Preface

The thesis entitled "Optical Characterization of Certain Transition Metal and Rare Earth Ions Doped Zinc Lead Borate Glasses" brings out the results on the spectroscopic properties of four transition metal (Cu$^{2+}$, Mn$^{2+}$, Co$^{2+}$ & Ni$^{2+}$) and four rare-earth (Eu$^{3+}$, Tb$^{3+}$, Sm$^{3+}$ & Dy$^{3+}$) ions doped ZnO-PbO-B$_2$O$_3$ optical glasses. Entire thesis has been written in SEVEN Chapters.

In the Chapter I, necessary theory relating to the spectral analysis of the transition metal and rare earth ions has been presented.

In the Chapters II, method of preparation of optical glasses, measurements concerning the optical absorption spectra, emission spectra, XRD, FTIR, and other related physical properties of the optical glasses studied have been described.

Chapter III brings out results on a new series of zinc lead borate (ZLB) glasses by varying ZnO content, to enhance UV transmission, in the chemical composition of $x$ZnO-15 PbO-(85-x) B$_2$O$_3$, where $x$ = 0, 5, 10, 15, 20, 25, 30, 35, 40 and 45 mol% ZnO. From the measurement of UV absorption spectra both the direct and indirect band gaps have been evaluated. Also different physical properties of a reference glass of 45ZnO-15PbO-40B$_2$O$_3$ have been studied. From the measurement of refractive indices at six different wavelengths, Cauchy's constants ($A=1.578743209$; $B=131832.33$ nm$^2$ and $C=-0.77756 \times 10^{10}$ nm$^4$) have been computed and a satisfactory correlation has been achieved between the theoretical and experimental results. Absorption spectra of Cu$^{2+}$ (45-x) ZnO-15PbO-40B$_2$O$_3$ (where x = 0.1, 0.2, 0.5 and 1.0 mol%) have shown two absorption bands at 428 nm ($^2B_{1g} \rightarrow ^2E_g$) and 777 nm ($^2B_{1g} \rightarrow ^2B_{2g}$). Emission spectra of (1.0 mol%) Cu$^{2+}$: ZLB have revealed two emission transitions at 400 and 493 nm with excitations at 288 and 316 nm. This Chapter has been published as an article:
Chapter-IV reports on the development and optical characterization of heavy metal oxide (HMO)-based transparent glasses in the chemical composition of $15\text{PbO}-40\text{B}_2\text{O}_3$ $(45-x)\text{ZnO}$-x $\text{TM}^{2+}$ ($=\text{Mn}^{2+}$ or $\text{Ni}^{2+}$ or $\text{Co}^{2+}$) (where $x = 0.2$, 0.5 mol%). For these glasses both absorption and emission spectra have been measured, in order to understand their optical performances. The XRD profiles have confirmed their glassy nature and the FTIR spectral features have been analyzed. From the emission spectra, a bright green emission (538 nm) from $\text{Mn}^{2+}$-glasses, an intense red emission (670 nm) from $\text{Ni}^{2+}$ and from $\text{Co}^{2+}$ (625 nm) glasses have been noticed very clearly. Based on the UV-absorption spectra of these materials, both direct and indirect band gaps have been computed. Apart from the spectral analysis, different physical properties of these glasses have also been carried out. Due to the presence of both PbO and ZnO, these glasses are found to be good moisture-resistant optical systems. Both optical and physical properties have been found to be more encouraging towards their use as novel luminescent optical materials. The contents of this Chapter have been published in the following journal:

Optical Characterization of $\text{Cu}^{2+}$ ion-doped Zinc–Lead–Borate glasses

Chapter-V presents the results on the spectral analysis of $\text{Eu}^{3+}$ or $\text{Tb}^{3+}$ ions (0.5 mol%) doped heavy metal oxide (HMO) based zinc lead borate glasses from the measurement of their absorption, emission spectra and also different physical properties. From the XRD, DSC profiles, the glass nature and glass thermal properties have been studied. The measured emission spectrum of $\text{Eu}^{3+}$ glass has revealed five transitions ($^5\text{D}_0\rightarrow^7\text{F}_0$, $^7\text{F}_1$, $^7\text{F}_2$, $^7\text{F}_3$ & $^7\text{F}_4$) at 578, 591, 613, 654 and 702 nm, respectively, with $\lambda_{\text{exct}} = 392$ nm ($^7\text{F}_0 \rightarrow^5\text{L}_6$). In the case of $\text{Tb}^{3+}$: ZLB glass, four emission transitions such as
(\(^4D_4 \rightarrow {}^7F_6, {}^7F_5, {}^7F_4 \text{ & } {}^7F_3\)) that are located at 489, 542, 585 and 622 nm, respectively, have been measured with \(\lambda_{\text{exc}} = 374\) nm. For all these emission bands decay curves have been plotted to evaluate their lifetimes and the emission processes that arise in the glasses have been explained in terms of energy level schemes.

**Optical characterization of Eu\(^{3+}\) & Tb\(^{3+}\) ions doped Zinc Lead Borate Glasses**

Chapter VI narrates the results of the analysis of Sm\(^{3+}\) or Dy\(^{3+}\) (0.5mol %) ions doped heavy metal oxide (HMO) based zinc lead borate (ZLB) glasses. Optical measurements such as absorption, emission spectra, lifetimes, XRD, DSC profiles have been carried out. The emission spectrum of Sm\(^{3+}\): ZLB has shown the emission transitions of \(^4G_5/2 \rightarrow {}^6H_5/2\) (563 nm), \(^4G_5/2 \rightarrow {}^6H_7/2\) (598 nm), \(^4G_5/2 \rightarrow {}^6H_9/2\) (646 nm), \(^4G_5/2 \rightarrow {}^6H_{11/2}\) (708 nm) with \(\lambda_{\text{exc}} = 401\) nm \((^6H_5/2 \rightarrow ^4F_{7/2})\). In the case of the Dy\(^{3+}\): ZLB glass, emission transitions of \(^4F_{9/2} \rightarrow {}^6H_{15/2}\) (485 nm), \(^4F_{9/2} \rightarrow {}^6H_{13/2}\) (575 nm) and \(^4F_{9/2} \rightarrow {}^6H_{11/2}\) (664 nm) with \(\lambda_{\text{exc}} = 447\) nm \((^6H_{15/2} \rightarrow ^4I_{15/2})\) have been identified. Energy level schemes relating to the emission mechanisms involved in Sm\(^{3+}\) and Dy\(^{3+}\) glasses have been given and the results presented in this Chapter are accepted for publication in the following journal as an article:

**Optical Characterization of Sm\(^{3+}\) and Dy\(^{3+}\): ZnO-PbO-B\(_2\)O\(_3\) Glasses**

Chapter VII summarizes the entire thesis results as the conclusion chapter and the contents of it have also been presented as an article:

**Optical Analysis of Certain Transition Metal and Rare Earth Ions Doped Zinc Lead Borate Glasses**
Optical characterization of Cu$^{2+}$ ion-doped zinc lead borate glasses

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Received 4 January 2005; accepted 14 April 2005

Abstract

We have developed a new series of zinc lead borate (ZLB) glasses by varying ZnO content, to enhance UV transmission, in the chemical composition of $x$ZnO·15PbO·(85−$x$)B$_2$O$_3$, where $x$ = 0.5, 1.0, 1.5, 2.0, 2.5, 3.0, 3.5, 4.0 and 4.5 mol% ZnO. From the measurement of UV absorption spectra both the direct and indirect band gaps have been evaluated. Also different physical properties of a reference glass of 45ZnO·15PbO·40B$_2$O$_3$ have been studied. From the measurement of refractive indices at six different wavelengths, Cauchy's constants ($A$ = 1.578743209; $B$ = 131382.33 nm$^2$ and $C$ = −0.77756 × 10$^{-5}$ nm$^4$) have been computed and a satisfactory correlation has been achieved between the theoretical and the experimental results. Absorption spectra of Cu$^{2+}$ (45−$x$)ZnO·15PbO·40B$_2$O$_3$ (where $x$ = 0.1, 0.2, 0.5 and 1.0 mol%) have shown two absorption bands at 428 nm ($^2$B$_{1g}$ → $^2$E$_g$) and 777 nm ($^2$B$_{1g}$ → $^2$B$_{2g}$). Emission spectra of (1.0 mol%) Cu$^{2+}$·ZLB have revealed two emission transitions at 400 and 493 nm with excitations at 288 and 316 nm.

Keywords: Cu$^{2+}$·ZLB glasses; Spectral analysis

I. Introduction

Luminescent materials with copper ions in crystalline glasses could display bright photoluminescence depending on the host materials [1]. Melts with B$_2$O$_3$ could exhibit viscosity
and lead to the formation of glasses [2]. It is reported that \( \text{B}_2\text{O}_3 \) is a good network former and \( \text{ZnO}, \text{PbO} \) are network modifiers and copper ions are in \( \text{Cu}^{2+} \) and \( \text{Cu}^+ \) valence states [3]. Since Cu element has got a polyvalence and also due to weak screening of its optical electrons, its spectrum could be dependent on the host glass composition [4]. \( \text{ZnO} \) is considered as a promising candidate as a host material with a wide band gap for its development as potential optical material [5]. The \( \text{Cu}^{2+} \) ion has \( 3d^94s^2 \) configuration where as \( \text{Cu}^+ \) ion will be in \( 3d^{10}4s^2 \) electronic configuration where electrons are present in the form of covalent bonds with the oxygen neighbors [6]. Electronic behavior as well as the optical, magnetic and structural properties of oxide glasses will depend on the relative ratio of the different valence states of the transition metal ions [7].

The co-ordination state of \( \text{Zn}^{2+} \) ions in oxide glasses strongly suggests that \( \text{ZnO}_4 \) polyhedra plays an important role in forming glass network. \( \text{Zn}^{2+} \) ions will improve mechanical properties and chemical resistivity through the formation of tetrahedral co-ordination. \( \text{ZnO} \) is an important component for the preparation of multi-component oxide glasses with a high thermal resistance against crystallization [8]. The stability of both \( \text{Cu}^+ \) and \( \text{Cu}^{2+} \) ions could be found to be sensitive to the glass environment. The valence state of copper affects not only chemical and physical properties but also the glass forming ability [9]. In the present work, we have developed and analyzed a new series of zinc lead borate (ZLB) glasses with and without \( \text{Cu}^{2+} \) ions to analyze their physical and optical properties.

2. Experimental studies

2.1. Glasses preparation

Reference glasses were developed by melt-quenching technique with a chemical composition of [\( x\text{ZnO} - 15\text{PbO} - (85-x)\text{B}_2\text{O}_3 \)], where \( x = 0, 5, 10, 15, 20, 25, 30, 35, 40 \) and 45 mol\%. We also developed copper glasses with a formula of [(45 - x)\( \text{ZnO} - 15\text{PbO} - 40\text{B}_2\text{O}_3 \)], where \( x = 0.1, 0.2, 0.5 \) and 1.0 mol\%. Reagent grade chemicals of \( \text{H}_3\text{BO}_3, \text{ZnO}, \text{PbO}_2 \) and \( \text{CuO} \) were used in the glasses preparation. Each batch (10 g) of chemical was powdered finely and mixed thoroughly and was later melt in an electrical furnace for an hour, at 950 °C. These melts were quenched in between two brass plates to have optical glasses in circular designs of 2-3 cm in diameter with a uniform thickness of 0.3 cm. Due to the homogeneous distribution of copper ions in the glasses, light blue to dark bluish-green color was noticed from all these glasses. All the optical glasses thus developed were annealed at 200 °C for an hour to remove thermal stains in the glasses. Fig. 1 shows a specimen photograph for \( \text{Cu}^{2+} \)-doped ZLB glasses and a reference glass.

2.2. Measurement of physical properties and optical spectra of glass

Glass densities were measured by using toluene as an immersion liquid based on the Archimedes's principle. Glass refractive indices were measured on a precision refractometer (Kahnew, Model GMR-I) by using the minimum deviation method between the wavelengths of 0.4 and 1.1 µm.

For a reference glass, X-ray diffraction (XRD) spectrum was obtained on a Shimadzu XD3A diffractometer with a Ni-filter and CuK\( \alpha \) (\( = 1.542 \) Å) radiation with an applied voltage of 30 kV.
and 20 mA anode current calibrated with Si at the rate of 2 °C/min. The FT-IR spectrum (4000-450 cm⁻¹) of the reference glass was recorded on a Bruker IFS 66 V FT-IR spectrometer with a KBr pellet. DSC measurement was carried out on a Netzsch STA 409C in the temperature range of 30-1200 °C, at the rate of 10 °C/min, under N₂ atmosphere. The optical absorption spectra (350-2500 nm) for all undoped glasses and for the four Cu²⁺-doped glasses (0.1, 0.2, 0.5 and 1.0 mol% CuO) in the range of 380-1100 nm were measured on a Varian Cary Win Spectrometer. Both the excitation and emission spectra of the 1.0 mol% Cu²⁺-doped glasses were measured in a steady state mode on a SPEX Fluorolog-2 (Model F-II) with a Data max software to acquire the data with a Xe arc lamp (150 W) as the excitation source.

