4.1. INTRODUCTION

In recent years, there has been an increasing interest to the lanthanide ions doped in different hosts to achieve favorable optical devices such as lasers, fiber amplifiers, light converters, sensors and hole burning high density memories [160, 161]. The optical spectrum of lanthanide ion is closely related to the particular local symmetry of the environment occupied by this ion in solid matrices. In glasses, they usually in homogeneously broadened band due to site-to-site variations in the local field action on the ions [162]. Glasses doped with rare earth ions are proving to be the best luminescent materials as they have high emission efficiencies. While the emission is originated from both 4f-4f as well as 4f-5d electronic transitions, the 4f-4f transitions gives sharp emission lines covering wide range of spectral region, from the ultraviolet (UV) to the infrared region (IR). These sharp emissions attracted potential applications in solid state lasers, optical fiber amplifiers and three dimensional display devices [163-165]. The emission quantum efficiencies of the rare earth ions are strongly dependent on phonon energy of the host material and active ion concentration. In recent years, among other oxide based glasses, borate glasses have been the subject of interest due to their high transparency, low melting point, high thermal stability and capability of accommodating large concentrations of rare earth ions [14,166-167].

In recent times, glasses containing Sm$^{3+}$ ions have stimulated extensive interest due to their potential application for high-density optical storage, under water communication and color displays [168,169]. Additionally, the Sm$^{3+}$ ions exhibit broad emission bands due to $^4\mathrm{G}_{5/2} \rightarrow ^6\mathrm{H}_1$ ($J = 5/2, 7/2, 9/2, 11/2$) transitions in any host matrix. Moreover, the phonon energies of hosts are not so critical to the orange-red emission at $\sim 600$ nm, because of the large energy difference of $^4\mathrm{G}_{5/2}$ meta-stable level to its next lower lying levels [64, 65]. The large gap between the $^4\mathrm{G}_{5/2}$ level and its sublevels permits the applications of sm$^{3+}$ ions in different glass hosts with large phonon energy. It is also well known that the intensities of emission bands of Sm$^{3+}$ ion in glasses depend on its concentration and glass composition [66]. In order to obtain optimum emission characteristics for device applications, the characteristic features of host as well as concentration dependent studies of Sm$^{3+}$ions are essential. The present work reports, the preparation and characterization of a new
series of trivalent samarium doped Zinc Alumino Bismuth Borate (ZnAlBiB) glasses, by using the techniques such as optical absorption, luminescence and decay curve measurements. The present study mainly focus on absorption, steady-state and time-resolved emission spectral measurements of Sm$^{3+}$ ions in ZnAlBiB glasses to select a good host material for solid state laser devices.

4.2. EXPERIMENTAL PROCEDURE

The glasses having composition 20ZnO - 10Al$_2$O$_3$ - (10-x) Bi$_2$O$_3$ - 60B$_2$O$_3$ + xSm$_2$O$_3$, (x= 0.1, 0.5, 1, 2, 2.5 mol %) were prepared by using normal melt-quenching technique. The glasses were abbreviated as ZnAlBiBSm01, ZnAlBiBSm05, ZnAlBiBSm10, ZnAlBiBSm15, ZnAlBiBSm20, and ZnAlBiBSm25 depending on rare earth concentration in these glasses from 0.1 to 2.5 mol%. The glasses were prepared by melt quenching method as described in Chapter 2. The absorption spectra were obtained from a JASCO model V-670 UV-vis-NIR spectrophotometer from 800 to 1700 nm with a resolution of 0.1nm. The photoluminescence (PL) emission and excitation spectra for all these glasses were recorded at room temperature using RF-5301 PC Spectrofluorophotometer. The emission from sample was coupled into a monochromator (Acton SP2300) coupled to CCD (charge coupled detector) through the appropriate lenses and filters. The high-resolution PL images were obtained from a modified 410nm CW diode laser coupled confocal microscope (Olympus, BX51) equipped with XY-piezo stage. Time-resolved PL measurements were recorded using an Edinburgh luminescence spectrometer (model F900) equipped with a microsecond xenon flash lamp as the source of excitation at 401 nm.

