Upconversion and Spectroscopic Properties of Rare Earth Codoped Lead Borate Glass Matrix

K. KRISHNA MURTHY GOUD1, CH. RAMESH2 and B. APPA RAO1

1Dept. of Physics, UCE (A), Osmania University, Hyderabad-500007 (T.S), India.
2Dept. of Physics, M G University, Nalgonda (T.S), India.

Abstract
To develop efficient upconversion laser materials in the visible region an active lead borate glasses doped with Er3+/Yb3+ rare earth ions (GEY) has been studied extensively. In this investigation characterization techniques like Optical absorption, FTIR and photoluminescence were recorded and the data was analyzed. To evaluate the values of $\Omega_2$, $\Omega_4$ and $\Omega_6$ Judd-Ofelt theory has been applied to the $f \leftrightarrow f$ transitions. Based on Judd–Ofelt theory branching ratio($\beta_r$) oscillator strength and the radiative life time($T_R$) values were determined. The upconversion spectra exhibited three emission bands at around 525 nm ($^{2}H_{11/2} \rightarrow ^{4}I_{15/2}$), 545nm ($^{4}S_{3/2} \rightarrow ^{4}I_{15/2}$) and 660nm ($^{4}F_{9/2} \rightarrow ^{4}I_{15/2}$). The energy transfer mechanism between Yb3+ and Er3+ was discussed very clearly. Comparing the data obtained in other Er3+/Yb3+ doped materials, the lead bismuth gallium borate glasses doped with 0.6 mol% of Er2O3/0.2 mol% of Yb2O3 ions are suitable materials for developing red upconversion lasers in the visible region.

Introduction
The addition of rare earths to the base glass matrix created a great interest in the researchers because of upconversion of infrared light to visible light. This feature leads to various applications like upconversion lasers, sensors, and optical displays1-3. Among different oxide glass compositions, the lead borate glass matrix doped with $f$ block elements are suitable systems for applications in optical devices of laser technology. The absorption and emission properties of rare earth ions in lead borate glass matrix are well reported in the literature4-6. Among various glass systems, heavy metal oxide glasses are good enough for the applications in non-linear optical instruments7.
The physical properties like thermal expansion coefficient, refractive index, glass transition temperature, chemical resistance and infrared transmittance of the glasses changes when heavy metal oxides like, Ga$_2$O$_3$ is introduced in to the glass matrix. The addition of heavy metal oxides makes the glass matrix good enough for the applications in photonic devices. Er$_2$O$_3$ is universally considered as an effective ion among different rare-earth ions that produce upconversion, and gives rather high efficiency. Energy transfer and excited state absorption mechanisms are most efficient in the case of Er$_3^+$ ions. Because of efficient energy transfer from Yb$^{3+}$ to Er$^{3+}$ ions, the sensitization of Er$^{3+}$ doped materials with Yb$^{3+}$ ions is a well-known method for increasing the optical pumping efficiency. In this task, we presented the spectral properties of Er$^{3+}$/Yb$^{3+}$ codoped lead bismuth gallium borate (GEY) glasses.

Experimental
Glasses with [100-(x+y)] [0.5PbO-0.25B$_2$O$_3$-0.20Bi$_2$O$_3$-0.05Ga$_2$O$_3$] -xEr$_2$O$_3$ -yYb$_2$O$_3$ with y = 0 for x = 0, 0.2 and y = 0.2 for x = 0 to 1.0 (step 0.2 mol%) are chosen for this investigation and the glass samples are marked as GE0Y0, GE2Y0, GE0Y2, GE2Y2, GE4Y2, GE6Y2, GE8Y2 and GE10Y2, respectively. All glasses were processed by universally accepted melt quenching method. With the help of JASCO Model V-670 UV–VIS–NIR spectrophotometer, optical absorption spectra of the present glass matrix were reported in the wavelength range 350–2000 nm. The FTIR spectra of glass samples were recorded on a BRUKER OPTICS, TENSOR-27 infrared spectrometer in the range 4000–400 cm$^{-1}$. Using JOBIN YVON Fluorolog-3 spectrofluorimeter, upconversion fluorescence spectra were obtained in the wavelength range 300-700 nm upon the incitement of 980 nm laser diode.

