Chapter-III
Section A

Emission Analysis of Pr$^{3+}$ & Tm$^{3+}$ ions doped B$_2$O$_3$-BaO-LiF/AlF$_3$ optical glasses
3A1 Introduction

The advantage of glasses over their crystalline counterpart includes physical isotropy, absence of grain boundaries and a possibility to continuously vary the compositions suitable to the requirements, as those are being used in a wide variety of applications [1-3]. In view of these advantages, over the past several years, a great deal of work has been carried out in literature by performing detailed analysis on different kinds of optical glasses based on oxides, phosphates, borates, halides and oxy-halides [4-9]. In recent years, an increasing interest has been devoted towards the development of fluoro- borate glasses because of their potential use in the production of infrared optical components and optical fibers. Besides this, borate glasses possess high ionic conductivity, the short range order around the network forming borons, the anomalous dependence of their structure on the molar fraction of oxide modifiers. Moreover borate glasses have been known as good and quite useful host matrices to accommodate in them the rare earth ions of oxides based on their good glass forming nature compared to several other conventional glassy systems [10-12]. These borate glass systems could work as good fluorescent host matrices and the boron oxygen groups dominantly contribute for their potential uses in the optoelectronic and non linear applications [13,14]. In our laboratory, we have recently undertaken to prepare highly transparent borate glasses (B$_2$O$_3$-BaO), and that are added with certain glass network modifiers (NWM) such as LiF and AlF$_3$. Addition of BaO has enhanced transparency, transmission and also mechanical properties of these B$_2$O$_3$-BaO-LiF/AlF$_3$ glassy systems. When rare earth ions are added to these glasses, they create a variety of dopant ion sites with a strong rare earth ion and host interaction, thus resulting in with more intense emission and absorption bands, which could be found to be Stark split [15-19]. Among the rare earth doped glasses, trivalent praseodymium ions (Pr$^{3+}$) have potential uses for laser optical materials development based on its energy level scheme in the UV, visible and near infrared wavelength regions [20,21]. Thulium (Tm$^{3+}$) ion doped glasses have widely been investigated as potential materials for their development as infrared optical systems (1.8 micro meters) blue (450nm) up conversion lasers and also in fiber optical amplifiers for the S band (1460-1530nm) region [22]. In the present thesis work in Section A of Chapter III, the results of the absorption, excitation and emission spectra of Pr$^{3+}$ & Tm$^{3+}$ doped B$_2$O$_3$-BaO-LiF/AlF$_3$ glasses

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and those two host reference glasses have also been analyzed to understand structural and thermal properties from the measurement of their XRD, FTIR and DTA-TG profiles.

3A2 Experimental Studies

Barium oxide (BaO) containing fluoro borate optical glasses with Pr\textsuperscript{3+} & Tm\textsuperscript{3+} ions were prepared by using a conventional melt quenching technique. The raw chemicals used were analytical grade such as H\textsubscript{3}BO\textsubscript{3}, BaCO\textsubscript{3}, LiF, AlF\textsubscript{3} and oxides of rare earths were used. Each batch with 10g of raw chemicals were thoroughly mixed and powdered using an agate mortar and pestle, each batch was melt in porcelain crucibles at 950°C in an tubular furnace for an hour. The chemical melts were quenched in between smooth surfaced brass plates to obtain optical glasses in 2cm diameter having thickness of 0.3cm and with 0.1 mol% Pr\textsuperscript{3+}: glass and with 0.2 mol% Tm\textsuperscript{3+}: glasses have demonstrated encouraging and intense spectral (absorption/emission) features, hence, those concentrations have been found to be optimum concentration to obtain the maximum optical performance from these glasses. For our easy reference those glasses are labeled as BBLi, BBAI, Pr\textsuperscript{3+}: BBLi, Pr\textsuperscript{3+}: BBAI, Tm\textsuperscript{3+}: BBLi and Tm\textsuperscript{3+}: BBAI respectively as has been given in the following table.

Table. 3A1: Compositions of the prepared glasses

<table>
<thead>
<tr>
<th>Glass type</th>
<th>Glass chemical composition</th>
</tr>
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<tbody>
<tr>
<td>BBLi</td>
<td>60B\textsubscript{2}O\textsubscript{3} - 10BaO - 30 LiF</td>
</tr>
<tr>
<td>BBAI</td>
<td>60B\textsubscript{2}O\textsubscript{3} - 10BaO - 30 AlF\textsubscript{3}</td>
</tr>
<tr>
<td>Pr\textsuperscript{3+}: BBLi</td>
<td>0.1 Pr : 59.9B\textsubscript{2}O\textsubscript{3} - 10BaO - 30 LiF</td>
</tr>
<tr>
<td>Pr\textsuperscript{3+}: BBAI</td>
<td>0.1 Pr : 59.9B\textsubscript{2}O\textsubscript{3} - 10BaO - 30 AlF\textsubscript{3}</td>
</tr>
<tr>
<td>Tm\textsuperscript{3+}: BBLi</td>
<td>0.2 Tm : 59.8B\textsubscript{2}O\textsubscript{3} - 10BaO - 30 LiF</td>
</tr>
<tr>
<td>Tm\textsuperscript{3+}: BBAI</td>
<td>0.2 Tm : 59.8B\textsubscript{2}O\textsubscript{3} - 10BaO - 30 AlF\textsubscript{3}</td>
</tr>
</tbody>
</table>

The XRD spectra of reference glasses were recorded on a Shimadzu - XD 3A diffractometer with a Ni-filter and CuK\textalpha{} (1.542Å) radiation with an operating voltage of 30KV and current of 20 mA with a Si detector at the 2θ values at the rate
of two degrees per minute. FTIR spectra of these samples were carried out on a Nicolet IR-200 Spectrophotometer using the KBr pellet technique in the range of 400-4000 cm\(^{-1}\). Thermal behaviors of the reference host glasses were carried out on a TG-DTA analysis (Comptec STA409PC) system from the room temperature up to 1000°C at a heating rate of 10°C/min in an N\(_2\) gas atmosphere. The Vis-NIR absorption spectra of Pr\(^{3+}\) & Tm\(^{3+}\) : fluoro-borate glasses were measured on a Varian-Cary-Win Spectrometer (JASCO V-570). Both excitation and emission spectra of these glass samples were recorded on a SPEX Fluorolog-2 fluorimeter (Model-II) attached with a Xe-arc lamp (150W) with the datamax software in acquiring spectral data. For the prominent emission bands thus measured, their lifetimes were also obtained with a phosphorimeter attachment to the main system with a Xe-flash lamp (25W) and a phosphorimeter attachment to the main system with a computer controller while measuring the decay curves.