3. Results and discussion

Fig. 2 confirms the amorphous nature of the reference glass in the composition of 45ZnO-15PbO-40B₂O₃. In Fig. 3, the UV absorption spectra are shown for different glasses with the chemical formulae of xZnO-15PbO (85-x)B₂O₃, where x = 0, 5, 10, 15, 20, 25, 30, 35, 40 and 45, in order to understand their UV transmission extension ability with the addition of ZnO content. Accordingly Fig. 4 presents a graphical representation of the UV transmission as a function of ZnO change. In order to understand the optically induced transitions, optical band gaps (both direct and indirect) have been computed from the UV absorption spectra of these glasses. We are aware of the fact that there are two kinds of optical transitions at the fundamental absorption edge. Both direct and indirect transitions, involve the interaction of an electromagnetic wave with an electron in the valence band. According to the literature, the optical absorption coefficient is given as [α = 2.303 × (OD)/λ], where OD is the optical density and "λ" is the thickness of the glass (cm). Optical band gaps for direct and indirect transitions can be obtained.
Fig. 3. UV absorption spectra of undoped ZnO-PbO-B₂O₃ glasses in varied contents of ZnO.

From $\alpha(h\nu) = B(h\nu - E_{opt})^n$ where $B$ is a constant, $h\nu$ vs. the energy and $E_{opt}$ is the optical band gap. For a direct transition $n = \frac{1}{2}$ and for an indirect transition $n = 2$. From the plots of $(ah\nu)^2$ and $(ah\nu)^{1/2}$ as function of photon energy $(h\nu)$, $E_{opt}$ values are obtained for direct and indirect
critnsitions, respectively. The respective values of $E_{\text{opt}}$ are obtained by extrapolating to $(zhv)^2 = 0$ for the direct transitions and $(zhv)^{1/2} = 0$ for the indirect transitions [10,11]. A plot of $E_{\text{opt}}$ against ZnO content shows that $E_{\text{opt}}$ increases linearly with an increase in ZnO content as shown in Fig. 5. The FT-IR spectrum of the reference glass is shown in Fig. 6. The structure of borate glasses consists of random network of BO$_3$ triangles with certain fractions of boroxol (six-membered) rings. In the infrared range, the vibrational modes of the borate network have three regions. Accordingly, 1200-1600 cm$^{-1}$ band could be the first region, which arises due to an asymmetric stretching relaxation of the B-O bond of trigonal BO$_3$ units, the second region is located at 800-1200 cm$^{-1}$ which is due to the B-O bond stretching of tetrahedral BO$_4$ units, and the third region is at 700 cm$^{-1}$ which is because of the bending of B-O-B linkages in the borate network. Thus, the band at 1330 cm$^{-1}$ is due to B-O stretching vibrations of (BO$_3$)$_2$ unit in metaborate chain and orthoborates. The peak observed at 900 cm$^{-1}$ is assigned to the B-O bond stretching of BO$_4$ units. The absorption band at 720 cm$^{-1}$ indicates the B-O-B bending vibration. In general, the absorption band at 806 cm$^{-1}$ is attributed to the boroxol ring in the borate glass network [9,12]. In the present study, the peak at 806 cm$^{-1}$ could not be found, which indicates the absence of boroxol ring in the glass network. Similarly, the band in the region of 3200-3600 cm$^{-1}$ is ascribed to the hydroxyl (or) water groups. The DSC thermogram for the reference glass is shown in Fig. 7 and from this, the glass transition temperature ($T_g = 420$ C), crystallization temperature ($T_c = 630$ C) and glass melting temperature ($T_m = 880$ C) are evaluated, and from these values the glass stability factor ($S = 210$ C), Hruby's parameter ($K_H = 0.84$) have been calculated using the necessary formulae that are already reported in the literature [13]. The glass
stability factor (S) addresses the glass stability and Hruby's parameter presents the stability of the glass against the devitrification. The measured refractive indices of the reference glass 45ZnO-15PbO-40B_2O_3 at different wavelengths are given in Table I.

Fig. 5. Direct and indirect optical band gaps of ZnO-PbO-B_2O_3 glasses with the change in ZnO content.

Fig. 6. FTIR spectrum of 45ZnO-15PbO-40B_2O_3 glass.
The Cauchy's formula of refractive index \((n)\) as a function of wavelength \((\lambda)\) is given by
\[
n(\lambda) = A + B/\lambda^2 + C/\lambda^4.
\] (1)

The values of refractive indices depend on the glass chemical composition and wavelengths \((\lambda \text{ nm})\) [14]. The Cauchy's constants in the present work are \(A = 1.578743209\), \(B = 131832.33 \text{ nm}^2\) and \(C = -0.77756 \times 10^{10} \text{ nm}^4\). A graph for theoretical refractive indices through the Cauchy's formula is shown in Fig. 8(a) and its dispersion curve is given in Fig. 8(b) which is obtained upon the differentiation of the Eq. (1) i.e., \(dn/d\lambda = -2B/\lambda^3 - 4C/\lambda^5\). For the reference glass, the value of \(dn/d\lambda\) is evaluated from the expression with the substitution of the value for \(B\) and \(C\), respectively.

\[
\frac{dn}{d\lambda} = \frac{-263664.66}{\lambda^3} + \frac{3.11024 \times 10^{10}}{\lambda^5}.
\]
It is found that $dn/d\lambda$ decreases with the wavelength change at a given temperature. The group index ($N_g$) of the glass could also be determined [15]. $N_g = n - 2dn/d\lambda$, the group refractive index ($N_g$) is necessary when a broad band or a modulated electromagnetic radiation is in use. The measured refractive indices ($n_d$) at 589.3 nm for CuO-doped 45ZnO-15PbO-40B$_2$O$_3$ glasses are
Table 2
Experimental refractive index data of CuO-doped (0.1, 0.2, 0.5 and 1.0 mol%) 45ZnO-15PbO-40B2O3 glass along with densities

<table>
<thead>
<tr>
<th>Copper glasses</th>
<th>Refractive index n_d (λ = 589.3 nm)</th>
<th>Density d (g/cm³)</th>
</tr>
</thead>
<tbody>
<tr>
<td>44.9ZnO-15PbO-40B2O3: 0.1CuO</td>
<td>1.9129</td>
<td>4.992</td>
</tr>
<tr>
<td>44.8ZnO-15PbO-40B2O3: 0.2CuO</td>
<td>1.9168</td>
<td>4.998</td>
</tr>
<tr>
<td>44.5ZnO-15PbO-40B2O3: 0.5CuO</td>
<td>1.9243</td>
<td>5.015</td>
</tr>
<tr>
<td>44.0ZnO-15PbO-40B2O3: 1.0CuO</td>
<td>1.9328</td>
<td>5.041</td>
</tr>
</tbody>
</table>

Fig. 9. Visible absorption spectra of (x = 0.1, 0.2, 0.5 and 1 mol%) Cu⁺⁺ (45-x)/ZnO-15PbO-40B2O3 glasses.

presented in Table 2 along with their densities. The optical absorption spectra of Cu⁺⁺ glasses are shown in Fig. 9 with two absorption bands at 428 and 777 nm, respectively. It is noticed that with an increase in CuO concentration from 0.1 to 1.0 mol%, intensities of absorption bands are also significantly increasing with a little shift in the band position towards the longer wavelength.

From the Ref. [16], it is found that a free ion term Cu⁺⁺ (3d⁹) is 2D and in octahedral crystal field it splits into 2E_g and 2T_2g. With 2E_g as the lower level and this 2E_g level splits due to Jahn-Teller effect. So Cu⁺⁺ is rarely found in regular octahedral site. Therefore, in the present work, Cu⁺⁺ is expected to be octahedrally co-ordinated with six oxygen atoms and the octahedron could be tetragonally distorted. Hence in the tetragonally distorted octahedral environment, the 2E_g level splits into 2A_1 and 2B_1 and the 2T_2g level as 2E_g and 2B_2 with the ground as 2B_1. Table 3 presents the electronic assignments made for the measured absorption bands with their FWHM values.
Table 3
Absorption spectrum data of CuO-doped (0.1, 0.2, 0.5 and 1.0 mol%) 45ZnO-15PbO-40B2O3 glass

<table>
<thead>
<tr>
<th>CuO (mol%)</th>
<th>Transition 2B1g→2Eg (nm)</th>
<th>Transition 2B1g→2B2g (nm)</th>
<th>Absorbance (a.u)</th>
<th>FWHM (Δλ) (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.1</td>
<td>414</td>
<td>765</td>
<td>0.1</td>
<td>170</td>
</tr>
<tr>
<td>0.2</td>
<td>419</td>
<td>768</td>
<td>0.2</td>
<td>240</td>
</tr>
<tr>
<td>0.5</td>
<td>423</td>
<td>772</td>
<td>0.3</td>
<td>320</td>
</tr>
<tr>
<td>1.0</td>
<td>428</td>
<td>777</td>
<td>0.4</td>
<td>370</td>
</tr>
</tbody>
</table>

Table 4
Various physical properties of CuO-doped (0.1, 0.2, 0.5 and 1.0 mol%) 45ZnO-15PbO-40B2O3 reference glass

<table>
<thead>
<tr>
<th>Properties</th>
<th>0.1 CuO</th>
<th>0.2 CuO</th>
<th>0.5 CuO</th>
<th>1.0 CuO</th>
</tr>
</thead>
<tbody>
<tr>
<td>Average molecular weight M(g)</td>
<td>167.297</td>
<td>167.295</td>
<td>167.289</td>
<td>167.289</td>
</tr>
<tr>
<td>Density d (g/cm³)</td>
<td>4.992</td>
<td>4.998</td>
<td>5.015</td>
<td>5.041</td>
</tr>
<tr>
<td>Thickness of the glass l (cm)</td>
<td>0.3</td>
<td>0.3</td>
<td>0.3</td>
<td>0.3</td>
</tr>
<tr>
<td>Refractive Index n (589.3 nm)</td>
<td>1.9129</td>
<td>1.9168</td>
<td>1.9243</td>
<td>1.9328</td>
</tr>
<tr>
<td>Dielectric constant ε</td>
<td>3.659</td>
<td>3.674</td>
<td>3.703</td>
<td>3.736</td>
</tr>
<tr>
<td>Molar volume V_m (cm³/mol)</td>
<td>33.513</td>
<td>33.472</td>
<td>33.358</td>
<td>33.184</td>
</tr>
<tr>
<td>Molar refractivity R_m (cm⁻¹)</td>
<td>15.747</td>
<td>15.774</td>
<td>15.808</td>
<td>15.827</td>
</tr>
<tr>
<td>Molar polarizability σ_m (Å³)</td>
<td>6.245</td>
<td>6.255</td>
<td>6.269</td>
<td>6.277</td>
</tr>
<tr>
<td>Copper ion concentration N (10²² ions/cm³)</td>
<td>0.179</td>
<td>0.359</td>
<td>0.903</td>
<td>1.815</td>
</tr>
<tr>
<td>Polaron radius r_p (Å)</td>
<td>3.3185</td>
<td>2.6294</td>
<td>1.935</td>
<td>1.533</td>
</tr>
<tr>
<td>Inter ionic distance r_i (Å)</td>
<td>12.141</td>
<td>15.323</td>
<td>4.8025</td>
<td>3.805</td>
</tr>
<tr>
<td>Field strength F (10⁶ cm⁻¹)</td>
<td>0.181613</td>
<td>0.28927</td>
<td>0.53412</td>
<td>0.85103</td>
</tr>
<tr>
<td>Glass optical basicity (A)</td>
<td>0.43713</td>
<td>0.437119</td>
<td>0.430533</td>
<td>0.43363</td>
</tr>
<tr>
<td>Glass oxide species (Å³), z_oxide = 11.018 + 0.567A_oxide + 0.783A_glass</td>
<td>1.41517</td>
<td>1.41549</td>
<td>1.41581</td>
<td>1.41483</td>
</tr>
</tbody>
</table>

In copper-doped glasses, the absorption band at 800 nm (2B1g→2Eg) is due to Cu⁺⁺ ion in octahedral co-ordination with a strong tetragonal distortion [12]. The present optical absorption studies of CuO-doped 45ZnO-15PbO-40B2O3 glasses confirm the presence of Cu⁺⁺ ions. Based on the measured densities, refractive indices and the molecular weight of (45-χ) ZnO-15PbO-40B2O3-χCuO (χ = 0.1, 0.2, 0.5 and 1.0 mol%) glasses, various other physical properties of these glasses have also been presented in Table 4. The necessary formulae of these factors have earlier been reported in the Refs. [10,13]. From Table 4, it is observed that the physical properties such as the average molecular weight, molar refractivity, mean molar volume, electronic polarizability, polaron radii, interionic distances are all decreasing with the change in glass composition.

