Chapter-IV

Emission Analysis of $\text{Cu}^{2+}$, $\text{Ni}^{2+}$, $\text{Co}^{2+}$, $\text{Mn}^{2+}$ & $\text{Cr}^{3+}$ ions doped $\text{B}_2\text{O}_3$-$\text{BaO}$-$\text{LiF}$ optical glasses
4.1 Introduction

We are aware of the fact that in comparison with the crystalline materials, glassy materials have several advantages and those could find a wide variety of applications in optoelectronic and other related optical materials development [1-9]. B2O3 has been a well known glass forming chemical and in recent years, an increasing interest has been shown towards the development of fluoro-borate glasses because of their potential use in the production of infrared optical components and optical fibres. 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 quite useful host matrices to accommodate them with the rare earth ions compared to several other conventional glassy systems [10–12]. These borate glass systems could be found as good host matrices and the boron oxygen groups dominantly contribute to their potential uses in certain optoelectronic and non linear applications [13, 14].

We have recently undertaken to prepare highly transparent borate glasses (B2O3-BaO), and that are added with certain glass network modifiers (NWM) such as and LiF and AlF3. Addition of BaO, it has enhanced transparency, transmission and also mechanical properties of these B2O3-BaO-LiF/AlF3 glasses. For the host reference glasses (without any luminescent ion), we have earlier measured their XRD,FTIR, DTA, and TG profiles in order to understand their structural and thermal properties. When rare earth ions (Pr3+, Tm3+, Sm3+, Dy3+, Eu3+, Tb3+ & Ho3+) are added to these glasses, they create a variety of dopant sites with a strong rare earth ion and host interaction, thus resulting in with more intense emission and absorption bands [15-17]. Glasses with the LiF content have shown more encouraging and significant results compared with the AlF3 glasses. By noticing these important trends, rare earths in those matrices are considered as dopant luminescent ions in the present work, it is intended to investigate spectral properties of B2O3-BaO-LiF glasses by adding five different transition metal (Cu2+, Ni2+, Co2+, Mn2+ & Cr3+) ions to understand their optical performance.
4.2 Experimental Studies

![Diagram showing different transition metal ions doped BBLi glasses](image)

**Fig. 4.1:** Host reference (undoped) and five different transition metal ions (Cr$^{3+}$, Co$^{2+}$, Mn$^{2+}$, Cu$^{2+}$ & Ni$^{2+}$) doped BBLi glasses.

Transition metal (Cu$^{2+}$, Ni$^{2+}$, Co$^{2+}$, Mn$^{2+}$ & Cr$^{3+}$) ions doped BBLi glasses were prepared by using a conventional melt quenching technique. The raw chemicals used were of analytical grade such as H$_3$BO$_3$, BaCO$_3$, LiF and the oxides of transition metals. Each of the batches with 10g of raw chemicals was thoroughly mixed and powdered using an agate mortar and pestle, each batch was thus melt in a porcelain crucible at 950°C in an tubular electrical furnace for an hour. The chemical melts were quenched in between smooth surfaced brass plates to obtain optical glasses of 2cm in diameter having a thickness of 0.3cm.

The Vis-NIR absorption spectra of Cr$^{3+}$, Ni$^{2+}$, Co$^{2+}$, Mn$^{2+}$ & Cr$^{3+}$ ions doped B$_2$O$_3$-BaO-LiF (BBLi) 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 (150W) with the datamax software in acquiring both the emission and excitation spectral data. Fig. 4.1 displays the developed optical glasses used in the present investigation.
4.3 Spectral analysis

