Luminescence Analysis of Eu$^{3+}$ and Tb$^{3+}$ ions doped Borate Zinc Magnesium Glasses

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Abstract: This paper reports on the spectral and optical analysis of Eu$^{3+}$ or Tb$^{3+}$ ions (0.2 mol%) doped Borate Zinc Magnesium (BZM) glasses from the measurement of their absorption, excitation and emission properties. The measured emission spectrum of Eu$^{3+}$:BZM glass has revealed five transitions ($^5D_0 \rightarrow ^7F_n$) at 579, 591, 613, 652, and 701 nm, respectively with $\lambda_{max} = 393$ nm ($^5D_1 \rightarrow ^5L_6$). In the case of Tb$^{3+}$:BZM glass, six emission transitions such as ($^5D_1 \rightarrow ^7F_4, ^7F_{5,6,7}$, and $^7F_3$) that are located at 414, 439, 488, 543, 585, and 621 nm respectively, have been measured with $\lambda_{max} = 377$ nm ($^5D_4 \rightarrow ^7F_{6,7}$). Energy level schemes relating to the emission mechanisms involved both in Eu$^{3+}$ and Tb$^{3+}$ glasses have been explained and also decay curves have been plotted in order to evaluate emission band lifetimes.

Keywords: Eu$^{3+}$ and Tb$^{3+}$ glasses, Optical properties

1. Introduction

Rare-earth ions doped glasses are important materials for bulk lasers, optical fibers, waveguide lasers and optical amplifiers [1]–[4]. Trivalent rare-earth ions Eu$^{3+}$ and Tb$^{3+}$ doped phosphate, silicate, germanate and telluride glasses have been developed for infrared active optical devices [5]–[9]. Recently, research focus on rare-earth doped glasses is limited to infrared optical devices, and there is a growing interest in visible optical devices [10]–[14]. With the increasing demand of various visible lasers and light sources, further investigations in other rare-earth ions, such as Dy$^{3+}$, Tb$^{3+}$, Sm$^{3+}$ and Eu$^{3+}$ ions, are becoming more significant [15]–[20].

Oxide glasses are attracting hosts for obtaining efficient luminescence in rare-earth ions. In them, borate based glasses are the most suitable ones for RE ion doping due to their high transparency, low melting point, high thermal stability and good RE ion solubility, easy preparation on large scale, shaping and cost effective properties [19], [20]. However, it is difficult to release efficient infrared to visible upconversion emission in borate based glasses due to high vibrational energy. On the other hand, the high vibrational energy in borate glass is not detrimental to the emission of Eu$^{3+}$ and Tb$^{3+}$ ions under normal 4f transitions and sometimes it can accelerate the relaxation process, which is necessary and beneficial for visible emissions [21].

Towards the development of luminescent glassy materials with certain transition or rare earth ions from literature it has been made quite clear that B$_2$O$_3$ could be used as a good network-former (NWF) and two other chemicals such as ZnO and MgO could be found as network-modifiers (NWM) when those are added to the B$_2$O$_3$ content. It has also been noticed that the presence of ZnO content in the glassy matrices, stability of the material becomes stronger, with a high thermal resistance against the crystallization [22].

Over the past several years, a great deal of work has been carried out to understand the spectral properties of different optical materials. We have recently studied the spectral properties of rare earth ions such as Sm$^{3+}$ and Dy$^{3+}$ in the B$_2$O$_3$-ZnO-MgO glasses and also reported structural properties of host glass [23]. In the present work, our main objective is to investigate the spectral properties of a couple of rare earth ions such as Eu$^{3+}$ and Tb$^{3+}$ ions in BZM glasses. Rare-earth ions (RE$^{3+}$) would generally be existing in the trivalent state, of which 4f configuration could be found relatively isolated and the next excited 4f configuration lies in the high energy level above the ground state of 4f configuration [24] and hence the electronic configuration causes the display of more sharp absorption or emission bands because of the intra f-f transitions. Among the various RE ions, it is well known that the Eu$^{3+}$ ion has an excited level $^5D_0$ to exhibit intense and sharp emission transitions with $^7F_0$ as the ground state and also this ion shows bright red colour emission having the transition $^5D_0 \rightarrow ^7F_2$. The Eu$^{3+}$ -doped glasses are attracting a great deal of interest because persistent spectral hole burning can be performed in the $^7F_0 \rightarrow ^5D_0$ transition of Eu$^{3+}$ at room temperature and also these have potential use in high-density optical storage. Another important one is Tb$^{3+}$ ion, which can show more intense transition with $^7F_{6,7}$ as the ground state and this ion emits more intense green colour emission ($^5D_4 \rightarrow ^7F_0$) and hence these have been used in the development of efficient green emitting phosphors and scintillating materials. Thus the rare earth ions such as Eu$^{3+}$ and Tb$^{3+}$ ions give strong luminescence in a variety of host lattices and hence it is interesting to study the photoluminescence properties of these ions doped Borate Zinc Magnesium glasses.

