Optical properties of Nd doped Bi$_2$O$_3$-PbO-Ga$_2$O$_3$ glasses

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Abstract: The optical properties of a new family of neodymium doped BPG (Bi$_2$O$_3$-PbO-Ga$_2$O$_3$) glasses are presented. We measured a high refractive index, of 2.5, and a transmission cutoff in the far infrared at 8 $\mu$m. 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. 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$_2$O$_3$-PbO-Ga$_2$O$_3$) 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$_2$O$_3$ 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 optoelectronic 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$_2$O$_3$, 24.9mol% Bi$_2$O$_3$, 56.7mol% PbO and 1mol% Nd$_2$O$_3$, 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).
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).](image1)

![Fig. 2. Absorption spectra of Nd:BPG glass (2.5mm thickness).](image2)

The probability rate of a radiative transition between two distinct multiplets $J$ and $J'$, can be obtained from the well known relation:
\[
A(J \rightarrow J') = \frac{64\pi^4e^2}{\lambda(2J + 1)\lambda^3} \frac{n(n^2 + 2)^2}{9} \sum_{r=2,4,6} \Omega_r \left| \langle SLJ | U^{(r)} | S'' L' J' \rangle \right|^2
\]

where \( \Omega \) 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 \( \Omega \) in Nd:YLF crystals [12]. The calculated values of \( \Omega \) for Nd:BPG are:

\[
\begin{align*}
\Omega_2 &= 0.95 \times 10^{-20} \text{cm}^2 \\
\Omega_4 &= 2.01 \times 10^{-20} \text{cm}^2 \\
\Omega_6 &= 4.30 \times 10^{-20} \text{cm}^2
\end{align*}
\]

![Excitation spectrum](image)

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

The \( \Omega_4/\Omega_6 \) ratio governs the branching ratio (\( \beta_R \)) 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 \( \Omega \) values and the matrix elements \( U^{(r)} \) 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:

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

For Nd:BPG glass, this value is 369\( \mu \)s.

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]:
in which $\tau_R$ represents the radiative lifetime and $\beta_R$ the branching ratio for the $4F_{3/2} \rightarrow 4I_{11/2}$ transition. So the peak emission cross-section of Nd:BPG corresponds to $1.1 \times 10^{-20}\text{cm}^2$ 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

<table>
<thead>
<tr>
<th>$4F_{3/2} \rightarrow$</th>
<th>$\lambda$ (nm)</th>
<th>$A_{\lambda \rightarrow J}$ (s$^{-1}$)</th>
<th>$\beta$ (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$4I_{15/2}$</td>
<td>1869</td>
<td>16.75</td>
<td>0.59</td>
</tr>
<tr>
<td>$4I_{13/2}$</td>
<td>1341</td>
<td>375.14</td>
<td>13.85</td>
</tr>
<tr>
<td>$4I_{11/2}$</td>
<td>1066</td>
<td>1349.04</td>
<td>49.82</td>
</tr>
<tr>
<td>$4I_{9/2}$</td>
<td>877</td>
<td>967.60</td>
<td>35.73</td>
</tr>
</tbody>
</table>

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 $1.1 \times 10^{-20}\text{cm}^2$, a spectral linewidth of 30nm, and a branching ratio of about 0.50. The $\Omega_4/\Omega_6$ 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 bandwidth makes Nd:BPG glasses a good candidate for laser action with interesting features for its use in short pulse generation under diode pumping.

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