The chromium ion, Cr$^{3+}$ ($d^3$), gives rise to the free ion terms of $^4F$, $^4P$, $^2G$ and several other doublet states, of which $^4F$ is the ground state. In an octahedrally coordinated system in the weak fields, $^4F$ splits as $^4A_{2g}(F)$, $^4T_{2g}(F)$ and $^4T_{1g}(F)$ whereas $^4P$ transforms as $^4T_{1g}(P)$. In the doublet states, $^2G$ splits as $^2A_{1g}(G)$, $^2E_g(G)$, $^2T_{1g}(G)$ and $^2T_{2g}(G)$. The weak field terms $^4A_{2g}(F)$, $^2E_g(G)$, $^2T_{1g}(G)$ and $^2T_{2g}(G)$ correspond to the lowest strong field configuration ($t_2g$)$^3$. The states $^4T_{1g}(F)$ and $^4T_{2g}(F)$ correspond to ($t_2g$)$^2$ ($e_g$)$^1$ and $^4T_{1g}(P)$ corresponds to ($t_2g$)$^1$($e_g$)$^2$. The ground state is $^4A_{2g}(F)$ at all strengths of the crystal field. Thus only three spin allowed transitions arise from $^4A_{2g}(F)$ to $^4T_{2g}(F)$, $^4T_{1g}(F)$ and $^4T_{1g}(P)$ states in addition to several spin forbidden transitions.

In a cubic crystalline field of low to moderate strength, the five d electrons of Mn$^{2+}$ ion are distributed in the $T_{2g}$ and $e_g$ orbitals, with three in the former and two in the latter. Thus, the ground state configuration is ($t_2g$)$^3$ ($e_g$)$^2$. This configuration gives rise to the electronic states, $^6A_{1g}$, $^4A_{1g}$, $^4E_g$, $^4T_{1g}$, $^4T_{2g}$ and to a number of doublet states of which $^6A_{1g}$ lies lowest according to Hund’s rule. The free ion levels of Mn$^{2+}$ in the order of an energy increasing are $^6S$, $^4G$, $^4P$, $^4D$ and $^4F$ etc. The energy level for Mn$^{2+}$ ion in octahedral environment (CN=6) are $^6A_{1g}$ ($^6S$), $^4T_{1g}$ ($^4G$), $^4T_{2g}$ ($^4G$), $^4E_g$ - $^4A_{1g}$ ($^4G$), $^4T_{2g}$ ($^4D$) and $^4E_g$ ($^4D$). The $^4E_g$ - $^4A_{1g}$ ($^4G$) and $^4E_g$ ($^4D$) levels have relatively less influence compared to the other levels by crystal field. It means that the relative sharp lines could be expected in the absorption or excitation spectrum, which is the criterion for assignments of levels for Mn$^{2+}$ ion. Since all the excited states of Mn$^{2+}$ ion (3d$^5$) will be either quartets or doublets, the optical absorption spectra of Mn$^{2+}$ ions will have only spin forbidden transitions [18,19].

Regarding Ni$^{2+}$ (3d$^8$) ion, it is generally a stable ion in a glass, under normal atmospheric conditions. All the spectra of Ni$^{2+}$ ions could be accounted for in terms of equilibrium between Ni$^{2+}$ ions in octahedral and tetrahedral symmetry [20] and it is reported that Ni$^{2+}$ ions should occur as octahedral sites in preference to tetrahedral
sites in a glass. The energy levels of Ni\(^{2+}\) ion in octahedral symmetry with a ground state of \(^3A_{2g}(F)\) are \(^3T_{2g}(F), \; ^1E(1D), \; ^3T_{1g}(F), \; ^1T_{2g}(D)\) and \(^3T_1(3P)\) etc. The energy levels of Ni\(^{2+}\) ion in octahedral symmetry are \(^3A_{2g} (F) \rightarrow ^4T_{2g} (F), ^3A_{2g} (F) \rightarrow ^3T_{1g} (F)\) and \(^3A_{2g} (F) \rightarrow ^3T_{1g} (P)\). In addition to these three spin allowed transitions, a spin-forbidden transition \(^3A_{2g} (F) \rightarrow ^1E_g (D)\), will appear as a weak absorption band.