3A3 Results and Discussion

![Graph](image_url)

**Fig. 3A.1:** UV-Vis Absorption spectra of BBLi and BBAI reference glasses
Fig. 3A.2: IR Absorption spectra of BBLi and BBAI reference glasses

Fig. 3A.1 shows that Li containing host glass has shown at least 20 nm enhancement in its UV transparency as 380 nm, compared to Al containing glass which filters out UV below 400 nm. Fig. 3A.2 reveals that even transmitting NIR up to 2500 nm, Li-containing glass is found to be better over Al-containing glass.

Fig. 3A.3: XRD spectral profiles of BBLi and BBAI reference glasses
The X-ray diffraction patterns of the BBLi & BBAI reference or host glasses are shown in Fig.3A.3, which confirms the amorphous nature of these glasses.

![X-ray diffraction patterns](image)

**Fig.3A.4:** FTIR spectra of BBLi and BBAI reference glasses

The FTIR spectra of the reference glasses are shown in Fig.3A.4. The structure of borate glasses consists of a random network of BO$_3$ triangles with certain fraction of boroxol (six membered) rings. In the infrared spectral region, the vibration modes of the borate network have three regions [23]. The 1200-1600 cm$^{-1}$ band is the first region, this is due to an asymmetric stretching relaxation of the B-O band of trigonal BO$_3$ units and the second region is located between 800 and 1200 cm$^{-1}$ and is due to the B-O bond stretching of tetrahedral BO$_4$ units and the last band around 700 cm$^{-1}$ is due to the bending of B-O-B linkages in the borate network [24,25]. Thus, the band around 1384 cm$^{-1}$ is due to B-O stretching vibrations of (BO$_3$)$_3^-$ units in metaborate chain and orthoborates. The peak observed at 994 cm$^{-1}$ is attributed to the B-O bond stretching of BO$_4$ units. The absorption band at 704 cm$^{-1}$ indicates the B-O-B bending vibrations. The peak at 574 cm$^{-1}$ could be due to loose BO$_4$ units. In general, the band at 806 cm$^{-1}$ is assigned to the boroxol ring in the borate glass network. In the present study, the peak at 806 cm$^{-1}$ is found to be
missing, which indicates the absence of a boroxol ring in the glass network. The band at 2358 cm\(^{-1}\) is assigned to the stretching vibration of O-H and the band in the region of 3200-3600 cm\(^{-1}\) is ascribed to a hydroxyl (or) water group. The absorption band at 3445 cm\(^{-1}\) is attributed to a symmetric OH stretching mode.

![Fig. 3A.5(a) DTA and TG profiles of BBLi host glass](image)

The thermal behaviors of the two host glasses are shown in Fig.3A.5(a&b). The DTA curve of the BBLi glass shows an endothermic peak at 134.6°C and another at 440°C two and finally a broad exothermic peak at 742°C. The first endothermic peak is related to the loss of OH and the decomposition of hydroxide. The point of slope change of the endothermic peak at higher temperature (440°C) indicates the glass transition temperature (\(T_g\)) as marked in the figure. The exothermic peak at 742°C is attributed to crystallization.
Similarly for BBA1 glass, $T_g$ and crystallization ($T_c$) peaks are detected at 411°C and 716°C respectively. The TG curve shows only a small weight loss about 1% in the complete range of investigation i.e., from 30°C to 1000°C in both the glasses studied.

**Fig.3A.6**: UV-Vis Absorption spectra of Pr$^{3+}$: BBLi & BBA1 glasses
The room temperature optical absorption spectra of BBLi:Pr$^{3+}$ and BBAI:Pr$^{3+}$ glasses in the UV-Vis range (350-650nm) and NIR range (900-2200nm) are shown in Figs.3A.6 & 3A.7 respectively. The absorption bands correspond to the transitions from the ground state $^3H_4$ to the upper states belonging to the 4$^2$ configuration of the Pr$^{3+}$ ions in the glasses and thus the bands are attributed to the transitions $^3H_4 \rightarrow ^1D_2$, $^3P_2$, $^3F_4$, $^3F_3$, $^3F_2$ that are located at 587 nm, 443 nm, 1431 nm, 1513 nm and 1879 nm respectively, with a decreasing order of energy, by following the assignment reports on Pr$^{3+}$ ion in other optical systems [26, 27]. It is clear from the Figs.3A.5 & 3A.6, that the overall appearance of the spectra of Pr$^{3+}$ ion in both the glasses are more similar from each other but the bands relative intensities are changing.
Fig. 3A.8: Excitation spectra of Pr$^{3+}$: BBLi & BBAI glasses

Fig. 3A.8 shows the excitation spectra of Pr$^{3+}$: BBLi & BBAI glasses. Excitation spectra have been monitored with an emission wavelength of $\lambda_{\text{em}} = 602$ nm and the excitation bands are assigned to the electronic transitions of $^3H_4 \rightarrow ^3P_2$ at 445 nm, $^3H_4 \rightarrow ^3P_1$ at 463 nm and $^3H_4 \rightarrow ^3P_0$ at 482 nm. These excitation bands are consistent with the absorption spectra [28].

Fig. 3A.9: Emission spectra of Pr$^{3+}$: BBLi & BBAI glasses

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Prominent excitation band at 445nm has been selected for the measurements of emission spectra of Pr\textsuperscript{3+}: BBLi & BBAl glasses showing a red emission ('\textsuperscript{1}D\textsubscript{2}→\textsuperscript{3}H\textsubscript{4}) at 602 nm as has been shown in Fig.3A.9.

