Optical properties of Nd doped Bi_2O_3-PbO-Ga_2O_3 glasses

Luciana R. P. Kassab, Sonia H. Tatumi, Cintia M. S. Mendes
Laboratório de Vidros e Datação, Faculdade de Tecnologia de São Paulo,Centro Estadual de Educação Tecnológica Paula Souza, Praça Coronel Fernando Prestes 30, CEP 01124-060, São Paulo, SP, Brazil
kassablm@mandic.com.br

Lilia C. Courrol, Niklaus U. Wetter
Centro de Lasers e Aplicações, Instituto de Pesquisas Energéticas e Nucleares, Comissão Nacional de Energia Nuclear, São Paulo, SP, Brazil
lcourrol@net.ipen.br

http://www.opticsexpress.org

Abstract: The optical properties of a new family of neodymium doped BPG (Bi_2O_3-PbO-Ga_2O_3) glasses are presented. We measured a high refractive index, of 2.5, and a transmission cutoff in the far infrared at 8µm. Three emission bands are observed centered at 877nm, 1066nm and 1341nm. The emission cross-section is $10^{-20}cm^2$ and the total spectral linewidth is 30nm at 1066nm. The Judd-Ofelt parameters are calculated and used to evaluate transition probability, radiative lifetime and branching ratios. The optical properties of these Nd:BPG glasses show promise for their use as a new active laser material.

OCIS code: (160.3380) Laser materials; (300.6360) Spectroscopy, laser

References and links

1. W. Koechner, *Solid State Laser Engineering* (Springer-Verlag, Berlin, 1996), Chap. 2 and Chap. 3.
2. R. Scheps, "Efficient Laser Diode Pumped Nd Lasers," Appl. Opt., **1,** 89-91 (1989).
3. N. P. Barnes, M. E. Storm, P. L. Cross, and M. W. Skolaut, "Efficiency of Nd Laser Materials with laser Diode Pumping," J. Quantum Electron., **26,** 558-569 (1990).
4. J. Nees et al.,"Ensuring Compactness, Reliability, and Scalability for the Next Generation of High-Field Lasers," J. Quantum Electron., **4,** 376-384(1998).
5. W. R. Dumbaugh, "Lead Bismuthate Glasses," Physics and Chemistry of Glasses, **19**, 121-125 (1978).
6. W. R. Dumbaugh, "Heavy Metal Oxides Glasses Containing Bi_2O_3," Physics and Chemistry of Glasses, **27**, 119-123 (1986).
7. J. G. Clemente, L. R. P. Kassab, S. H. Tatumi, "Study of Glasses Containing Heavy Metal and Gallium Oxides," in *Proceedings of the 4th Brazilian Symposium on Glasses and Related Materials* (Ouro Preto, MG, Brazil, 1999), pp. 27.
8. F. Donald Bloss, *An Introduction to the Methods of Optical Crystallography* (Holt, Rinehart and Winston, Inc, USA, 1961).
9. B. R. Judd, "Optical Absorption Intensities of Rare-Earth Ions," Phys. Rev., **127**, 750 (1962).
10. G. S. Ofelt, "Intensities of Crystal Spectra of Rare-Earth Ions," J. Chem. Phys, **37**, 511 (1962).
11. C. Y. Chen, W. A. Sibley, D. C. Yeh and C. A. Hunt, "The optical properties of Er^{3+} and Tm^{3+} in $KCaF_3$ Crystal," J. of Luminesc., **43**, 185-194 (1989).
12. C. Li, Y. Guyot, C. Linares, R. Moncorgé, M. F. Joubert, "Radiative Transition Probabilities of Trivalent Rare-Earth Ions in $LiYF_4$," in *Proceedings on Advanced Solid-State Lasers*, Albert A. Pinto, Tso Yee Fan, Vol. V of OSA Proceedings Series (Optical Society of America, New Orleans, LA., 1993), pp. 91-95.
13. Y. Guyot, H. Manaa, J. Y. Rivoire, R. Moncorgé, N. Garnier, E. Descroix, M. Bom, P. Laporte, "Excited-State-Absorption and Upconversion Studies of Nd^{3+} doped single crystals $Y_3Al_5O_{12}$, $YLiF_4$ and $LaMgAl_{11}O_{19}$", Phys. Rev. B, **51**, 784-799 (1995).
14. R. R. Petrin, M. L. Kliewer, J. T. Beasley, R. C. Powell, I. D. Aggarwal, R. C. Ginther, "Spectroscopy and Laser Operation of Nd:ZBAN Glass," J. Quantum Electron., **27,** 1031-1038 (1991).
15. W. T. Carnall, H. Crosswhite, H. M. Crosswhite , private communication (1977).
16. Y. Guyot, R. Moncorgé, L. D. Merkle, A. Pinto, B. MacIntosy, H. Verdun, "Luminescence properties of Y_2O_3 single crystals doped with Pr^{3+} or Tm^{3+} and codoped with Yb^{3+} , Tb^{3+} or Ho^{3+} ions," Optical Materials, **5**, 127-136 (1996).
17. M. J. Weber, "Science and Technology of Laser Glass," J. Non-Cryst. Solids, **123**, 208-222 (1990).