3.1. Optical basicity of the glasses

The optical basicity of an oxide glass defines the ability of the glass to donate negative charge to the probe ion. An optical basicity of glass can also be predicted from its composition. The basicity

...
moderating parameter is obtained from \( \eta = 1.36(X_i - 0.26) \), where \( X_i \) is the Pauling electronegativity of the cation [17]. The optical basicity and electronic polarizability of the oxide species \( \text{oxide}^{(-i)} \) of the glass compositions are evaluated [14] and listed out in Table 4. It is observed that the optical basicity values of the glasses are decreasing with CuO content change. For all cations present in the glass matrices, optical basicity moderating parameters and optical basicity are given in Table 5.

Fig. 10 reveals the excitation and Fig. 11 shows the emission spectrum of 1.0 mol% CuO-doped 45ZnO-15PbO-40B₂O₃ glass. According to theory [18], oxide-based glasses could show charge transfer bands in the UV region due to UV absorption by the oxygen ligands around the cations, which normally fall in the wavelength range of 250-350 nm. Accordingly, for the (1 mol%) Cu²⁺:44ZnO-15PbO-40B₂O₃ glass two excitation bands at 288 and 316 nm have been observed. These are due to charge transfer phenomena caused by \( \text{O}^{2-} \) with an UV radiation exposure. The emission spectra have been obtained with the two excitation wavelengths at 288 and 316 nm. With
$\lambda_{\text{exi}} = 288 \text{ nm}$, two emission peaks at 400 and 493 nm have been found; with $\lambda_{\text{exi}} = 316 \text{ nm}$, these emission peaks are relatively more intense bands. The emission at 493 nm is found to be shifted towards the longer wavelength depending upon the increase in excitation wavelength and the line width. Such an observation has earlier been made [6,19] and it is due to the existence of multi-site structures of copper ions. The emission at 493 nm could be found unchanged with the change in excitation wavelengths. These emissions at 400 and 493 nm are due to Cu$^{2+}$ ions in the glass. However, according to the earlier investigations [20], emission at 493 nm arises due to a localized excitation of an isolated Cu$^{2+}$ ion (there is a short lived transfer of an electron from a neighboring oxygen to the copper ion). In Table 4, various physical properties of the copper-doped glasses have been presented for a comparison as a function of CuO content.

4. Conclusions

In brief, it is concluded that with an incremental addition of ZnO into glass matrices of PbO·B$_2$O$_3$, gradual extension of UV radiation transmission has been achieved. Due to the presence of both Zn and Pb, glasses are found to be more stable, transparent and bubble free and they possess good resistance towards humidity in the laboratory conditions for months together. Keeping in view these encouraging properties, one specimen glass has been selected to examine its amorphous nature through XRD spectrum. For the same glass, FTIR profile has also been measured to investigate the glass bonding nature. A good comparison has been made between the measured refractive indices and theoretically evaluated data, upon the computation of Cauchy's constants ($A$, $B$, $C$) for this reference glass. Both absorption and emission spectra
have revealed the presence of Cu$^{2+}$ ions in the glasses investigated. Both for the reference
glass and Cu$^{2+}$ glasses, refractive indices and densities have been measured. We suggest that
these glasses have potential applications to carry on further research work with several other
transition metal ions as the dopant ions in our extension studies to analyze their optical
performances.

Acknowledgements

One of us (ATR) would like to thank his research colleague Mr. G. Lakshminarayana and also
Dr. KPC. Gandhi, Director of FSL, Hyderabad, India for his kind permission and co-operation
in the present work.

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Optical characterization of Mn$^{2+}$, Ni$^{2+}$ and Co$^{2+}$ ions doped zinc lead borate glasses

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Received 19 May 2005; accepted 6 February 2006

Abstract

This paper reports on the development and optical characterization of heavy metal oxide (HMO)-based transparent glasses in the chemical composition of 15PbO-40B$_2$O$_3$-(45-x)ZnO-x TM$^{2+}$ (x = Mn$^{2+}$ or Ni$^{2+}$ or Co$^{2+}$) (where x = 0.2, 0.5 mol%). For these glasses both absorption and emission spectra have been measured, in order to understand their optical performances. The XRD profiles have confirmed their glassy nature and the FTIR spectral features have been analyzed. From the emission spectra, a bright green emission (531 nm) from Mn$^{2+}$-doped glasses, an intense red emission (670 nm) from Ni$^{2+}$ and from Co$^{2+}$ (825 nm) glasses have been noticed very clearly. Based on the UV-absorption spectra of these materials, both direct and indirect band gaps have been computed. Apart from the spectral analysis, different physical properties of these glasses have also been carried out. Due to the presence of both PbO and ZnO, these glasses are found to be good moisture-resistant optical systems. Both optical and physical properties have been found to be more encouraging towards their use as novel luminescent optical materials.

Keywords: Mn$^{2+}$; Ni$^{2+}$ and Co$^{2+}$ glasses - spectral analysis

1. Introduction

Over the past one decade a great deal of work has been carried to understand the emission properties of various rare earth ions doped optical materials [1-9]. Regarding transition metal ions doped materials, only a little work has so far been reported [10-14]. In order to examine the significance and importance of heavy metal oxide (HMO)-based glasses, we have recently investigated the optical properties and reported certain important results on the Cu$^{2+}$-ZPB glasses [15] and wherein it is reported that B$_2$O$_3$ functions as a good network-former and ZnO, PbO are working as network-modifiers and transition metal ions are mostly in divalent valence states. Keeping in view the encouraging properties we obtained from Cu$^{2+}$-ZPB glasses, it has been considered to systematically analyze the optical characteristic parameterization of yet another three more divalent transition metal ions such as Mn$^{2+}$ (3d$^5$), Co$^{2+}$ (3d$^7$) and Ni$^{2+}$ (3d$^8$), as these ions are also potentially luminescent like the Cu$^{2+}$ ions. Therefore, the present paper brings out the results of the
absorption, excitation and emission spectra of the above given transition ions and these glasses are further analyzed by the application of optical tools such as XRD, DSC and FTIR measurements apart from the determination of various physical properties of these glassy materials.

2. Experimental studies

2.1. Glass preparation

Mn$^{2+}$, Ni$^{2+}$ and Co$^{2+}$ ions doped in zinc lead borate (ZPB) glasses were prepared in the following chemical compositions:

- $40B_2O_3 - 15PbO - (45-x)ZnO - xMnO_2$,
- $40B_2O_3 - 15PbO - (45-x)ZnO - xNiO$,
- $40B_2O_3 - 15PbO - (45-x)ZnO - xCoCl_2$,

where $x = 0.2$ and $0.5$ mol%. The chemicals used were reagent grade of $H_2BO_3$, $ZnO$, $PbO$, $MnO_2$, $NiO$, $H_2O$ and $CoCl_2$. All weighed chemicals were finely powdered and then mixed thoroughly before each of the batches (10 g) was melted by using suitable ceramic crucibles in an electrical furnace at 950°C for an hour. These melts were quenched in between two brass plates and 2.3 cm diameter optical glass discs with a uniform thickness of 0.3 cm were obtained. Due to the homogenous distribution of Mn$^{2+}$, Ni$^{2+}$, and Co$^{2+}$ ions in the glass matrices, these glasses are in bright colors. The Mn$^{2+}$ glasses have been found to be in "pink", Co$^{2+}$ glasses in "blue" and Ni$^{2+}$ glasses in "brown" colors and these glasses were annealed at 200°C for an hour in order to remove thermal strains.

2.2. Measurements

Glass densities were measured with toluene as an immersion solvent using Archimedes' principle. Abbe refractometer was used to measure the glass refractive index with a sodium vapor lamp (589.3 nm). X-ray diffraction (XRD) spectra were measured on a Shimadzu XD3A diffractometer with a Ni-filter and CuK$_{α}$ ($\lambda = 1.5418\,\text{Å}$) radiation at an applied voltage of 30 kV and 20 mA anode current, which was calibrated with Si at the rate of 2°/min. The FT-IR spectra (4000-450 cm$^{-1}$) were recorded on a Bruker IFS 66 V FT-IR spectrometer with KBr pellets. DSC profiles were recorded on a Netzsch STA 409C system in the temperature range of 30-1200°C, at the rate of 10°C/min, under $N_2$ gas atmosphere. The optical absorption spectra of Mn$^{2+}$, Co$^{2+}$ and Ni$^{2+}$ glasses were measured on a Varian-Cary Win Spectrophotometer. Both the excitation and emission spectra of Mn$^{2+}$, Co$^{2+}$ and Ni$^{2+}$ glasses were measured on a SPEX Fluorolog-2 (Model II) with a Data max Software to acquire the data with a Xe-arc lamp (150 W) as the excitation source. Table 1 lists out various physical properties of Mn$^{2+}$, Co$^{2+}$ and Ni$^{2+}$ doped ZPB glasses. Following the mathematical expressions that are made available in literature [16,17], we have computed these physical quantities and documented accordingly in Table 1 for a comparison. For 0.5 mol% Mn$^{2+}$, Co$^{2+}$ and Ni$^{2+}$ ions doped glasses, from the glass transition temperature $T_g$ (°C), crystallization temperature $T_c$ (°C), and melting temperature $T_m$ (°C) values, the glass stability factor ($S$), Hruby’s parameter ($K_p$) have been calculated as was reported earlier [16], and the results are given in Table 1. The glasses' stability factor demonstrates that these glasses are more stable and the Hruby’s parameter describes the stability of these glasses against the devitrification.

3. Theory

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 orbitals. Thus, its ground state configuration is $(t_{2g})^3(e_g)^2$. This configuration yields to energy levels such as $^6A_{1g}$, $^4A_{1g}$, $^4E_g$, $^4T_{1g}$, $^4T_{2g}$ and to a number of doublet states of which $^4A_{1g}$ lies lowest according to Hund’s rule. The free ion levels of
Mn$^{2+}$ are arranged as follows, based on their energy: $^4S, ^4G, ^4P, ^4D$ and $^4F$, etc., and these energy levels in octahedral environment (CN = 6) are $^5A_1g$ ($^4S$), $^3T_2g$ ($^4G_1$), $^1T_1g$ ($^4G_2$), $^3E_g$ ($^4A_1g$), $^1T_2g$ ($^4E_1g$) and $^3T_1g$ ($^4T_2g$). The $^3E_g-^1A_1g$ ($^4G$) and $^3T_2g$ ($^4E_1g$) levels have relatively less influence compared to the other levels by the 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$^5$) would either be quartets or doublets, the optical absorption spectra of Mn$^{2+}$ ion-doped materials have only spin forbidden transitions [17,18]. In octahedral co-ordination, Co$^{2+}$ free ion ground state $^4F$ splits into the $^4T_1$, $^4T_2$ and $^4A_2$ states with the $^4T_1$ state as the lowest. With regards to Co$^{2+}$, this co-ordination has three bands which correspond to the spin allowed transitions $^4T_1(F) ightarrow ^4T_2(F)$, $^4T_1(F) ightarrow ^4A_2(F)$ and $^4T_1(F) ightarrow ^4T_1(P)$. The $^4T_1(F) ightarrow ^4A_2(F)$ transition 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 $^4T_1$ ($^4F$), $^2T_2$ ($^4F$), $^2E_2$ ($^4G$) and $^2T_1$ ($^4P$), etc., with the ground state of $^4A_2$ ($^4F$). In a tetrahedral symmetry, Co$^{2+}$ ion-doped materials mainly show two spin-forbidden transitions $^4A_1$ ($^4F$) $\rightarrow$ $^4T_1(P)$ and $^4A_1$ ($^4F$) $\rightarrow$ $^4T_1$ ($^4F$), 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 [19,20]. Regarding Ni$^{2+}$ (3d$^8$) ion, it is generally a stable ion in 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 [21] 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 $^4A_{1g}$ (F) are $^2T_2g$ (F), $^4E_1g$ (D), $^2T_2g$ (F), $^4T_2g$ (D) and $^2T_1g$ (P). The energy levels of Ni$^{2+}$ ion in octahedral symmetry are $^4A_{1g}$ (F) $\rightarrow$ $^2T_2g$ (F), $^4A_{1g}$ (F) $\rightarrow$ $^4T_2g$ (F) and $^4A_{1g}$ (F) $\rightarrow$ $^2T_1g$ (F). In addition to these three spin allowed transitions, a spin-forbidden transition $^4A_{2g}$ (F) $\rightarrow$ $^4E_2$ (D) will appear as a weak absorption band.