Fig.3A.10: Decay curves of the emission at 602 nm of Pr\textsuperscript{3+}:BBLi & BBAl glasses with $\lambda_{\text{exci}}=445$ nm

Fig.3A.10 presents the decay curves of emission band ('\textsuperscript{1}D\textsubscript{2}→\textsuperscript{3}H\textsubscript{4}) at $\lambda_{\text{exci}}=445$nm and their lifetimes as 0.125ms and 0.092ms of Pr\textsuperscript{3+} glasses. An energy level scheme is given in Fig.3A11 to explain the excitation and emission mechanism of these Pr\textsuperscript{3+} glasses [33-35].

Fig.3A.11: Emission level scheme of Pr\textsuperscript{3+}:BBLi & BBAl glasses
The room temperature absorption spectra of Tm$^{3+}$: BBLi and Tm$^{3+}$: BBAI glasses were recorded in the range 350-900nm (UV-Vis) and 900-2200(NIR), and are shown in Figs.3A.12&13 respectively.

Fig.3A.12: UV-Vis Absorption spectra of Tm$^{3+}$: BBLi & BBAI glasses

Fig.3A.13: IR Absorption spectra of Tm$^{3+}$: BBLi & BBAI glasses
It consists five transitions from the $^3H_6$ ground state to the different higher levels $^1G_4, ^3F_3, ^3H_4, ^3H_5$ and $^2F_4$ at 469 nm, 685 nm, 790 nm, 1206 nm and 1644 nm respectively. Energy levels that are higher than $^1G_4$, are not observed because of the intrinsic band gap absorption in the host glass [29, 30].

Fig. 3A.14: Excitation spectra of Tm$^{3+}$: BBLi & BBAI glasses

Fig.3A.15: Emission spectra of Tm$^{3+}$: BBLi & BBAI glasses
Fig. 3A.16: Decay curves of the emission at 454 nm of Tm$^{3+}$: BBLi & BBAI glasses with $\lambda_{\text{excl}} = 355$ nm

Fig. 3A.17: Emission level scheme of Tm$^{3+}$: BBLi & BBAI glasses
The UV excitation spectrum of Tm$^{3+}$: BBLi & BBAl glasses are shown in Fig.3A.14 with an excitation band at about 355nm, which corresponds to the transition of $^3H_6\rightarrow^1D_2$ of Tm$^{3+}$ ion [31-33]. The emission spectra obtained at $\lambda_{\text{exci}}$ = 355nm are shown in Fig.3A.15. The emission bands of these Tm$^{3+}$ doped glasses were found at 454nm and 480nm, which correspond to the transitions of $^1D_2\rightarrow^3F_4$ and $^1G_4\rightarrow^3H_6$ respectively. Fig 3A.16 presents the decay curves of the emission band ($^1D_2\rightarrow^3F_4$) with an excitation wavelength at 355nm and their lifetimes of Tm$^{3+}$ glasses as 0.035ms and 0.029ms. An energy level scheme is given in Fig.3A17 to explain the excitation and emission mechanism of these Tm$^{3+}$ glasses [33-35].

3A4 Conclusions

It is concluded that due to the addition of LiF and AlF$_3$ into B$_2$O$_3$-BaO glasses, transparent, stable, moisture resistant and an extended UV & NIR wavelengths have been noticed. More particularly Li containing glass has shown its better performance not only in physical properties and but also in optical spectra measurements with more clear profiles compared with Al$^{3+}$ containing glass. We have analyzed absorption, excitation, emission, lifetimes of bright emission bands. Also we have employed XRD, FTIR and tools, to understand their structural and thermal properties. It has been more clear to summarize that red emission from Pr$^{3+}$ glasses and bright blue emission from Tm$^{3+}$ glasses have been noticed under an UV source and also from the emission spectral measurements. These luminescent glasses are suggested to be prominent optical materials.
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Chapter-III
Section B

Emission Analysis of Sm$^{3+}$ & Dy$^{3+}$ ions doped B$_2$O$_3$-BaO-LiF/AlF$_3$ optical glasses
3B.1 Introduction

Over the past several years, a great deal of work has been carried out in the development and characterization of a wide variety of optical glasses [1-5]. In recent years, a special interest has been evinced towards the production of fluoro-borate glasses because of their potential use in the production of infrared optical components. Besides this, borate glasses possess high ionic conductivity, the short range order around the network forming borons and the anomalous dependence of their structure on the molar fraction of oxide modifiers. Moreover, borate glasses with their good glass forming nature have been identified as more useful host matrices to accommodate the required quantity of rare earth ions compared to several other conventional glassy systems [6-8]. Thus, these borate glass systems could work as good fluorescent host matrices and the boron-oxygen groups dominantly contribute for their potential uses in the optoelectronic and non-linear applications. Barium borate glasses (B$_2$O$_3$-BaO) with a couple of network modifiers (NWMs) of LiF and AlF$_3$ have been developed earlier [9]. When rare earth ions are added into these glassy matrices, they are generating different dopant sites, thus causing a strong interaction between the rare earth ions and host matrices and hence such a situation results-in with more intense absorption and emission spectral features, which could sometimes be observed to be Stark splitting [10-12]. In the present section, the luminescence performance in Sm$^{3+}$ or Dy$^{3+}$: B$_2$O$_3$-BaO-LiF/AlF$_3$ optical glasses has been investigated. For the reference glasses to understand their structural and thermal properties measurements of XRD, FTIR and DTA-TG have been carried out and results are presented in Section B of the Chapter III.

3B.2 Experimental Studies

Sm$^{3+}$ or Dy$^{3+}$ ions incorporated four optical glasses were developed following the procedures as was already described in Chapter II of this thesis and also in the earlier section to understand their optical properties

The NIR optical absorption spectra (900nm-2200nm) of Sm$^{3+}$ & Dy$^{3+}$: fluoro-borate glasses were measured on a Varian-Cary-Win Spectrophotometer (JASCO V-570). Both the excitation and emission spectra of these glasses were
recorded on a SPEX Fluorolog-2 Fluorimeter (Model-II) with a Xe-arc lamp (150W) in the wavelength region of 300nm-500nm for excitation and 500nm-750nm for emission spectra respectively. Emission decay curves were obtained with a phosphorimeter attachment to the system fitted with a Xe-flash lamp (50W) in the place of CW source.

