Rare Earth Doped Photonic Glass Materials for the Miniaturization and Integration of Optoelectronic Devices

Ju H. Choi¹, Alfred Margaryan², Ashot Margaryan², Wytze van der Veer³ and Frank G. Shi¹

¹University of California Irvine, Dept. of Chemical and Materials Science Irvine, CA 92697
²AFO Research Inc., P.O. Box 1934, Glendale, CA 91209
³University of California Irvine, Dept of Chemistry, Irvine, CA 92697
¹Phone: 949.824.7385, Fax: 949.824.2541
¹Email: juc@uci.edu

Abstract

Er³⁺ doped alkaline-free glass systems based on MgF₂-BaF₂-Ba(PO₃)₂-Al(PO₃)₃ (MBBA system), was investigated with the aim of using as high gain media. The absorption spectra were recorded to obtain the intensity parameters (Ω_i) which are found to be Ω₂= 4.47×10⁻²⁰ cm², Ω₄=1.31×10⁻²⁰ cm², Ω₆=0.81× 10⁻²⁰ cm² for the MBBA system. The emission cross section for the ⁴I₁₃/₂ → ⁴I₁₅/₂ transition is determined by the Fuchtbauer-Ladenburg method and found to be 2.35 ×10⁻²⁰ cm² for the MBBA systems. Comparison of the measured spectroscopic values to those of Er³⁺ transitions in other glass hosts suggests that new MBBA systems are good candidates for broadband compact optical fiber and waveguide amplifier applications.

Keywords: Rare earth ion, Fluorophosphate glass

1.0 Introduction

The use of compact lasers has attracted increasing interest operating in the infrared region for optical communications, medical and eye-safe light detecting and ranging applications in the visible region for data storage, undersea communications [1-3]. With the development of 980nm laser diodes, the diode pumped solid state lasers can provide a compact and efficient device with the advantage of easy coupling with fiber integrated optical systems. Specifically, the optically excited luminescence originating from the dipole-forbidden ⁴I₁₃/₂ → ⁴I₁₅/₂ transition of Er³⁺ has a wavelength of 1.54 μm that matches one of the minimum loss windows of commercial silica-based optic fibers. Typical Er³⁺ doped fiber amplifiers utilize approximately several meters of silica fiber doped with a few hundred ppm weight Er³⁺ ions [4].

In the construction of integrated light amplifiers it is desirable to obtain the maximum gain with minimum component size. In order to evaluate the potential for compact laser media, we conducted a systematic investigation of the spectroscopic properties of Er³⁺ doped MBBA system. The previous results on Nd³⁺, Yb³⁺ doped fluorophosphate glass systems already showed the strong potentials for each characteristics transitions of rare earth ions [5-9] to develop new host materials with a high emission cross section for compact gain media. We obtained intensity parameters, the radiative lifetime and gain coefficient for the ⁴I₁₃/₂ → ⁴I₁₅/₂ transition of Er³⁺. Finally, the potential of these systems for short fiber amplifiers or planar waveguides is evaluated by comparison to other reported glass hosts.

2.0 Experimental procedures

2.1 Glass formation:

The batch materials of 40MgF₂-40BaF₂-10Ba(PO₃)₂-10Al(PO₃)₃ system (the MBBA system) was purchased from reagent grade materials (City Chemicals, except for Er₂O₃, Spectrum Materials), all have better than
99.99% purity. The ingredients of the glasses were weighed with 0.1% accuracy and mixed thoroughly for 3 hours. Next, the raw mixed materials were melted in a vitreous carbon crucible in Ar-atmosphere at 1200 - 1250 °C. The melt was quenched by pouring it in a room temperature stainless steel mold. Next, the samples were annealed below the glass transition temperature, around 400 - 430 °C, to remove internal stress, which was verified by examination with a polariscope (Rudolph Instruments). The samples for optical and spectroscopic measurements were cut and polished to a size of 15×10×2mm³.

2.2 Spectroscopic measurements:

The refractive index \( n_D \) of the samples was measured at 588 nm, using an Abbe refractometer (ATAGO). The absorption spectra were obtained at room temperature in the range of 400-1700 nm with a Perkin-Elmer photo spectrometer (Lambda 900). The lifetime and fluorescence spectrum of both samples was recorded using a chopped Ti:Sapphire laser (Coherent 890) tuned to 800 nm, pumped by the 514 nm line of an Ar laser (Innova 300), see Figure 3. The fluorescence signal was recorded with a 0.25 m monochromator (Oriel 77200), using a InGaAs PIN detector (Thorlabs DET 410), a trans-impedance amplifier and a Lock-In amplifier (Oriel Merlin 70100). The lifetimes of both samples, was recorded with the same system, recording the temporal behavior of the fluorescence signal with a 100 MHz digital Oscilloscope.

3.0 Results and discussion

3.1 Optical properties

The value of \((n_D-n_C)\) and Abbe number \((\nu_d)\) normally describes dispersion in glasses as below

\[
\nu_d = \frac{(n_D - 1)}{(n_F - n_C)} \tag{1}
\]

where \(n_D, n_F\) and \(n_C\) are the refractive indices at the D, C and F spectral lines. The variation of refractive index as a function of rare earth dopant concentration was systematically investigated in previous work. 2wt% of Er\(^{3+}\) doped MBBA system was used in this work. The refractive index \(n_D\), and Abbe number are 1.5885 and 68.1, respectively.

