OPTICAL PROPERTIES OF Eu$^{3+}$ & Tb$^{3+}$: TeO$_2$-B$_2$O$_3$-P$_2$O$_5$-CdO GLASSES

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Abstract: This paper reports on the development and spectral results of europium (Eu$^{3+}$) and terbium (Tb$^{3+}$) optical glasses in the following chemical composition.

20TeO$_2$ – 49.5B$_2$O$_3$ – 10CdO – 10P$_2$O$_5$ – 10AlF$_3$-0.5 Eu$_2$O$_3$
20TeO$_2$ – 49.5B$_2$O$_3$ – 10CdO – 10P$_2$O$_5$ – 10AlF$_3$-0.5 Tb$_2$O$_7$

From the measurements of X-ray diffraction (XRD), glass amorphous nature and thermal properties of these glasses have been carried out. From the XRD, the glass nature have been studied. The measured emission spectrum of Eu$^{3+}$ glasses have revealed five transitions (4D$_{0}$→F$_{0}$, F$_{1}$, F$_{2}$, F$_{3}$ & F$_{4}$) at 579, 591, 613, 652 & 701 nm respectively with $\lambda_{exc}$ = 392nm (4F$_{9/2}$→4L$_{6}$) . In the case of Tb$^{3+}$ glasses four emission transitions such as 4F$_{5/2}$→ (F$_{6}$, F$_{7}$, F$_{8}$ & F$_{9}$) that are located at 489, 543, 584 and 621nm respectively have been measured with $\lambda_{exc}$=376nm (4F$_{9/2}$→G$_{8}$). Emission mechanisms that are arised in the glasses have been explained in terms of energy level diagrams.

Index Terms - Spectral analysis; Eu$^{3+}$; glasses; Tb$^{3+}$; glasses; emission; excitation.

I. INTRODUCTION

Over the past several years, a great deal of work has been done on TeO$_2$ based glasses. TeO$_2$ glass system are well known for their good chemical durability, thermal stability, high refractive index, high transparency in the infrared region and low phonon energy values$^{1,2}$. It has been well known that a pure TeO$_2$ chemical does not form a glass but it does so, when it is mixed with certain other oxides such as B$_2$O$_3$, P$_2$O$_5$ and CdO etc. Further, the glasses upon addition of AlF$_3$ as the network modifiers (NWM), could strengthen (or) enhance certain electrical, thermal and optical properties. Due to these properties of the glasses, they were considered as the best materials for optical applications$^{3-5}$. Further, these glasses are considered as very good materials for hosting lasing ions like transition metal or rare earth ions due to their good chemical durability, thermal stability and certain other oxides such as B$_2$O$_3$, P$_2$O$_5$, and CdO etc.

II EXPERIMENTAL STUDIES

2.1. Preparation of glasses

The chemicals used in the preparation of glasses were of reagent grade. The chemical compositions of these Eu$^{3+}$ and Tb$^{3+}$ ions doped glasses are as follows.

20TeO$_2$ – 49.5B$_2$O$_3$ – 10CdO – 10P$_2$O$_5$ – 10AlF$_3$-0.5 Eu$_2$O$_3$
20TeO$_2$ – 49.5B$_2$O$_3$ – 10CdO – 10P$_2$O$_5$ – 10AlF$_3$–0.5 Tb$_2$O$_7$

All the chemicals were finely powdered and then mixed thoroughly. Each batch weighing 10g was melted by using alumina crucibles in an electric furnace at 950°C, for an hour. These melts were quenched in between two brass plates. The obtained glasses were of 2-3 cm in diameter with a uniform thickness of 0.3 cm. These glasses were annealed at 200°C for an hour in order to remove the thermal strains.

2.2. Measurement of physical properties and optical spectra of cadmium phoso boro tellurite glasses

Powder X-ray diffraction (XRD) spectrum was obtained on a Shimadzu XD3A – diffractometer with a Ni-filter and CuK$\alpha$ ($\lambda=1.542$ A$^0$) radiation at an applied voltage of 30kV and 20mA anode current, calibrated with Si at the rate of 2$^\circ$/min. The optical absorption spectra (350 – 1100 nm) of the reference glasses were measured on a Varian-Cary Win spectrophotometer. Both the excitation and the emission spectra of the 0.5 mol% Eu$^{3+}$ and Tb$^{3+}$ doped glasses were measured under the steady state mode on a SPEX Fluorolog-2 Fluorimeter (model F-II) with a Xe-arc lamp (150W) as the excitation source and spectral data was obtained based on the Datamax software.
III. RESULTS AND DISCUSSION

3.1. Reference glasses

Fig.1 confirms the amorphous nature of the reference glass in the composition of 20TeO$_2$ – 50B$_2$O$_3$ – 10CdO - 10 P$_2$O$_5$- 10AlF$_3$. Figs.2 shows the UV optical absorption spectra of reference glasses. From the absorption spectrum of 20TeO$_2$ – 50B$_2$O$_3$ – 10CdO - 10 P$_2$O$_5$- 10AlF$_3$ glass, the optical band gap ($E_{opt}$) values are determined the following way.