3B.3 Results and Discussion

The absorption spectra of Sm$^{3+}$: BBLi and Sm$^{3+}$: BBAI optical glasses are shown in Fig. 3B.1. The observed absorption bands have been assigned to the electronic transitions concerned based on the reports that are available in the literature on both Sm$^{3+}$ and Dy$^{3+}$ ions doped glasses to analyse them appropriately.

![Absorption spectra of Sm$^{3+}$: BBLi and BBAI glasses](image)

Fig. 3B.1: NIR absorption spectra of Sm$^{3+}$: BBLi and BBAI glasses

Generally, ground state absorption transitions with in the Sm$^{3+}$ ions are electric dipole (ED) natured, which could obey a selection rule: $\Delta J \leq 6$ except for the $^6H_{5/2} \rightarrow ^4F_{7/2}$, $^4G_{5/2}$ transitions which are, magnetic dipole (MD) natured, obeying the selection rules: $\Delta J = 0, \pm 1[13-15]$. It has been noticed that both Sm$^{3+}$: BBLi and Sm$^{3+}$: BBAI glasses have revealed eight absorption bands of $^6H_{5/2} \rightarrow ^4F_{11/2}$, $^6F_{9/2}$, $^6F_{7/2}$, $^6F_{5/2}$, $^6F_{3/2}$, $^6H_{15/2}$, $^6F_{1/2}$ and $^6H_{13/2}$ that are located at 947, 1077, 1223, 1370,
The absorption band corresponding to the transition $^6H_{15/2} \rightarrow ^{4}F_{9/2}$ (1263 nm) shows the highest intensity and the remaining transitions appear with appreciable intensity.

**Fig. 3B.2:** (a) Excitation (b) Emission spectra of Sm$^{3+}$: BBLi and BBAl glasses

Fig. 3B.2(a) presents the excitation spectra of Sm$^{3+}$: BBLi and BBAl glasses with seven excitation bands, which are assigned to the electronic transitions of $^6H_{5/2} \rightarrow ^4H_{7/2}$, $^6H_{5/2} \rightarrow ^4K_{13/2}$, $^6H_{5/2} \rightarrow ^4F_{9/2}$, $^6H_{5/2} \rightarrow ^4F_{7/2}$, $^6H_{5/2} \rightarrow ^4F_{5/2}$, $^6H_{5/2} \rightarrow ^4G_{9/2}$, $^6H_{5/2} \rightarrow ^4I_{9/2}$, and $^6H_{5/2} \rightarrow ^4F_{3/2}$ located at 359 nm, 372 nm, 401 nm, 419 nm, 439 nm, 482 nm and 527 nm respectively. Fig. 3B.2(b) shows the emission spectra of 0.1 mol% Sm$^{3+}$: BBLi and Sm$^{3+}$: BBAl glasses with an excitation at $\lambda_{exc} = 401$ nm ($^6H_{5/2} \rightarrow ^4I_{9/2}$). The emission transitions of Sm$^{3+}$ glasses are located at 565 nm ($^4G_{5/2} \rightarrow ^6H_{7/2}$), 601 nm ($^4G_{5/2} \rightarrow ^6H_{9/2}$), 648 nm ($^4G_{5/2} \rightarrow ^6H_{9/2}$) and 710 nm ($^4G_{5/2} \rightarrow ^6H_{7/2}$), respectively. Among the emission transitions, significant orange emission is due to the $^4G_{5/2} \rightarrow ^6H_{7/2}$ transition at 601 nm revealing three components and similarly another band at 565 nm also with three components and these split components are probably due to the Stark splitting energy levels though there is another possibility of transitions from $^4F_{3/2}$ and $^4G_{7/2}$ levels to some of the lower levels which could not be ruled out. The energy of the exciting spectral lines is larger than the excitation energy of these ($^4F_{3/2}$ and $^4G_{7/2}$) levels and they may also be populated by a relaxation process as it happens with the $^4G_{5/2}$ level.
Fig. 3B.3 Decay curves of the emission transition (601 nm) of Sm$^{3+}$: BBLi and BBAl glasses with $\lambda_{\text{exc}} = 401$ nm.

For the Sm$^{3+}$ glasses, Fig. 3B.3 presents the decay curves which are plotted for the prominent emission transition $^4G_{5/2} \rightarrow ^6H_{7/2}$ at 601 nm with an excitation wavelength of 401 nm. The lifetime was found to be 2.568 and 2.564 ms respectively.

Fig. 3B.4 Energy level diagram of Sm$^{3+}$: BBLi and BBAl glasses.
Fig. 3B.4 describes the energy level scheme involved in the emission process. In Fig. 3B.5, absorption spectra of Dy$^{3+}$: BBLi and Dy$^{3+}$: BBAl optical glasses are shown. There are four absorption bands with $^6H_{15/2}$ as the ground state to the upper energy states of $^6F_{7/2}$, $^6H_{7/2}$, $^6F_{9/2}$ and $^6H_{11/2}$ identified at the wavelengths of 895 nm, 1081 nm, 1263 nm and 1665 nm, respectively [16]. In Dy$^{3+}$: BBLi and BBAl glasses, the absorption band at 1263 nm is more intense among the measured absorption bands which is a hypersensitive transition of the $^6H_{15/2} \rightarrow ^6F_{9/2}$, obeying the selection rules [17].

![Absorption spectra of Dy$^{3+}$: BBLi and BBAl glasses](image)

Fig. 3B.5-Absorption spectra of Dy$^{3+}$: BBLi and BBAl glasses

![Excitation and emission spectra of Dy$^{3+}$: BBLi and BBAl glasses](image)

Fig. 3B.6-Excitation and emission spectra of Dy$^{3+}$: BBLi and BBAl glasses
Fig. 3B.6 (a) shows the excitation spectrum of 0.1 mol% Dy\(^{3+}\): BBLi and Dy\(^{3+}\): BBAI glasses with a monitoring strong emission band located at 578 nm. The spectra shown exhibited six excitation peaks which are assigned to the electronic transitions of \(6\text{H}_{15/2} \rightarrow 4\text{i}_{15/2}\) (347 nm), \(6\text{H}_{15/2} \rightarrow 4\text{i}_{11/2}\) (362 nm), \(6\text{H}_{15/2} \rightarrow 4\text{i}_{13/2}\) (387 nm), \(6\text{H}_{15/2} \rightarrow 4\text{G}_{11/2}\) (423 nm), \(6\text{H}_{15/2} \rightarrow 4\text{i}_{15/2}\) (448 nm) and \(6\text{H}_{15/2} \rightarrow 4\text{F}_{9/2}\) (470 nm).