#19101 - $15.00 US
Received January 16, 2000; Revised February 10, 2000

1. Introduction

With the development of powerful diode lasers emitting around 800nm, spectroscopic studies of insulating laser materials doped with Nd^{3+} were renewed. The concentration levels of the active ion in glasses can be made very high and therefore short glass samples can absorb almost all the pump radiation of diodes leading to very efficient laser operation [1]. Most solid state Nd laser systems pumped by high power diode lasers are now standard tools for many applications due to their high efficiencies [2,3]. Special interest for wide-bandwidth laser glasses has recently come from the search for better high-field lasers [4] where the bandwidth sets the ultimate limit to how short the laser pulse can get.

In this paper we report the spectroscopic properties of Nd doped BPG (Bi_2O_3-PbO-Ga_2O_3) glasses produced at the Laboratory of Glasses and Datation at the Faculty of Technology of São Paulo (FATEC-SP).

In BPG glasses, lead and bismuth oxides do not form glasses by themselves and Ga_2O_3 plays the role of the system stabilizer. The well known [5,6,7] main characteristics of BPG glasses are the transmission into the far infrared region, the high refractive index and the nonlinear optical behavior. The principle of forming glass with infrared transmission to longer wavelengths is based on the use of compounds whose cation-anion bond is relatively weak, giving a low fundamental vibration frequency. BPG glasses have potential applications in optoeletronic circuits as ultrafast switches, infrared windows, optical isolators and also in advanced computer because of the characteristics mentioned above.

The optical properties of Nd doped BPG glasses are studied by means of absorption, luminescence and the associated lifetime and refractive index measurements. The Judd-Ofelt parameters are calculated and used to evaluate transition probability, radiative lifetime and branching ratios for the fluorescent levels; cross-section calculations are performed at 1066nm.

2. Experimental Procedure

The starting materials, which are 17.6mol% Ga_2O_3, 24.9mol% Bi_2O_3, 56.7mol% PbO and 1mol% Nd_2O_3, are melted in air at 1000°C for approximately one hour, using Pt crucibles. They are then poured onto preheated brass molds for a quick solidification and annealed at 250°C for 3 hours, producing dark red colored transparent samples. The samples are cut in slabs of 2.5mm thickness and then polished. Measurements of transmission in the infrared region are performed by means of a Jasco Spectrometer. The refractive index is determined by means of the "apparent depth method" [8]. This method relates the optical thickness (apparent thickness) of a transparent specimen to its physical thickness. Specimen surfaces must be polished, flat and parallel and thickness should be at least 2.5mm. We used a Carl Zeiss microscope with a 10x objective lens to measure the refractive index. The infrared pumping is performed with a GaAlAs laser diode (Spectra Diode Labs - model SDL-2382-P1). This diode system contains a broad-area semiconductor laser with 4W of continuous output power operating at 797nm. The diode laser beam is collimated by a diffraction-limited, N.A.=0.5, f=8mm objective, corrected by a 3x anamorphic prism pair (both from *Melles Griot*) and focused by a single f=10cm lens. Close to the focus, and for a depth of focus of 2mm, the beam has a rectangular profile, with transverse dimensions of approximately 120μm x 60μm. During the emission measurements, the sample is pumped by the diode laser beam chopped at 40Hz and focused onto the sample with a 10cm focal length lens. The visible Nd emission is detected with a Ge detector and analyzed with a 0.5m (Spex) monochromator. The luminescence signal was processed using a EG&G7220 lock-in amplifier. The lifetimes of excited Nd^{3+} ions are measured using a pulsed laser excitation (4ns) from a OPO pumped by a frequency doubled Nd:YAG laser. The time-dependence signal is detected by a fast S-1 extended type photomultiplier detector and analyzed using a signal processing Box-Car averager (PAR 4402).

#19101 - $15.00 US
Received January 16, 2000; Revised February 10, 2000

3. Results

Figure 1 shows the transmission spectrum in the infrared region in which we can see the cutoff wavelength of about 8μm; the presence of the OH-band at 3.25μm can also be observed. Figure 2 shows the absorption spectrum of the sample doped with neodymium. We notice four Nd^{3+} absorption bands at approximately 580, 750, 800 and 880nm and a bulk absorption in the blue. In Figure 3 we show the three emission bands centered at 877nm, 1066nm and 1341nm. These emissions correspond respectively to the following laser transitions: $^4F_{3/2}\rightarrow{}^4I_{9/2}$, $^4F_{3/2}\rightarrow{}^4I_{11/2}$ and $^4F_{3/2}\rightarrow{}^4I_{13/2}$. The fluorescence lifetime measured, associated to these transitions is of 110μs. The spectral linewidth of the fluorescent emission spectrum at 1066nm was measured to be 30nm. So Nd:BPG glass has an emission band at 1066nm, broader than most of other glass hosts [1], and offers considerable potential for wavelength tunability and generation of short laser pulses.

