Spectroscopic Properties of Sm\(^{3+}\) Doped in Yttrium Zinc Lithium Bismuth Borate Glasses

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ABSTRACT

Glass sample of Zinc Lithium Bismuth Borate \((20-x)\) Bi\(_2\)O\(_3\):15Li\(_2\)O: 15ZnO:10 Y\(_2\)O\(_3\): 40 B\(_2\)O\(_3\): x Sm\(_2\)O\(_3\) (where x=1,1.5,2 mol\%) have been prepared by melt-quenching technique. The amorphous nature of the prepared glass samples was confirmed by X-ray diffraction. Optical absorption and fluorescence spectra were recorded at room temperature for all glass samples. The various interaction parameters like Slater-Condon, bonding and Lande’s parameters have been computed. Judd-Ofelt intensity parameters and laser parameters have also been calculated. The values of spontaneous emission probability \((A)\) and stimulated emission cross-section\((\sigma_p)\) are found to be maximum for the transition \((^4S_{5/2} \rightarrow ^6H_{5/2})\), \((^4S_{5/2} \rightarrow ^6H_{7/2})\), \((^4S_{5/2} \rightarrow ^6H_{9/2})\) and \((^4S_{5/2} \rightarrow ^4I_{15/2})\) for glass YZnLiBiB SM 02, suggest that glass YZnLiBiB SM 02 better compared to the other two glass systems.

**Keywords:** Yttrium zinc lithium bismuth borate glasses, Energy interaction parameters, Optical properties, Judd-Ofelt analysis.

1. INTRODUCTION

Bismuth borate glasses are very important because of their technological and scientific application\(^1\)\(^-\)\(^3\). Rare earth doped transparent bismuth borate glasses and glass ceramics are of increasing interests in various optical applications, because of their superior optical, liner, non liner and electrical properties\(^4\)\(^,\)\(^5\).

Glasses based on heavy metal oxides \((\text{Bi}_2\text{O}_3)\) have received increased attention due to their manifold possible application in the field of glass ceramics, optoelectronics and reflecting windows\(^6\)\(^-\)\(^8\). Bismuth borate glasses are also possessing broad range of applications in the fields of optical fiber amplifiers, laser materials, photonic switches and layers for optical devices\(^9\)\(^-\)\(^10\). Furthermore, Sm\(^{3+}\) ion is one of the most important active ions in the rare earth family due to its convenient closely lying energy level structure\(^11\).
The present work reports on the preparation and characterization of rare earth doped heavy metal oxide (HMO) glass systems for lasing materials. We have studied on the absorption and emission properties of $\text{Sm}^{3+}$ doped yttrium zinc lithium bismuth borate glasses. The intensities of the transitions for the rare earth ions have been estimated successfully using the Judd-Ofelt theory. The laser parameters such as radiative probabilities($A$), branching ratio ($\beta$), radiative life time($\tau_R$) and stimulated emission cross section($\sigma_p$) are evaluated using J.O. intensity parameters($\Omega_\lambda$, $\lambda=2,4,6$).

### 2. EXPERIMENTAL TECHNIQUES

#### Preparation of glasses

The following $\text{Sm}^{3+}$ doped bismuth borate glass samples (20-x) $\text{Bi}_2\text{O}_3:15\text{Li}_2\text{O}:15\text{ZnO}:10\text{Y}_2\text{O}_3:40\text{B}_2\text{O}_3$ x $\text{Sm}_2\text{O}_3$ (where x=1,1.5 and 2 mol%) have been prepared by melt-quenching method. Analytical reagent grade chemical used in the present study consist of $\text{Bi}_2\text{O}_3$, $\text{Li}_2\text{O}$, $\text{ZnO}$, $\text{Y}_2\text{O}_3$, $\text{B}_2\text{O}_3$ and $\text{Sm}_2\text{O}_3$. They were thoroughly mixed by using an agate pestle mortar. Then melted at 1050°C by an electrical muffle furnace for 2h., After complete melting, the melts were quickly poured in to a preheated stainless steel mould and annealed at temperature of 350°C for 2h to remove thermal strains and stresses. Every time fine powder of cerium oxide was used for polishing the samples. The glass samples so prepared were of good optical quality and were transparent. The chemical compositions of the glasses with the name of samples are summarized in Table 1.