Co\(^{2+}\) has the electronic configuration of argon and in addition seven electrons in the 3d state (3d\(^7\)). According to Hund's rule the ground state is a \(^4F_{9/2}\) state, i.e. a state which has an orbital degeneracy of 7. In octahedral co-ordination Co\(^{2+}\) free ion ground state \(^5F\) splits into the \(^4T_1, \; ^4T_2\) and \(^4A_2\) states with the \(^4T_1\) state as the lowest. Co\(^{2+}\) ion in this co-ordination has three bands which correspond to the spin allowed transitions \(^4T_1(F) \rightarrow ^4T_2 (F), ^4T_1 (F) \rightarrow ^4A_2 (F)\) and \(^4T_1 (F) \rightarrow ^4T_1 (P)\). The \(^4T_1(F) \rightarrow ^4A_2 (F)\) could be seen in a low intensity due to a forbidden two-electron jump. In a tetrahedral symmetry, the energy levels of Co\(^{2+}\) ion are \(^4T_2 (1F), ^4T_1 (1F), ^2E_2 (2G)\) and \(^4T_1 (1P)\) etc., with the ground state of \(^4A_2 (1F)\). In a tetrahedral symmetry, Co\(^{2+}\) ion doped materials mainly show two-spin forbidden transitions \(^4A_1 (1F) \rightarrow ^4T_1 (P)\) and \(^4A_2 (1F) \rightarrow ^4T_1 (1F)\) respectively. The high intensity of the tetrahedrally co-ordinated band could be attributed to the mixing of the 3d-orbitals with 4p-orbitals and ligand orbitals [21, 22].

The free ion term Cu\(^{2+}\) (3d\(^9\)) is \(^2D\) in a octahedral crystal field, splits into \(^2E_g\) and \(^2T_{2g}\). \(^2E_g\) generally splits due to Jahn - Teller effect and therefore, Cu\(^{2+}\) is rarely found in regular octahedral site. Accordingly, in the present investigation, Cu\(^{2+}\) is taken to be octahedrally coordinated by six oxygen atoms and the octahedron is tetragonally distorted. Therefore in the tetragonally distorted octahedral environment, the \(^2E_g\) level splits into \(^2A_1\) and \(^2B_1\) and \(^2T_{2g}\) levels into \(^2E\) and \(^2B_2\), the ground state being \(^2B_1\)[23].
4.4 Results and Discussion

a) \(\text{Cr}^{3+} (3d^3): \text{BBLi glass:}\)

Fig. 4.2: Absorption spectrum of \(\text{Cr}^{3+}: \text{BBLi glass}\)

Fig. 4.2 shows an absorption spectrum of \(\text{Cr}^{3+}: \text{BBLi glass}\). A broader absorption band has been observed that is superimposed with three weaker bands at 620 nm, 648 nm, and 684 nm respectively, which are assigned to the spin allowed \((^4A_2g(F) \rightarrow ^4T_{2g}(F)), (^4A_2g(F) \rightarrow ^2T_{1g}(G))\) and \((^4A_2g(F) \rightarrow ^2E_g(G))\) transitions, following the literature reports [24-27]. The \(^2E\) and \(^2T\) states acquire their spin-allowed characters via spin orbit interaction with a broad iso-energetic \((^4A_2g(F) \rightarrow ^4T_{2g}(F))\) transition[27]. Based on the absorption band positions, energy level structure factors such as Racah (\(B = 972 \text{ cm}^{-1}, C = 2631 \text{ cm}^{-1}\)) parameters and Crystal field factor (\(Dq = 1536 \text{ cm}^{-1}\)) have been evaluated for the \(\text{Cr}^{3+}: \text{BBLi optical glass}\).
Fig. 4.3: (a) Excitation and (b) Emission spectra of Cr$^{3+}$:BBLi glass

Fig. 4.3 presents both the excitation and emission spectra of Cr$^{3+}$: BBLi glass with an excitation at 558 nm ($^4A_2g(F)\rightarrow ^4T_{2g}(F)$) [28]. A couple of emission bands at 607 nm ($^2T_{1g}(F)\rightarrow ^4A_{2g}(F)$) and 624 nm ($^4T_{2g}(F)\rightarrow ^4A_{2g}(F)$) [27] have been measured.

b) Mn$^{2+}$ (3d$^5$):BBLi glass

Fig. 4.4: Absorption spectrum of Mn$^{2+}$:BBLi glass

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Fig. 4.4 shows the absorption spectrum of Mn$^{2+}$:BBLi glass with an absorption band at 467 nm which is due to the transition of ($^6A_{1g}(S) \rightarrow ^4T_{1g}(G)$) [29] ion in an octahedral symmetry. By using the energy of this band, the crystal field factor ($D_q = 2145$ cm$^{-1}$) of the Mn$^{2+}$: BBLi glass has been evaluated.