4.3. RESULTS AND DISCUSSION:

4.3.1. Absorption spectra and Judd-Ofelt analysis

The optical absorption spectra of Sm$^{3+}$ions doped ZnAlBiB glass measured in the spectral range 800-1700nm is shown in Figure.4.1. The absorption spectra of all the titled glasses are similar to each other except variation in intensities which are due to variation in concentration of Sm$^{3+}$ ions and glass composition [170]. The room temperature optical absorption spectra in NIR region for the titled glasses consists of several inhomogeneous broadened bands assigned to f-f transitions from the ground
$^6\text{H}_{5/2}$ state to various excited states of Sm$^{3+}$ ions in the host glass. Due to strong absorption of the titled glasses in the UV region, several peaks disappeared in the visible spectral region. The band positions along with their assignments of transitions for the ZnAlBiB glass are given in Table 4.1. On the other hand, the transitions to $^6\text{H}$ and $^6\text{F}$ spectral terms are spin allowed in the NIR region. Most of the transitions were due to electric dipole interactions only with the selection rule $|\Delta J|\leq0$, but a few transitions contains magnetic dipole contribution following the selection rule $\Delta J=0, \pm1$ [88]. To have an idea about the nature of Sm$^{3+}$-ligand bond, nephelauxetic ratios ($\beta$) and bonding parameter ($\delta$) have been evaluated using the Eq. (1.3 &1.4). The bonding will be covalent or ionic depending upon the positive or negative sign of $\delta$. The bonding parameters ($\delta$) are found to be negative (-0.0126, -0.0113, -0.0111, -0.0108, -0.0106, -0.0105) for the titled glasses indicates the ionic nature of the Sm–O bond. Moreover, the ionic nature gradually decreases with the decrease in Bi$_2$O$_3$ content. Similar ionic nature has been observed in other reported Sm$^{3+}$-doped glasses [168, 171, 172].

The Judd–Ofelt (JO) theory [78, 79] has been applied for seven well-defined absorption transitions such as $^6\text{H}_{5/2} \rightarrow ^6\text{F}_{11/2}$, $^6\text{F}_{9/2}$, $^6\text{F}_{7/2}$, $^6\text{F}_{5/2}$, $^6\text{F}_{3/2}$, $^6\text{F}_{15/2}$, and $^6\text{F}_{1/2}$ observed in the wavelength range 800–1700nm. The experimental oscillator strengths ($f_{\text{exp}}$) were determined from the absorption spectra by using the procedure outline in Chapter-I of this thesis. From $f_{\text{exp}}$ and squared reduced matrix elements using least square analysis, JO intensity parameters ($\Omega_2$, $\Omega_4$ and $\Omega_6$) are obtained for the titled glass matrices and in turn used to obtain calculated oscillator strengths ($f_{\text{cal}}$). Table 4.1 presents the experimental and calculated oscillator strengths along with $\delta$ rms values for all the ZnAlBiB glasses. Very small rms deviations obtained between experimental and calculated oscillator strengths indicates the validity of JO theory. The experimental oscillator strengths ($f_{\text{exp}}$) observed for ZnAlBiBSm10 glass is relatively much higher than the other titled glasses as presented in Table 4.1. The JO intensity parameters and their trend ($\Omega_6>\Omega_4>\Omega_2$) for the titled glasses have been presented in Table 4.2. According to Jorgensen and Judd [88] and Jorgensen and Reisfeld [153], $\Omega_2$ is a covalency-dependent parameter, whereas $\Omega_4$ and $\Omega_6$ are structure-dependent parameters. From the Table 4.2 it can be observed that, the $\Omega_2$ value is found to be high for ZnAlBiBSm10 glass. The lower $\Omega_2$ values for the Sm$^{3+}$ ions in the present glasses is an indication of weaker covalency of Sm–O bond under
more centro-symmetric or asymmetric environment around Sm\(^{3+}\) ions [173]. The high magnitude of \(\Omega_6\) indicates low rigidity of the present titled glasses compared to various other glasses presented in Table 4.2 [167, 174, 175].

Figure 4.1. Absorption spectra of Sm\(^{3+}\) ions doped ZnAlBiB glasses. The inset shows the absorption edge details of ZnAlBiBSm10 glass.
Table 4.1. Measured ($f_{\text{exp}} \times 10^6$) and calculated ($f_{\text{cal}} \times 10^6$) oscillator strengths of Sm$^{3+}$ ions doped ZnAlBiB glasses.

