Spectral and thermal analysis of Sm$^{3+}$ and Dy$^{3+}$: B$_2$O$_3$-BaO-LiF/AlF$_3$ glasses

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Optical and thermal properties of Sm$^{3+}$ and Dy$^{3+}$: B$_2$O$_3$-BaO-LiF/AlF$_3$ glasses have been studied. These optical materials have been characterized from the measurement of their XRD, FTIR, absorption, excitation, emission spectra and DTA-TG profiles. From the recorded photoluminescence spectra of samarium (Sm$^{3+}$) glasses, four emission transitions; $^6$G$_{5/2} \rightarrow ^4$H$_{5/2}$ (565 nm), $^6$G$_{5/2} \rightarrow ^4$H$_{7/2}$ (601 nm), $^6$G$_{5/2} \rightarrow ^4$H$_{9/2}$ (648 nm) and $^6$G$_{5/2} \rightarrow ^4$H$_{11/2}$ (710 nm) with $\lambda_{exc} = 401$ nm ($^4$F$_{9/2}$ $\rightarrow ^4$F$_{7/2}$) have been observed. In the case of dysprosium (Dy$^{3+}$) glasses, three emission transitions; $^4$F$_{9/2}$ $\rightarrow ^4$H$_{15/2}$ (485 nm), $^4$F$_{9/2}$ $\rightarrow ^4$H$_{13/2}$ (578 nm) and $^4$F$_{9/2}$ $\rightarrow ^4$H$_{11/2}$ (667 nm) with $\lambda_{exc} = 448$ nm ($^4$H$_{11/2}$ $\rightarrow ^4$I$_{15/2}$) have been observed. For the prominent emissions only, the decay curves have been recorded in order to evaluate their lifetimes. The materials nature, structural trends and thermal properties have also been analyzed through the measurement of their XRD, FTIR and TG-DTA profiles.

Keywords: RE$^{3+}$ glasses, Spectral analysis, Thermal analysis

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 paper, the luminescence performance in Sm$^{3+}$ or Dy$^{3+}$: B$_2$O$_3$-BaO-LiF/AlF$_3$ optical glasses has been investigated.

2 Experimental Details

Two reference (host) glasses that are labeled as BBLi and BBAl are without dopant ions. Also, Sm$^{3+}$ or Dy$^{3+}$ ions incorporated four optical glasses were developed for their characterization (Table 1). Each of these chemical batches in 10g each was prepared by using high purity laboratory reagent chemicals of H$_2$BO$_3$, BaCO$_3$, LiF, AlF$_3$, Sm$_2$O$_3$ and Dy$_2$O$_3$ in good purity. All these weighed chemicals were thoroughly mixed by using an agate mortar and a pestle, and each time the mixed chemical powder was transferred into a porcelain crucible and melted in an electrical furnace at a temperature of 950° for about an hour. The melts were quenched in between smooth surfaced brass plates for obtaining transparent and clear glasses in circular form with 2 cm diameter and an uniform thickness of 0.3cm for each of these glasses.

The XRD profiles were recorded on a Shimadzu XD 3A Diffractmeter with a Ni-filter and CuK$\alpha$ (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 were recorded using a Nicolet IR-200 Spectrophotometer with KBr pellet in the range 4000 to 400 cm⁻¹. The thermal decomposition behaviours of the glasses were studied on a TG-DTA analysis (Comptec STA409PC) system up to 1000°C at a heating rate of 10°C/min in an N₂ gas atmosphere. The absorption spectra of Sm³⁺ and Dy³⁺: fluoro-borate glasses were measured on a Varian-Cary-Win Spectrometer (JASCO V-570). Both excitation and emission spectra of these glasses were recorded on a SPEX Fluorolog-2 Fluorimeter (Model-II) attached with a Xe-arc lamp (150 W) 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 (50 W).

3 Results and Discussion

Fig. 1 shows the XRD profiles of host glasses (BBLi and BBAl) confirming their amorphous nature. The FTIR spectra of the host glasses are shown in Fig. 2. The structure of vitreous borate consists of a random network of BO₃ triangles with certain fraction of boroxol (six membered) rings but with the inclusion of the network modifiers, formation of BO₄ tetrahedra takes place in the borate glass network. In the infrared spectral region, the vibrational modes of borate networks show three regions. In the first region, 1200-1600 cm⁻¹ band is due to an asymmetric stretching relaxation of the B-O bond of trigonal BO₃ units, the band in the second region is located between 800 and 1200 cm⁻¹ and is due to the B-O bond stretching of tetrahedral BO₄ units and in third region a band at 700 cm⁻¹ is due to the bending of B-O-B linkages in the borate network. Thus, BBLi and BBAl containing host glasses without the dopant rare earth ions have demonstrated the presence of three principle bands located at 1384, 994 and 704 cm⁻¹ along with a small band at 574 cm⁻¹. The band around 1384 cm⁻¹ is arising from B-O stretching vibrations of (BO₃)³⁻ units in metaborate chain and orthoborates. The peak observed at 994 cm⁻¹ is attributed to the B-O bond stretching of BO₄ units. The absorption band at 704 cm⁻¹ indicates the B-O-B

