonant laser excitations to determine the mechanism involved in the energy transfer in the up-conversion processes. The excitation system consists of a tunable optical parametric oscillator (OPO from OPOTEK) pumped by the second harmonic of a Q-switched Nd-YAG laser from Quantel. Laser excitation at 797 nm was applied to excite the $^4F_{5/2}$ of Nd^{3+}. This laser system delivers pulses of typical energy of 10 mJ with time duration of 4 ns and frequency of 10 Hz and can be tuned from 680 to 2000 nm. The pumped area in the sample was approximately 1 mm^2. The time-dependence luminescence of the acceptor was detected by an InSb (77 K) infrared detector (Judson model J10D) with a fast preamplifier (response time of 0.5 μs) and analyzed using a signal-processing box-car averager (PAR 4402) or a 200 MHz digital oscilloscope (Tektronix TDS 410). The relative errors in the emission measurements are estimated to be ±5%, errors in the lifetime measurements are ±10%.

3. Results

The absorption spectrum of the Nd^{3+} results from the transitions of the ground state, $^4I_{9/2}$, to various excited states. Fig. 1 shows the absorption spectrum at room temperature for the lead fluoroborate glass doped with 1.75 wt% of Nd_2O_3. It is important to note that the transparency region for this glass begins at 470 nm.

The results obtained from the emission (Fig. 2) and lifetime measurements show that the optimum sample for laser operation at 1060 nm is the one with 1.75 wt% Nd_2O_3. In the sample containing 3.49 wt% of Nd_2O_3 concentration quenching due to ion–ion interaction was observed. The $^4F_{3/2} \rightarrow {}^4I_{11/2}$ transition has the greatest potential for laser application with fluorescence peak at 1060 nm. Table 1 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 [12]; L223, a fluorophosphate

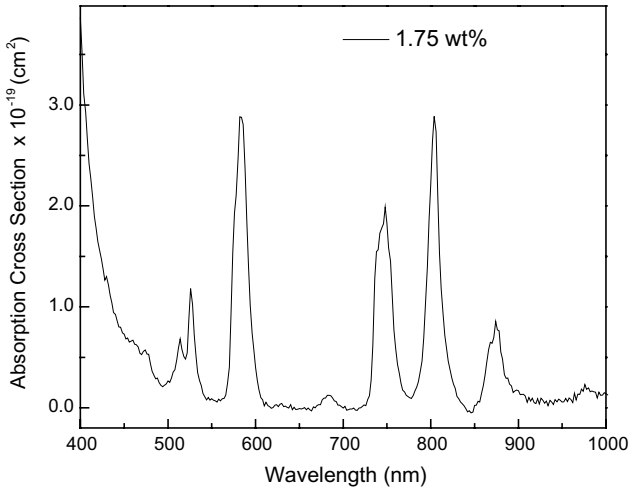

Fig. 1. Absorption spectrum at room temperature for the lead fluoroborate glass doped with 1.75 wt% of Nd_2O_3.

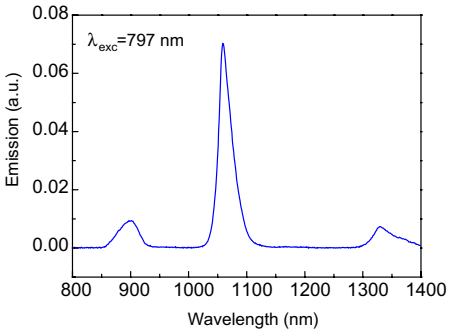

Fig. 2. Emission spectra obtained exciting the lead fluoroborate glasses doped with 1.75 wt% at 797 nm ($^4F_{3/2} \rightarrow {}^4I_{11/2}$ transition).

Table 1
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)
Fluorzirconate [13]	3.0	1049	450	26.4
P107 [12]	3.9	1054	322	26.5
L-223 [12]	3.5	1054	371	27.2
ZBAN [8]	3.2	1048	360	27.8
Lead fluoroborate [7]	3.6	1060	313	30.4

glass [12]; ZBAN, a heavy metal fluoride glass [8] and a fluorozirconate glass [13].

