Optical absorption and fluorescence properties of Dy$^{3+}$: SFB glasses

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Optical absorption and fluorescence properties of Dy\(^{3+}\): SFB glasses

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Abstract : This paper presents the preparation and spectroscopic characterization of Dy\(^{3+}\)-doped sodium fluoroborate (SFB) glasses of the type \((50-x)\) B\(_2\)O\(_3\) + 25 Na\(_2\)O + 10 CaF\(_2\) + 10 AlF\(_3\) + 5 LaF\(_3\) + x DyF\(_3\) (x = 0.01, 0.1, 0.5, 1.0, 2.0 and 4.0 mol%). By measuring the area under absorption bands, the experimental oscillator strengths are determined. The Judd-Ofelt (J-O) intensity parameters \(\Omega_\lambda\) (\(\lambda = 2, 4, 6\)) are evaluated by the least square fit method. These phenomenological parameters are used to predict luminescence properties of the lanthanide ions in SFB glasses. Photoluminescence spectra and lifetimes of \(4F_{9/2}\) level of Dy\(^{3+}\) ions in these glasses have been measured by exciting with 348 nm line of xenon flash lamp. The measured decay curves exhibit single exponential at lower concentrations of 0.01, 0.1, 0.5 and 1.0 mol% and non-exponential at higher concentrations of 2.0 and 4.0 mol%. The predicted \(\tau_R\) and \(\beta_R\) values of \(4F_{9/2}\) transition are compared with the experimentally measured values. From the magnitude of stimulated emission cross sections (\(\sigma_s\)), branching ratios (\(\beta_{\lambda}\)), multiphonon relaxation rates (\(W_{\text{MP}}\)), the most potential laser transitions are identified and the utility of these glasses as laser active material is discussed.

1. INTRODUCTION
Fluoride based glasses are promising host materials for applications in photonics such as frequency upconverters, optical amplifiers [1-2]. Optical absorption and fluorescence studies of rare earth ions doped glasses found wide applications in the field of lasers and telecommunications. This study mainly includes the absorption, emission and lifetime measurements of Dy\(^{3+}\)-doped sodium fluoroborate (SFB) glasses in order to know their utility for solid state laser devices. Lanthanum is a common constituent of ceramics and glasses which acts as glass former at low concentrations. The addition of AlF\(_3\) improves the optical quality with a tendency to devitrify during cooling because of their strong ionic bonding [3]. In general, borate glasses exhibit lower thermal expansion coefficients, higher densities, stronger bonding and denser packing [4].
2. EXPERIMENTAL DETAILS

Glass samples were prepared with chemical composition of (50-x) B_2O_3 + 25 Na_2O + 10 CaF_2 +10 AlF_3 + 5 LaF_3 + x DyF_3, where x = 0.01, 0.1, 0.5, 1.0, 2.0, and 4.0 mol%. Homogeneous mixture of reagent grade chemicals were melted in an electric furnace at 1050 °C in platinum crucible for one hour and subsequently annealed at 360°C for seven hours to remove thermal strains. Absorption spectra of Dy^{3+} doped SFB glasses were recorded in the wavelength range 340-1800 nm region using a Varian Cary 5E UV-VIS-NIR spectrophotometer. By exciting the samples at 386 nm, visible photoluminescence spectra as well as lifetime measurements were recorded using JOBIN YVON Fluorolog-3 spectrofluorimeter.

3. RESULTS AND DISCUSSIONS

3.1. Absorption spectra and J-O analysis

UV-VIS and NIR room temperature absorption spectra of SFB glasses containing 1.0 mol% of Dy^{3+} are shown in figures 1 (a) and (b) respectively. The areas under the absorption peaks are used to determine experimental oscillator strengths and the J-O parameters are obtained by the least squares fit [5, 6]. The evaluated Ω_2, Ω_4 and Ω_6 parameters are found to be 4.55, 2.11 and 1.78 (x10^{-20} cm^2) respectively. The small δ_{rms} deviations of ±0.68×10^{-6} indicates a good fit between calculated and measured oscillator strengths. The spectral intensities of certain transitions of rare earth ions are found to be very sensitive to the environment which are called as hypersensitive transitions obeying the selection rules J ≤ 2, ΔL ≤ 2 and ΔS =0 [7]. In the case of Dy^{3+} ion the ^4H_{15/2} → ^4I_{11/2} is the hypersensitive transition. The evaluated J-O parameters obtained in the present glass are also comparable with different host glasses [8-11]

![Figure 1](image1.png)

**Figure 1.** Absorption spectra of 1.0 mol% Dy^{3+} doped SFB glass: (a) UV-VIS, (b) NIR.

3.2. Photoluminescence spectra

Figure 2 presents the emission spectra of 0.01, 0.1, 0.5, 1.0, 2.0 and 4.0 mol% of Dy^{3+} doped SFB glass samples obtained by exciting the samples at 386 nm corresponding to ^4I_{15/2} → ^4I_{13/2} transition. The spectra consists of three emission peaks at 483, 574 and 664 nm corresponding to ^4F_{9/2} → ^4H_{J}, with J = 15/2, 13/2 and 11/2 transitions respectively. The emission mechanism of Dy^{3+} ions in SFB glasses is shown in figure 3. The emission intensities of Dy^{3+} in SFB glasses increase with the concentration upto 1.0 mol% and beyond that concentration quenching has been observed. The yellow
(\(^4F_{9/2} \rightarrow ^6H_{13/2}\)) to blue \(^4F_{9/2} \rightarrow ^6H_{15/2}\) intensity ratios increase up to 1.0 mol%. Beyond 1.0 mol% of Dy\(^{3+}\), yellow-blue intensity ratios decrease due to fluorescence quenching. From the emission spectra the peak wavelengths (\(\lambda_p\)), effective linewidths (\(\Delta \lambda_{\text{eff}}\)), stimulated emission cross-sections (\(\sigma_e\)) and the measured branching ratios (\(\beta_m\)) are determined. In the present work, the radiative transition probabilities (\(A_R\)), measured branching ratios (\(\beta_m\)) and stimulated emission cross-sections (\(\sigma_e\)) for \(^4F_{9/2} \rightarrow ^6H_J (J=11/2,13/2,15/2)\) transition in 1.0 mol% of Dy\(^{3+}\)-doped SFB glass are compared with other reported glasses and presented in table 1 [12-14]. For \(^4F_{9/2} \rightarrow ^6H_{15/2}\) transition the branching ratio is high when compared to other reported systems.