<table>
<thead>
<tr>
<th>Transitions from $^6H_{5/2}$</th>
<th>Energy (cm$^{-1}$)</th>
<th>ZnAlBiBSm01</th>
<th>ZnAlBiBSm05</th>
<th>ZnAlBiBSm10</th>
<th>ZnAlBiBSm15</th>
<th>ZnAlBiBSm20</th>
<th>ZnAlBiBSm25</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>$f_{\text{exp}}$</td>
<td>$f_{\text{cal}}$</td>
<td>$f_{\text{exp}}$</td>
<td>$f_{\text{cal}}$</td>
<td>$f_{\text{exp}}$</td>
<td>$f_{\text{cal}}$</td>
</tr>
<tr>
<td>$^6F_{11/2}$</td>
<td>10570</td>
<td>0.27</td>
<td>0.56</td>
<td>0.67</td>
<td>1.71</td>
<td>1.43</td>
<td>0.52</td>
</tr>
<tr>
<td>$^6F_{9/2}$</td>
<td>9267</td>
<td>3.09</td>
<td>3.38</td>
<td>3.67</td>
<td>3.72</td>
<td>7.57</td>
<td>8.51</td>
</tr>
<tr>
<td>$^6F_{7/2}$</td>
<td>8156</td>
<td>4.63</td>
<td>4.41</td>
<td>4.91</td>
<td>4.88</td>
<td>11.3</td>
<td>10.6</td>
</tr>
<tr>
<td>$^6F_{5/2}$</td>
<td>7293</td>
<td>1.39</td>
<td>1.44</td>
<td>1.62</td>
<td>1.62</td>
<td>2.23</td>
<td>2.72</td>
</tr>
<tr>
<td>$^6F_{3/2}$</td>
<td>6784</td>
<td>0.57</td>
<td>0.64</td>
<td>0.73</td>
<td>0.75</td>
<td>2.03</td>
<td>1.53</td>
</tr>
<tr>
<td>$^6H_{15/2}$</td>
<td>6535</td>
<td>0.16</td>
<td>0.02</td>
<td>0.09</td>
<td>0.03</td>
<td>0.30</td>
<td>0.07</td>
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<tr>
<td>$^6F_{1/2}$</td>
<td>6305</td>
<td>0.05</td>
<td>0.003</td>
<td>0.04</td>
<td>0.03</td>
<td>0.16</td>
<td>0.44</td>
</tr>
<tr>
<td>$\delta_{\text{rms}}(\times 10^{-6})$</td>
<td></td>
<td>± 0.186</td>
<td>± 0.039</td>
<td>± 0.533</td>
<td>± 0.269</td>
<td>± 0.217</td>
<td>± 0.139</td>
</tr>
<tr>
<td>Re refractive index (n)</td>
<td></td>
<td>1.790</td>
<td>1.800</td>
<td>1.802</td>
<td>1.804</td>
<td>1.807</td>
<td>1.809</td>
</tr>
<tr>
<td>Density (d) (gm/cc)</td>
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<td>3.936</td>
<td>3.935</td>
<td>3.924</td>
<td>3.910</td>
<td>3.911</td>
<td>3.904</td>
</tr>
<tr>
<td>Sample Thickness (t) (mm)</td>
<td></td>
<td>1.53</td>
<td>1.53</td>
<td>1.53</td>
<td>1.53</td>
<td>1.53</td>
<td>1.53</td>
</tr>
</tbody>
</table>
Table 4.2. Comparison of Judd-Ofelt parameters ($\times 10^{-20}$ cm$^2$) and their trend for Sm$^{3+}$ ions in different glasses.

<table>
<thead>
<tr>
<th>Glass Composition</th>
<th>$\Omega_2$</th>
<th>$\Omega_4$</th>
<th>$\Omega_6$</th>
<th>Trend</th>
<th>References</th>
</tr>
</thead>
<tbody>
<tr>
<td>ZnAlBiBSm01</td>
<td>0.009 ± 0.095</td>
<td>2.27 ± 0.031</td>
<td>3.35 ± 0.012</td>
<td>$\Omega_6 &gt; \Omega_4 &gt; \Omega_2$</td>
<td>Present Work</td>
</tr>
<tr>
<td>ZnAlBiBSm05</td>
<td>0.091 ± 0.008</td>
<td>2.55 ± 0.001</td>
<td>3.69 ± 0.002</td>
<td>$\Omega_6 &gt; \Omega_4 &gt; \Omega_2$</td>
<td>Present Work</td>
</tr>
<tr>
<td>ZnAlBiBSm10</td>
<td>1.171 ± 0.231</td>
<td>4.14 ± 0.059</td>
<td>8.52 ± 0.014</td>
<td>$\Omega_6 &gt; \Omega_4 &gt; \Omega_2$</td>
<td>Present Work</td>
</tr>
<tr>
<td>ZnAlBiBSm15</td>
<td>0.015 ± 0.012</td>
<td>2.82 ± 0.004</td>
<td>4.26 ± 0.004</td>
<td>$\Omega_6 &gt; \Omega_4 &gt; \Omega_2$</td>
<td>Present Work</td>
</tr>
<tr>
<td>ZnAlBiBSm20</td>
<td>0.021 ± 0.014</td>
<td>2.55 ± 0.005</td>
<td>4.18 ± 0.001</td>
<td>$\Omega_6 &gt; \Omega_4 &gt; \Omega_2$</td>
<td>Present Work</td>
</tr>
<tr>
<td>ZnAlBiBSm25</td>
<td>0.013 ± 0.188</td>
<td>2.65 ± 0.051</td>
<td>4.07 ± 0.157</td>
<td>$\Omega_6 &gt; \Omega_4 &gt; \Omega_2$</td>
<td>Present Work</td>
</tr>
<tr>
<td>LPG 12</td>
<td>0.880</td>
<td>3.93</td>
<td>4.66</td>
<td>$\Omega_6 &gt; \Omega_4 &gt; \Omega_2$</td>
<td>[167]</td>
</tr>
<tr>
<td>LSG 12</td>
<td>0.770</td>
<td>6.39</td>
<td>7.09</td>
<td>$\Omega_6 &gt; \Omega_4 &gt; \Omega_2$</td>
<td>[167]</td>
</tr>
<tr>
<td>CdBiB</td>
<td>0.040</td>
<td>2.84</td>
<td>6.03</td>
<td>$\Omega_6 &gt; \Omega_4 &gt; \Omega_2$</td>
<td>[174]</td>
</tr>
<tr>
<td>PbF$_2$-TeO$_2$-B$_2$O$_3$</td>
<td>0.210</td>
<td>1.42</td>
<td>1.87</td>
<td>$\Omega_6 &gt; \Omega_4 &gt; \Omega_2$</td>
<td>[175]</td>
</tr>
</tbody>
</table>
4.3.2. Emission spectra and radiative properties