2. Experimental Studies

2.1 Glasses Preparation

Following are the Eu$^{3+}$ or Tb$^{3+}$ ions (0.2 mol%) doped Borate Zinc Magnesium (BZM) glasses along with a reference glass (RG):
The optical absorption spectra of Rare earth ions doped glasses were measured by using SPEX Fluorolog-2 Fluorimeter (JASCO V-570). Both the excitation and emission spectra have been measured in 10 g batch each separately, thoroughly mixed and finely powdered using agate mortar and pestle. Then each batch of chemical mix was transferred into porcelain crucible and melted in an electric furnace for an hour at 980 °C separately. Those melts were quenched in between two smooth surfaced brass plates to obtain circular glass discs of 2-3 cm in diameter with 0.3 cm in thickness. The host (Reference) BZM glass was transparent and colourless, under an UV source Eu³⁺-doped glass did exhibit red emission and Tb³⁺-doped glass green emissions respectively. Fig. 1 displays the glasses developed in the present work.

2.2 Characterizations

The optical absorption spectra of Rare earth ions doped glasses were measured on a Varian-Cary Win spectrometer (JASCO V-570). Both the excitation and emission spectra have been measured by using SPEX Fluorolog-2 Fluorimeter (Model-II) with Datamax software to acquire the data with Xe-flash lamp (150W) as the excitation source. A Xe-flash lamp with a phosphorimeter attachment was used to measure the lifetimes of the emission transitions of Eu³⁺ and Tb³⁺ glasses.

3. Results and Discussion

3.1 Eu³⁺: BZM glass

The Vis and NIR optical absorption spectrum of 0.2 mol% Eu³⁺ doped BZM glass is shown in Fig. 2, with five absorption bands such as 1F₀ → 1L₀ (394 nm), 1F₀ → 1D₁ (526 nm), 1F₀ → 1F₆ (2094 nm) and 1F₁ → 1F₆ (2205 nm) respectively [25]. The 1F₁ ↔ 1D₂ absorption and emission bands are spin forbidden and hence they are very weak [26]. The close examination of band positions (1F₀ → 1F₆, 1F₁ → 1F₆) reveals that the energy gap between 1F₀ and 1F₁ levels is ~240 cm⁻¹ which is comparable to other Eu³⁺ doped glasses.

3.2 Tb³⁺: BZM glass

The excitation spectrum of the 0.2 mol % Eu³⁺:BZM glass, monitoring emission at 613 nm, which corresponds to the 1D₀ → 1F₂ transition. From this spectrum, six excitation bands which could be assigned to the electronic transitions of 1F₀ → 1D₁ at 360 nm, 1F₀ → 1L₂ at 380 nm, 1F₀ → 1L₆ at 393 nm, 1F₀ → 1D₁ at 413 nm, 1F₀ → 1D₂ at 463 nm and 1F₀ → 1D₃ at 532 nm are identified. Among these, the prominent excitation band 1F₀ → 1L₆ at 393 nm has been chosen to measure the emission spectrum of Eu³⁺: BZM glass.