The absorption coefficient ‘α’, near the edge of each curve is determined at wavelength intervals of 5 nm for linear region and 2 nm for the non-linear region, using the relation.

$$\alpha = \text{ln}(I/I_0)/t \quad \text{(1)}$$

where ‘t’ is the thickness of each sample and ln(I/I$_0$) corresponds to the absorbance. The relation between α and photon energy of incident radiation, hv is given by the following relation.

$$\alpha = \text{Const}_1 \cdot (hv - E_{opt})^2/\text{hv} \quad \text{--------> (2)}$$

where $E_{opt}$ is the energy of the optical band gap. The above relation can be written as

$$\alpha = \text{Const}_2 \cdot (hv)^{1/2} \quad \text{--------> (3)}$$

Using the relation (3), the $E_{opt}$ values are determined by extrapolation of the linear region of the plots of ($\alpha \cdot hv^{1/2}$) against hv to ($\alpha \cdot hv^{1/2}$)=0 shown in Fig 3. The values of $E_{opt}$ is found to be 2.8eV.

The relation between ‘α’ and Urbach energy ($\Delta E$) is given by the well known Urbach law and is given by

$$\alpha = \text{Const}_3 \cdot \exp(hv/\Delta E) \quad \text{--------> (4)}$$

$\Delta E$ is usually interpreted as the width of the tail of the localized states in the band gap.

The relation (4) can be rewritten as

$$\text{ln} \alpha = (hv/\Delta E) - \text{Const}_4 \quad \text{--------> (5)}$$

Urbach plots are the plots where the natural logarithm of absorption coefficients, $\text{ln} \alpha$ is plotted against photon energy hv. In the present study, Urbach plot for a typical glass 20TeO$_2$ – 50B$_2$O$_3$ – 10CdO - 10 P$_2$O$_5$- 10AlF$_3$ is shown in Fig 4. The values of Urbach energy ($\Delta E$) are calculated by determining the slopes of the linear regions of the curves and taking their reciprocals. The values of $\Delta E$ is found to be 0.25eV.

3.2. Eu$^{3+}$: glasses

The XRD pattern of the glass Eu$^{3+}$ (0.5 mol %): 20TeO$_2$ – 49.5B$_2$O$_3$ – 10CdO - 10 P$_2$O$_5$-10AlF$_3$ is shown in Fig.5, which confrirms the amorphous nature of the glass. The excitation spectrum of Eu$^{3+}$ glass is shown in Fig.8. It shows four excitation bands at 360 nm ($^{5}F_{0} \rightarrow ^{5}D_{2}$), 379 nm ($^{5}F_{0} \rightarrow ^{7}G_{6}$), 392 nm ($^{5}F_{0} \rightarrow ^{5}L_{6}$) and 412 nm ($^{5}F_{0} \rightarrow ^{5}D_{4}$). Out of these, a prominent excitation band at 392 nm ($^{5}F_{0} \rightarrow ^{7}L_{6}$) is selected to measure the emission spectra of Eu$^{3+}$: glasses. Emission spectra of Eu$^{3+}$ glasses is shown in Fig.7. It represents five emission transitions at 579 nm ($^{5}D_{0} \rightarrow ^{7}F_{2}$ nm), 591nm ($^{5}D_{0} \rightarrow ^{7}F_{1}$), 613 nm ($^{5}D_{0} \rightarrow ^{7}F_{2}$), 652 nm ($^{5}D_{0} \rightarrow ^{7}F_{3}$) and 701 nm ($^{5}D_{0} \rightarrow ^{7}F_{4}$) and are in good agreement with those reported in the literature.$^{16,17}$ In the case of Eu$^{3+}$: glasses narrow emission bands arise due to the shielding effect of 4f$^6$ electrons by 5s and 5p electrons in outer shells in the Eu$^{3+}$ ion. Among these five emission bands, the transition $^{5}D_{0} \rightarrow ^{7}F_{2}$ shows a strong red emission at a wavelength of 613 nm. Here, the $^{5}D_{0} \rightarrow ^{7}F_{2}$ transitions are electric dipole transitions and the red emission ($^{5}D_{0} \rightarrow ^{7}F_{2}$) is a hypersensitive transition which follows the selection rule of $\Delta J = \pm 2$. The transition $^{5}D_{0} \rightarrow ^{7}F_{1}$ is considered as a magnetic dipole transition with the selection rule $\Delta J = \pm 1$. The emission mechanism in Eu$^{3+}$: glasses are shown in Fig.8. Finally it can be found that Eu$^{3+}$: glasses are good candidates for novel optical materials.