The emission spectra of Dy\(^{3+}\) (0.1 mol%): BBLi and BBAI glasses are also given in Fig. 6(b). The emission spectra shown three emission peaks at 485 nm (blue), 578 nm (yellow) and 667 nm (red) corresponding to the transitions of \(4\text{F}_{9/2} \rightarrow 6\text{H}_{15/2}\), \(4\text{F}_{9/2} \rightarrow 6\text{H}_{13/2}\) and \(4\text{F}_{9/2} \rightarrow 6\text{H}_{11/2}\). Among these transitions, \(4\text{F}_{9/2} \rightarrow 6\text{H}_{13/2}\) (578 nm) is dominating over the other two, while \(4\text{F}_{9/2} \rightarrow 6\text{H}_{11/2}\) has the lower intensity. The \(4\text{F}_{9/2} \rightarrow 6\text{H}_{13/2}\) transition belongs to a hypersensitive transition with \(\Delta J = 2\) which is a forced electric dipole transition being allowed only at low symmetry with no inversion center[18]. Fig. 3B.7 presents the decay curves which are plotted for the prominent emission transition \(4\text{F}_{9/2} \rightarrow 6\text{H}_{13/2}\) with an excitation wavelength of 448 nm and the lifetimes are found to be 0.985 and 0.895 ms respectively.

![Decay curves of the emission transition (578 nm) of Dy\(^{3+}\): BBLi and BBAI glasses with \(\lambda_{\text{excl}} = 448\) nm](image)

Fig. 3B.7- Decay curves of the emission transition (578nm) of Dy\(^{3+}\): BBLi and BBAI glasses with \(\lambda_{\text{excl}} = 448\) nm.
3B.4 Conclusions

Systematic analysis of the structural, thermal and luminescence properties alongside absorption spectra of Sm$^{3+}$ or Dy$^{3+}$ ions containing new glass systems of B$_2$O$_3$-BaO-LiF or AlF$_3$ has been carried out. The results as presented here are of importance and interest in the progress of the identification of newer optical glasses for applications as potential luminescent amorphous materials.
3B.5 References

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Chapter- III
Section-C

Emission Analysis of Eu$^{3+}$, Tb$^{3+}$ & Ho$^{3+}$
ions doped B$_2$O$_3$-BaO-LiF/AlF$_3$
optical glasses
3C1 Introduction

Over the past several years, a great deal of work has been carried out in the development and characterization of a wide variety of optical glasses for different applications [1-9]. In recent years, a special interest has been focused towards the production of fluoro-borate glasses because of their potential applications as luminescent materials [10-12]. It is interesting to mention that these borate glasses having boron-oxygen groups which could be dominantly contributing in luminescence phenomenon thus these glasses have been identified as potential optical materials for their use in optoelectronics. We have earlier carried out a preliminary study in understanding the emission spectra of two rare earth (Pr³⁺ & Tm³⁺) ions doped separately in barium borate (B₂O₃-BaO) glasses with a couple of network modifiers (NWMs) namely LiF & AlF₃ [13]. Now, it is aimed to undertake yet another three rare earth ions such as Eu³⁺, Tb³⁺ and Ho³⁺ ions that are doped individually in the same [13] host glass matrices of B₂O₃-BaO-LiF/AlF₃ to understand their emission performance. Since these ions are known to be prominently visible color luminescent ions (Eu³⁺ for red, Tb³⁺ for green and Ho³⁺ for bluish green) upon their excitation in the UV region, we have undertaken these ions in the present work to study their emission performances.

3C2 Experimental Studies

Glasses Preparation

Two types of reference host glasses (abbreviated as BBLi and BBAl ) without dopant rare earth ions were prepared in the following chemical compositions by means of a conventional melt quenching method:

<table>
<thead>
<tr>
<th>Type</th>
<th>Composition</th>
</tr>
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<tbody>
<tr>
<td>BBLi</td>
<td>60B₂O₃ - 10BaO - 30 LiF</td>
</tr>
<tr>
<td>BBAl</td>
<td>60B₂O₃ - 10BaO - 30 AlF₃</td>
</tr>
</tbody>
</table>

Accordingly, into these two types of host glass matrices, three rare earth ions such as Eu³⁺, Tb³⁺ & Ho³⁺ were incorporated each of them separately, hence the following six luminescent optical glasses were prepared for the present
investigation alongside the above two reference glasses. The following six glasses were labeled appropriately based on the availability of the luminescent rare earth ion and the other host glass chemicals.

<table>
<thead>
<tr>
<th>Ion</th>
<th>Batch Chemicals</th>
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<tbody>
<tr>
<td>Eu³⁺: BBLi</td>
<td>0.1 Eu³⁺: 59.9B₂O₃ - 10BaO - 30 LiF</td>
</tr>
<tr>
<td>Eu³⁺: BBAI</td>
<td>0.1 Eu³⁺: 59.9B₂O₃ - 10BaO - 30 AlF₃</td>
</tr>
<tr>
<td>Tb³⁺: BBLi</td>
<td>0.1 Tb³⁺: 59.9B₂O₃ - 10BaO - 30 LiF</td>
</tr>
<tr>
<td>Tb³⁺: BBAI</td>
<td>0.1 Tb³⁺: 59.9B₂O₃ - 10BaO - 30 AlF₃</td>
</tr>
<tr>
<td>Ho⁶⁺: BBLi</td>
<td>0.1 Ho⁶⁺: 59.9B₂O₃ - 10BaO - 30 LiF</td>
</tr>
<tr>
<td>Ho⁶⁺: BBAI</td>
<td>0.1 Ho⁶⁺: 59.9B₂O₃ - 10BaO - 30 AlF₃</td>
</tr>
</tbody>
</table>

The raw chemicals used were of analytical grade H₂BO₃, BaCO₃, LiF, AlF₃ and the oxides of rare earths studied. Each batch with 10g of raw chemicals was thoroughly mixed and powdered using an agate mortar and pestle. Each of these batch chemicals was melt in a porcelain crucible at 950°C for an hour in a tubular electrical furnace. The chemical melts were quenched in between smooth surfaced brass plates to obtain transparent clear glasses in 2cm diameter having 0.3 cm thickness.