In Fig. 3, we shown the energy level diagram of the neodymium ion showing the up-conversion processes under diode laser pumping at 797 nm and the anti-Stokes emissions usually observed for this kind of excitation. The anti-Stokes emission spectrum obtained is

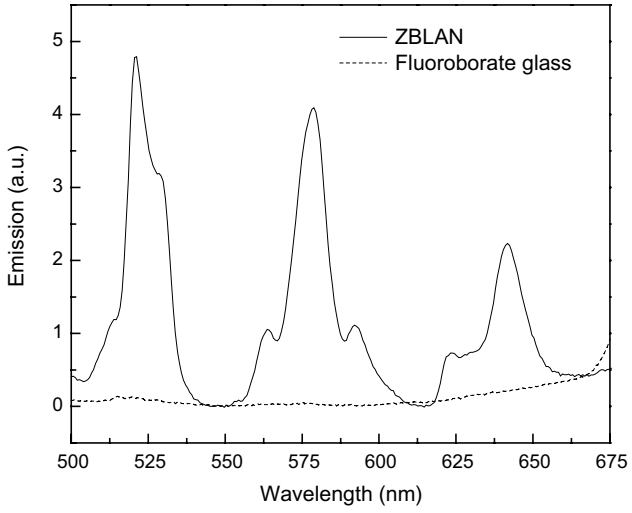

Fig. 3. Anti-Stokes fluorescence of ZBLAN and lead fluoroborate glass doped with 1.75 wt% Neodymium, in the blue–green spectral region under 797 nm excitation. Both samples have the same thickness and the emission spectra were obtained with the same pumping and detection conditions.

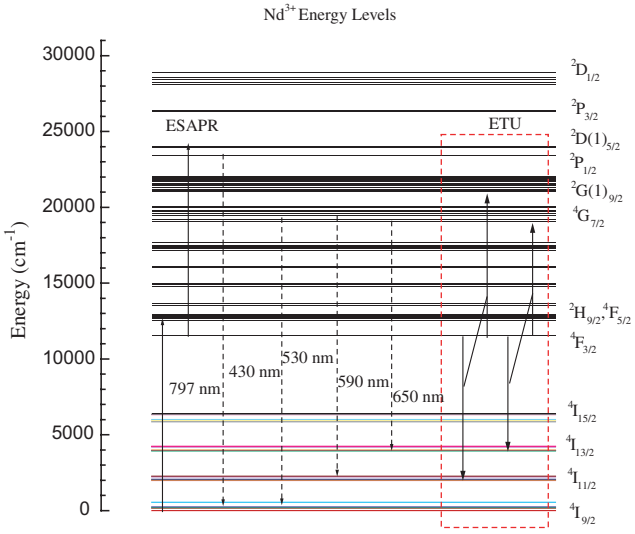

Fig. 4. Energy level diagram of Nd, showing the up-conversion processes under diode laser pumping at 797 nm and observed anti-Stokes emissions.