Fig. 4.5: (a) Excitation and (b) Emission spectra of Mn$^{2+}$: BBLi glass

Fig. 4.5 presents both the excitation and emission spectra of Mn$^{2+}$:BBLi glass with an emission band at 580 nm and it is assigned to the spin forbidden ($^4T_{1g}$ (G) $\rightarrow ^6A_{1g}(S)$) transition with an excitation at 380 nm ($^6A_{1g}(S) \rightarrow [^1A_{1g}(G), ^4E_{g}(G)]$) [30], has been observed from the Mn$^{2+}$:BBLi glass.
c) Ni\(^{2+}\) (3d\(^{1}\)) : BBLi glass

Fig.4.6: Absorption spectrum of Ni\(^{2+}\): BBLi glass

Fig.4.6 shows the absorption spectrum of Ni\(^{2+}\):BBLi glass, displaying an absorption band at 434 nm which is assigned to the spin allowed transition \((^3A_2_g(F) \rightarrow ^3T_{1g}(P))\) [27] and also a weak absorption band at 827 nm which is a spin forbidden d-d transition of \(^3A_2_g(F) \rightarrow ^1E_g(D)\) [31]. The crystal field parameter \(D_q=2074\) cm\(^{-1}\) from the absorption peak at 434 nm.

Fig.4.7: (a) Excitation and (b) Emission spectra of Ni\(^{2+}\): BBLi glasses
Fig. 4.7 presents an emission at 518 nm ($^1T_{2g}(G) \rightarrow ^3A_{2g}(F)$) [32] and a weaker emission at 582 nm ($^3T_{1g}(F) \rightarrow ^3A_{2g}(F)$) [33], upon excitation at 415 nm ($^3A_{2g}(F) \rightarrow ^3T_{1g}(P)$).

d) $\text{Co}^{2+} (3d^7)$: BBLi glass

![Absorption Spectrum of Co$^{2+}$: BBLi Glass](image)

Fig. 4.8: Absorption spectrum of Co$^{2+}$: BBLi glass

Fig. 4.8 shows an absorption spectrum of Co$^{2+}$: BBLi glass with an absorption band at 589 nm and another at 1449 nm, these two bands are assigned to spin-forbidden transitions of $^4A_{2g}(F) \rightarrow ^4T_{1g}(P)$ and $^4A_{2g}(F) \rightarrow ^4T_{1g}(F)$ respectively [34,35]. Measured absorption band at 589 nm, has resulted in with the crystal field ($Dq=1697 \text{ cm}^{-1}$) factor of Co$^{2+}$: BBLi glass.

e) $\text{Cu}^{2+} (3d^9)$: BBLi glass

Fig. 4.9 shows the absorption spectrum of Cu$^{2+}$: BBLi glass revealing a broad absorption band at 794 nm ($^2B_{1g} \rightarrow ^2B_{2g}$) [31] transition. From the energy of the broad band at 794 nm, the crystal field factor ($Dq = 1259 \text{ cm}^{-1}$) has also been computed.
Fig. 9: Absorption spectrum of Cu$^{2+}$: BBLi glass

4.5 Conclusions

In summary, it is concluded that a novel fluoro borate glasses (B$_2$O$_3$-BaO-LiF) have been prepared incorporated with different transitions metal ions. Both absorption and emission spectra of transition metal (Cr$^{3+}$, Mn$^{2+}$, Ni$^{2+}$, Co$^{2+}$ & Cu$^{2+}$) ions doped B$_2$O$_3$-BaO-LiF glasses have successfully been measured and analysed.
4.6 References

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