Figure 4.2 shows the excitation spectra of titled glasses in the region 325–500 nm by monitoring the emission at 598 nm. As shown in Figure 4.2, the excitation spectra contain several excitation bands in visible region. This indicates that the commercial UV-blue laser diodes and blue-bluish-green light emitting diodes (LEDs) can be used as pumping sources for the Sm$^{3+}$-doped ZnAlBiB glasses [176].

![Excitation spectra of Sm$^{3+}$ ions doped ZnAlBiB glasses.](image)

The emission spectra of the Sm$^{3+}$ doped ZnAlBiB glasses recorded in the spectral range 500-750nm by exciting with 410nm (24390 cm$^{-1}$) CW laser is shown in Figure 4.3. The confocal images shown by ZnAlBiB glasses when excited at 410nm using CW laser are also shown in Figure 4.3. The emission spectra exhibit four emission bands corresponding to $^4G_{5/2} \rightarrow ^6H_{5/2}$ (563 nm), $^4G_{5/2} \rightarrow ^6H_{7/2}$ (598nm), $^4G_{5/2} \rightarrow ^6H_{9/2}$ (645nm), and $^4G_{5/2} \rightarrow ^6H_{11/2}$ (704nm) transition irrespective of variation in concentration. Among the four observed bands, the $^4G_{5/2} \rightarrow ^6H_{7/2}$ is more intense and $^4G_{5/2} \rightarrow ^6H_{11/2}$ is found to be weak in intensity. From, Figure 4.3, it can be seen that the emission spectral intensity of Sm$^{3+}$ ions in the titled glasses increases gradually up to 1 mol% of Sm$^{3+}$ ions and then decreases gradually for all the peaks. This
concentration quenching observed at 1 mol% of $\text{Sm}^{3+}$ ions in these glasses may be due to enhanced interaction between $\text{Sm}^{3+}$ ions and also between $\text{Sm}^{3+}$ ions with host defects leading to the cross-relaxations among the active ions [177]. These samples have a very distinct orange-red luminescence, which is mainly due to the luminescence of the intense $^4G_{5/2} \rightarrow {^6}H_{7/2}$ transition at 598nm (16722 cm$^{-1}$) and $^4G_{5/2} \rightarrow {^6}H_{9/2}$ at 645nm(15503 cm$^{-1}$). These transitions are useful in high-density optical storage, color displays and medical diagnostics.

The intensity of orange-red luminescence shown by ZnAlBiB glasses increases with increase in concentration up to 1 mol% of $\text{Sm}^{3+}$ ions and then decreasing. To get further confirmation for this, we have recorded confocal PL images for all the ZnAlBiB glasses. From the confocal PL images shown in Figure. 4.3, it can be observed that the orange-red emission intensity is maximum for 1 mol% of $\text{Sm}^{3+}$ ions. This result is in consistent with the emission spectra given by the titled glasses. The emission transition may be electric dipole or magnetic dipole allowed that results from an interaction of an electron in an atom with the electromagnetic field. We believe that the $^4G_{5/2} \rightarrow ^6H_{5/2}$ (563 nm) is predominantly due to magnetic dipole in character whereas the transition $^4G_{5/2} \rightarrow ^6H_{9/2}$ (644 nm) is predominantly due to electric dipole in character. A transition $^4G_{5/2} \rightarrow ^6H_{7/2}$ (598 nm) is principally present’s electric dipole in character, although the transition is magnetic dipole allowed. Higher intensity of the electric dipole transition exhibit more asymmetric nature. In the present work, the spectral intensity of the electric dipole induced transition $^4G_{5/2} \rightarrow ^6H_{9/2}$ of the $\text{Sm}^{3+}$ ion is higher than the magnetic transition $^4G_{5/2} \rightarrow ^6H_{5/2}$. The relative intensities of these transitions are known to be sensitive to the variations in the local environment surrounding $\text{Sm}^{3+}$ ions [178]. It indicates that the asymmetric nature is predominant in the titled glasses, which is further confirmed through the lower $\Omega_2$ JO intensity parameter. Other emission band located at 645nm is an electric dipole forced transition and its intensity is also sensitive to the changes in the local field around rare earth ion [179].
Figure 4.3. PL images of Sm$^{3+}$ ions doped ZnAlBiB glasses and their corresponding emission spectra.