Results and Discussion
The optical absorption spectra of all prepared glasses was shown in Figure 1. The spectra exhibits intense absorption band at 980 nm because of $^4I_{15/2} \rightarrow ^4I_{11/2}$ and $^2F_{7/2} \rightarrow ^2F_{5/2}$ transitions of Er$^{3+}$ and Yb$^{3+}$, respectively. The supplementary absorption bands are due to the contribution of 4f-4f transitions of Er$^{3+}$ ions from the ground ($^4I_{15/2}$) level to the higher levels at 488nm ($^4F_{7/2}$), 521nm ($^4H_{11/2}$), 545nm ($^4S_{3/2}$), 652nm ($^4P_{5/2}$), 798nm ($^4I_{15/2}$) and 1510nm ($^4I_{13/2}$). With the augmentation in the enrichment of Er$^{3+}$ ions, the enhancement in the intensities of all bands was noticed to increase.

The enhancement in the value of cut-off wavelength upto 0.6 mol% of Er$_2$O$_3$ ions and decrement beyond this concentration of Er$_2$O$_3$ was noticed in the Fig. 1: Optical absorption spectra of GEY glasses.

Table 1: Values of cut off wavelength, $E_{opt}$ and $\Delta E$ of GEY glasses codoped with Er$^{3+}$/Yb$^{3+}$.

<table>
<thead>
<tr>
<th>S. No.</th>
<th>Sample code</th>
<th>Cut-off wavelength (nm)</th>
<th>$E_{opt}$ (eV) $\pm 0.01$</th>
<th>$\Delta E$ (eV) $\pm 0.001$</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>GE0Y0</td>
<td>400</td>
<td>3.02</td>
<td>0.152</td>
</tr>
<tr>
<td>2</td>
<td>GE2Y0</td>
<td>408</td>
<td>2.96</td>
<td>0.148</td>
</tr>
<tr>
<td>3</td>
<td>GE0Y2</td>
<td>409</td>
<td>2.95</td>
<td>0.148</td>
</tr>
<tr>
<td>4</td>
<td>GE2Y2</td>
<td>419</td>
<td>2.89</td>
<td>0.144</td>
</tr>
<tr>
<td>5</td>
<td>GE4Y2</td>
<td>425</td>
<td>2.85</td>
<td>0.139</td>
</tr>
<tr>
<td>6</td>
<td>GE6Y2</td>
<td>431</td>
<td>2.8</td>
<td>0.135</td>
</tr>
<tr>
<td>7</td>
<td>GE8Y2</td>
<td>427</td>
<td>2.83</td>
<td>0.138</td>
</tr>
<tr>
<td>8</td>
<td>GE10Y2</td>
<td>423</td>
<td>2.86</td>
<td>0.141</td>
</tr>
</tbody>
</table>
amplification of bonding artifacts and NBOs in the glass network up to 0.6 mol% of \( \text{Er}_2\text{O}_3 \). More likely in this concentration region the Ga\(^{3+}\) ions may take network establish locations with GaO\(^4\) units and interchange with BO\(^4\) units. Such concatenation may incur a decrement in the firmness of the glass network and causes the decrease in the optical band gap as noticed. Judd-Ofelt theory helps in the analyzation of the radiative transitions within the confines of \( 4f^n \) configuration of a rare earth ion. The Judd-Ofelt parameters \( \Omega_\lambda \) \((\lambda = 2, 4 \text{ and } 6)\) and different spectroscopic parameters, in particular radiative lifetime, oscillator strength and branching ratios \( (\beta_r)\) were determined by applying standard equations\(^{15-22}\). The values of various radiative parameters are presented in Table 2 and Table 3.

According to literature\(^{23,24}\), \( \Omega_2 \) is associated with the symmetry of the rare earth site while \( \Omega_6 \) is inversely proportional to the covalency of Er-O bond. The Er-O bond is supposed to be dependent on the local basicity around the rare-earth sites, which can be adjusted by the configuration or complex of the host material. It is strongly entrenched that an emission level with \( \beta_r \) value above 50% turn into a possible laser radiation. Based on info on radiative transitions in the present glasses, the transition \( ^4\text{F}_{9/2} \rightarrow ^4\text{I}_{15/2} \) has the high degree of \( \beta_r \) apart from different transitions. As a result this transition may be treated as a acceptable laser transition. The order of Judd-Ofelt parameters in the present glass system is \( \Omega_4 > \Omega_2 > \Omega_6 \).