#### Table 1

<table>
<thead>
<tr>
<th>Sample</th>
<th>Glass composition (mol %)</th>
</tr>
</thead>
<tbody>
<tr>
<td>YZnLiBiB (UD)</td>
<td>20 $\text{Bi}_2\text{O}_3$; 15$\text{Li}_2\text{O}$; 15$\text{ZnO}$; 10$\text{Y}_2\text{O}_3$; 40$\text{B}_2\text{O}_3$</td>
</tr>
<tr>
<td>YZnLiBiB (SM1)</td>
<td>19 $\text{Bi}_2\text{O}_3$; 15$\text{Li}_2\text{O}$; 15$\text{ZnO}$; 10$\text{Y}_2\text{O}_3$; 40$\text{B}_2\text{O}_3$; 1 $\text{Sm}_2\text{O}_3$</td>
</tr>
<tr>
<td>YZnLiBiB (SM1.5)</td>
<td>18.5$\text{Bi}_2\text{O}_3$; 15$\text{Li}_2\text{O}$; 15$\text{ZnO}$; 10$\text{Y}_2\text{O}_3$; 40$\text{B}_2\text{O}_3$; 1.5 $\text{Sm}_2\text{O}_3$</td>
</tr>
<tr>
<td>YZnLiBiB (SM2)</td>
<td>18 $\text{Bi}_2\text{O}_3$; 15$\text{Li}_2\text{O}$; 15$\text{ZnO}$; 10$\text{Y}_2\text{O}_3$; 40$\text{B}_2\text{O}_3$; 2 $\text{Sm}_2\text{O}_3$</td>
</tr>
</tbody>
</table>

YZnLiBiB (UD) -Represents undoped Yttrium Zinc Lithium Bismuth Borate glass specimens
YZnLiBiB (SM) -Represents $\text{Sm}^{3+}$ doped Yttrium Zinc Lithium Bismuth Borate glass specimens

#### 3. THEORY

#### 3.1 Oscillator Strength

The intensity of spectral lines are expressed in terms of oscillator strengths using the relation

$$f_{\text{expt.}} = 4.318 \times 10^{-9} \int \varepsilon (\nu) d \nu$$

where, $\varepsilon (\nu)$ is molar absorption coefficient at a given energy $\nu$ (cm$^{-1}$), to be evaluated from Beer–Lambert law.
Under Gaussian Approximation, using Beer–Lambert law, the observed oscillator strengths of the absorption bands have been experimentally calculated\textsuperscript{13}, using the modified relation:

\[ P_m = 4.6 \times 10^{-9} \times \frac{1}{c} \log \frac{I_0}{I} \times \Delta \nu_{1/2} \]  

(2)

where \( c \) is the molar concentration of the absorbing ion per unit volume, \( I \) is the optical path length, \( \log I_0/I \) is absorbtivity or optical density and \( \Delta \nu_{1/2} \) is half band width.

### 3.2 Judd-Ofelt Intensity Parameters

According to Judd\textsuperscript{14} and Ofelt\textsuperscript{15} theory, independently derived expression for the oscillator strength of the induced forced electric dipole transitions between an initial \( J \) manifold \( |4f^N (S, L) J\rangle \) level and the terminal \( J' \) manifold \( |4f^N (S'L') J'\rangle \) is given by:

\[
\frac{8 \pi^2 m c \nu}{3h(2J + 1)n} \left[ \frac{(n^2 + 2)^2}{9} \right] \times S(J, J')
\]  

(3)