![Figure 2. Emission spectra of SFB glasses doped with different concentrations of Dy\(^{3+}\) ion.](image)

**Table 1.** Comparison of radiative transition probabilities (\(A_R\)), measured branching ratios (\(\beta_m\)) and stimulated emission cross-sections (\(\sigma_e \times 10^{-2}\)) for the \(^4F_{9/2} \rightarrow ^6H_J (J=15/2,13/2,11/2)\) transitions of Dy\(^{3+}\) ions in various glass matrices.

<table>
<thead>
<tr>
<th>Glass</th>
<th>(^4F_{9/2} \rightarrow ^6H_{15/2})</th>
<th>(^4F_{9/2} \rightarrow ^6H_{13/2})</th>
<th>(^4F_{9/2} \rightarrow ^6H_{11/2})</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>(A_R)</td>
<td>(\beta_m)</td>
<td>(\sigma_e)</td>
</tr>
<tr>
<td>SFB [Present]</td>
<td>143</td>
<td>0.54</td>
<td>0.02</td>
</tr>
<tr>
<td>LBTAF [12]</td>
<td>161</td>
<td>0.55</td>
<td>0.02</td>
</tr>
<tr>
<td>Lithium Fluoroborate [13]</td>
<td>267</td>
<td>0.30</td>
<td>0.13</td>
</tr>
<tr>
<td>YSGG Laser host[14]</td>
<td>174</td>
<td>0.41</td>
<td>-</td>
</tr>
</tbody>
</table>

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3.3. Measured lifetimes

The luminescence decay profiles of $^4F_{9/2}$ metastable state of Dy$^{3+}$ ion at different concentrations in SFB glass are shown in figure 4. The fluorescence decay curves exhibit single-exponential nature for concentrations of 0.01, 0.1, 0.5, 1.0, 2.0 mol % and non-exponential behavior at concentration of 4.0 mol%. The intensity of decay curve of 4 mol % is analyzed according to the reaction [15]

$$I(t) = A_1 \exp (-t/\tau_1) + A_2 \exp (-t/\tau_2)$$  \hspace{1cm} \text{(1)}

where $A_1$ and $A_2$ are constants and $\tau_1$ and $\tau_2$ are the lifetimes of two channels responsible for the decay. Non-exponential behaviour at higher concentrations of Dy$^{3+}$ ions may be due to the energy transfer between the Dy$^{3+}$ ions. The energy transfer process is also shown in Fig.3. The fluorescence decay curves exhibit single exponential nature in the concentration range of 0.01-2.0 mol% and the lifetimes are determined accordingly. The non-exponential nature of decay curves, observed for higher concentrations (4.0 mol %) of Dy$^{3+}$ ions is fitted to double exponential (Eq.1) and this may be due to energy transfer through cross relaxation:

$$^4F_{9/2} + ^6H_{15/2} \rightarrow ^4F_{5/2} + ^4F_{11/2}$$

The cross relaxation process can be explained as, when an excited Dy$^{3+}$ ion at $^4F_{9/2}$ state relaxes to $^4F_{5/2}$, it excites or transfers its energy to the near by Dy$^{3+}$ ion at the ground $^6H_{15/2}$ state to the higher $^4F_{11/2}$ state. Later both the ions quickly decay non-radiatively to the ground state. The radiative lifetime ($\tau_0$) of excited $^4F_{9/2}$ level of 1.0 mol% Dy$^{3+}$- doped SFB glass calculated from J-O analysis is found to be 1255$\mu$s.

The measured lifetimes from decay curve analysis are 998, 1021, 957, 847, 711, 396 $\mu$s for 0.01, 0.1, 0.5, 1.0, 2.0 and 4.0 mol% concentrations respectively. The difference between experimental and calculated lifetimes of 1.0 mol% Dy$^{3+}$-doped glasses may be due to cross relaxation. The evaluated quantum efficiency of $^4F_{9/2}$ level is 67% for 1.0 mol% Dy$^{3+}$-doped SFB glasses.
4. CONCLUSIONS

The UV-VIS luminescence characteristics of Dy$^{3+}$ ion in SFB glasses have been analyzed. The large stimulated emission cross-section of $15.34 \times 10^{-22}$ cm$^2$ for $^4F_{9/2} \rightarrow ^6H_{13/2}$ transition corresponding to 574 nm supports that the present glass host is a good candidate for laser active material. The decay profiles of the Dy$^{3+}$- doped SFB glasses are found to be single exponential for lower concentrations up to 2.0 mol% suggesting negligible interaction among Dy$^{3+}$ ions and becomes non-exponential at higher concentrations due to energy transfer between Dy$^{3+}$ ions. In the present work, the evaluated radiative parameters $\sigma_r$ and $b_m$ suggest that the 1.0 mol% Dy$^{3+}$ doped glass may be used for two channels emission in the blue (483nm) and yellow (574nm) regions.

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