Table 1 — Compositions of the prepared glasses

<table>
<thead>
<tr>
<th>Glasses labelling</th>
<th>Glasses chemical compositions (mol %)</th>
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<tbody>
<tr>
<td>BBLi</td>
<td>60B₂O₃ - 10BaO - 30LiF</td>
</tr>
<tr>
<td>BBAl</td>
<td>60B₂O₃ - 10BaO - 30AlF₃</td>
</tr>
<tr>
<td>SmBBLi</td>
<td>0.1Sm₂O₃ - 59.9B₂O₃ - 10BaO - 30LiF</td>
</tr>
<tr>
<td>SmBBAl</td>
<td>0.1Sm₂O₃ - 59.9B₂O₃ - 10BaO - 30AlF₃</td>
</tr>
<tr>
<td>DyBBLi</td>
<td>0.1Dy₂O₃ - 59.9B₂O₃ - 10BaO - 30LiF</td>
</tr>
<tr>
<td>DyBBAl</td>
<td>0.1Dy₂O₃ - 59.9B₂O₃ - 10BaO - 30AlF₃</td>
</tr>
</tbody>
</table>

Fig. 1 — XRD profiles of BBLi and BBAl host glasses
bending vibrations. The peak at 574 cm\(^{-1}\) could be due to loose BO\(_4\) units. From Fig. 2, it is evidenced that, there exists a distinctive difference in the relative intensities of the peaks due to B-O bonds of BO\(_3\) and BO\(_4\) functional units in BBLi and BBAl glasses. The ratio of the intensities of two bands \([I(BO_4)/I(BO_3)]\) could be found varying with the type of modifier (Li or Al) ion present in the glass system. The values thus evaluated are found to be 0.81 and 0.95 for BBLi and BBAl glasses respectively, indicating that the relative fraction of BO\(_4\) units could be more in the barium borate glass with Li\(^+\) ions than in the glass with Al\(^{3+}\) ions. 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.

The thermal behaviours of the two host glasses are shown in Fig. 3. The DTA curve of the BBLi glass shows an endothermic peak at 134.6\(^\circ\)C and two exothermic peaks at 223 and 440\(^\circ\)C and finally a broad exothermic peak at 742\(^\circ\)C. The first
endothermic peak is related to the loss of OH and the decomposition of hydroxide. The exothermic peaks are attributed to oxide crystallization. The TG curve shows only a small weight loss of 1% in the complete range of investigation i.e., from 30 to 1000°C in both the glasses studied.

The absorption spectra of Sm³⁺: BBLi and Sm³⁺: BBAl optical glasses are shown in Fig. 4. The observed absorption bands correspond to the transitions from the ground state of Sm³⁺ namely ⁶H₅/₂ to the various upper energy states of the rare earth ion investigated. Generally, ground state absorption transitions with in the Sm³⁺ ions are electric dipole (ED) natured, which could obey a selection rule: ΔJ ≤ 6 except for the ⁹H₄/₂ → ⁴F₇/₂, ⁴G₉/₂ transitions which are, magnetic dipole (MD) natured, obeying the selection rules: ΔJ = 0,±1⁴⁻¹⁸. It has been noticed that both Sm³⁺: BBLi and Sm³⁺: BBAL glasses have revealed eight absorption bands of ⁶H₅/₂ → ⁶F₁₁/₂, ⁶F₉/₂, ⁶F₇/₂, ⁶F₅/₂, ⁶F₃/₂, ⁶H₁₅/₂, ⁶F₁/₂ and ⁶H₁₃/₂ that are located at 947, 1077, 1223, 1370, 1470, 1521, 1585 and 1780 nm respectively. The absorption band corresponding to the transition ⁶H₁₅/₂ → ⁴F₉/₂ (1263 nm) shows the highest intensity and the remaining transitions appear with appreciable intensity. Fig. 5(a) presents the excitation spectra of Sm³⁺: BBLi and BBAl glasses with seven excitation bands, which are, ⁶H₅/₂ → ⁴H₇/₂, ⁶H₅/₂ → ⁴K₃/₂, ⁶H₅/₂ → ⁴F₇/₂, ⁶H₅/₂ → ⁴P₅/₂, ⁶H₅/₂ → ⁴G₉/₂, ⁶H₅/₂ → ⁴I₉/₂, and ⁶H₅/₂ → ⁴F₃/₂ transitions at 359, 372, 401, 419, 439, 482 and 527 nm respectively. Fig. 5(b) shows the emission spectra of 0.1 mol% Sm³⁺: BBLi and Sm³⁺: BBAl glasses with an excitation wavelength of λₑˣᶜᵣᵣ = 401 nm (⁶H₅/₂ → ⁴F₇/₂). The emission transitions of Sm³⁺ glasses are located at 565 nm (⁴G₅/₂ → ⁶H₅/₂), 601 nm (⁴G₅/₂ → ⁶H₇/₂), 648 nm (⁴G₅/₂ → ⁶H₉/₂) and 710 nm (⁴G₅/₂ → ⁶H₁₁/₂), respectively. Among the emission transitions, significant orange emission is due to the ⁴G₅/₂ → ⁶H₇/₂ 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 ⁴F₃/₂ and ⁴G₇/₂ 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 (⁴F₃/₂ and ⁴G₇/₂) levels and they may also be populated by a relaxation process as it happens with the ⁴G₅/₂ level. For the Sm³⁺ glasses, Fig. 6 presents the decay curves which are plotted for the prominent emission transition ⁴G₅/₂ → ⁶H₇/₂ at 601 nm with an excitation wavelength of 401 nm. The lifetime was found to be 2.568 and 2.564 ms respectively. Fig. 7 describes the energy level scheme involved in the emission process.
Fig. 5 — (a) Excitation (b) Emission spectra of Sm$^{3+}$: BBLi and BBAl glasses