Among the four emission transitions, the $^4G_{5/2} \rightarrow ^6H_{7/2}$ and $^4G_{5/2} \rightarrow ^6H_{9/2}$ transitions of ZnAlBiBSm10 glass are more intense. The JO parameters obtained by least square fit are used to predict the radiative properties such as the radiative transition probability ($A_R$), total radiative transition probability ($A_T$), radiative lifetime ($\tau_R$) and branching ratios ($\beta_R$) using the corresponding expression given in Chapter 1, and the values are given in Table 4.3. The peak stimulated emission cross section ($\sigma_{se}$) of an emission band have been evaluated using Eq. (1.28), and are given in Table 4.4, along with emission peak wavelength ($\lambda_p$) and effective bandwidth ($\Delta\lambda_p$). The large stimulated emission cross-section is an attractive feature for low-threshold, high gain laser applications, which are utilized to obtain CW laser action. Among the four emission transitions, the $^4G_{5/2} \rightarrow ^6H_{7/2}$ transition has high stimulated emission cross-section for all the titled glasses. From the same Table 4.4 it can also be seen that ZnAlBiBSm10 glass exhibits higher stimulated emission cross-section among all the glasses studied. The luminescence branching ratio ($\beta_R$) is another important parameter and plays an important role in deciding the lasing potentiality of an emission transition. It is well
known that, an emission transition having the $\beta_R$ greater than 50% is consider to be more potential for laser emission [180]. Hence In the present glass systems, $^4G_{5/2} \rightarrow ^6H_{7/2}$ transition satisfies the above conditions required for a good laser transition. The experimental branching ratios ($\beta_{exp}$) are estimated from the ratio of individual area of the corresponding emission band to that of the total integrated area under all the emission peaks.

The experimental branching ratios ($\beta_{exp}$) of all the titled glasses are given in Table 4.4. From the magnitude of calculated branching ratios ($\beta_R$) given in Table 4.4, it is evident that the $^4G_{5/2} \rightarrow ^6H_{7/2}$ and $^4G_{5/2} \rightarrow ^6H_{9/2}$ transitions are more intense compared to other transitions and therefore the ZnAlBiB glasses may be used for the development of light emitting diodes (LEDs) in optical communication. The laser characteristic parameters such as branching ratio ($\beta_R$) and stimulated emission cross-section ($\sigma_{se}$) for the ZnAlBiBSm10 glass compared with other different glass hosts are given in Table 4.5 [134, 172, 174, 181-184]. The higher $\beta_R$ and $\sigma_{se}$ values obtained for ZnAlBiBSm10 glass speaks the potentiality of that glass for visible lasing action at around 598 nm when compared with other reported glasses (Table 4.5). The optical gain is a critical parameter to predict the amplification of the laser medium. From the Table 4.4, it is evident that, the $^4G_{5/2} \rightarrow ^6H_{7/2}$ transition of ZnAlBiBSm10 glass has the higher stimulated emission cross sections ($\sigma_{se}$), optical gain ($\sigma_{se} \times \tau_R$) and gain bandwidth values ($\sigma_{se} \times \Delta\lambda_p$) which could be a favorable feature for the development of visible laser at around 598 nm, which is highly useful in deep-water communications [185].
Table 4.3. Radiative transition probability ($A_R$) (s$^{-1}$), radiative branching ratio ($\beta_R$) and total radiative transition probability ($A_T$) (s$^{-1}$) for Sm$^{3+}$ ions doped ZnAlBiB glasses