Where, the line strength \( S(J, J') \) is given by the equation

\[
S(J, J') = e^2 \sum_{\lambda=2, 4, 6} \Omega_\lambda <4f^N(S, L) J \parallel U^{(\lambda)} \parallel 4f^N(S', L') J'>^2
\]  

(4)

In the above equation \( m \) is the mass of an electron, \( c \) is the velocity of light, \( \nu \) is the wave number of the transition, \( h \) is Planck’s constant, \( n \) is the refractive index, \( J \) and \( J' \) are the total angular momentum of the initial and final level respectively, \( \Omega_\lambda \ (\lambda = 2, 4, 6) \) are known as Judd-Ofelt intensity parameters which contain the effect of the odd-symmetry crystal field terms, radial integrals and energy denominators. \( \parallel U^{(\lambda)} \parallel^2 \) are the matrix elements of the doubly reduced unit tensor operator calculated in intermediate coupling approximation. \( \Omega_\lambda \) parameter can be obtained from least square fitting method\textsuperscript{16}.

### 3.3 Radiative Properties

The \( \Omega_\lambda \) parameters obtained using the absorption spectral results have been used to predict radiative properties such as spontaneous emission probability (A) and radiative life time (\( \tau_r \)), and laser parameters like fluorescence branching ratio (\( \beta_R \)) and stimulated emission cross section (\( \sigma_p \)).

The spontaneous emission probability from initial manifold \( |4f^N (S', L') J'> \) to a final manifold \( |4f^N (S, L) J\rangle \) is given by:

\[
A([S', L'] J'; (S, L) J] = \frac{64 \pi^2 v^3}{3h(2J+1)} \left[ \frac{n(n^2+2)^2}{9} \right] \times S(J', J)
\]  

(5)

Where, \( S(J', J) = e^2 [\Omega_2 \parallel U^{(2)} \parallel^2 + \Omega_4 \parallel U^{(4)} \parallel^2 + \Omega_6 \parallel U^{(6)} \parallel^2] \)

The fluorescence branching ratio for the transitions originating from a specific initial manifold \( |4f^N (S', L') J'> \) to a final many fold \( |4f^N (S, L) J\rangle \) is given by
β [(S’, L’) J’; (S, L) J ] = \sum_{S’ L’ J’}^{A_{[(S’, L’) J’; (S, L)]}} \frac{A}{A_{[(S’, L’) J’; (S, L)]}}

(6)

where, the sum is over all terminal manifolds.

The radiative life time is given by

\[ \tau_{rad} = \sum_{S L J} A[(S’, L’) J’; (S, L)] = A_{Total}^{-1} \]

(7)

where, the sum is over all possible terminal manifolds. The stimulated emission cross-section for a transition from an initial manifold \(|4f N (S’, L’) J’>\) to a final manifold \(|4fN (S, L) J >\) is expressed as

\[ \sigma_p(\lambda_p) = \frac{\lambda_p^2}{8\pi c n^2 \Delta \lambda_{eff}} \times A[(S’, L’) J’; (S, L)] \]

(8)

where, \(\lambda_p\) the peak fluorescence wavelength of the emission band and \(\Delta \lambda_{eff}\) is the effective fluorescence line width.

3.4 Nephelauxetic Ratio (β) and Bonding Parameter (b_{1/2})

The nature of the R-O bond is known by the Nephelauxetic Ratio (\(\beta’\)) and Bonding Parameters (\(b_{1/2}\)), which are computed by using following formulae\(^{17,18}\). The Nephelauxetic Ratio is given by

\[ \beta’ = \frac{v_a}{v_g} \]

(9)

where, \(v_a\) and \(v_g\) refer to the energies of the corresponding transition in the glass and free ion, respectively. The value of bonding parameter (\(b_{1/2}\)) is given by

\[ b_{1/2} = \left(1 - \beta’^2\right)^{1/2} \]

(10)

4. RESULT AND DISCUSSION

4.1 XRD Measurement

Figure 1 presents the XRD pattern of the sample contain - B\(_2\)O\(_3\) which is show no sharp Bragg’s peak, but only a broad diffuse hump around low angle region. This is the clear indication of amorphous nature within the resolution limit of XRD instrument.