4. Results and discussion

4.1 Section A: Mn$^{2+}$-doped ZPB glasses

The XRD pattern of 0.5 Mn$^{2+}$-ZPB glass has been given in Fig. 1, which confirms the glass amorphous nature. The UV absorption edge has been used to evaluate the optical transition and electronic band structures of optical materials. Two types of optical (both direct and indirect) transitions could occur at the fundamental absorption edge of these materials. For direct optical transition, $\pi(\nu) = \mu(\nu - E_{opt})^2/\nu$ could
be the formulae where $n = \frac{1}{2}$ for allowed transitions, $B$ is the constant and $E_{opt}$ the direct optical band gap, for indirect transitions $a(h\nu) = B(h\nu - E_{opt})^n/h\nu$ where $n = 2$ for allowed transitions and $E_{opt}$ is the indirect optical band gap by using the above two equations, by plotting $(a(h\nu))^2$ and $(a(h\nu))^2$ as a function of photon energy ($h\nu$), optical energy band gaps ($E_{opt}$) for indirect and direct transitions are determined. From UV-absorption spectra (Fig. 2) of Mn$^{2+}$ glasses, both direct and indirect band gaps have been calculated [22,23]. The visible absorption spectra of Mn$^{2+}$:ZPB glasses are shown in Fig. 3, with a broad absorption band at 470 nm ($^6A_{1g} (S) \rightarrow ^4T_{1g} (G)$) of Mn$^{2+}$ ions in octahedral symmetry [17,24]. These transitions are spin and parity forbidden for electric dipole radiation in an octahedral environment, hence the absorption bands are very weak. Fig. 4 shows the excitation spectra of Mn$^{2+}$:ZPB glasses. We are aware of the fact that Mn$^{2+}$ d-d absorption transitions are difficult to be pumped as those are forbidden by spin and parity for
Electric dipole radiation in octahedral symmetry. Charge transfer (CT) bands could occur when a valance electron is transferred from the ligand towards the unoccupied orbitals of the metallic cation and those are parity allowed and occur generally in the UV and vacuum UV region, which are mainly vibronic in character [25]. Zn$^{2+}$ ions may act as whole electron trapping centers for Mn$^{2+}$-doped glasses. Excitation band at 263 nm, second excitation band at 346 nm and the third band at 392 nm have been measured. The sharp excitation band at 263 nm is assigned to $^{6}A_{1g}(S)\rightarrow ^{4}A_{2g}(F)$, the band at 346 nm is assigned to the $^{6}A_{1g}(S)\rightarrow 4T_{2g}(D)$ of Mn$^{2+}$ ion, which exists in the UV-region in absorption spectrum. Similarly, the excitation band at 392 nm could coincide with the energy of $^{2}A_{1g}(S)\rightarrow ^{4}T_{2g}(G)$ absorption transition of Mn$^{2+}$ ion [18]. The excitation band at 392 nm is low in sharpness and intensity compared with 263 nm band. Under an UV source, Mn$^{2+}$:ZPB glasses have shown bright green color and it is strongly dependent on the co-ordination
environment of Mn$^{3+}$ in the host matrix, and it emits a green light when it is tetrahedrally co-ordinated (CN = 4), whereas it emits red in octahedral co-ordination (CN = 6). The emission spectra (Fig. 5) of Mn$^{3+}$:ZPB glass with excitation at 263 nm have exhibited a broad green band at 538 nm (0.2 mol%) and 536 nm (0.5 mol%) and these are assigned to the spin forbidden $^4T_{2}(G) \rightarrow ^6A_1 (S)$ transition of isolated Mn$^{3+}$ ions in tetrahedral symmetry (weak crystal field) [18,26]. According to Tanabe–Sugano diagrams for 3d$^5$ ions with decreasing crystal field strength, a blue shift of the $^4T_{1g} \rightarrow ^6A_1$ optical transition occurs [27,28]. An energy level scheme has been given in Fig. 6 to explain the mechanism involved in the emission process in the Mn$^{3+}$:ZPB glasses.

![Energy level scheme](image)

Fig. 6. Emission process in Mn$^{3+}$ :ZPB glasses.

![XRD profile](image)

Fig. 7. XRD profile of Ni$^{2+}$:ZPB glass.
4.2. Section B: Ni$^{2+}$-doped ZPB glasses

The XRD pattern of Ni$^{2+}$-ZPB glass has been presented in Fig. 7, which confirms the amorphous nature. From the UV-absorption spectra (Fig. 8) of Ni$^{2+}$-ZPB glasses, both direct and indirect optical band gaps have been calculated. The visible absorption spectra of Ni$^{2+}$ glasses have been shown in Fig. 9. A sharp absorption band at 424 nm, broad absorption band at 810 nm and a small band at 880 nm have been measured, and these are assigned to the spin allowed transition $^3A_{2g} \rightarrow T_{1g}(P)$ (424 nm), spin-forbidden transition $^3A_{2g}(F) \rightarrow ^1E_g(D)$ (810 nm) and spin allowed transition $^3A_{2g}(F) \rightarrow ^1T_{1g}(F)$ (880 nm) of Ni$^{2+}$ ions in octahedral co-ordination, respectively. According to ligand field theory, the lowest multiplet term $^3F$ of the free Ni$^{2+}$ ions splits into different levels through the anisotropic Host materials can affect the level splitting of...
Ni$^{2+}$ ion and hence the luminescence of the doped glass could be associated with the d-d optical transitions $^3A_{2g}(F) \rightarrow ^3T_{1g}(F)$, $^1E_g(D)$ and $^3T_{1g}(P)$, $^1T_{2g}(D) \rightarrow ^3T_{1g}(F)$ and $^3T_{2g}(F)$, so the energy levels of the excitation states of Ni$^{2+}$ are different with the matrices change [29-32]. Usually, two kinds of environments around Ni$^{2+}$ are proposed as octahedral and tetrahedral sites. In this system, the site symmetry around Ni$^{2+}$ can be ascribed to the former case that Ni$^{2+}$ is an ion with an exceptionally large crystal field stabilization energy (CFSE), particularly in an octahedral field. In fact, the d-d transitions of the tetrahedral complexes are electric dipole allowed; whereas those of the octahedral complexes are electric dipole forbidden, and which

![Excitation Spectrum of Ni$^{2+}$-ZPB Glass](image1.png)

**Fig. 10.** Excitation spectrum of Ni$^{2+}$-ZPB glass.

![Emission Spectra of Ni$^{2+}$-ZPB Glasses](image2.png)

**Fig. 11.** Emission spectra of Ni$^{2+}$-ZPB glasses.
occur mainly due to the static or dynamic distortions from the regular octahedral geometry, which partially removes the inversion center. Moreover, those could also be magnetic dipole allowed. As a consequence, their oscillator strengths are several orders of magnitude lower than that of tetrahedral. The excitation spectrum of 0.2 mol% Ni\textsuperscript{2+}:ZPB glass has been given in Fig. 10 with an emission \( \lambda_{em} = 670 \) nm. A sharp excitation band at 420 nm has been obtained which coincides with the absorption transition \( ^3A_2g (F) \rightarrow ^3T_1g (P) \) of Ni\textsuperscript{2+}-doped samples. The CT excitation bands at 374, 343, 321 nm for 0.2 mol\% Ni\textsuperscript{2+}-doped samples are observed. Fig. 11 presents the emission spectra of Ni\textsuperscript{2+} samples at an excitation with 420 nm. It reveals emissions at the green (577 nm) and at the red (670 nm) wavelengths. Following the energy levels of Ni\textsuperscript{2+} ions in octahedral sites, these emissions in green and red regions are assigned to \( ^1T_{2g} (D) \rightarrow ^1A_{2g} (F) \) and \( ^1T_{2g} (D) \rightarrow ^3T_{1g} (F) \) electronic transitions, respectively. At this excitation (420 nm), both the samples show emission peaks at the same position. However, the relative intensities of these peaks are changing considerably with Ni\textsuperscript{2+} ions concentration change. The green broad (577 nm) emission intensity is low compared to the sharp red band

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Fig. 12. Energy level scheme for emission process in Ni\textsuperscript{2+}:ZPB glass.

Fig. 13. XRD profile of Co\textsuperscript{2+}:ZPB glass.
(670 nm) emission intensity. For 0.2 mol% Ni^{2+} doped sample, green band intensity is slightly high compared to the red emission. But for 0.5 mol% Ni^{2+} sample, red emission increases considerably compared to the broad green emission intensity. Fig. 12 explains the mechanism involved in the emission process of Ni^{2+}:ZPB glass.

4.3. Section C: Co^{2+}-doped ZPB glasses

The XRD pattern of the Co^{2+}:ZPB glass has been shown in Fig. 13, which confirms the amorphous nature. Based on the UV absorption spectra of Co^{2+}:ZPB glasses (Fig. 14), both direct and indirect optical band gaps
have been calculated. The visible absorption spectra of Co$^{2+}$ glasses are shown in Fig. 15 and an absorption band at 590 nm and a broad absorption band centered at about 1466 nm could be noticed, and these are assigned to spin-forbidden transitions $^4A_2 ( ^4F) \rightarrow ^4T_1 ( ^4P)$ and $^4A_2 ( ^4F) \rightarrow ^4T_1 ( ^4P)$ of tetrahedrally co-ordinated Co$^{2+}$ ions [20,29]. The spectra of cobalt materials, their optical properties in the near infrared (1.3–1.6 μm) [ $^4A_2 ( ^4F) \rightarrow ^4T_1 ( ^4P)$] region of tetrahedrally co-ordinated Co$^{2+}$ ions are considered more important. The excitation spectra of Co$^{2+}$ glasses are shown in Fig. 16, with $\lambda_{em} = 625$ nm assigned to $^4A_2 \rightarrow ^4T_1 ( ^4P)$ transition of tetrahedrally co-ordinated Co$^{2+}$ ions. The metastable $^2E ( ^2G)$ energy level is assigned to the $^4A_2$ one of the tetrahedrally co-ordinated Co$^{2+}$ ion. Broad luminescence bands at 581 nm (0.2 mol%) and at 582 nm (0.5 mol%) have been attributed to the electric dipole allowed transition from the

![Fig. 16. Excitation spectra of Co$^{2+}$/ZPB glasses with emission at 630 nm.](image_url)

![Fig. 17. Emission spectra of Co$^{2+}$/ZPB glasses with $\lambda_{em} = 580$ nm.](image_url)
thermally populated \(^{4}T_{1}\) \((^{4}P)\) [30]. Fig. 17 shows emission spectra of Co\(^{2+}\)-ZPB glasses excited at 580 nm with an emission band at 631 nm (0.2 mol\%) and 625 nm (0.5 mol\%), which is assigned to the transition \(^{2}E\) (\(^{2}G\)) \(\rightarrow\) \(^{4}A_{2}\) \((^{4}P)\) of Co\(^{2+}\) ion in tetrahedral co-ordination [29]. Fig. 18 presents an energy level scheme to explain the emission phenomenon in Co\(^{2+}\)-ZPB glasses. The FTIR spectral features of Mn\(^{2+}\), Ni\(^{2+}\) and Co\(^{2+}\)-doped ZPB glasses have been measured, however; specimen profiles of Mn\(^{2+}\)-ZBS glasses are shown in Fig. 19. The FTIR band positions and their assignments along with the data concerning various physical property characteristic factors and also full-width at half-maximum (FWHM) data pertaining to the emission bands of these luminescent glasses are listed in Tables 1-7 for a comparison of the results thus obtained in the present study on these potential luminescent transition metal ions doped zinc lead borate optical glass systems.

Fig. 18. Energy level scheme for emission process in Co\(^{2+}\)-ZPB glass.