<table>
<thead>
<tr>
<th>Transition</th>
<th>$^4G_{5/2} \rightarrow$</th>
<th>ZnAlBiBSm01</th>
<th>ZnAlBiBSm05</th>
<th>ZnAlBiBSm10</th>
<th>ZnAlBiBSm15</th>
<th>ZnAlBiBSm20</th>
<th>ZnAlBiBSm25</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$A_R$</td>
<td>$\beta_R$</td>
<td>$A_R$</td>
<td>$\beta_R$</td>
<td>$A_R$</td>
<td>$\beta_R$</td>
<td>$A_R$</td>
</tr>
<tr>
<td>$^6H_{5/2}$</td>
<td>27</td>
<td>0.08</td>
<td>28</td>
<td>0.08</td>
<td>33</td>
<td>0.04</td>
<td>29</td>
</tr>
<tr>
<td>$^6H_{7/2}$</td>
<td>169</td>
<td>0.53</td>
<td>186</td>
<td>0.53</td>
<td>360</td>
<td>0.54</td>
<td>210</td>
</tr>
<tr>
<td>$^6H_{9/2}$</td>
<td>53</td>
<td>0.16</td>
<td>62</td>
<td>0.17</td>
<td>141</td>
<td>0.21</td>
<td>67</td>
</tr>
<tr>
<td>$^6H_{11/2}$</td>
<td>34</td>
<td>0.11</td>
<td>38</td>
<td>0.11</td>
<td>73</td>
<td>0.10</td>
<td>44</td>
</tr>
</tbody>
</table>

$A_T = 315$  $A_T = 348$  $A_T = 668$  $A_T = 386$  $A_T = 370$  $A_T = 372$
4.3.3 Emission lifetime analysis

Analysis of emission decay curves gives the information about lifetimes of an excited state of a rare earth ion in any host composition. The decay curves for the $^4\text{G}_{5/2}$ fluorescent level of Sm$^{3+}$ ions in ZnAlBiB glasses with different concentration of Sm$^{3+}$ ions have been carried out at room temperature by controlling the emission at 598 nm corresponding to $^4\text{G}_{5/2} \rightarrow ^6\text{H}_{7/2}$ transition upon excitation at 401 nm. Figure 4.4 shows the emission decay profiles of 598 nm orange-red emission for all the glasses corresponding to $^4\text{G}_{5/2} \rightarrow ^6\text{H}_{7/2}$ transition. An excited rare earth ion may relax to the ground state through radiative transition and/or phonon emission or by transferring the excess energy to a nearby rare earth ion for a combination of relaxation. From Figure 4.4, it is observed that the decay profiles of $^4\text{G}_{5/2}$ level are single exponential for lower concentration and non-exponential for the higher concentration of Sm$^{3+}$ ion.

The experimental lifetimes ($\tau_{\text{exp}}$) measured from the decay curves for $^4\text{G}_{5/2}$ levels are presented in Table 4.4 along with radiative lifetimes ($\tau_{R}$). The $\tau_{\text{exp}}$ values for $^4\text{G}_{5/2}$ level found to be decreasing with increasing the concentration of Sm$^{3+}$ ions. The decrease in the experimental lifetime values and the conversion of decay curves from exponential to non-exponential with increasing concentration of Sm$^{3+}$ ions is the characteristic feature for the existence of concentration quenching. These results are also in consistent with the concentration dependent emission spectral study (Figure 4.3). The luminescence intensity quenching and non-exponential behavior of decay curves beyond 1 mol% of Sm$^{3+}$ ion concentration in the titled glasses are due to non-radiative energy transfer between Sm$^{3+}$ ions.
Table 4.4. Emission peak wavelength ($\lambda_p$(nm)), effective band width ($\Delta\lambda_p$(nm)), experimental branching ratio ($\beta_{exp}$), stimulated emission cross-section ($\sigma_{se}$(x $10^{-22}$) (cm$^2$)), gain bandwidth ($\sigma_{se}\times\Delta\lambda_p$(x$10^{-28}$), optical gain ($\sigma_{se}\times\tau_R$)(x$10^{-25}$) and O/R ratios for the emission transitions of Sm$^{3+}$ ions doped ZnAlBiB glasses. Experimental, radiative lifetimes ($\tau_{exp}$, $\tau_R$)(μs) and quantum efficiency ($\eta$)(%) of $^4G_{5/2}$ transition for different concentrations of Sm$^{3+}$ ions doped ZnAlBiB glasses are given separately.