Fig. 1 X-ray diffraction pattern of \(\text{Bi}_2\text{O}_3: \text{Li}_2\text{O}: \text{ZnO}: \text{Y}_2\text{O}_3: \text{B}_2\text{O}_3: \text{Sm}_2\text{O}_3\)
4.2 FTIR Transmission spectra

The FTIR spectra are presented in Figure 2 and the possible mechanism bands was tabulated in Table 2.

![FTIR Transmission spectra](image)

**Fig. 2 IR transmission spectra for Bi\(_2\)O\(_3\); Li\(_2\)O; Zn\(_2\)O; Y\(_2\)O\(_3\); B\(_2\)O\(_3\); Sm\(_2\)O\(_3\) glasses**

The BO\(_3\) triangles are corner bonded in a random network\(^9\). The present set of glasses show very strong transmission bands in the region 470-500, 640-695, 950-1000, 1250-1320 and 2340-2500 cm\(^{-1}\). In borate glasses it has been reported that the bands observed in the region 470-525 cm\(^{-1}\) are due to the variation metal cations such as Zn\(^{2+}\). Whereas, the bands observed in the range 990-1020 cm\(^{-1}\) are assigned due to B-O bond stretching of the tetrahedral BO\(_4\) units. The bands observed around 665-705 cm\(^{-1}\) are due to the bending mode of B-O-B vibrations\(^{20}\). In the present glass system, the intermerging bonds observed in the region 1280-1360 cm\(^{-1}\) are assigned to the asymmetric stretching of B-O bond in the trigonal units. The bands observed in the region 2360-2500 cm\(^{-1}\) are due to hydroxol group\(^{20}\).

<table>
<thead>
<tr>
<th>Peak position (cm(^{-1}))</th>
<th>Assignment</th>
</tr>
</thead>
<tbody>
<tr>
<td>470-500 cm(^{-1})</td>
<td>Variation metal cations such as Zn(^{2+})</td>
</tr>
<tr>
<td>640-695 cm(^{-1})</td>
<td>Bending of B-O-B linkage</td>
</tr>
<tr>
<td>950-1000 cm(^{-1})</td>
<td>B-O stretching of BO(_4) tetrahedra</td>
</tr>
<tr>
<td>1250-1320 cm(^{-1})</td>
<td>Asymmetric stretching of B-O of trigonal</td>
</tr>
<tr>
<td>2340-2500 cm(^{-1})</td>
<td>Indication of OH groups</td>
</tr>
</tbody>
</table>

4.3 Absorption Spectrum

The absorption spectra of Sm\(^{3+}\) doped YZnLiBiB glass specimens have been presented in Figure 3 in terms of optical density \(\log (I/I_0)\) versus wavelength (nm), where I and I\(_0\) are intensities of the radiation transmitted through doped specimens and undoped specimens of
equal thickness. Ten absorption bands have been observed from the ground state \(^6\text{H}_{\frac{5}{2}}\) to excited states \(^6\text{F}_{\frac{1}{2}}, ^6\text{F}_{\frac{7}{2}}, ^6\text{F}_{\frac{9}{2}}, ^6\text{G}_{\frac{7}{2}}, ^4\text{I}_{\frac{9}{2}}, ^6\text{M}_{\frac{7}{2}}, (^6\text{P}^2, ^4\text{P})_{\frac{5}{2}}, ^4\text{F}_{\frac{7}{2}}, ^4\text{D}_{\frac{1}{2}}, \) and \((^4\text{D}, ^6\text{P})_{\frac{5}{2}}\) for Sm\(^{3+}\) doped YZnLiBiB glasses.

Fig. (3) Absorption spectrum of Sm\(^{3+}\) doped YZnLiBiB (01) glass

The experimental and calculated oscillator strength for Sm\(^{3+}\) ions in YZnLiBiB glasses are given in Table 3.