3.2. Absorption spectrum properties of Er\(^{3+}\) in MBBA system.

![Figure 1: The absorption cross section of Er\(^{3+}\) in the range of 300nm to 1700nm.](image)

The absorption spectrum of Er\(^{3+}\) ion consists of 11 absorption bands centered at 1532, 804, 650, 544, 520, 488, 451, 406, 377, 365, and 356 nm, corresponding to the absorptions from the ground state \(4f_{15/2}\) to the excited states in the \(4f^{11}\) electronic configuration respectively. The radiative nature of trivalent rare earth ions in a variety of laser host materials is usually investigated using the Judd-Ofelt model \([10, 11]\). The observed oscillator strengths \(f_{med}\) at each absorption peak is calculated by integration the optical absorption spectra over each peak, as given by following expression Eq. (2):

\[
f_{med} = \frac{mc^2}{\pi \varepsilon^2 N} \int \frac{\alpha(\lambda)}{\lambda^2} d\lambda . \tag{2}
\]

Here \(c\) is the velocity of light, \(N\) is the Er\(^{3+}\) ion concentration (ion/cm\(^3\)), \(\alpha(\lambda) (=2.303D_0(\lambda)/d)\) is the optical absorption coefficient at a particular absorption wavelength \(\lambda\), which is calculated from the sample thickness \(d\) and the measured absorption density \(D_0(\lambda)\). The oscillator strengths as predicted by Judd-Ofelt model \(f_{cal}\) were also calculated. The oscillator strengths of the observed electronic transition are due to three interactions, electrical dipole \((ed)\), magnetic dipole \((md)\) and electric quadrupole \((eq)\). In most instances in the Er\(^{3+}\) system, the oscillator
strength of the eq component is of the order of $10^{-10}$, and the md component is of the order of $10^{-8}$. These contributions are thus unimportant compared with the ed contribution to the oscillator strength, which is in the order of $10^{-6}$ [1]. However, a significant contribution of the md component is involved for the $4I_{15/2} \rightarrow 4I_{13/2}$ absorption transition for the Er$^{3+}$. Therefore, theoretical oscillator strengths $f(aJ, bJ')$ of the $J \rightarrow J'$ transition at the mean frequency $\nu$ is given for both the electric and the magnetic dipole transition by below Eq. (3)

$$f_{ed}(aJ, bJ') = \frac{g^*/m_e}{3(2J+1)\hbar^2 n^4} \left[ \chi_{ed}(aJ, bJ') + \chi_{md}(aJ, bJ') \right]$$ (3)

where $m_e$ is the mass of the electron. $e$ and $h$ are the charge of the electron and plank’s constant, respectively. $\chi_{ed} = n(n^2+2)^2/9$ and $\chi_{md} = n^3$ are local field corrections and are functions of the refractive index n of the medium. $S_{ed}$ and $S_{md}$ are the electrical dipole and the magnetic dipole line strength respectively.

### 3.2. Intensity parameters & quality factor

The Judd-Ofelt intensity parameters were determined by a least squares fit of the theoretical (free ion) oscillator strengths to the measured (glass matrix) values obtained from optical absorption spectra. By fitting the measured oscillator strengths $f_{med}$ to the calculated values $f_{cal}$ we obtained the following values for three Judd-Ofelt parameters $\Omega_2 = 4.47 \times 10^{-20}$ cm$^2$, $\Omega_4 = 1.31 \times 10^{-20}$ cm$^2$ and $\Omega_6 = 0.81 \times 10^{-20}$ cm$^2$ are obtained for the MBBA system. The deviation $\delta_{rms}$ of the fits was 8.52 $\times 10^{-6}$, which indicates that these fits are reliable. In Table I [12-15] these values are compared to those for other reported laser glasses. The value of $\Omega_2$ indicates the strength of the covalent binding between the tri-valent rare earth ion and the host material [16, 17]. The value of $\Omega_2$ of the MBBA systems is smaller than those of BK20 oxide glass and phosphate glass, which show strong co-valent bonds. The measured value is higher than that of ZBLAN, which has a very high fluoride content causing strong ionic bonds and thus weaker co-valent bonds. The values of $\Omega_2$ of the MBBA system are comparable to those of other fluorophosphate glass with similar fluorine content.

The effect of co-valent bonding between the Er$^{3+}$ ions and the host material can be understood in terms of the Judd-Ofelt parameters. In case of a Er$^{3+}$ doped system the $t=2$ transition matrix elements $|U_{ij}|^2$ of the transitions between the $4I_{11/2}$, $4I_{13/2}$ and $4I_{15/2}$ states are very small. The quality of these transitions for laser operation is thus characterized by $\Omega_4$ and $\Omega_6$ via the spectroscopic quality factor $Q (=\Omega_4/\Omega_6)$, as introduced by Kaminskii [18]. The Q values are found to be 1.62 for the MBBA system. These values are larger than those found in most laser glasses as well as in FP20, see Table I. The MBBA glass system is thus better suitable for laser applications than other published glass systems.