<table>
<thead>
<tr>
<th>Transition</th>
<th>Parameters</th>
<th>ZnAlBiBSm01</th>
<th>ZnAlBiBSm05</th>
<th>ZnAlBiBSm10</th>
<th>ZnAlBiBSm15</th>
<th>ZnAlBiBSm20</th>
<th>ZnAlBiBSm25</th>
</tr>
</thead>
<tbody>
<tr>
<td>$^4G_{5/2} \rightarrow ^6H_{5/2}$</td>
<td>$\lambda_p$</td>
<td>563</td>
<td>563</td>
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<tr>
<td> </td>
<td>$\Delta\lambda_p$</td>
<td>12.5</td>
<td>10.15</td>
<td>10.15</td>
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<td>10.15</td>
<td>12.5</td>
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<td>0.09</td>
<td>0.10</td>
<td>0.11</td>
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<td>0.17</td>
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<td>$\sigma_{se}$</td>
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<td>1.34</td>
<td>1.17</td>
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<td>1.16</td>
<td>1.36</td>
<td>1.19</td>
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<td>598</td>
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<tr>
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<td>13.28</td>
<td>12.5</td>
<td>14.06</td>
<td>14.06</td>
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<td>$\sigma_{se}\times\Delta\lambda_p$</td>
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<td>$\sigma_{se}\times\tau_R$</td>
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<td>22.1</td>
<td>23.6</td>
<td>21.0</td>
<td>21.2</td>
<td>19.0</td>
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<td>$\Delta\lambda_P$</td>
<td>$\beta_{\text{exp}}$</td>
<td>$\sigma_{\text{se}}$</td>
<td>$\sigma_{\text{se}} \Delta\lambda_P$</td>
<td>$\sigma_{\text{se}} \tau_R$</td>
<td>$(^{4}G_{5/2} \rightarrow ^{6}H_{7/2})/(^{4}G_{5/2} \rightarrow ^{6}H_{5/2})$$(O/R)$</td>
</tr>
<tr>
<td>------------------</td>
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<td>$^{4}G_{5/2} \rightarrow ^{6}H_{9/2}$</td>
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<td>15.62</td>
<td>0.35</td>
<td>2.42</td>
<td>3.78</td>
<td>7.65</td>
<td>1.57</td>
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<td>644</td>
<td>14.06</td>
<td>0.35</td>
<td>3.11</td>
<td>4.37</td>
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<td>2.84</td>
<td>4.44</td>
<td>7.69</td>
<td>21.87</td>
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<td>2.90</td>
<td>4.53</td>
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<td>3.55</td>
<td>3.79</td>
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<td>2.07</td>
<td>7.43</td>
<td>3.09</td>
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<td>4.18</td>
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<td>26.56</td>
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<td>26.56</td>
<td>0.03</td>
<td>1.6</td>
<td>4.26</td>
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</table>

Emission characteristics of $^{4}G_{5/2} \rightarrow ^{6}H_{7/2}$ transition

<table>
<thead>
<tr>
<th></th>
<th>$\tau_R$</th>
<th>$\tau_{\text{exp}}$</th>
<th>$\eta$</th>
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<tr>
<td></td>
<td>3167</td>
<td>1696</td>
<td>53</td>
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<td>2866</td>
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<td>1125</td>
<td>43</td>
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<tr>
<td></td>
<td>2700</td>
<td>1115</td>
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</tr>
<tr>
<td></td>
<td>2683</td>
<td>1096</td>
<td>40</td>
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</tbody>
</table>

98
From Table 4.4, it can be observed that the experimental lifetimes ($\tau_{exp}$) are found to be less than radiative lifetimes ($\tau_R$). The deviation of the experimental lifetimes ($\tau_{exp}$) from the radiative lifetimes ($\tau_R$) obtained by using the JO theory was probably not related to the multi-phonon relaxation, considering the larger energy gap between $^4G_{5/2}$ level and the next lower level $^6F_{11/2}$ compared to the phonon energy. The discrepancy of lifetimes between experimental and radiative lifetime values is rather ascribed to the non-radiative energy transfer through cross-relaxation, which increases with the concentration of Sm$^{3+}$ ions [180].

In case of RE$^{3+}$ ions, luminescence quantum efficiency ($\eta$) is the ratio of measured lifetime ($\tau_{exp}$) to the radiative lifetime ($\tau_R$), i.e.,

$$\eta = \frac{\tau_{exp}}{\tau_R} \times 100 \%$$

The quantum efficiency thus calculated for all the glasses are given in Table 5. Among all the glasses studied, the quantum efficiency obtained for ZnAlBiBSm10 was found to be 77% for $^4G_{5/2}$ level. Such quantum efficiency value observed for ZnAlBiBSm10 glass compared with other glasses are given in Table 4.5 [134, 172, 174,181-184]. From Table 4.4, it is evident that ZnAlBiBSm10 glass is competent enough for visible laser emission at 598 nm with its quantum efficiency value more than the reported glasses.