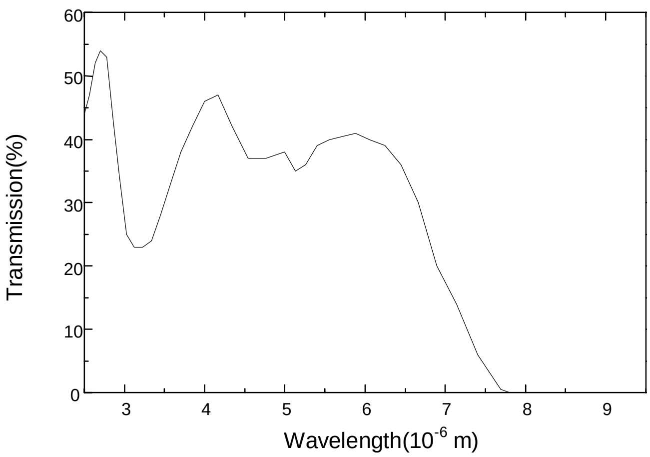

Fig. 1. Transmission in the infrared region for the BPG glass doped with neodymium (2.5mm thickness).

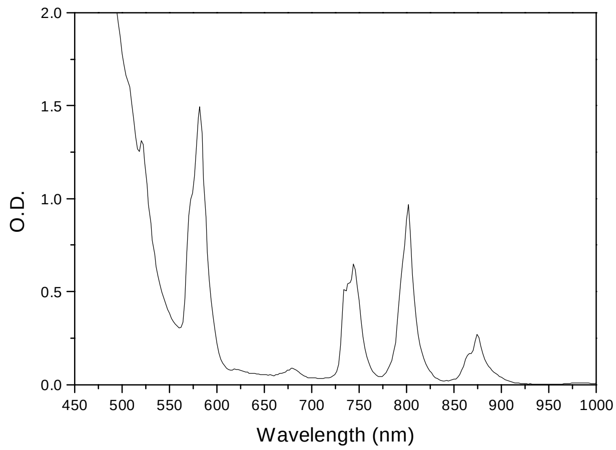

Fig. 2. Absorption spectra of Nd:BPG glass (2.5mm thickness).

The probability rate of a radiative transition between two distinct multiplets J and J', can be obtained from the well known relation :

$$A(J \rightarrow J') = \frac{64\pi^4 e^2}{3h(2J+1)\lambda^3} \frac{n(n^2+2)^2}{9} \sum_{t=2,4,6} \Omega_t \left| \left\langle SLJ \left| U^{(t)} \right| S''L'J' \right\rangle \right|^2 \qquad (1)$$

where Ω_t are the Judd-Ofelt parameters which depend on the strength and symmetry of the local field. Analysis of oscillator strengths of dipole-forced electronic transitions of 3+ rare-earth ions in solids are widely used by means of the Judd-Ofelt theory [9,10,11]. The same approach is used to calculate Ω_t in Nd:YLF crystals [12]. The calculated values of Ω_t for Nd:BPG are:

$\Omega_2 = 0.95 \times 10^{-20} cm^2$
$\Omega_4 = 2.01 \times 10^{-20} cm^2$
$\Omega_6 = 4.30 \times 10^{-20} cm^2$

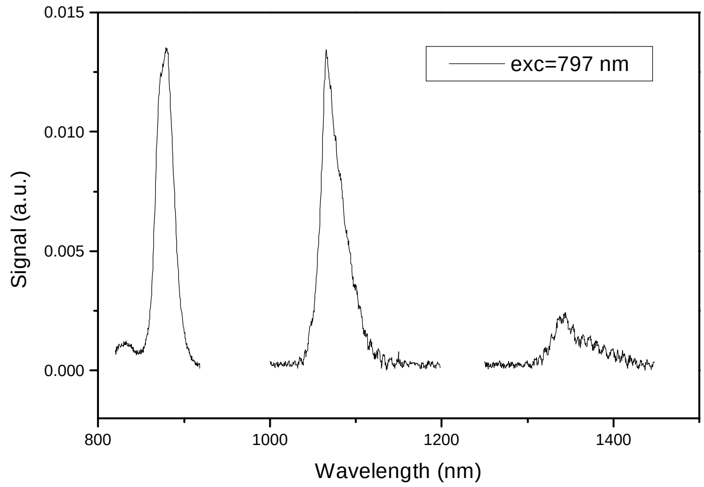

Fig. 3. Room temperature fluorescence spectrum of Nd:BPG glass under diode laser excitation at 797nm.