Fig. 4 shows the emission spectrum of Eu³⁺:BZM glass, monitoring emission at 613 nm, which corresponds to the 1D₀ → 1F₂ transition. The intense emission bands in the range 570-725 nm caused by the 1D₀ → 1F₁ transition. In particular, only the intense emission band 1D₀ → 1F₂ (701 nm) was reported previously in literature [24]. In Eu³⁺, due to the shielding effect of 4f⁶ electrons by 5s and 5p electrons in the outer shells, sharp and narrow emission peaks could thus be observed. Due to high non-radiative relaxation from excited states of energy higher than 1D₀ state, the intense emission bands in the range 570-725 nm caused by the 1D₀ → 1F₁ (591 nm), 1D₀ → 1F₂ (613 nm), 1D₀ → 1F₃ (652 nm) and 1D₀ → 1F₄ (701 nm) transitions are electric dipole (ED) transitions.
transition that follows the selection rule of $\Delta J = 2$ and shows a bright emission from Eu$^{3+}$-doped glasses. Another transition $^3\text{D}_0 \rightarrow ^7\text{F}_1$ with $\Delta J = 1$ has been identified as magnetic dipole (MD) transition [27] and it is chosen as the reference one, because it is less affected by the changes in the local environment of Eu$^{3+}$ ions and can be used for the estimation of transition probabilities. The absence of emissions starting from the excited levels of $^5\text{D}_{J(=1,2,3)}$ is due to the high energy phonons found the glasses, i.e. when the Eu$^{3+}$ ions are excited to any level above the $^3\text{D}_0$, there is a fast non-radiative multiphonon relaxation to this level [28].

Thus the emissions from $^3\text{D}_J \rightarrow ^7\text{F}_J$ to $^7\text{F}_J$ are several orders less than that of $^3\text{D}_0 \rightarrow ^7\text{F}_2$. The luminescence intensity ratio (R) between electric($^3\text{D}_0 \rightarrow ^7\text{F}_2$) and magnetic($^3\text{D}_0 \rightarrow ^7\text{F}_1$) dipole transitions provide valuable information about the red color ($^3\text{D}_0 \rightarrow ^7\text{F}_2$) richness in comparison with orange ($^3\text{D}_0 \rightarrow ^7\text{F}_1$) color in developing red laser sources. The intensity ratio R is a measure of the strength of covalent/ionic bonding between Eu$^{3+}$ and surrounding ligands and informs about local symmetry around europium ions. The higher the value of R, lower the symmetry around the Eu$^{3+}$ ions and the higher the Eu-O covalence and vice versa [29]. Generally, it is known that the luminescence intensity ratio value is < 1.0 for symmetric and > 1.0 for non-centrosymmetric surroundings. For the Eu$^{3+}$: BZM glass the R value is found to be 1.98, which indicates that the Eu$^{3+}$ ions are located in an asymmetric environment. The emission mechanism (Energy level diagram) of Eu$^{3+}$ ions in the BZM glass is represented in Fig. 5.

Fig. 6 presents the decay curve of the Eu$^{3+}$: BZM glass, which is plotted for the prominent emission transition $^3\text{D}_0 \rightarrow ^7\text{F}_2$ at 613 nm with an excitation wavelength of 393 nm. The decay curve exhibited an exponential nature and its lifetime has found to be 1.81 ms

### 3.2 Tb$^{3+}$: BZM glass

The room temperature optical absorption spectrum of 0.2 mol% Tb$^{3+}$-doped BZM glass recorded in the range 450-2300 nm is shown in Fig. 7. The absorption spectrum contains four bands at 485 nm, 1886 nm, 1934 nm and 2207 nm corresponding to $^7\text{F}_6 \rightarrow ^5\text{D}_4$, $^7\text{F}_4$, $^7\text{F}_2$ and $^7\text{F}_1$ transitions respectively. The location and assignment of the band positions has been done according to Carnall et al. [30]. All these transitions are due to electric dipole interaction following the selection rules, $\Delta S = 0$, $|\Delta L| \leq 6$ and $|\Delta J| \leq 6$ [31]. Among these observed transitions, $^7\text{F}_6 \rightarrow ^7\text{D}_4$ transition is very weak and located in the visible region and the rest of the transitions $^7\text{F}_6 \rightarrow ^7\text{F}_J$ ($J = 1, 2, 3$) are intense and located in the near infra-red region. From the absorption spectrum, it is
noticed that the absorption transitions corresponding to $^{7}F_{6} \rightarrow ^{7}F_{1}$ and $^{7}F_{6} \rightarrow ^{7}F_{1}$ are overlapped.