### Table 3: Measured and calculated oscillator strength \((P_m \times 10^6)\) of Sm\(^{3+}\) ions in YZnLiBiB glasses.

<table>
<thead>
<tr>
<th>Energy level from (^6\text{H}_{\frac{5}{2}})</th>
<th>Glass YZnLiBiB(SM01)</th>
<th>Glass YZnLiBiB(SM1.5)</th>
<th>Glass YZnLiBiB(SM02)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>(P_{\text{exp}})</td>
<td>(P_{\text{cal}})</td>
<td>(P_{\text{exp}})</td>
</tr>
<tr>
<td>(^6\text{F}_{\frac{1}{2}})</td>
<td>1.53</td>
<td>1.59</td>
<td>1.52</td>
</tr>
<tr>
<td>(^6\text{F}_{\frac{7}{2}})</td>
<td>5.50</td>
<td>5.56</td>
<td>5.40</td>
</tr>
<tr>
<td>(^6\text{F}_{\frac{9}{2}})</td>
<td>3.77</td>
<td>3.86</td>
<td>3.76</td>
</tr>
<tr>
<td>(^4\text{G}_{\frac{7}{2}})</td>
<td>0.12</td>
<td>0.12</td>
<td>0.10</td>
</tr>
<tr>
<td>(^4\text{I}_{\frac{9}{2}})</td>
<td>1.20</td>
<td>1.19</td>
<td>1.10</td>
</tr>
<tr>
<td>(^4\text{M}<em>{\frac{7}{2}}), (^4\text{G}</em>{\frac{9}{2}}) (^4\text{I}_{\frac{5}{2}})</td>
<td>0.25</td>
<td>0.25</td>
<td>0.23</td>
</tr>
<tr>
<td>((^6\text{P}^2, ^4\text{P})<em>{\frac{5}{2}}, ^4\text{L}</em>{\frac{3}{2}})</td>
<td>1.29</td>
<td>1.33</td>
<td>1.28</td>
</tr>
<tr>
<td>(^6\text{F}<em>{\frac{1}{2}}, ^6\text{P}</em>{\frac{3}{2}}, ^4\text{K}_{\frac{3}{2}})</td>
<td>5.60</td>
<td>5.72</td>
<td>5.40</td>
</tr>
<tr>
<td>(^4\text{D}<em>{\frac{1}{2}}, ^4\text{P}</em>{\frac{3}{2}}, ^4\text{L}_{\frac{1}{2}})</td>
<td>2.38</td>
<td>2.45</td>
<td>2.36</td>
</tr>
<tr>
<td>(^4\text{D}<em>{\frac{3}{2}}), ((^4\text{D}, ^6\text{P})</em>{\frac{5}{2}})</td>
<td>2.40</td>
<td>3.51</td>
<td>2.38</td>
</tr>
<tr>
<td>r.m.s. deviation</td>
<td>±0.4180</td>
<td>±0.4143</td>
<td>±0.4159</td>
</tr>
</tbody>
</table>

Computed values of \(F_2\), Landé’s parameter \((\zeta_4)\), Nephiiauxetic ratio\((\beta')\) and bonding parameter\((b^{1/2})\) for Sm\(^{3+}\) ions in YZnLiBiB glass specimen are given in Table 4.
Table 4: $F_2, \xi_{4f}, \beta'$ and $b^{1/2}$ parameters for Samarium doped glass specimen.