The FTIR spectra of GEY glass system codoped with \( \text{Er}^{3+}/\text{Yb}^{3+} \) was shown in figure 2. The band cited at \( \sim 482 \text{ cm}^{-1} \) is attributed to the bending vibrations of Bi\(_2\)O\(_3\) pyramidal units and also because of the presence of PbO\(_4\) units\(^{25}\). A band was identified at \( \sim 613 \text{ cm}^{-1} \), which is produced by the vibrations of B-O-B linkages. Asymmetric stretching vibrations of B-O bands in BO\(_4\) units produces a band at \( \sim 930 \text{ cm}^{-1} \). The band identified at \( \sim 1250 \text{ cm}^{-1} \) is because of asymmetric stretching vibrations of BO\(_3\) units\(^{27}\). From figure 2 it was noticed that, the intensity of band corresponding to GaO\(^4\) tetrahedral groups increases from 0 mol% of \( \text{Er}_2\text{O}_3 \) to 0.6 mol% of \( \text{Er}_2\text{O}_3 \); beyond 0.6 mol% of \( \text{Er}_2\text{O}_3 \) the trend is reverse. This is due to the fact that Ga\(^{3+}\) ions go into alternative positions with GaO\(^4\) structural units and alter the glass structure up to 0.6 mol%. Within this concentration Ga\(^{3+}\), separate the rare-earth ions from rare earh-O-rare earh bonds and convert into Ga-O-rare earh. Like that declustering effect leads to the large gap between rare earth ions and may favors the increment of fluorescence emission.

### Table 2: Radiative life time \( (T_R) \) and branching ratios \( (\beta_r) \) of Er\(^{3+}\) in GEY glasses.

<table>
<thead>
<tr>
<th>Transitions</th>
<th>( \beta_r ) (%)</th>
<th>( T_R ) (ms)</th>
</tr>
</thead>
<tbody>
<tr>
<td>( ^2\text{H}<em>{11/2} \rightarrow ^4\text{I}</em>{15/2} )</td>
<td>14</td>
<td>0.74</td>
</tr>
<tr>
<td>( ^4\text{S}<em>{9/2} \rightarrow ^4\text{I}</em>{15/2} )</td>
<td>16</td>
<td>0.8</td>
</tr>
<tr>
<td>( ^4\text{G}<em>{9/2} \rightarrow ^4\text{I}</em>{15/2} )</td>
<td>52</td>
<td>2.76</td>
</tr>
</tbody>
</table>

### Table 3: Experimental and evaluated oscillator strength values of \( \text{Er}_2\text{O}_3 \) in GEY glass system.

<table>
<thead>
<tr>
<th>Transition from ( ^4\text{I}<em>{15/2} ) to ( ^4\text{I}</em>{j} )</th>
<th>( f_{\text{exp}}(x) \times 10^6 )</th>
<th>( f_{\text{cal}}(x) \times 10^6 )</th>
</tr>
</thead>
<tbody>
<tr>
<td>4I(_{13/2})</td>
<td>0.982</td>
<td>0.976</td>
</tr>
<tr>
<td>4I(_{11/2})</td>
<td>0.549</td>
<td>0.558</td>
</tr>
<tr>
<td>4I(_{9/2})</td>
<td>0.446</td>
<td>0.441</td>
</tr>
<tr>
<td>4I(_{7/2})</td>
<td>1.207</td>
<td>1.219</td>
</tr>
<tr>
<td>4I(_{5/2})</td>
<td>0.328</td>
<td>0.312</td>
</tr>
<tr>
<td>2H(_{11/2})</td>
<td>4.435</td>
<td>4.442</td>
</tr>
<tr>
<td>4F(_{7/2})</td>
<td>1.163</td>
<td>1.171</td>
</tr>
<tr>
<td>r.m.s. deviation</td>
<td>±0.091</td>
<td></td>
</tr>
</tbody>
</table>

Fig. 2: FTIR spectra of GEY glass matrix.
Figure 3 represents the upconversion emission spectra of present glasses obtained in the wavelength region 500 –700nm upon the incitement of 980nm laser source. Three emission bands at 525nm, 545 nm and 660nm were exhibited by the spectra. It was noticed that the upconversion luminescence intensity of red emission (660nm) is higher than the upconversion luminescence intensity of green emission (525 and 545nm). It was also noticed that the green radiation is feeble and red radiation is of high intense.