**Figure 7:** Absorption spectrum of (0.2 mol %) Tb$^{3+}$: BZM glass

Fig. 8 presents the excitation spectrum of 0.2 mol% Tb$^{3+}$-doped BZM glass, monitoring emission at 543 nm. The observed excitation bands are due to the 4f→4f transitions of Tb$^{3+}$ ions [32]. In the 300–525 nm wavelength range, several excitation bands are identified which are assigned to the electronic transitions of $^{7}F_{6} \rightarrow (^{5}H_{7}, ^{5}D_{0,1})$ at 317 nm, $^{7}F_{6} \rightarrow (^{5}G_{5}, ^{5}L_{4})$ at 339 nm, $^{7}F_{6} \rightarrow (^{5}L_{9}, ^{5}G_{4})$ at 352 nm, $^{7}F_{6} \rightarrow (^{5}D_{10})$ at 369 nm, $^{7}F_{6} \rightarrow (^{5}G_{6}, ^{5}D_{3})$ at 377 nm and $^{7}F_{6} \rightarrow ^{5}D_{4}$ at 484 nm respectively [33]-[36]. Only the prominent excitation peak at 377 nm ($^{7}F_{6} \rightarrow ^{5}G_{6}$) has been chosen to measure the emission spectrum of Tb$^{3+}$: BZM glass.

**Figure 8:** Excitation spectrum of (0.2 mol %) Tb$^{3+}$: BZM glass

Fig. 9 shows the emission spectrum recorded for Tb$^{3+}$:BZM glass fixing the excitation wavelength at 377 nm. Normally, Tb$^{3+}$ ions doped materials exhibit strong luminescence bands in blue ($^{5}D_{3} \rightarrow ^{7}F_{4}$) and green ($^{5}D_{4} \rightarrow ^{7}F_{5}$) spectral regions. In Tb$^{3+}$ ions doped glass hosts, the emission below 480 nm originate from $^{5}D_{3}$ level and the emission above 480 nm originate from $^{5}D_{4}$ levels. The emission bands centered at 414nm and 439m are assigned to $^{5}D_{3} \rightarrow ^{7}F_{3}$ and $^{5}D_{3} \rightarrow ^{7}F_{4}$ transitions, while the other bands peaked at 488, 543, 585 and 621 nm are attributed to the $^{5}D_{4} \rightarrow ^{7}F_{J}$ (J= 6, 5, 4 and 3) transitions respectively [37]-[39]. The weak blue emission at 488 nm corresponding to the transition $^{5}D_{4} \rightarrow ^{7}F_{6}$ obeys the magnetic dipole transition selection rule of $\Delta J = \pm 1$ [40], [41]. Laporte-forbidden transition $^{5}D_{4} \rightarrow ^{7}F_{5}$ observed at 543 nm gives very intense green emission [37].

**Figure 9:** Emission spectrum of (0.2 mol %) Tb$^{3+}$: BZM glass

Fig. 10 describes the energy level scheme for the emission process with the 377 nm excitation wavelength. Fig. 11 presents the decay curve, which is plotted for the prominent emission transition $^{5}D_{4} \rightarrow ^{7}F_{5}$ at 543 nm with an excitation wavelength 377nm. The decay curve exhibited a single exponential in nature and its life time has found to be 2.23 ms.

**Figure 10:** Energy level scheme of all the observed excitation and emission transitions of Tb$^{3+}$: BZM glass
4. Conclusion

In summary, it could be concluded that highly transparent, moisture resistant and stable 0.2 mol% of Eu$^{3+}$ or Tb$^{3+}$ ions doped Borate Zinc Magnesium glasses have been developed. Optical analysis of these glasses has been carried out based on the measurements of absorption, excitation and emission spectra. Apart from analyzing the optical properties of these glasses, we have watched a bright red (Eu$^{3+}$; BZM glasses) and a green (Tb$^{3+}$; BZM glasses) emissions from these glasses when those are placed under an UV source. We have plotted the decay curves of the bright emission bands of Eu$^{3+}$ or Tb$^{3+}$; BZM glasses. It could be suggested that these BZM glasses are highly potential enough towards the display of red (Eu$^{3+}$) and green (Tb$^{3+}$) luminescent colors. Such primary (red, green) colors emitting materials are of significant importance in the development of emission rich optical systems.

References