<table>
<thead>
<tr>
<th>Glasses</th>
<th>$\Omega_2$ (10$^{-20}$ cm$^2$)</th>
<th>$\Omega_4$ (10$^{-20}$ cm$^2$)</th>
<th>$\Omega_6$ (10$^{-20}$ cm$^2$)</th>
<th>$\Omega_4/\Omega_6$</th>
<th>Ref</th>
</tr>
</thead>
<tbody>
<tr>
<td>BK20</td>
<td>5.66</td>
<td>1.84</td>
<td>1.18</td>
<td>1.56</td>
<td>12</td>
</tr>
<tr>
<td>ZBLAN</td>
<td>2.20</td>
<td>1.40</td>
<td>0.91</td>
<td>1.54</td>
<td>13</td>
</tr>
<tr>
<td>Phosphate</td>
<td>6.65</td>
<td>1.52</td>
<td>1.11</td>
<td>1.34</td>
<td>14</td>
</tr>
<tr>
<td>FP20</td>
<td>4.71</td>
<td>1.61</td>
<td>1.62</td>
<td>0.99</td>
<td>15</td>
</tr>
<tr>
<td>MBBA</td>
<td>4.47</td>
<td>1.31</td>
<td>0.81</td>
<td>1.62</td>
<td>Current work</td>
</tr>
</tbody>
</table>

**Table I:** Comparison of Judd-Ofelt parameters of Er$^{3+}$ doped MBBA system and other reported laser glasses

#### 3.3 The emission cross section and gain coefficient of the $4I_{13/2} \rightarrow 4I_{15/2}$ transition.

The efficiency of a laser transition is evaluated by considering stimulated emission cross-section ($\sigma_{em}(\lambda)$). In this work,
σ_{em}(λ) was determined from the emission spectrum using Fuchtbauer-Ladenburg method (FL) [19]

$$\sigma_{em} = \frac{\beta_{J\rightarrow J'} \lambda_p^2 A_{nu}}{8\pi c n(\lambda_p) \Delta \lambda_{eff}}$$  \hspace{1cm} (4)

where $\lambda_p$ is the peak wavelength of the emission, $\lambda_{eff}$ is the width of the emission line, $\beta_{J\rightarrow J'}$ is the branching ration, which is in case of the $^4I_{13/2} \rightarrow ^4I_{15/2}$ transition equal to 1, $c$ is the speed of light in vacuums, and $n(\lambda_p)$ is the refractive index at emission peak wavelength. In our case an effective line width is used instead of the full width at half maximum to compensate for the asymmetric profile of the emission line. Fig. 2 shows the absorption cross section, $\sigma_{abs}(\lambda)$, and the emission cross section, $\sigma_{em}(\lambda)$, determined by FL method.

![Figure 2: Absorption cross section and measured emission cross section of Er^{3+} in the MBBA system.](image)

For the MBBA system, the peak absorption cross sections of $\sigma_{abs}(\lambda)$ turned out to be $1.58 \times 10^{-20}$ cm$^2$ and the peak emission cross sections of $\sigma_{em}(\lambda)$ are $1.86 \times 10^{-20}$ cm$^2$. Comparing the Er$^{3+}$ ion to a simplified two level system, we assume the population is either in the $^4I_{15/2}$ ground state or the $^4I_{13/2}$ excited state. In this case the optical gain properties are directly associated with the absorption and emission cross sections. Gain spectra is shown in Fig. 3 as a function of the population inversion $\gamma$, using the relation below

$$G(\lambda) = \gamma \sigma_{em}(\lambda) - (1 - \gamma) \sigma_{abs}(\lambda)$$ \hspace{1cm} (5)

Using this equation, we calculated the gain spectra as shown in Fig. 3.

![Figure 3: Gain coefficient in the eye-safe range of Er^{3+} in the MBBA system](image)

Note that the gain will be positive at 1536 nm, when the population inversion is larger than 0.5. The maximum value for the gain is achieved in the case of complete population inversion ($\gamma = 1$), in this case cross section for stimulated emission is $2.35 \times 10^{-20}$ cm$^2$ for the MBBA system.

4.0 Conclusions

The novel MBBA system was successfully developed and the absorption and emission spectra of Er$^{3+}$ were measured and analyzed. Three intensity parameters are found to be $\Omega_2 = 4.47 \times 10^{-20}$ cm$^2$, $\Omega_4 = 1.31 \times 10^{-20}$ cm$^2$, $\Omega_6 = 0.81 \times 10^{-20}$ cm$^2$ for the MBBA system. The strong emission bands were observed at 1536 nm and the effective bandwidths were found to be 91 nm. Emission cross section determined by FL method for the $^4I_{13/2} \rightarrow ^4I_{15/2}$ transition are found to be $2.35 \times 10^{-20}$ cm$^2$ and population inversion of above 50% were obtained. These spectroscopic results show that these novel materials are strong candidates for developing broadband optical amplifiers and compact fiber lasers.
References