**Measurements**

Both excitation and emission spectra of these glasses were recorded on a SPEX Fluorolog-2 Fluorimeter (Model-II) attached with a Xe-arc lamp (150W) with the Datamax software in acquiring the spectral data. Emission decay curves were measured with a phosphorimeter attachment to the system with a Xe-flash lamp (50W).

**3C3 Results and Discussion**

Fig.3C1 presents both excitation and emission spectra of Eu³⁺: BBLi/BBAI glasses. The excitation spectrum of the sample shows peaks corresponding to the transitions from ground state to different excited states of 4f⁶ configuration of Eu³⁺ ions. The transitions are assigned appropriately to ⁷F₀→⁵F₂ (304nm), ⁷F₀→⁵D₄
(360nm), $^7F_0 \rightarrow ^5G_2$ (381nm), $^7F_0 \rightarrow ^5L_6$ (392nm), $^7F_0 \rightarrow ^5D_3$ (414nm), $^7F_0 \rightarrow ^5D_2$ (463nm), and $^7F_0 \rightarrow ^5D_1$ (531nm) respectively.

Fig.3C1: Excitation and emission spectra of Eu$^{3+}$: BBLi & BBAl glasses

Among all excitation bands, the $^7F_0 \rightarrow ^5L_6$ (392nm) has been a prominent one and with which the emission spectrum has been obtained showing emission transitions at 580nm ($^5D_4 \rightarrow ^7F_0$), 593nm ($^5D_4 \rightarrow ^7F_1$), 655nm ($^5D_4 \rightarrow ^7F_3$) and 704nm ($^5D_4 \rightarrow ^7F_4$). Among those five emission bands, the transition $^5D_0 \rightarrow ^7F_2$ (615nm) has shown a strong red emission which is considered as a hypersensitive transition following the selection rules of $\Delta J=2$. In glassy materials due to the absence of a centre of symmetry a mixing of the 4f orbitals with opposite parity could be taking place and hence an electric dipole transition (ED) would be found more intense [17-18] resulting a bright red emission. The absence of emission from the excited levels of $^5D_{j=1,2,3}$ could be due to the presence of high energy phonons (~1380 cm$^{-1}$) from glasses. Under this condition, when the Eu$^{3+}$ ions are excited to and levels above the $^5D_0$ level, there could be a fast non radiative multiphonon relaxation takes place from those levels to $^5D_0$ level from where the radiative transitions to the ground multiplet. Therefore, $^5D_0 \rightarrow ^7F_1$ emission transitions intensities could be considered to represent the total emission intensity of the Eu$^{3+}$ glass studied as was reported earlier in literature [19].
Fig.3C2: Decay curves of the red emission at 615nm of EU$^{3+}$: BBLi & BBAl glasses ($\lambda_{\text{exc}}$= 392nm)

Fig.3C2 presents the decay curves as well as the lifetime of the prominent emission transition $^5\text{D}_0 \rightarrow ^7\text{F}_2$ emission (615 nm) with an excitation wavelength 392 nm. Fig.3C3 shows excitation and emission spectra of Tb$^{3+}$ :BBLi/BBAl glasses. The excitation spectrum shows a sharp peak at 376 nm due to the transition $^7\text{F}_6 \rightarrow ^5\text{G}_6$ along with a small component at 350nm ($^7\text{F}_6 \rightarrow ^5\text{D}_2$). The prominent excitation band at 376nm has been chosen to measure the emission spectra of Tb$^{3+}$: BBLi/BBAl glasses and has revealed four emission peaks at 491nm, 547nm, 588nm and 624nm which are assigned to transitions $^5\text{D}_4 \rightarrow ^7\text{F}_6$, $^5\text{D}_4 \rightarrow ^7\text{F}_5$, $^5\text{D}_4 \rightarrow ^7\text{F}_4$ and $^5\text{D}_4 \rightarrow ^7\text{F}_3$ respectively [20-21]. The emission transitions are all found to be intense and sharp due to the f-f inner shell transitions, from the excited level to the lower level such as $^5\text{D}_4 \rightarrow ^7\text{F}_3$ ($J=3-6$) for Tb$^{3+}$ arises from the Laporte-forbidden transitions [22]. Here, green emission at 547nm ($^5\text{D}_4 \rightarrow ^7\text{F}_4$) obeys the magnetic dipole transition selection rule of $\Delta J=\pm1$ and found to be more intense.
Fig. 3C3: Excitation and emission spectra of Tb\(^{3+}\): BBLi & BBA1 glasses

Fig. 3C4: Decay curves of the green emission at 547nm of Tb\(^{3+}\): BBLi & BBA1 glasses (\(\lambda_{ex}=376\text{nm}\) )
Fig 3C4 presents the decay curves of the green emission (547nm) for both the glasses studied. Fig 3C5a shows excitation and emission spectra of Ho$^{3+}$:BBLi/BBAI glasses. The excitation spectrum of Ho$^{3+}$ glass reveals an excitation band at 389 nm ($^5$I$_{5}$→$^5$G$_{4}$). In the Fig 3b, a prominent green emission has been observed at 519 nm ($^5$F$_{4}$→$^5$I$_{6}$) with $\lambda_{\text{ex}}$ = 389 nm. Two distinct local maxima are present which reflect the closely spaced $^5$F$_{3}$ and $^5$S$_{2}$ stark manifolds of Ho$^{3+}$ [23].