shown in Fig. 4, where the group of emission lines at 430 nm ($^2P_{1/2} \rightarrow {}^4I_{9/2}$), 530 nm ($^4G_{7/2} \rightarrow {}^4I_{9/2}$), 590 nm ($^4G_{7/2} \rightarrow {}^4I_{11/2}$) and 650 nm ($^4G_{7/2} \rightarrow {}^4I_{13/2}$), observed in ZBLAN glass doped with 0.5 mol% (used only for comparisons), is not observed in lead fluoroborate glass. Under pumping with 797 nm, the Nd ions are excited to the $^2H_{9/2}$, $^4F_{5/2}$ manifold, from which they relax to the metastable $^4F_{3/2}$ level that has fluorescence lifetimes of 450 μs and 313 μs for ZBLAN and fluoroborate, respectively. A second photon of 797 nm can excite Nd ions from the $^4F_{3/2}$ level to the $^2D(1)_{5/2}$ manifold which transfers its energy to the thermal excitation of the fluoroborate glasses. In the ZBLAN glass the excited Nd ions relax mainly to the $^4G_{7/2}$ level. Another excitation can be induced by a 797 nm photon re-absorption, which excites the $^2P_{3/2}$ level, being one of the possibilities due to the $^4F_{5/2} \rightarrow {}^2P_{3/2}$ transition. These processes are indicated as ESAPR (excited state absorption of pumping radiation). There are also energy transfer up-conversion (ETU) processes involving two Nd^{3+} ions, leaving one ion in either the $^4G_{7/2}$ and manifolds or the $^2G(1)_{9/2}$ multiplet and the other ion in the states $^4I_{13/2}$ or $^4I_{11/2}$, respectively. The absences of the anti-Stokes emissions for lead fluoroborate glasses, probably are due to an energy transfer mechanism from $^2P_{1/2}$ Nd^{3+} level to the glass matrix with an emission quenching. This fact allow us consider that ETU process occurs and no emission returns to $^4F_{5/2}$ level.

4. Discussion

The ETU process, in which an excited ion transfers non-radiatively its energy to an already excited neighbor

ion, is one of the most efficient up-conversion mechanisms [14]. ETU has been observed in a variety of systems, and in the majority of them it is the dominant process [15]. The local symmetry of the system and the dopant concentration determine the spatial distribution as well as the interaction of the ion pairs which formed the host lattice.

The most important ETU processes are [9]:

$$(k_1) \quad {}^4F_{3/2} \rightarrow {}^4F_{11/2}{:}{}^4F_{3/2} \rightarrow {}^2G(1)_{9/2}$$

$$(k_2) \quad {}^4F_{3/2} \rightarrow {}^4F_{11/2}{:}{}^4F_{3/2} \rightarrow {}^4G_{7/2}$$

The ETU up-conversion processes can reduce the population of the upper level causing a lifetime shortening. As a consequence, there is an increase of the laser threshold and a reduction of the energy storage efficiency. The time dependence of the $^4F_{3/2}$ population can be derived from the following rate equation:

$$\frac{dN}{dt} = -\frac{N}{\tau} - 2K_{ETU}N^2, \tag{1}$$

where N is the population density, τ is the fluorescence lifetime in the absence of up-conversion, and K_{ETU} is the macroscopic ETU parameter. With $N(t=0) = N_0$, integration yields [16]

$$N(t) = \frac{N_0 \exp(-t/\tau)}{1 + 2K_{ETU}N_0\tau[1 - \exp(-t/\tau)]}. \tag{2}$$

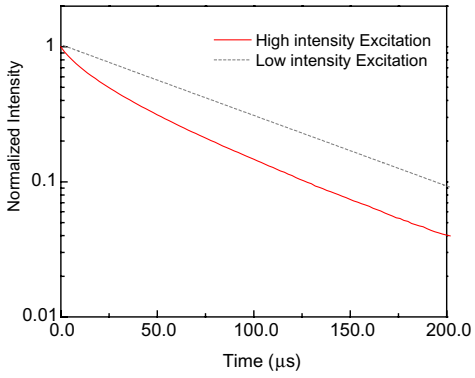

Fig. 5. Decay of the infrared fluorescence from the $^4F_{3/2}$ level for weak excitation (upper curve) and strong excitation (lower curve) for the lead fluoroborate glass doped with 1.75 wt%.

So, when there is no up-conversion, the decay is purely exponential, whereas for $K_{ETU} \neq 0$, and as K_{ETU} $N_0\tau$ increases, the decay time is shortened.