Fig. 19. FTIR spectra of Mn\(^{2+}\)-ZPB glasses.
**Table 1**

Physical properties of Mn"\(^{2+}\) (0.2, 0.5 mol%) Co"\(^{2+}\) (0.2, 0.5 mol%), Ni"\(^{2+}\) (0.2, 0.5 mol%) PbO-ZnO-B_2O_3 (ZPB) glasses

<table>
<thead>
<tr>
<th>Physical property parameters</th>
<th>Results</th>
</tr>
</thead>
<tbody>
<tr>
<td>Average molecular weight, (M(g))</td>
<td>167.309</td>
</tr>
<tr>
<td>Density, (\rho(g/cm^3))</td>
<td>4.973</td>
</tr>
<tr>
<td>Refractive index, (n_d) (599.3 nm)</td>
<td>1.910</td>
</tr>
<tr>
<td>Transition metal ion concentration, (N_1) ((10^2) ions/cm(^3))</td>
<td>0.3580</td>
</tr>
<tr>
<td>Polaron radius, (r_p) ((A^*))</td>
<td>2.6399</td>
</tr>
<tr>
<td>Interionic distance, (r_i) ((A^*))</td>
<td>15.297</td>
</tr>
<tr>
<td>Field strength, (F(\text{MV/cm}))</td>
<td>0.2983</td>
</tr>
<tr>
<td>Oxygen packing density (mol/cm(^3))</td>
<td>53.5616</td>
</tr>
<tr>
<td>Direct optical band gap (eV)</td>
<td>3.05</td>
</tr>
<tr>
<td>Indirect optical band gap (eV)</td>
<td>2.95</td>
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<tr>
<td>Glass transition temperature, (T_g) ((^\circ\text{C}))</td>
<td>426.7</td>
</tr>
<tr>
<td>Crystallization temperature, (T_c) ((^\circ\text{C}))</td>
<td>531.7</td>
</tr>
<tr>
<td>Temperature of setting, (T_s) ((^\circ\text{C}))</td>
<td>790.0</td>
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<tr>
<td>Glass stability factor, (S = T_s - T_g) ((^\circ\text{C}))</td>
<td>105</td>
</tr>
<tr>
<td>Hruby’s parameter ((K_{GR}) = \frac{T_c - T_g}{T_s - T_g})</td>
<td>0.3987</td>
</tr>
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</table>

**Table 2**

The IR transmission spectral peak positions and assignments in the range of (450-4000 cm\(^{-1}\)) for Mn"\(^{2+}\)-ZPB glass

<table>
<thead>
<tr>
<th>Mn&quot;(^{2+}) (mol%)</th>
<th>Peak positions (cm(^{-1}))</th>
<th>Assignments (Ref. [15])</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.2</td>
<td>534</td>
<td>Loose BO(_4) units and ZnO(_4) bonds</td>
</tr>
<tr>
<td>0.5</td>
<td>523, 538</td>
<td></td>
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<tr>
<td>0.2</td>
<td>695.85, 880</td>
<td>B-O-B bending vibrations</td>
</tr>
<tr>
<td>0.5</td>
<td>696.94, 887</td>
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<tr>
<td>0.2</td>
<td>1383.98</td>
<td>B-O stretching vibrations of (BO(_3))(^2-) units in meta, orthorate chains</td>
</tr>
<tr>
<td>0.5</td>
<td>1382.84</td>
<td></td>
</tr>
<tr>
<td>0.2</td>
<td>1600, 1635</td>
<td>Asymmetric stretching relaxation of the B-O band of trigonal BO(_3) unit</td>
</tr>
<tr>
<td>0.5</td>
<td>1720</td>
<td></td>
</tr>
<tr>
<td>0.2</td>
<td>3435.74, 3780</td>
<td>Molecular, water groups</td>
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<tr>
<td>0.5</td>
<td>3435.77</td>
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</table>

**Table 3**

FWHM (nm) the emission bands of Mn"\(^{2+}\)-ZPB glass

<table>
<thead>
<tr>
<th>Mn&quot;(^{2+}) (mol%)</th>
<th>Excitation (nm)</th>
<th>Emission (nm) (4T_{1g} (G) \rightarrow 4A_{1g} (S))</th>
<th>Emission band FWHM (nm)</th>
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</thead>
<tbody>
<tr>
<td>0.2</td>
<td>263</td>
<td>530</td>
<td>15</td>
</tr>
<tr>
<td>0.5</td>
<td>530</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

5. Conclusion

In summary, it is concluded that we have developed highly transparent and brightly colored Mn"\(^{2+}\), Co"\(^{2+}\), and Ni"\(^{2+}\) ions doped ZnO-PbO-B_2O_3 (ZPB) glasses for evaluating their optical potential as luminescent
Table 4
The FTIR transmission spectral peak positions and their assignments for Ni\(^{2+}\)-ZPB glass in the range from 4000 to 450 cm\(^{-1}\)

<table>
<thead>
<tr>
<th>Ni(^{2+}) ion concentration (mol%)</th>
<th>Peak positions (cm(^{-1}))</th>
<th>Assignments (Ref. [15])</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.2</td>
<td>476, 518, 598</td>
<td>Loose BO(_4) units and ZnO(_4) bonds</td>
</tr>
<tr>
<td>0.5</td>
<td>534.6</td>
<td>B-O-B bending vibrations</td>
</tr>
<tr>
<td>0.2</td>
<td>698.82, 875.76</td>
<td>B-O stretching vibrations of (BO(_3))^(^-) units in meta, orthohborate chains</td>
</tr>
<tr>
<td>0.5</td>
<td>698.44, 897.06</td>
<td></td>
</tr>
<tr>
<td>0.2</td>
<td>136.3</td>
<td>Asymmetric stretching relaxation of the H-O band of trigonal BO(_3) units</td>
</tr>
<tr>
<td>0.5</td>
<td>1763.61</td>
<td></td>
</tr>
<tr>
<td>0.2</td>
<td>3435.16</td>
<td>Molecular, water groups</td>
</tr>
<tr>
<td>0.5</td>
<td>3435.44</td>
<td></td>
</tr>
</tbody>
</table>

Table 5
FWHM (nm) values for the emission bands of Ni\(^{2+}\)-ZPB glass

<table>
<thead>
<tr>
<th>Ni(^{2+}) ion concentration (mol%)</th>
<th>Excitation (nm)</th>
<th>Emission band (nm)</th>
<th>Emission band FWHM (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.2</td>
<td>420</td>
<td>(^{1}T_{2g}) (D) \rightarrow (^{1}A_{2g}) (F)</td>
<td>10 (green)</td>
</tr>
<tr>
<td>0.5</td>
<td>420</td>
<td>(^{1}T_{2g}) (D) \rightarrow (^{1}T_{2g}) (F)</td>
<td>5 (red)</td>
</tr>
</tbody>
</table>

Table 6
The FTIR transmission spectral peak positions and their assignments for Cu\(^{2+}\)-ZPB glass in the range from 4000 to 450 cm\(^{-1}\)

<table>
<thead>
<tr>
<th>Cu(^{2+}) ion concentration (mol%)</th>
<th>Peak positions (cm(^{-1}))</th>
<th>Assignment (Ref. [15])</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.2</td>
<td>534.55</td>
<td>Loose BO(_4) units and ZnO(_4) bonds</td>
</tr>
<tr>
<td>0.5</td>
<td>535.76, 598.75</td>
<td>B-O-B bending vibrations</td>
</tr>
<tr>
<td>0.2</td>
<td>699.95, 982.90</td>
<td>B-O stretching vibrations of (BO(_3))^(^-) units in meta, orthohborate chains</td>
</tr>
<tr>
<td>0.5</td>
<td>664.64, 705, 887.02</td>
<td></td>
</tr>
<tr>
<td>0.2</td>
<td>1197.90, 1367.51</td>
<td>B-O stretching vibrations of (BO(_3))^(^-) units in meta, orthohborate chains</td>
</tr>
<tr>
<td>0.5</td>
<td>1199.41, 1367.22</td>
<td></td>
</tr>
<tr>
<td>0.2</td>
<td>1634.38</td>
<td>Asymmetric stretching relaxation of the B-O band of trigonal BO(_3) units</td>
</tr>
<tr>
<td>0.5</td>
<td>1647.79, 1735</td>
<td></td>
</tr>
<tr>
<td>0.2</td>
<td>3435.64</td>
<td>Molecular, water groups</td>
</tr>
<tr>
<td>0.5</td>
<td>3435.43, 3747.57</td>
<td></td>
</tr>
</tbody>
</table>

Table 7
FWHM (nm) values for the emission bands of Cu\(^{2+}\)-ZPB glass

<table>
<thead>
<tr>
<th>Cu(^{2+}) ion concentration (mol%)</th>
<th>Excitation (nm)</th>
<th>Emission (nm) (^{2}E) ((^{2}G)) \rightarrow (^{4}A_{2g}) ((^{4}F))</th>
<th>Emission band FWHM (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.2</td>
<td>580</td>
<td>631</td>
<td>13</td>
</tr>
<tr>
<td>0.5</td>
<td>580</td>
<td>625</td>
<td>7</td>
</tr>
</tbody>
</table>

materials based on their absorption, excitation, emission spectral results. All the features given in various figures and the results tabulated in different tables of the present work are considered to be more useful results towards the progress of transition metal ions doped optical glasses. Due to the availability of Zn and Pb ions
in the ZPB glasses, they have been found to possess good resistance towards the humidity conditions in the laboratory even up to several months together. XRD profiles have confirmed their glassy nature more clearly and the FTIR profiles have been used to understand the bonding nature of these glasses. The analysis made through various optical tools strongly suggest that these glasses have potential applications as luminescent optical materials.

Acknowledgments

One of us (A. T. R.) would like to thank his research colleague Mr. G. Lakshminarayana and also Dr. K. P. C. Gandhi, Director of FSL, Hyderabad, India for his kind permission and cooperation in the present work.

References


Optical characterization of Eu$^{3+}$ and Tb$^{3+}$ ions
doped zinc lead borate glasses

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Received 18 October 2005; accepted 27 February 2006

Abstract

This paper reports on the spectral analysis of Eu$^{3+}$ or Tb$^{3+}$ ions (0.5 mol%) doped heavy metal oxide (HMO) based zinc lead borate glasses from the measurement of their absorption, emission spectra and also different physical properties. From the XRD, DSC profiles, the glass nature and glass thermal properties have been studied. The measured emission spectrum of Eu$^{3+}$ glass has revealed five transitions ($^5D_{0} \rightarrow ^7F_{1}$, $^7F_{2}$, $^7F_{3}$, $^7F_{4}$, and $^7F_{6}$) at 578, 591, 613, 654 and 702 nm, respectively, with $\lambda_{max} = 592$ nm ($^5D_{0} \rightarrow ^7F_{1}$). In the case of Tb$^{3+}$-ZLB glass, four emission transitions such as ($^5D_{4} \rightarrow ^7F_{1}$, $^7F_{2}$, $^7F_{3}$, $^7F_{4}$, and $^7F_{6}$) that are located at 489, 541, 585 and 622 nm, respectively, have been measured with $\lambda_{max} = 541$ nm. For all these emission bands decay curves have been plotted to evaluate their lifetimes and the emission processes that arise in the glasses have been explained in terms of energy level schemes.

Keywords: Zinc lead borate glasses; Optical properties

1. Introduction

Towards the development of luminescent glassy materials with certain transition or rare earth ions from literature it has been made quite clear that Bi$_2$O$_3$ could be used as a good network-former (NWF) and two other chemicals such as ZnO and PbO could be found as network-modifiers (NWM) when these are added to the Bi$_2$O$_3$ content. It has also been noticed that the presence of ZnO content in the glassy matrix, stability of the material becomes stronger, with a high thermal resistance against the crystallization [1]. Over the past several years, a great deal of work has been carried out to understand the spectral properties of different optical materials [2–9]. We have recently reported the results concerning the optical properties of certain divalent transition metal ions namely Cu$^{2+}$-ZLB glass [10] and Mn$^{2+}$, Co$^{2+}$ and Ni$^{2+}$-ZLB glass [11]. 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 ZLB glasses. Rare-earth ions (RE$^{3+}$) would generally be existing in the trivalent state, of which the 4f$^{1}$ configuration could be found relatively isolated and the next excited 4f$^{1}$-5d configuration lies in the high energy level above the ground state of the 4f$^{1}$ configuration [4] and hence the electronic configuration causes the display of more sharp absorption or emission bands because of the intra-f-transitions. For quite sometime it has been known that rare earth ions doped optical glassy materials have attracted a great deal of attention in different laboratories for a wide variety of applications [12–16]. The red color emitting rare earth ion namely Eu$^{3+}$ (4f$^{1}$) ion has a lower lying excited level ($^5D_{0}$) to reveal intense and sharp emission transitions [13] with the $^3D_{0}$ as the ground state. Similarly the green color-emitting ion namely Tb$^{3+}$ (4f$^{1}$) could reveal more bright and line-like excitation and emission bands [17,18] with $^5D_{4}$ as the ground state in the UV-vis wavelength region.

2. Experimental studies

2.1. Glasses preparation

The chemicals used were reagent grade of H$_3$BO$_3$, ZnO, PbO, Eu$_2$O$_3$, Er$_2$O$_3$ and Tb$_2$O$_3$. The chemical compositions of these Eu$^{3+}$ and Tb$^{3+}$ (0.5 mol%) doped glasses are as follows:

40Bi$_2$O$_3$-15PbO-44.5ZnO-0.5Eu$_2$O$_3$ (Eu$^{3+}$: ZLB glass)
Glass densities were measured with the tolerance as the immersion liquid by applying the conventional Archimedes principle. An Abbe-refractometer was employed to measure the glass refractive index with a sodium Abbe-refractometer. Glass densities were measured on a Netzsch STA 409C system in the temperature range of 30–1200°C, at the rate of 10°C/min, under N2 gas atmosphere. The optical absorption spectra of Eu3+ and Tb3+ glasses were measured on a Varian-Cary Win Spectrophotometer. Both the excitation and emission spectra of Eu3+ and Tb3+ were measured on a SPEX Fluorolog-2 (Model-F-11) fitted with a Xe-arc lamp (150 W) and the spectral data was acquired based on the Datamax software on the computer system. To measure the lifetimes of the emission bands from this system, Xe-flash lamp was arranged to the system alongside a phosphorimeter attachment. Table 1 presents different physical properties of Eu3+ and Tb3+ doped ZLB glasses that were computed based on the different mathematical expressions reported earlier in literature [12, 19]. For 0.5 mol% Eu3+ and Tb3+ ions doped glasses, the values of glass transition (Tg), crystallization (Tc) and melting (Tm) temperatures were located and from these parameters, glass stability factors (S) and also related Hubry's parameters (Kh) were computed [12] and the obtained results are given in Table 1. The glass stability factor clearly indicates that these glasses posses more stability, whereas, Hubry's parameter describes the stability of the glass against the devitrification.  