Fig 6 describes the decay curves of the emission transition $^5$F$_{4}$→$^5$I$_{6}$ along with the lifetime results. It is well known that the lifetime of an emission level is inversely proportional to the probability per unit time that the ion will exit from that excited level. In other words, the population of an excited level decays exponentially with a time constant equal to the lifetime [24-27]. When there are several pathways for the population to decay, the total probability is the sum of the individual probabilities for each pathway. The two main pathways for decay are radiative and nonradiative, and hence the lifetime is given by the network modifying and forming ions, therefore an effective influence is possible only from Li$^+$ in luminescence properties of the rare earth ions in such optical glasses. Where $\tau$ is the total lifetime, $\tau_r$ is the radiative lifetime, and $\tau_{nr}$ is the non-radiative lifetime.

$$\tau^{-1} = \tau_r^{-1} + \tau_{nr}^{-1}$$
Fig. 3C6: Decay curves of the bluish green emission at 519nm of Ho\textsuperscript{3+}: BBLi & BBAl glasses (\(\lambda_{\text{exc}} = 389\text{nm}\))

Table 3C1: Measured lifetimes (\(\tau_m\) in ms) and decay constants (\(k\) in \(10^3\text{s}^{-1}\)) or inverse of the lifetimes (\(\tau_m^{-1}\)) of the intense emissions of RE\textsuperscript{3+} (Eu\textsuperscript{3+}, Tb\textsuperscript{3+} & Ho\textsuperscript{3+}):B\textsubscript{2}O\textsubscript{3}-BaO-LiF/AlF\textsubscript{3} Glasses

<table>
<thead>
<tr>
<th>Emission parameters</th>
<th>Eu\textsuperscript{3+} doped</th>
<th>Tb\textsuperscript{3+} doped</th>
<th>Ho\textsuperscript{3+} doped</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>B\textsubscript{2}O\textsubscript{3}-BaO-LiF/AlF Glasses</td>
<td>B\textsubscript{2}O\textsubscript{3}-BaO-LiF/AlF Glasses</td>
<td>B\textsubscript{2}O\textsubscript{3}-BaO-LiF/AlF Glasses</td>
</tr>
<tr>
<td></td>
<td>Red Emission ((^1\text{D}_0 \rightarrow ^3\text{F}_2))</td>
<td>Green Emission ((^3\text{D}_4 \rightarrow ^3\text{F}_5))</td>
<td>Bluish Green Emission ((^3\text{F}_4 \rightarrow ^3\text{I}_4))</td>
</tr>
<tr>
<td>(\lambda_{\text{emiss}})</td>
<td>with (\lambda_{\text{exc}} = 615\text{nm}) &amp; (\lambda_{\text{exc}} = 547\text{nm}) &amp; (\lambda_{\text{exc}} = 519\text{nm})</td>
<td></td>
<td></td>
</tr>
<tr>
<td>(\text{LiF})</td>
<td>(3.06)</td>
<td>(3.00)</td>
<td>(0.65)</td>
</tr>
<tr>
<td>(\text{AlF}_3)</td>
<td>(2.52)</td>
<td>(2.69)</td>
<td>(0.36)</td>
</tr>
<tr>
<td>(T_m) (m.sec)</td>
<td>(0.326)</td>
<td>(0.333)</td>
<td>(1.538)</td>
</tr>
<tr>
<td>(K = T_m \cdot 10^3\text{s}^{-1})</td>
<td>(0.396)</td>
<td>(0.371)</td>
<td>(2.777)</td>
</tr>
</tbody>
</table>

The radiative lifetime arises from the fluorescence from an excited level to all the levels below it. Non-radiative lifetime depends largely on the glass.
composition and the coupling between the vibrations of the lattice ions and the states of the rare earth ions. Decay curves are observed to be exponential and 1/e lifetimes have been computed. Table 1 gives the results concerning the measured lifetimes ($\tau_m$), and also the inverse of the lifetimes ($\tau^{-1}$) of the intense emissions of the rare earth glasses studied. Results clearly demonstrate the better performance with Li containing glasses with all three rare-earth ions as luminescent ions in the glasses. LiF has particularly been more effective as the glass network modifier in enhancing emission results compared with AlF$_3$ containing glasses. It is due to the monovalent nature of Li$^+$ ions which behave highly mobile over the trivalent Al$^{3+}$ ions in the glass matrices investigated.

3C4 Conclusions

In summary, the barium fluoro-borate glasses containing two different modifiers (LiF, Al$_2$O$_3$) doped with Eu$^{3+}$, Tb$^{3+}$ and Ho$^{3+}$ ions have successfully been prepared and analyzed from their measured luminescence spectra. Also XRD, DTA and FTIR tools have been employed to understand their thermal and structural properties. An intense red emission from Eu$^{3+}$ glasses, bright green emissions from Tb$^{3+}$ glasses and bluish-green emissions from Ho$^{3+}$ glasses have been noticed under an UV source and also from the measured emission profiles. Based on those results it could be suggested that Li containing glasses a more promising and potential luminescent optical systems.
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Chapter-III
Section D

Emission Analysis of Er$^{3+}$ & Nd$^{3+}$ ions doped B$_2$O$_3$-BaO-LiF/AlF$_3$ optical glasses
3D1 Introduction

Borate glasses have been known as good host materials to accommodate them with the rare earth ions easily and encouragingly [1-3]. Besides this, Borate glasses are found to be more suitable optical materials with high transparency and high thermal stability [4]. Earlier, Barium borate glasses (B₂O₃-BaO) added with a couple of network modifiers (NWMs) of LiF & AlF₃ have been developed for which XRD, FTIR and DTA-TG studies have been carriedout. Quite recently, we have investigated the spectral properties of rare earth ions like Pr³⁺, Tm³⁺, Sm³⁺, Dy³⁺, Eu³⁺, Tb³⁺ & Ho³⁺ doped in BBLi glasses [5-7]. Alongside investigations on RE³⁺:BBLi glasses certain transition metal ions such as Cu²⁺,Ni²⁺,Co²⁺,Mn²⁺ & Cr³⁺ doped BBLi glasses have also been studied [8]. The glasses containing LiF have shown more encouraging results compared with the AlF₃ available glasses. Our preliminary investigations have shown all these rare earth doped glasses as potentially visible colour luminescent materials. Since the BBLi glasses are found to be good quality and significantly important optical glasses, in the present short communication, we have made an attempt to study two more rare earth ions (Nd³⁺, Er³⁺) in understanding their both absorption and NIR emission spectral properties.