The temporal evolution of the infrared emission of the $^4F_{3/2} \rightarrow {}^4F_{9/2}$ transition was obtained by exciting the samples with an OPO laser at 800 nm, and emission lifetime was measured at 1064 nm. At low excitation conditions (2 mJ, 4 ns), the decay for the $^4F_{3/2}$ level is nearly exponential (Fig. 5 shows decay for low excitation (upper curve) for the lead fluoroborate glass doped with 1.75 wt%), except in the 3.49wt% sample. At greater power excitation (12 mJ, 4 ns) an increasing non-exponential decay appears. By fitting an experimental decay function to the $^4F_{3/2}$ level, with Eq. (2), it was possible to obtain the macroscopic ETU parameter shown in Table 2. These results are in agreement with the ones obtained for other glass matrices where the loss inducing parameter was found to be in the range $(1–2) \times 10^{-20}$ cm^3 [17]. If we plot the K_{ETU} parameter (cm^3/s) as a function of neodymium concentration, it non-linear behavior. However $W_{ETU} = K_{ETU}\tau$ (s^{-1}), or ETU probability, is a quadratic function of Nd concentration, as observed in the log–log plot shown in Fig. 6.

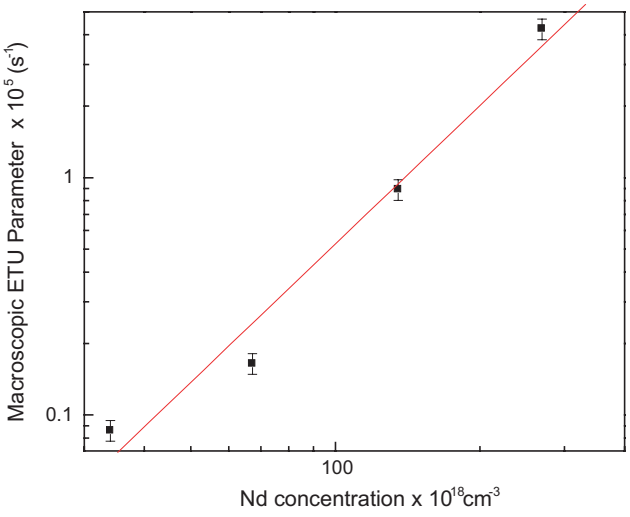

Fig. 6. The macroscopic ETU parameter as a function of neodymium concentration.

Table 2
Spectroscopic properties, laser parameters and results of the macroscopic ETU parameters of samples employed in this study

[Nd] wt%	τ_{exp} (ms)	σ_{em} (10^{-20} cm^2)	$\Delta\lambda_{EFF}$ (nm)	[Nd] (10^{18} cm^{-3})	[N$_0$] (10^{19} cm^{-3})	K_{ETU} (10^{-16} cm^3/s)
0.044	0.08 ± 0.01	2.3 ± 0.2	47.6	3.39	0.06	Not measurable
0.088	0.08 ± 0.01	2.9 ± 0.2	38.0	6.80	0.15	Not measurable
0.440	0.08 ± 0.01	3.1 ± 0.2	35.1	34.00	0.50	2.6 ± 0.2
0.870	0.07 ± 0.01	3.4 ± 0.2	32.5	67.19	1.17	2.4 ± 0.2
1.750	0.06 ± 0.01	3.6 ± 0.2	30.4	135.20	1.85	6.6 ± 0.6
3.490	0.03 ± 0.01	–	–	269.50	2.98	15.7 ± 1.5
ZBLAN[13]	–	3.0	26.4	250.00	–	46.0

5. Conclusion

The study of the pump related up-conversion processes in Nd laser glasses shows that this process is detected under typical diode laser pumping intensities. From the analysis of the temporal evolution of infrared emission from the $^4F_{3/2}$ level, we have estimated the macroscopic ETU parameter for the samples studied. These parameters are consistent with those previously reported in different glasses. The sample with 1.75 wt% of Nd_2O_3 presents emission cross-section of 3.6×10^{-20} cm^2 at 1060 nm, fluorescence lifetime of 90 μs and effective fluorescence bandwidth of 30.43 nm. For this sample the K_{ETU} was estimated to be approximately 6.6×10^{-16} cm^3/s.

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