<table>
<thead>
<tr>
<th>Glass Specimen</th>
<th>$F_2$</th>
<th>$\xi_{4f}$</th>
<th>$\beta'$</th>
<th>$b^{1/2}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sm$^{3+}$</td>
<td>358.82</td>
<td>1258.16</td>
<td>0.9337</td>
<td>0.1821</td>
</tr>
</tbody>
</table>

In the Yttrium Zinc Lithium Bismuth Borate glasses (YZnLiBiB) $\Omega_2, \Omega_4$ and $\Omega_6$ parameters decrease with the increase of x from 1 to 2 mol%. The order of magnitude of Judd-Ofelt intensity parameters is $\Omega_2 > \Omega_4 > \Omega_6$ for all the glass specimens. The spectroscopic quality factor ($\Omega_4/\Omega_6$) related with the rigidity of the glass system has been found to lie between 1.06 and 1.11 in the present glasses.

The values of Judd-Ofelt intensity parameters are given in Table 5.

Table 5: Judd-Ofelt intensity parameters for Sm$^{3+}$ doped YZnLiBiB glass specimens

<table>
<thead>
<tr>
<th>Glass Specimen</th>
<th>$\Omega_2$(pm$^2$)</th>
<th>$\Omega_4$(pm$^2$)</th>
<th>$\Omega_6$(pm$^2$)</th>
<th>$\Omega_4/\Omega_6$</th>
</tr>
</thead>
<tbody>
<tr>
<td>YZnLiBiB(SM01)</td>
<td>4.11</td>
<td>3.94</td>
<td>3.55</td>
<td>1.11</td>
</tr>
<tr>
<td>YZnLiBiB(SM1.5)</td>
<td>4.08</td>
<td>3.79</td>
<td>3.52</td>
<td>1.08</td>
</tr>
<tr>
<td>YZnLiBiB(SM02)</td>
<td>4.05</td>
<td>3.70</td>
<td>3.48</td>
<td>1.06</td>
</tr>
</tbody>
</table>

4.4. Fluorescence Spectrum

The fluorescence spectrum of Sm$^{3+}$ doped in yttrium zinc lithium bismuth borate glass is shown in Figure 4. There are four broad bands observed in the Fluorescence spectrum of Sm$^{3+}$ doped yttrium zinc lithium bismuth borate glass. The wavelengths of these bands along with their assignments are given in Table 6. The peak with maximum emission intensity appears at 604nm and corresponds to the ($^4G_{5/2} \rightarrow ^6H_{7/2}$) transition.

![Fluorescence Spectrum](image_url)
Table6: Emission peak wave lengths (λρ), radiative transition probability (A_rad), branching ratio (β), stimulated emission cross-section (σ_p) and radiative life time (τ_r) for various transitions in Sm³⁺ doped YZnLiBiB glasses

<table>
<thead>
<tr>
<th>Transition</th>
<th>YZnLiBiB SM 01</th>
<th>YZnLiBiB SM 1.5</th>
<th>YZnLiBiB SM 02</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>λ_ρ (nm)</td>
<td>A_rad (s⁻¹)</td>
<td>β</td>
</tr>
<tr>
<td>G_{5/2}→H_{1/2}</td>
<td>712</td>
<td>35.386</td>
<td>0.1079</td>
</tr>
<tr>
<td>G_{5/2}→H_{11/2}</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>G_{7/2}→H_{1/2}</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>G_{7/2}→H_{11/2}</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

5. CONCLUSION

In the present study, the glass samples of composition (20–x) Bi₂O₃:15Li₂O:15ZnO:10Y₂O₃: 40B₂O₃:xSm₂O₃ (where x = 1, 1.5, 2 mol %) have been prepared by melt-quenching method. The fairness of the fitting approximation is examined by the root mean square deviation. Low r.m.s.deviation values clearly indicate the accuracy of fitting. The values of spontaneous emission probability (A) and stimulated emission cross-section (σ_p) are found to be maximum for the transition (4G_{5/2}→4H_{5/2}), (4G_{5/2}→4H_{7/2}), (4G_{5/2}→4H_{9/2}) and (4G_{5/2}→6H_{11/2}) for glass YZnLiBiB SM 02, suggest that glass YZnLiBiB SM 02 better compared to the other two glass systems (YZnLiBiB SM 1, YZnLiBiB SM 1.5).

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