The Ω_4/Ω_6 ratio governs the branching ratio (β_R) from $^4F_{3/2}$ state. The lower the value of this ratio, the stronger the $^4F_{3/2} \rightarrow {}^4I_{11/2}$ emission around 1060nm. The obtained value is 0.47 for Nd:BPG; for Nd:YAG crystals, this value is 0.54 [13] and for Nd:ZBAN glass is 0.64 [14]. By using the Ω_t values and the matrix elements $U^{(t)}$ for Nd^{3+} obtained from the literature [15], it is possible to calculate the radiative transition probabilities for all the laser emissions which are relevant for the diode pumped Nd-laser system. These values are shown in table 1.

The radiative lifetime of an excited state (J) can be obtained by:

$$\tau_R = \sum_J \left[A(J, J') \right]^{-1} \qquad (2)$$

For Nd:BPG glass, this value is 369μs.

We should remark that the fluorescent emission observed at 877nm occurs at a lower wavelength than normally observed in other neodymium doped hosts and has a considerable branching ratio value when compared with the 1066nm emission.

The stimulated emission cross-section at the peak of $^4F_{3/2} \rightarrow {}^4I_{11/2}$ transition is obtained from the fluorescence lineshape by using the expression [16]:

Received January 16, 2000; Revised February 10, 2000

$$\sigma(\lambda) = \frac{\lambda^5 \beta_R}{8\pi n^2 c \tau_R} \frac{I(\lambda)}{\int \lambda I(\lambda) d\lambda} \tag{3}$$

in which τ_R represents the radiative lifetime and β_R the branching ratio for the $4F_{3/2} \rightarrow {}^4I_{11/2}$ transition. So the peak emission cross-section of Nd:BPG corresponds to 1.1 x 10^{-20}cm^2 as shown in Figure 4. This value is comparable to other silicates used as laser glasses [17].

Table 1. Transition probability and branching ratios of Nd:BPG glasses

${}^4F_{3/2} \rightarrow$		λ (nm)	$A_{J \rightarrow J'}(s^{-1})$	β(%)
	${}^4I_{15/2}$	1869	16.75	0.59
	${}^4I_{13/2}$	1341	375.14	13.85
	${}^4I_{11/2}$	1066	1349.04	49.82
	${}^4I_{9/2}$	877	967.60	35.73

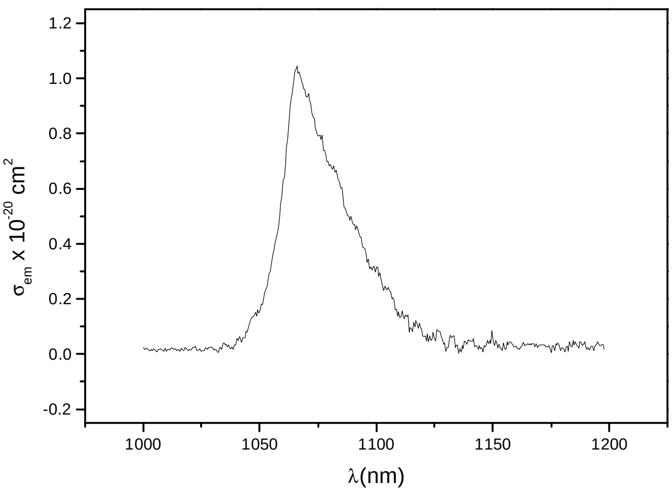

Fig. 4. Emission cross section of Nd:BPG glass for 1066nm.

4. Conclusion

The optical properties of neodymium doped BPG glasses are presented in this work. This is, to our knowledge, the first time that this host is doped with rare-earth ions. At fixed, 1mol% Nd-doping level, we measured three emission bands centered at 877nm, 1066nm and 1341nm when pumping at 797nm. The main emission line at 1066nm shows a cross-section of 1.1 x 10^{-20}cm^2 , a spectral linewidth of 30nm, and a branching ratio of about 0.50. The Ω_4/Ω_6 ratio is 0.47; for Nd:YAG crystals, this value is of 0.54 and for Nd:ZBAN glass of 0.64. We also detected no upconversion fluorescence and the sample exhibited a very good mechanical resistance under high-brightness, diode laser pumping. The bulk absorption in the blue limits the efficiency of this material under xenon flash lamp pumping whereas the broad emission bandwith makes Nd:BPG glasses a good candidate for laser action with interesting features for its use in short pulse generation under diode pumping.

Acknowledgments

We would like to thank the support from Fundação de Amparo à Pesquisa do Estado de São Paulo (FAPESP) and also Dr. Ana R. Blak from Instituto de Física da USP for the measurements of transmission in the infrared region.