Figure 4.4. Decay curves of the prominent emission transition at 598 nm for Sm$^{3+}$ ions doped ZnAlBiB glasses.
Table 4.5. Comparison of branching ratio ($\beta_R$), stimulated emission cross section ($\sigma_{se} \times 10^{-22} \text{ cm}^2$) and quantum efficiency ($\eta$) (%) of $^4G_{5/2} \rightarrow ^6H_{7/2}$ transition for $\text{Sm}^{3+}$ ion in different glass hosts.

<table>
<thead>
<tr>
<th>Transition ($^4G_{5/2} \rightarrow ^6H_{7/2}$)</th>
<th>$\beta_R$</th>
<th>$\sigma_{se}$</th>
<th>$\eta$ (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>ZnAlBiBSm10 (Present Work)</td>
<td>0.54</td>
<td>15.8</td>
<td>77</td>
</tr>
<tr>
<td>LSG [134]</td>
<td>0.41</td>
<td>8.20</td>
<td>-</td>
</tr>
<tr>
<td>L5FBS [172]</td>
<td>0.46</td>
<td>5.74</td>
<td>-</td>
</tr>
<tr>
<td>N4BS [174]</td>
<td>0.43</td>
<td>8.78</td>
<td>74</td>
</tr>
<tr>
<td>30 mol % Pbo [175]</td>
<td>0.51</td>
<td>6.92</td>
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</tr>
<tr>
<td>LCZSF [181]</td>
<td>0.44</td>
<td>12.6</td>
<td>57</td>
</tr>
<tr>
<td>RTFP (LiTFP) [182]</td>
<td>0.53</td>
<td>6.91</td>
<td>-</td>
</tr>
<tr>
<td>Tellurite Glass [183]</td>
<td>0.49</td>
<td>3.6</td>
<td>-</td>
</tr>
<tr>
<td>ZFBP [184]</td>
<td>-</td>
<td>3.44</td>
<td>-</td>
</tr>
</tbody>
</table>

4.3.4. CIE Chromaticity coordinates

In order to understand the color emitted by the $\text{Sm}^{3+}$ doped ZnAlBiB glasses, the chromaticity coordinates values are evaluated from the emission spectra following the procedure outlined in the commission International de l’Eclaiage France CIE system [185]. The emission spectra obtained by intrinsic excitation have mainly three parts. A small part spread in green region, a main part spread in the orange to red region and a third part spread in red region. Out of these parts, a main part which is spread in the orange to red is more intense than the other parts. Figure 4.5 represents the CIE plot with color coordinates of $\text{Sm}^{3+}$ in ZnAlBiB glasses when excited at 410nm wavelength using CW laser. From Figure 4.5 it is observed that the CIE coordinates for all the ZnAlBiB glasses falls in orange-red region. As shown in Figure 4.5, among all the glasses, the CIE chromaticity coordinates for ZnAlBiBSm10 glass is much nearer to the orange-red region. This result is in consistent with the confocal images.
recorded for ZnAlBiBSm10 glass (Figure.4.3). This indicates that the present titled glasses are potential materials for the familiar cation of red component of white light emitting diodes in solid state lighting applications.

![Figure.4.5. CIE color chromaticity diagram for Sm$^{3+}$ ions doped ZnAlBiB glasses.](image)

4.4. CONCLUSION

ZnAlBiB glasses doped with different concentration of Sm$^{3+}$ ions were prepared by the conventional melt quenching technique. The JO parameters evaluated from the measured absorption spectra of these glasses are used to calculate radiative properties of Sm$^{3+}$ ions. The excitation spectra for the titled glasses exhibit several excitation bands in visible region ranging from 325-500 nm. This indicates that, the commercial UV-blue laser diodes and bluish-green light emitting diodes are suitable as pumping sources for the titled glasses. The emission spectra recorded by monitoring the excitation at 410 nm using CW laser in the titled glasses gives four emission bands in visible region. Among them $^4G_{5/2} \rightarrow ^6H_{7/2}$ is more intense and $^4G_{5/2} \rightarrow ^6H_{7/2}$ is moderate for all the glasses and are responsible for the distinct orange-red emission. This result is in consistent with the confocal photoluminescence images recorded for all ZnAlBiB
glasses. Based on the emission spectra, high stimulated emission cross-sections, branching ratios and quantum efficiencies observed for $^4\text{G}_{5/2}\rightarrow^6\text{H}_{7/2}$ transition for all these glasses suggest the feasibility of using these materials as visible lasers in orange-red (598nm) visible region. The CIE chromaticity coordinates evaluated from the emission spectra for all these glasses also confirms the same thing. From the measured emission cross-sections, branching radios, quantum efficiencies, con-focal photoluminescence images and CIE chromaticity coordinates evaluated, it was concluded that 1 mol% of Sm$^{3+}$ ion concentration is optimum in ZnAlBiB glasses for the development of orange-red visible lasers (598nm) in principle.