### Table 1  

<table>
<thead>
<tr>
<th>Eu3+ (0.5 mol%)</th>
<th>Tb3+ (0.5 mol%)</th>
<th>ZnO-PbO-B2O3 glasses</th>
</tr>
</thead>
<tbody>
<tr>
<td>Physical properties of Eu3+ (0.5 mol%) and Tb3+ (0.5 mol%)</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>Physical quantities</td>
<td>Results</td>
</tr>
<tr>
<td></td>
<td>Average molecular weight, M (g)</td>
<td>168.65</td>
</tr>
<tr>
<td></td>
<td>Density, d (g/cm³)</td>
<td>4.992</td>
</tr>
<tr>
<td></td>
<td>Reflective index, nα (589.3 nm)</td>
<td>1.9129</td>
</tr>
<tr>
<td></td>
<td>Rare-earth ion concentration, N (10²² ions/cm³)</td>
<td>0.8925</td>
</tr>
<tr>
<td></td>
<td>Interionic distance, r (Å)</td>
<td>4.820</td>
</tr>
<tr>
<td></td>
<td>Glass transition temperature, Tg (°C)</td>
<td>421.2</td>
</tr>
<tr>
<td></td>
<td>Crystallization temperature, Tc (°C)</td>
<td>544.3</td>
</tr>
<tr>
<td></td>
<td>Temperature of melting, Tm (°C)</td>
<td>873.1</td>
</tr>
<tr>
<td></td>
<td>Glass stability factor, S = Tg − Tc (°C)</td>
<td>143.1</td>
</tr>
<tr>
<td></td>
<td>Hubry s parameter, Kh = (Tg − Tc)/(Tm − Tg)</td>
<td>0.466</td>
</tr>
</tbody>
</table>

**Fig. 1.** Photograph showing both (A) reference and (B) Eu3+–ZLB glass and (C) Tb3+–ZLB glass.

**Fig. 2.** XRD profile of Eu3+–ZLB glass.

The X-ray diffraction pattern of the glass Eu3+: 44.5ZnO–15PbO–40B2O3 is shown in Fig. 2, which con-
firms the glass amorphous nature and the DSC thermogram of the Eu$^{3+}$ glass is shown in Fig. 3, and from this we have identified the glass transition [$T_g$], crystallization [$T_c$], and the melting [$T_m$] temperatures. The absorption spectrum of Eu$^{3+}$ ion is shown in Fig. 4, with four weak absorption bands such as $T_0 \rightarrow T_1$ (392 nm), $T_0 \rightarrow T_2$ (462 nm), $T_0 \rightarrow T_3$ (530 nm) and $T_0 \rightarrow T_4$ (580 nm), the assignments have been made following a recently published article [19]. Excitation spectrum of Eu$^{3+}$ glass (Fig. 5) shows four excitation bands such as $T_0 \rightarrow T_1$ (358 nm), $T_0 \rightarrow T_2$ (374 nm), $T_0 \rightarrow T_3$ (392 nm), $T_0 \rightarrow T_4$ (412 nm). Among these, a prominent excitation band $T_0 \rightarrow T_4$ at 392 nm has been chosen to measure the emission spectrum of Eu$^{3+}$-ZLB glass (Fig. 6) with five emission transitions of $T_4 \rightarrow T_0$ (578 nm), $T_4 \rightarrow T_3$ (591 nm), $T_4 \rightarrow T_2$ (613 nm), $T_4 \rightarrow T_1$ (654 nm), $T_4 \rightarrow T_0$ (702 nm) as was reported previously in literature [20,21]. Due to the shielding effect of 4f electrons by 5s and 5p electrons in outer shells in the Eu$^{3+}$ ion, narrow emission bands are arising. Among these five emission bands the transition $T_4 \rightarrow T_0$ (613 nm) has shown a strong red emission. The $T_4 \rightarrow T_3$ transitions are electric dipole (ED) transitions and the red emission ($T_4 \rightarrow T_0$) is a hypersensitive transition that follows the selection rule of $\Delta J = 2$ and another transition $T_4 \rightarrow T_1$ with $\Delta J = 1$ could be found as a magnetic dipole transition [21]. In glassy materials, due to the absence of a centre of symmetry, a mixing of the 4f orbitals with opposite parity orbitals could be taking place and therefore electric dipole transitions would be arising [21,22]. The absence of emissions from the excited levels of $^5D_{J=1,2,3}$ could be due to the presence of high energy phonons in the glasses, i.e. when the Eu$^{3+}$ ions are excited to any level above the $^5D_0$, there could be a fast non-radiative multiphonon relaxation takes place at this level and also because of the fact that emission from $^5D_{J=2,3}$ to the $^5F_2$ levels would be found several orders of magnitude smaller compared to that of $^5D_0 \rightarrow T_2$ transitions, hence the emissions from these three excited states could not take place and so those could remain to suppressed. Therefore, $\sum T_4 \rightarrow T_J$ F$_2$ emission intensities could be considered to represent the total emission intensity of the Eu$^{3+}$ glass studied, as was done earlier in literature [21]. Fig. 7 explains the emission mechanism process in
The X-ray diffraction pattern of the glass Eu³⁺:ZLB glass is shown in Fig. 9, which confirms the glass amorphous nature and the DSC thermogram for the

![XRD profile of Tb³⁺:ZLB glass.](image)

Fig. 9. XRD profile of Tb³⁺:ZLB glass.

Table 2

<table>
<thead>
<tr>
<th>Emission transitions</th>
<th>λ_p (nm)</th>
<th>Δλ_p (nm)</th>
<th>τ_m (ns)</th>
<th>σ² (10⁹) cm²</th>
</tr>
</thead>
<tbody>
<tr>
<td>Eu³⁺:ZLB glass</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>2D₁₀ → T₁₀</td>
<td>578</td>
<td>4</td>
<td>1.90</td>
<td>0.929</td>
</tr>
<tr>
<td>2D₁₀ → T₁₂</td>
<td>591</td>
<td>14</td>
<td>1.67</td>
<td>0.189</td>
</tr>
<tr>
<td>2D₁₀ → T₁₂</td>
<td>643</td>
<td>13</td>
<td>2.35</td>
<td>0.168</td>
</tr>
<tr>
<td>2D₁₀ → T₁₄</td>
<td>654</td>
<td>8</td>
<td>1.21</td>
<td>0.686</td>
</tr>
<tr>
<td>2D₁₀ → T₁₂</td>
<td>792</td>
<td>12</td>
<td>1.48</td>
<td>0.514</td>
</tr>
<tr>
<td>Tb³⁺:ZLB glass</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>3D₁₄ → T₁₀</td>
<td>489</td>
<td>12</td>
<td>1.44</td>
<td>0.120</td>
</tr>
<tr>
<td>3D₁₄ → T₁₂</td>
<td>542</td>
<td>11</td>
<td>2.38</td>
<td>0.119</td>
</tr>
<tr>
<td>3D₁₄ → T₁₄</td>
<td>585</td>
<td>13</td>
<td>3.39</td>
<td>0.277</td>
</tr>
<tr>
<td>3D₁₄ → T₁₄</td>
<td>622</td>
<td>10</td>
<td>1.02</td>
<td>0.532</td>
</tr>
</tbody>
</table>

Fig. 8 presents the decay curves of the emission bands of Eu³⁺:ZLB glass along with their lifetimes in the same figure.

3.2. Tb³⁺:ZLB glass

The X-ray diffraction pattern of the glass Tb³⁺ (0.5mol%): 44.5ZnO-15PbO-40B₂O₃ is shown in Fig. 10, which confirms the glass amorphous nature and the DSC thermogram for the

![Decay curves of the emission transitions of Eu³⁺:ZLB glass.](image)

Fig. 8. Decay curves of the emission transitions of Eu³⁺:ZLB glass.

![Decay curves of the emission transitions of Tb³⁺:ZLB glass.](image)

Fig. 10. Decay curves of the emission transitions of Tb³⁺:ZLB glass.
In 1011 ran MHI

Excitation spectrum of Th\textsuperscript{3+} glass with two excitation peaks, \(\text{Th}^{3+} \rightarrow \text{H}_{4+} (292 \text{ nm})\) and \(\text{Th}^{3+} \rightarrow \text{G}_{6} (374 \text{ nm})\) based on the energy levels reported earlier \([23,24]\). Fig. 11 shows the emission spectrum of the Th\textsuperscript{3+} glass with \(\lambda_{ex} = 374 \text{ nm}\). The emission transitions are all found to be intense and shapeless bands due to the f–f inner shell transitions, from the excited level in the lower level such as \(\text{D}_{4} \rightarrow \text{F}_{3} \) (0–6) for Th\textsuperscript{3+}. The intense green emission is at 542 nm, which arises from the Laporte-forbidden \(\text{D}_{4} \rightarrow \text{F}_{3}\) transition \([23]\). From emission spectrum, transitions such as \(\text{D}_{4} \rightarrow \text{F}_{5} (489 \text{ nm}), \text{D}_{4} \rightarrow \text{F}_{3} (542 \text{ nm}), \text{D}_{4} \rightarrow \text{F}_{4} (585 \text{ nm}), \text{D}_{4} \rightarrow \text{F}_{5} (622 \text{ nm})\) has been identified \([23–25]\).
The transition \(\text{D}_{4} \rightarrow \text{F}_{3}\) obeys the magnetic dipole transition selection rule of \(\Delta J = \pm 1\) \([26–28]\) and Fig. 14 describes the emission process with the 374 nm excitation wavelength. Fig. 15 presents the decay curves of the emission transitions of the Th\textsuperscript{3+}\text{-ZLB} glass. As has been carried out for the Eu\textsuperscript{3+}\text{-ZLB} glass, for the emission bands of Th\textsuperscript{3+}\text{-ZLB} glass also, the stimulated emission cross-sections \((\sigma^E \text{ cm}^2)\) have been calculated and the results are given in Table 2.

![Absorption spectrum of Th\textsuperscript{3+}\text{-ZLB} glass](image)

![Excitation spectrum of Th\textsuperscript{3+}\text{-ZLB} glass](image)

![Emission spectrum of Th\textsuperscript{3+}\text{-ZLB} glass](image)

![Emission process in Th\textsuperscript{3+}\text{-ZLB} glass](image)
determine the emission watched red colors glasses. Thus based on various results documented the measurement of the absorption, excitation, and emission spectra. Glass amorphous nature and thermal properties have been understood from the measurement of XRD, DSC profiles. Apart from analyzing the optical properties of these glasses, we have watched a bright red (Eu$^{3+}$-ZLB glass) and a green (Th$^{4+}$-ZLB glass) emissions from these glasses when those are placed under an UV source. We have plotted the decay curves in order to determine the emission lifetimes and use those to compute the simulated emission cross-sections for the glasses studied and thus based on various results documented in Tables 1 and 2 and from Figs. 1–15, we could suggest these heavy metal oxide based glasses are highly potential enough towards the display of green (Th$^{4+}$) and red (Eu$^{3+}$) haminescence colors. Such primary (green, red) colors enabling materials are of significant importance in the development of emission rich optical systems.

Acknowledgements

One of us (ATR) would like to thank his research colleague Mr. G. Lakshminarayana and also Dr. K.P.C. Gandhi, Director, FSL, Hyderabad, India, for his kind permission and co-operation in the present work.

References

Optical characterization of Sm$^{3+}$ and Dy$^{3+}$:ZnO−PbO−B$_2$O$_3$ glasses

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Received 30 May 2006; accepted 31 August 2006

Abstract

Here, we present the results of the analysis of Sm$^{3+}$ or Dy$^{3+}$ (0.5 mol%) doped heavy metal oxide (HMO)-based zinc lead borate (ZLB) glasses. Optical measurements such as absorption, emission spectra, lifetime, XRD, DSC profiles have been carried out. The emission spectrum of Sm$^{3+}$:ZLB has shown the emission transitions of $^{4}S_{3/2} ightarrow ^{4}P_{3/2}$ (579 nm), $^{4}S_{3/2} ightarrow ^{4}P_{5/2}$ (592 nm), $^{4}S_{3/2} ightarrow ^{4}D_{5/2}$ (708 nm) with $^{4}P_{3/2}$ (476 nm) and $^{4}P_{5/2}$ (492 nm). In the case of the Dy$^{3+}$:ZLB glass, emission transition of $^{4}H_{11/2} ightarrow ^{4}I_{15/2}$ (485 nm), $^{4}H_{11/2} ightarrow ^{4}I_{13/2}$ (571 nm) and $^{4}H_{11/2} ightarrow ^{4}I_{15/2}$ (664 nm) with $^{4}F_{3/2}$ (579 nm) and $^{4}F_{5/2}$ (587 nm) have been identified. Energy level schemes relating to the emission mechanisms involved in Sm$^{3+}$ and Dy$^{3+}$ glasses have been given.