Fig. 6 — Decay curves of the emission transition (601 nm) of Sm$^{3+}$: BBLi and BBAl glasses with $\lambda_{exci} = 401$ nm
Fig. 7 — Energy level diagram of Sm$^{3+}$: BBLi and BBAl glasses

Fig. 8 — Absorption spectra of Dy$^{3+}$: BBLi and BBAl glasses
Fig. 8, absorption spectra of Dy$^{3+}$: BBLi and Dy$^{3+}$: BBAl optical glasses are shown. There are four absorption bands with $^6\text{H}_{15/2}$ as the ground state to the upper energy states of $^6\text{F}_{7/2}$, $^6\text{H}_{7/2}$, $^6\text{F}_{9/2}$ and $^6\text{H}_{11/2}$ identified at the wavelengths of 895, 1081, 1263 and 1665 nm, respectively. 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 $^6\text{H}_{15/2} \rightarrow ^6\text{F}_{9/2}$, obeying the selection rules. Fig. 9(a) shows the excitation spectrum of 0.1 mol% Dy$^{3+}$: BBLi and Dy$^{3+}$: BBAl glasses with a monitoring strong emission band located at 578 nm. The spectra shown exhibited

Fig. 9 — (a) Excitation and (b) emission spectra of Dy$^{3+}$: BBLi and BBAl glasses

Fig. 10 — Decay curves of the emission transition (578 nm) of Dy$^{3+}$: BBLi and BBAl glasses with $\lambda_{\text{exci}} = 448$ nm

Fig. 11 — Energy level diagram of Dy$^{3+}$: BBLi and BBAl glasses
six excitation peaks which are assigned to the electronic transitions of $^6H_{15/2} \rightarrow ^4I_{15/2}$ (347 nm), $^6H_{15/2} \rightarrow ^4I_{11/2}$ (362 nm), $^6H_{15/2} \rightarrow ^4I_{13/2}$ (387 nm), $^6H_{15/2} \rightarrow ^4G_{11/2}$ (423 nm), $^6H_{15/2} \rightarrow ^4I_{15/2}$ (448 nm) and $^6H_{15/2} \rightarrow ^4F_{9/2}$ (470 nm). The emission spectra of Dy$^{3+}$ (0.1 mol%): BBLi and BBAl glasses are also given in Fig. 9(b). The emission spectra shown three emission peaks at 485 nm (blue), 578 nm (yellow) and 667 nm (red) corresponding to the transitions of $^4F_{9/2} \rightarrow ^6H_{15/2}$, $^4F_{9/2} \rightarrow ^6H_{13/2}$ and $^4F_{9/2} \rightarrow ^6H_{11/2}$. Among these transitions, $^4F_{9/2} \rightarrow ^6H_{13/2}$ (578 nm) is dominating over the other two, while $^4F_{9/2} \rightarrow ^6H_{11/2}$ has the lower intensity. The $^4F_{9/2} \rightarrow ^6H_{13/2}$ 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\(^2\). Fig. 10 presents the decay curves which are plotted for the prominent emission transition $^4F_{9/2} \rightarrow ^6H_{13/2}$ with an excitation wavelength of 448 nm and the lifetimes are found to be 0.985 and 0.895 ms respectively. Fig. 11 describes the energy level scheme involved in the emission process.

4 Conclusions

A 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.

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