3D2 Experimental Studies

Glasses Preparation

Transparent, stable and colorless reference glass (BBLi) in the chemical composition of 60B₂O₃-10BaO-30LiF, light violet colored Nd³⁺:BBLi glass (0.1 mol%Nd³⁺:59.9B₂O₃-10BaO-30LiF) and pale pink colored Er³⁺: BBLi glass (0.1 mol%Er³⁺:59.9B₂O₃-10BaO-30LiF) have been developed by employing the quenching method. These three optical glasses are displayed in Fig.1. Each of these chemical batches was in 10g by using high purity (99.9%) laboratory reagent chemicals of H₃BO₃, BaCO₃, LiF, Nd₂O₃ and Er₂O₃. All these weighed chemicals were thoroughly mixed in an agate mortar and a pestle, and each time the mixed chemicals were transferred into a porcelain crucible and were melt in electrical furnace at a temperature of 950° for an hour each time. The chemicals melts were
quenched in between two smooth surfaced brass plates for obtaining transparent and air bubble free clear glasses in circular form with 2 cm in diameter and with a uniform thickness of 0.3cm.

![Image of glasses being quenched](image)

**Fig.1:** Photograph of both the reference and $\text{RE}^{3+} (=\text{Er}^{3+} \text{ or } \text{Nd}^{3+})$: BBLi glasses

**Measurements**

The absorption spectra of $\text{Nd}^{3+}$ & $\text{Er}^{3+}$: BBLi glasses were measured on a Varian-Cary-Win Spectrometer (JASCO V-570). NIR photoluminescence spectra of the $\text{Nd}^{3+}$ & $\text{Er}^{3+}$: BBL glasses were measured on a Horiba Triax-550 grating monochromator (JOBIN YVONHORIBA) equipped with a liquid nitrogen cooled InGaAs photo detector (Electro - Optical- System –Inc) in the wavelength range 800-1700 nm and a lock-in-amplifier (SR 830 DSP, Standard Research Systems) with an Ar$^+$ laser (514.5 nm) (LEXEL MODEL 85 ION LASER, 5Mw-200mW) as the excitation source.

**3D3 Results and Discussion**

The optical absorption spectrum of $\text{Nd}^{3+}$ glass is shown in Fig.2 which exhibits at 428 nm, 440 nm, 457 nm, 470 nm, 508 nm, 522 nm, 579 nm, 621 nm, 672 nm, 741 nm, and 800 nm which correspond to the electronic transitions of $^4I_{9/2} \rightarrow ^2D_{5/2}$, $^4I_{9/2} \rightarrow ^2P_{1/2}$, $^4I_{9/2} \rightarrow ^4G_{11/2}$, $^4I_{9/2} \rightarrow ^4D_{3/2}$, $^4I_{9/2} \rightarrow ^4G_{9/2}$, $^4I_{9/2} \rightarrow ^4G_{7/2}$, $^4I_{9/2} \rightarrow ^2G_{7/2}$, $^4I_{9/2} \rightarrow ^4H_{11/2}$, $^4I_{9/2} \rightarrow ^4F_{9/2}$, $^4I_{9/2} \rightarrow ^4F_{7/2}$ and $^4I_{9/2} \rightarrow ^4F_{5/2}$ respectively as was done earlier for other $\text{Nd}^{3+}$ optical materials in literature[9-12].

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Fig. 3D2: Absorption spectrum of Nd³⁺: BBLi Glass

Fig. 3D3: NIR emission spectrum of Nd³⁺: BBLi Glass

Fig. 3D3 shows the NIR emission spectrum of Nd³⁺: BBLi glass, with three emission bands at 902 nm, 1074 nm and 1344 nm corresponding to the $^4F_{3/2} \rightarrow ^4I_{9/2}$, $^4F_{3/2} \rightarrow ^4I_{11/2}$ and $^4F_{5/2} \rightarrow ^4I_{13/2}$ transitions. Fig. 3D4 shows the absorption spectrum of
Er\textsuperscript{3+}:B\textsubscript{2}O\textsubscript{3}-BaO-LiF glass in Vis-NIR regions and absorption bands are assigned to the electronic transitions, that are observed at 448 nm, 485 nm, 517 nm, 541 nm, 648 nm, 970 nm (1489 nm and 1528 nm) which correspond \( ^4 \text{I}_{15/2} \rightarrow ^4 \text{F}_{5/2}, \) \( ^4 \text{I}_{15/2} \rightarrow ^4 \text{F}_{7/2}, \) \( ^4 \text{I}_{15/2} \rightarrow ^2 \text{H}_{11/2}, \) \( ^4 \text{I}_{15/2} \rightarrow ^4 \text{S}_{3/2}, \) \( ^4 \text{I}_{15/2} \rightarrow ^4 \text{F}_{9/2}, \) \( ^4 \text{I}_{15/2} \rightarrow ^4 \text{I}_{11/2}, \) and \( ^4 \text{I}_{15/2} \rightarrow ^4 \text{I}_{13/2} \) transitions, as was done in literature[13-15]

![Absorption spectra of Er\textsuperscript{3+}: BBLi Glass](image1)

**Fig. 4:** Absorption spectra of Er\textsuperscript{3+}: BBLi Glass

![Emission spectrum of Er\textsuperscript{3+}: BBLi Glass](image2)

**Fig. 3D5** presents emission spectrum of Er\textsuperscript{3+}: BBLi glass with an excitation from Ar\textsuperscript{+} laser (514.5 nm).

![Emission spectrum of Er\textsuperscript{3+}: BBLi Glass](image3)

**Fig. 3D5:** NIR emission spectrum of Er\textsuperscript{3+}: BBLi Glass
Conclusions

Absorption spectra of Nd\textsuperscript{3+}:BBLi and Er\textsuperscript{3+}:BBLi glasses have successfully been analysed. By using an Ar\textsuperscript{+} laser (514.5nm), emission spectra of these two rare earths containing glasses have been measured and their spectra have appropriately been assigned to the electronic transitions. Based on their emission spectral features, such optical glasses could be suggested as potential materials for their use both in the progress of glass lasers and optoelectronics.
3D5 References

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