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Keywords: Sm$^{3+}$ and Dy$^{3+}$ glasses; Emission analysis

1. Introduction

Importance of HMO (heavy metal oxide) glasses has earlier been reported in literature [1−4]. Heavy metal oxide (PhO) based highly transparent optical glass systems in the general composition of $\text{ZnO}−15\text{PbO}−(85−x)\text{B}_2\text{O}_3$ with $x = 0, 5, 10, 15, . . . , 45\%$ have recently been developed by us with Cu$^{2+}$ (3d$^9$) as the dopant transition metal ion for its systematic optical characterization [5]. Subsequently, in the same host, we have also investigated three more transition metal ions such as Mn$^{2+}$ (3d$^{5}$), Co$^{2+}$ (3d$^{6}$), and Ni$^{2+}$ (3d$^{8}$) for their optical analysis [6]. Later, we have made an attempt to analyze the luminescence spectral properties of two rare earth ions such as Eu$^{3+}$ (4f$^1$) and Tb$^{3+}$ (4f$^3$) in these HMO glasses, have shown interesting and encouraging results have been reported by us quite recently [7]. These two rare earth ions have shown prominent emissions (red and green) in the visible wavelength region. In the present work our main objectives are to study both the absorption and photoluminescence spectral properties of two other important rare earth ions: Sm$^{3+}$ (4f$^1$) and Dy$^{3+}$ (4f$^1$) as they have strong absorption bands in the NIR wavelengths (800−2200 nm) and intense emission bands in the visible (550−730 nm) region.

2. Experimental studies

2.1. Glass preparation

Following are the Sm$^{3+}$ or Dy$^{3+}$ (0.5 mol%) doped zinc lead based borate (ZLB) glasses along with a reference glass (RG):

- Sm$^{3+}$:ZLB-44.52ZnO-15PbO-40B$_2$O$_3$;
- Dy$^{3+}$:ZLB-44.52ZnO-15PbO-40B$_2$O$_3$;
- RO:ZLB-45.02ZnO-15PbO-40B$_2$O$_3$.

The starting materials used in the present work were reagent grade chemicals of H$_2$BO$_3$, ZnO, PbO, Sm$_2$O$_3$ and Dy$_2$O$_3$. All the weighed chemicals were powdered, finely and mixed thoroughly before each batch (10 g) was melted in ceramic crucibles in an electrical furnace for 1 h, at 950 °C. These melts were quenched in between two brass plates to obtain optical glasses in circular design (2−3 cm) in diameter with a thickness of 0.3 cm. These glasses thus obtained were all annealed at 200 °C for 1 h, to remove possible thermal strains in the glasses. Fig. 1 presents the photographs of Sm$^{3+}$, Dy$^{3+}$ glasses and the reference glass as well.

2.2. Measurements

Glass densities were measured with terthane as an immersion liquid, Abbe refractometer was used to measure the glass.
refractive index at Na lamp (589.3 nm) wavelength. Powder X-ray diffraction spectra were obtained on a Shimadzu XD3A diffractometer with a Ni filter and Cu Kα (1.5418 Å) radiation with an applied voltage of 30kV and 20 mA anode current calibrated with Si at the rate of 2° C/min⁻¹. DSC profiles were carried out on a Netzsch STA 409 C in the temperature range of 30–1200°C, at the rate of 10°C/min⁻¹, under the N₂-gas atmosphere. The optical absorption spectra (400–2500 nm) were measured on a Varian–Cary Win spectrometer. The excitation and emission spectra were obtained on a SPEX Fluorolog-2 Fluorimeter (Model-II) with a Datamax software to acquire the data with a Xe-arc lamp (150 W) as the excitation source. A Xe-flash lamp with a phosphorimeter attachment has been used to measure the lifetimes of the emission transitions of Sm³⁺ and Dy³⁺ glasses. Table 1 presents the physical properties of Sm³⁺ and Dy³⁺ ions doped glasses. From the DSC profile, the values of T_p, T_c, and T_m were evaluated, and from these the values of glass stability factor (S), Hruby’s parameter (K_H) were calculated and the results are given in Table 1.

### Table 1

<table>
<thead>
<tr>
<th>Physical property</th>
<th>Results</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sm³⁺ (0.5 mol%)</td>
<td>Dy³⁺ (0.5 mol%)</td>
</tr>
<tr>
<td>Average molecular weight, M (g)</td>
<td>168.635</td>
</tr>
<tr>
<td>Density, d (g/cm³)</td>
<td>4.992</td>
</tr>
<tr>
<td>Refractive index, n (589.3 nm)</td>
<td>1.9120</td>
</tr>
<tr>
<td>Rare earth ion concentration, N</td>
<td>0.8915</td>
</tr>
<tr>
<td>Polarization radius, r_p (Å)</td>
<td>1.9431</td>
</tr>
<tr>
<td>Ionic distance, r (Å)</td>
<td>4.822</td>
</tr>
<tr>
<td>Field strength, F (x 10⁵ cm⁻²)</td>
<td>0.7047</td>
</tr>
<tr>
<td>Direct optical band gap (eV)</td>
<td>2.96</td>
</tr>
<tr>
<td>Indirect optical band gap (eV)</td>
<td>2.83</td>
</tr>
<tr>
<td>Glass transition temperature, T_g (°C)</td>
<td>421.2</td>
</tr>
<tr>
<td>Crystallization temperature, T_c (°C)</td>
<td>575.74</td>
</tr>
<tr>
<td>Melting temperature, T_m (°C)</td>
<td>1075.6</td>
</tr>
<tr>
<td>Glass stability factor, S = T_g - T_f (°C)</td>
<td>154.54</td>
</tr>
<tr>
<td>Hruby’s parameter, K_H = (T_c - T_f)/(T_m - T_g)</td>
<td>0.321</td>
</tr>
</tbody>
</table>

3. Results and discussion

3.1. Sm³⁺:ZLB glass

The X-ray diffraction pattern of the (0.5 mol%) Sm³⁺:4.4ZrO₁₋₁PrO₄O₂ glass is shown in Fig. 2, which confirms its amorphous nature. The differential scanning calorimeter (DSC) thermogram for the Sm³⁺:glass is shown in Fig. 3, from this, glass transition temperature (T_g), crystallization temperature (T_c), and melting temperature (T_m) are located and the data are presented in Table 1. Both the direct and indirect optical band gap has also been computed from the UV absorption spectra of Sm³⁺:glass following the procedure given by us earlier [5] and the results are presented in listed out in Table 1. The X-ray-NIR absorption spectrum of Sm³⁺ ion is shown in Fig. 4, with intense absorption bands in the NIR region. All transitions in the absorption spectrum of Sm³⁺ start from the ground state 5H₅ of the various upper states [8]. Absorption bands have been assigned to the transition of 5H₅ → 5F₁₂, 5F₁₀, 5F₉, 5F₇, 5F₅, 5H₃, H₃, and 5F₁₂ at 945, 1083, 1232, 1379, 1482, 1541 and 1592 nm, respectively [9]. Optical densities of the seven absorption bands have been measured and the data are given in Table 2.

![Fig. 1. Photographs of glasses: a reference glass RG, Sm³⁺ and Dy³⁺:ZLB glasses.](image)

![Fig. 2. XRD spectrum of Sm³⁺:ZLB glass.](image)
excitation at 401 nm has been selected for the measurement of emission spectrum of Sm$^{3+}$-glass. When the $4f_{5/2}$ level (401 nm) of Sm$^{3+}$ is excited, the initial population relaxes finally to the $4f_{7/2}$ level, between $4f_{5/2}$ and $4f_{7/2}$ levels; there are several levels with smaller energy differences, which encourage their efficient non-radiative relaxation leading to the population of the $4f_{5/2}$ state [10]. This state is separated from the next lower lying $4f_{11/2}$ by about 7000 cm$^{-1}$, which makes the multi phonon relaxation as negligible. Thus it could be stated that radiative transitions and relaxations by non-radiative energy transfer could be considered as two main processes, which could finally depopulates the $4f_{5/2}$ state [11]. Fig. 6 presents emission spectrum of Sm$^{3+}$-glass, with four emission transitions, of $^4G_{5/2} ightarrow ^4H_{5/2}$ (563 nm), $^4G_{5/2} ightarrow ^4H_{11/2}$ (590 nm), $^4G_{7/2} ightarrow ^4H_{15/2}$ (646 nm), and $^4G_{7/2} ightarrow ^4H_{11/2}$ (708 nm) transitions. Among these four, the transition $^4G_{5/2} ightarrow ^4H_{5/2}$ (590 nm) has shown a strong emission. The Sm$^{3+}$-glass shows a bright orange-redish emission under an UV source [12-14]. The transition $^4G_{5/2} ightarrow ^4H_{11/2}$ with $\Delta \varepsilon \geq 1$ is a magnetic dipole (MD) allowed but it is an electric dipole (ED) dominated. The another transition $^4G_{7/2} ightarrow ^4H_{11/2}$ is purely an electric dipole transition [15,16]. Generally the intensity ratio between ED and MD transition could be used to measure the symmetry of the local environment of the trivalent 4f ions. Greater the intensity

Table 2
Absorption bands of Sm$^{3+}$ and Dy$^{3+}$-ZLB glasses

<table>
<thead>
<tr>
<th>Energy (cm$^{-1}$)</th>
<th>Optical density (a.u.)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$^4F_{5/2}$</td>
<td>10,904</td>
</tr>
<tr>
<td>$^4F_{7/2}$</td>
<td>9,233</td>
</tr>
<tr>
<td>$^4F_{9/2}$</td>
<td>8,116</td>
</tr>
<tr>
<td>$^4F_{11/2}$</td>
<td>7,251</td>
</tr>
<tr>
<td>$^4F_{13/2}$</td>
<td>6,747</td>
</tr>
<tr>
<td>$^4H_{11/2}$</td>
<td>6,489</td>
</tr>
<tr>
<td>$^4F_{15/2}$</td>
<td>6,281</td>
</tr>
</tbody>
</table>

Absorption bands from the ground $^3H_{5/2}$ Dy$^{3+}$-ZLB glass

<table>
<thead>
<tr>
<th>Energy (cm$^{-1}$)</th>
<th>Optical density (a.u.)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$^4F_{5/2}$</td>
<td>11,245</td>
</tr>
<tr>
<td>$^4F_{7/2}$</td>
<td>12,422</td>
</tr>
<tr>
<td>$^4F_{9/2}$</td>
<td>11,037</td>
</tr>
<tr>
<td>$^4F_{11/2}$</td>
<td>9,124</td>
</tr>
<tr>
<td>$^4F_{13/2}$</td>
<td>7,839</td>
</tr>
<tr>
<td>$^4F_{15/2}$</td>
<td>5,949</td>
</tr>
</tbody>
</table>
of the ED transitions; more the asymmetry nature [17]. The transition \( \text{Gd}^{3+} \rightarrow \text{H}_{\text{a}} \) which is an electric dipole in nature has more intensity over the MD transition \( \text{Gd}^{3+} \rightarrow \text{H}_{\text{b}} \) which specifies the asymmetric nature of glass host. The Fig. 7 presents the decay curves of the emission transitions of \( \text{Sm}^{3+}:\text{ZLB} \) glass with the lifetimes. From the measured fluorescence emission spectrum, the emission peak wavelength \( \lambda_{\text{p}} \), lifetimes \( \tau_{\text{p}} \) full width at half maximum (FWHM), \( \Delta \lambda_{\text{p}} \) are calculated and with these prominent intensity ratio \( \text{r}_{\text{Gd}^{3+}} = \text{Gd}^{3+} \rightarrow \text{H}_{\text{a}} \text{Gd}^{3+} \rightarrow \text{H}_{\text{a}} \), \( \text{Gd}^{3+} \rightarrow \text{H}_{\text{b}} \text{Gd}^{3+} \rightarrow \text{H}_{\text{b}} \), \( \text{Gd}^{3+} \rightarrow \text{H}_{\text{c}} \text{Gd}^{3+} \rightarrow \text{H}_{\text{c}} \), \( \text{Gd}^{3+} \rightarrow \text{H}_{\text{d}} \text{Gd}^{3+} \rightarrow \text{H}_{\text{d}} \) gives more information about the covalency and site symmetry [18] and results are listed out in Table 3.

Fig. 8 describes the energy level scheme involved in the emission process with \( \lambda_{\text{em}} = 401 \text{ nm} \).