3.3. Tb$^{3+}$: glasses

The XRD pattern of the glass Tb$^{3+}$ (0.5 mol %): 30TeO$_2$ – 49.5B$_2$O$_3$ – 10CdO-10 P$_2$O$_5$ is shown in Fig.9, which confirms the amorphous nature of the glass. Excitation spectrum of Tb$^{3+}$: glass is shown in Fig.10. It indicates three excitation peaks at 350 nm ($^{5}D_{0} \rightarrow ^{5}D_{2}$), 369 nm ($^{5}D_{0} \rightarrow ^{7}L_{6}$) and 376 nm ($^{5}D_{0} \rightarrow ^{7}G_{6}$) which are noted by the energy levels reported earlier.$^{18,19}$ The emission spectra of Tb$^{3+}$: glasses with $\lambda_{exc}=376$ nm is shown in Fig.11. All the emission transitions are found to be intense and sharp bands due to the f-f inner shell transitions. From the emission spectra, the transitions at 489 nm ($^{5}D_{4} \rightarrow ^{7}F_{2}$), 543 nm ($^{5}D_{4} \rightarrow ^{7}F_{3}$), 584 nm ($^{5}D_{4} \rightarrow ^{7}F_{4}$) and 621 nm ($^{5}D_{4} \rightarrow ^{7}F_{5}$) are identified and are in good agreement with those reported in the literature.$^{16,21}$ Here, the intense green emission at 543 nm arises due to the Laporte-forbidden $^{5}D_{4} \rightarrow ^{7}F_{3}$ transition.$^{18}$ The transition $^{5}D_{4} \rightarrow ^{7}F_{2}$ at 489 nm is considered as the magnetic dipole transition which follows the selection rule of $\Delta J = \pm 1$. The emission mechanism in Tb$^{3+}$: glasses with $\lambda_{exc}=376$ nm is shown in Fig.12.

IV. CONCLUSION

We have developed highly transparent, moisture resistant and more stable Eu$^{3+}$ and Tb$^{3+}$ ions doped TeO$_2$ – B$_2$O$_3$ – P$_2$O$_5$ – CdO – AlF$_3$ glasses. From XRD the glass amorphous nature has been studied. Optical analysis of these glasses has been carried out based on the absorption, excitation and emission spectra. Further, we have identified a bright red and green emission from Eu$^{3+}$ and Tb$^{3+}$ doped glasses respectively under an UV source. The emission mechanisms that arise in these glasses is also explained in terms of the energy level diagrams. The Figs.1-12, we have suggested that the Eu$^{3+}$ and Tb$^{3+}$ ions doped glasses are highly potential enough towards the display of red (Eu$^{3+}$) and green (Tb$^{3+}$) colours and are widely used for display applications.

V. ACKNOWLEDGMENT

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REFERENCES

Figure 1. XRD profile of $20\text{TeO}_2 - 50\text{B}_2\text{O}_3 - 10\text{CdO} - 10\text{P}_2\text{O}_5 - 10\text{AlF}_3$ reference glass

Figure 2. UV absorption spectra of $20\text{TeO}_2 - 49.5\text{B}_2\text{O}_3 - 10\text{CdO} - 10\text{P}_2\text{O}_5 - 10\text{AlF}_3$ glass
Figure 3. $(\alpha h \nu)^{1/2}$ as a function of photon energy $h\nu$ for $30\text{TeO}_2 - 50\text{B}_2\text{O}_3 - 10\text{CdO} - 10\text{P}_2\text{O}_5$ glass.

Figure 4. $\ln \alpha$ plotted against photon energy $h\nu$ for $30\text{TeO}_2 - 50\text{B}_2\text{O}_3 - 10\text{CdO} - 10\text{P}_2\text{O}_5$ glass.
Figure 5. XRD profile of Eu\(^{3+}\): 30TeO\(_2\) – 50B\(_2\)O\(_3\) – 10CdO - 10 P\(_2\)O\(_5\) glass

Figure 6. Excitation spectrum of Eu\(^{3+}\): 20TeO\(_2\) – 49.5B\(_2\)O\(_3\) – 10CdO - 10 P\(_2\)O\(_5\) - 10AlF\(_3\) glass
Figure 7. Emission spectra of Eu$^{3+}$: $20\text{TeO}_2 - 49.5\text{B}_2\text{O}_3 - 10\text{CdO} - 10\text{P}_2\text{O}_5 - 10\text{AlF}_3$ glass

Figure 8. Energy level scheme for emission process in Eu$^{3+}$: $20\text{TeO}_2 - 49.5\text{B}_2\text{O}_3 - 10\text{CdO} - 10\text{P}_2\text{O}_5 - 10\text{AlF}_3$ glass
Figure 9. XRD profile of Tb\(^{3+}\): 20TeO\(_2\) – 49.5B\(_2\)O\(_3\) – 10CdO - 10 P\(_2\)O\(_5\)-10AlF\(_3\) glass

Figure 10. Excitation spectrum of Tb\(^{3+}\): 20TeO\(_2\) – 49.5B\(_2\)O\(_3\) – 10CdO - 10 P\(_2\)O\(_5\)-10AlF\(_3\) glass
Figure 11. Emission spectra of Tb$^{3+}$: 20TeO$_2$ – 49.5B$_2$O$_3$ – 10CdO - 10 P$_2$O$_5$-10AlF$_3$ glass

Figure 12. Energy level scheme for emission process in Tb$^{3+}$: 20TeO$_2$ – 49.5B$_2$O$_3$ – 10CdO - 10 P$_2$O$_5$-10AlF$_3$ glass