The results showed that the intensity of green and red radiations increases with increase in the concentration of Er$_2$O$_3$ upto 0.6 mol% and beyond this concentration decrease in the intensity was observed. As per literature in an upconversion, the increment in the intensity of emitted radiation ($I_{up}$) increases in proportion to the nth power of infrared excitation intensity ($I_{IR}$), i.e.,

$$I_{up} \propto I_{IR}^n$$

where n represents the number of infrared photons absorbed to emit one photon in the visible region. The value of 'n' can be determined from plot of log $I_{up}$ versus log $I_{IR}$. This plot gives a straight line and the slope of this straight line represents the value of 'n'. The log-log plot for the 525 nm, 545 nm and 660 nm emission was shown in figure 4 (a), (b) and (c), respectively. From figure 4 (a), (b) and (c), the value of 'n' for 525 nm, 545 nm and 660 nm emission bands was calculated and got around two. Hence, two photon absorption is responsible for green and red radiations.

Figure 5 illustrates the energy transfer mechanisms for the emissions in the Er$^{3+}$/Yb$^{3+}$ codoped glasses.
upon the incitement of 980 nm laser source. The energy transfer mechanism between Er\textsubscript{3+} and Yb\textsubscript{3+} mainly involves ground state absorption (GSA), energy transfer (ET) and excited state absorption (ESA). The energy transfer mechanism which is responsible for the green and red emissions was explained in detail in our previous papers.

From the Upconversion spectra, it was noticed that the intensity of green emissions centered at 525 nm and 545 nm are very small. This may be due to the radiation less transition of the erbium ions at \(^4\text{S}_{3/2}\) level to \(^4\text{F}_{9/2}\) level in large number.

The \(^4\text{I}_{15/2}\) level is populated owing to the radiation less transition from the upper \(^4\text{I}_{11/2}\) level. In addition to this, the radiation less transition from \(^4\text{S}_{3/2}\) level, which is populated by means of the mechanism explained earlier, to the \(^4\text{F}_{9/2}\) level also contributes to the red emission. As per the discussion made earlier, the phonon energy also plays a significant role and it can affect the upconversion intensity: with the increase of the phonon energy in Er\textsubscript{3+}/Yb\textsubscript{3+} co-doped glasses the red emission increases more than that of green by means of the mechanism explained above. The previous researchers reported that Ga\textsubscript{2}O\textsubscript{3} influences the increase in the intensity of red emission than that of green emission.

**Conclusions**

For the investigation of spectroscopic properties at room temperature, lead bismuth gallium borate glasses were prepared with different dopant (Er\textsuperscript{3+}/Yb\textsuperscript{3+}) ion concentrations. The incorporation of Er\textsuperscript{3+}/Yb\textsuperscript{3+} in the present glass matrix was evidenced by the studied characterization techniques. The Judd–Ofelt intensity parameters \(\Omega\) \((t=2,4,6)\), oscillator strength, branching ratio \((\beta)\), and the radiative lifetime values were calculated and analyzed. For the transition \(^4\text{F}_{9/2} \rightarrow ^4\text{I}_{15/2}\) at 660 nm, the branching ratio \((\beta)\) showed highest value among other transitions. Therefore, this transition is considered as suitable transition for the development of upconversion lasers. The upconversion bands representing to weak green and intense red emissions at around 525nm, 545 nm and 660nm, respectively, were detected upon the incitement of 980nm laser source. ESA and the ET were primarily connected with the upconversion processes. It was noticed that the increment in the energy transfer efficiency takes place with Er\textsuperscript{3+} content, and reaches maximum for the 0.6 mol% Er\textsuperscript{3+}/0.2 mol% Yb\textsuperscript{3+} co-doped glass. From the upconversion spectra it was found that, the red emission is more influenced than the green emission. Two-photon absorption process is responsible for the green and red emissions. The probability of radiation less transition of Er\textsuperscript{3+} ions from \(^4\text{F}_{11/2} \rightarrow ^4\text{I}_{13/2}\) is enough higher than the probability of upconversion to the upper \(^4\text{F}_{9/2}\) level as a result of the longer lifetime of the \(^4\text{I}_{13/2}\) level compared to the lifetime of the \(^4\text{I}_{11/2}\) level, which influences the radiation less transition \(^4\text{I}_{11/2} \rightarrow ^4\text{I}_{13/2}\) to take place more easily. Hence, the intensity of red emission is intensified than that of green emission. With increase in the concentration of Er\textsuperscript{3+} upto 0.6 mol%, the intensity of green emission increased slightly, while the red emission intensity increases to a larger extent when compared with that of green emission. The results obtained provide useful information for choice of Er and Yb concentration as well as for modelling and optimising the performance of upconversion lasers based Er\textsuperscript{3+}/Yb\textsuperscript{3+} codoped lead bismuth gallium borate glasses.
References