### 3.2. Dy\(^{3+}\) glass

X-ray diffraction pattern of the 0.5 mol% \( \text{Dy}^{3+}:44.5\% \text{ZnO}-15\% \text{B}_{2} \text{O}_{3} \) glass is shown in Fig. 9 which confirms its amorphous nature. The DSC thermogram for the \( \text{Dy}^{3+}\)-glass is shown in Fig. 10 and from this glass transition \( \left( T_{\text{g}} \right) \), crystallization \( \left( T_{\text{c}} \right) \) and melting \( \left( T_{\text{m}} \right) \) temperatures have been identified and the results are shown in Table 1. Both the direct and the indirect

| Table 3 | Emission peak wavelength \( \lambda_{\text{p}} \), full-width at half-maximum (FWHM, \( \Delta \lambda_{\text{p}} \)), lifetimes \( \tau_{\text{p}} \) of different emission transitions of \( \text{Sm}^{3+} \) and \( \text{Dy}^{3+} \) glasses |
|-----------------|-----------------|-----------------|-----------------|
| Emission transitions | \( \lambda_{\text{p}} \) (nm) | \( \Delta \lambda_{\text{p}} \) (nm) | \( \tau_{\text{p}} \) (ns) |
| (i) \( \text{Sm}^{3+:\text{ZnO}-15\% \text{B}_{2} \text{O}_{3}} \) glass measured with \( \lambda_{\text{em}} = 401 \text{ nm} \) | \( \text{Gd}^{3+} \rightarrow \text{H}_{\text{a}} \) | 593 | 11 | 1.45 |
| | \( \text{Gd}^{3+} \rightarrow \text{H}_{\text{b}} \) | 598 | 17 | 1.85 |
| | \( \text{Gd}^{3+} \rightarrow \text{H}_{\text{c}} \) | 646 | 18 | 1.55 |
| | \( \text{Gd}^{3+} \rightarrow \text{H}_{\text{d}} \) | 708 | 9 | 1.00 |
| | \( \text{Gd}^{3+} \rightarrow \text{H}_{\text{a}} \text{Gd}^{3+} \rightarrow \text{H}_{\text{a}} \) | 1049 | 0.005 | 0.24 |
| (ii) \( \text{Dy}^{3+:\text{ZnO}-15\% \text{B}_{2} \text{O}_{3}} \) glass measured with \( \lambda_{\text{em}} = 447 \text{ nm} \) | \( \text{F}_{\text{a}} \rightarrow \text{H}_{\text{a}} \) | 445 | 18 | 0.23 |
| | \( \text{F}_{\text{a}} \rightarrow \text{H}_{\text{a}} \) | 575 | 17 | 0.85 |
| | \( \text{F}_{\text{a}} \rightarrow \text{H}_{\text{a}} \) | 664 | 16 | * |
| | \( \text{F}_{\text{a}} \rightarrow \text{H}_{\text{a}} \text{F}_{\text{a}} \rightarrow \text{H}_{\text{a}} \) | 50.00 | 27,500 | 1.82 |

* Not measurable.
characterisation of materials. Orange glasses have been involved in the enrichment of their emission schemes appropriately. Based on the physical mechanism in Fig. 15, it is now concluded that, we have successfully developed brightly luminescent novel glasses, it could be suggested that both the rare earth glasses are brightly luminescent novel optical materials.

Acknowledgements

One of us (ATR) would like to thank Dr. K.P.C. Gandhi, Director, FSL and Dr. T.S.H. Murthy, Joint Director, FSL, Hyderabad, India for their kind cooperation and encouragement in the present work.

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Solid State Physics

Proceedings of the
DAE Solid State Physics Symposium

December 26-30, 2006

Barkatullah University, Bhopal


Editors
K.G. Bhushan  Amitabh Das  S.K. Gupta

Sponsored by
Board of Research in Nuclear Sciences
Department of Atomic Energy
Government of India
Optical analysis of certain transition metal and rare-earth ions doped zinc lead borate glasses

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Abstract

This paper reports on the optical analysis of certain transition metal and rare earth ions doped zinc lead borate glasses. Absorption spectra of Co\textsuperscript{II}, ZLB glass shows two absorption bands at 428 nm and 777 nm and two emission bands at 400 nm and 493 nm with excitation at 288 nm and 316 nm respectively. For Mn\textsuperscript{II}: glass a broad absorption band at 470 nm, and for Ni\textsuperscript{II}: glass three absorption bands at 424 nm, 810 nm, and 880 nm have been observed. For Co\textsuperscript{II} glass two absorption bands at 590 nm and 1465 nm. For Mn\textsuperscript{II}: glass with \(\lambda_{\text{exc}} = 263\) nm, a bright green emission at 538 nm transition. For Ni\textsuperscript{II}: glass, a green emission at 777 nm and red emission at 670 nm belong to \(\lambda_{\text{em}} = 477\) nm. For Co\textsuperscript{II} glass with \(\lambda_{\text{exc}} = 590\) nm a red emission. For Tm\textsuperscript{III} glass, five emission transitions at 578 nm, 591 nm, 613 nm, 654 nm, and 702 nm respectively at \(\lambda_{\text{exc}} = 392\) nm. For Tm\textsuperscript{III} glass, four emissions such as at 489 nm, 542 nm, 585 nm, and 622 nm with \(\lambda_{\text{em}} = 374\) nm have been measured. For Sm\textsuperscript{III} glass, emission bands of (563 nm), (598 nm), and (708 nm) at \(\lambda_{\text{em}} = 401\) nm have been recorded. From Dy\textsuperscript{III} glass, a bright yellow emission at 575 nm has been found, apart from (485 nm), and (664 nm) emissions at \(\lambda_{\text{em}} = 447\) nm.

RESULTS AND DISCUSSION

Fig.1 shows the absorption spectra of (25-x)ZnO-15PbO-30B\textsubscript{2}O\textsubscript{3}-xCoO (x= 0.1, 0.2, 0.5, and 1.0 mol %) glasses revealing bands at 428 nm (\(E_{\text{B}_{1g}}\) \(\rightarrow E_{\text{g}}\), 777 nm (\(E_{\text{B}_{1g}}\) \(\rightarrow E_{\text{g}}\), and 577 nm (\(E_{\text{B}_{1g}}\) \(\rightarrow E_{\text{g}}\)). Fig.2 shows the emission spectra obtained with two excitation wavelengths at 288 nm and 316 nm respectively. With \(\lambda_{\text{exc}} = 288\) nm, two emissions at 400 nm and 493 nm at \(\lambda_{\text{em}} = 516\) nm. The emission at 493 nm is shifted towards the longer wavelength depending upon the excitation wavelength. Such an observation has earlier been made due to the existence of multi-site structures of copper ions. The emissions at 400 nm, 493 nm are due to Cu\textsuperscript{II} ions in the glass. However, according to the earlier investigations [2], the emission at 493 nm arises due to a localized excitation of an isolated Cu\textsuperscript{II} ion (there is a short lived transfer of an electron from neighboring oxygen to the copper ion). The visible absorption spectra of Mn\textsubscript{II} glasses are shown in Fig. 3, with a broad absorption bands at 470 nm (\(A_{\text{II}}\) \(\rightarrow A_{\text{g}}\), 577 nm (\(A_{\text{II}}\) \(\rightarrow A_{\text{g}}\)) of Mn\textsubscript{II} ions in octahedral symmetry [3]. Fig.4 shows the emission spectra of Mn\textsubscript{II} glasses and the green emission color strongly depends on the coordination environment of Mn\textsuperscript{II} \(E_{\text{g}}\) in the host matrix. In Figs 5 & 6, both absorption and emission spectra of Ni\textsuperscript{II}: ZLB glasses are shown. A sharp absorption band at 424 nm, broad absorption band at 810 nm and a small band at 880 nm have been measured, and these are assigned to the spin allowed transition \(A_{\text{II}} \rightarrow E_{\text{g}}\) (424 nm), spin forbidden transition \(A_{\text{II}} \rightarrow E_{\text{g}}\) (810 nm) and spin forbidden transition \(A_{\text{II}} \rightarrow E_{\text{g}}\) (880 nm) of Ni\textsuperscript{II} ions in octahedral co-ordination, respectively [4].

According to the energy levels of Ni\textsuperscript{II} ions transitions in octahedral sites, the emission in green and red regions are assigned to (577 nm) \(A_{\text{II}} \rightarrow E_{\text{g}}\) (670 nm) \(A_{\text{II}} \rightarrow E_{\text{g}}\) transitions respectively. At 420 nm excitation, 0.2 mol% Ni\textsuperscript{II} doped sample green band intensity is slightly higher compared to the red emission. But for 0.5mol% Ni\textsuperscript{II} sample, red emission increases considerably compared to the broad green emission intensity. Figs 7 & 8 present the absorption and emission spectra of Co\textsuperscript{II}: ZLB glasses. From Fig.7 absorption bands at 590 nm and 1466 nm have been observed and are assigned to \(A_{\text{II}} \rightarrow A_{\text{g}}\) (428 nm) and \(A_{\text{II}} \rightarrow A_{\text{g}}\) (708 nm). Mn\textsuperscript{II} glass with five transitions of \(A_{\text{II}} \rightarrow E_{\text{g}}\) (577nm), \(A_{\text{II}} \rightarrow E_{\text{g}}\) (591nm), \(A_{\text{II}} \rightarrow E_{\text{g}}\) (613nm), \(A_{\text{II}} \rightarrow E_{\text{g}}\) (654nm), \(A_{\text{II}} \rightarrow E_{\text{g}}\) (702nm). Due to the shielding effect of 6f electron by 5S and 5P electrons in outer shells in the Eu\textsuperscript{II} ions, narrow emission bands are produced. Among these five emission bands \(A_{\text{II}} \rightarrow E_{\text{g}}\) (613nm) has shown a strong red color. The \(A_{\text{II}} \rightarrow E_{\text{g}}\) transitions are electric dipole (ED) transitions. In particular, the red emission \(A_{\text{II}} \rightarrow E_{\text{g}}\) is the hypersensitive transition that follows the selection rules of \(\Delta S = 2\). Another transition \(A_{\text{II}} \rightarrow E_{\text{g}}\), with \(\Delta S = 1\) has been identified as a magnetic dipole (MD) [5]. Fig.8 shows...
the emission spectrum of the Tb$^{3+}$ ion, with $\lambda_{\text{em}} = 374$ nm. The emission transitions reveal sharp emission bands due to the f-f transitions such as $^5D_{4} \rightarrow ^7F_{4}$ (374 nm) for Tb$^{3+}$. Bands with smaller widths and larger amplitudes ranging from 480 nm to 630 nm are observed. These originate from Tb$^{3+}$ ions and bands with the largest amplitude have a maximum at 544 nm. The emission transitions of the Tb$^{3+}$ ion with $\lambda_{\text{exc}} = 374$ nm reveal sharp emission bands due to the f-f transitions such as $^5D_{4} \rightarrow ^7F_{4}$ (374 nm), $^5D_{2} \rightarrow ^7F_{4}$ (542 nm), $^5D_{2} \rightarrow ^7F_{4}$ (585 nm), $^5D_{4} \rightarrow ^7F_{3}$ (622 nm). The most significant green transition is $^5D_{4} \rightarrow ^7F_{4}$, which obeys the magnetic dipole transition selection rules. The predominance of the magnetic dipole transition $^5D_{4} \rightarrow ^7F_{4}$ of Tb$^{3+}$ satisfying the selection rule of $\Delta J = \pm 1$. Fig. 11 presents emission spectrum of Sm$^{3+}$ glass, with $\lambda_{\text{em}} = 401$ nm with four emissions of $^6H_{14} \rightarrow ^{4}I_{12}$ (563 nm), $^4G_{9/2} \rightarrow ^{4}I_{12}$ (598 nm), $^4G_{7/2} \rightarrow ^{4}I_{12}$ (644 nm), and $^4G_{5/2} \rightarrow ^{4}I_{12}$ (708 nm). The Sm$^{3+}$ glass shows a bright orange-red emission under an UV source. Fig. 12 shows the emission spectrum of Dy$^{3+}$ ZLB glass at $\lambda_{\text{exc}} = 447$ nm with three emissions such as $^4F_{7/2} \rightarrow ^{4}I_{15/2}$ (485 nm), $^4F_{9/2} \rightarrow ^{4}I_{15/2}$ (575 nm) and $^4F_{5/2} \rightarrow ^{4}I_{15/2}$ (664 nm).}

**CONCLUSION**

In summary, it is concluded that, we have successfully developed highly transparent and more stable Zinc lead borate (ZLB) glasses doped with transition metal (Cu$^{2+}$, Mn$^{2+}$, Co$^{2+}$ and Ni$^{2+}$) and rare-earth (Eu$^{3+}$, Tb$^{3+}$, Sm$^{3+}$ and Dy$^{3+}$) ions and analyzed their absorption and emission spectral properties in order to evaluate their emission performance for their application as brightly fluorescent optical glass systems.

**REFERENCES**


