OPTICAL PROPERTIES OF Eu^{3+}&Tb^{3+}: TeO_2-B_2O_3-P_2O_5-CdO GLASSES

[1]M.V.Ramanaiah, [2]B.Sudhakar Reddy,
[1]Reader in Physics, [2]Reader in Physics
[1,2] Department of Physics,
[1,2] S.V.Degree College, Kadapa-516003, Andhra Pradesh, India

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.

$20TeO_2 – 49.5B_2O_3 – 10CdO – 10P_2O_5 – 10AlF_3$-0.5 Eu_2O_3
$20TeO_2 – 49.5B_2O_3 – 10CdO – 10\ P_2O_5 – 10AlF_3$-0.5 Tb_4O_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 ($^5D_0 \rightarrow {}^7F_0$, $^7F_1$, $^7F_2$, $^7F_3$ & $^7F_4$) at 579, 591, 613, 652 & 701 nm respectively with λ_{exci} = 392nm ($^7F_0 \rightarrow {}^5L_6$) . In the case of Tb^{3+} glasses four emission transitions such as $^5D_4 \rightarrow$ ($^7F_6$, $^7F_5$, $^7F_4$ & $^7F_3$) that are located at 489, 543, 584 and 621nm respectively have been measured with λ_{exci} =376nm ($^7F_6 \rightarrow {}^5G_6$). Emission mechanisms that are araised in the glasses have been explained in terms of energy level diagrams.

IndexTerms - 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.TeO2 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_2O_3, P_2O_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 components such as the IR domes, optical fibers and laser windows[3-9]. Further, these glasses are considered as very good materials for hosting lasing ions like transition metal or rare earth ions, since these provide a low phonon energy environment to minimize the non-radiative losses. Rare earth ions (RE^{3+}) would generally be exciting in trivalent state, of which the $4f^n$ configuration could found relatively isolated and the next exited $4f^{n-1}$ 5d configuration lies in the high energy level above the ground state of the $4f^n$ configuration[10]. Hence the electronic configuration causes the display of more sharp emission bands due to the intra f-f transitions. For quite sometime, it has been known that rare-earth ions doped optical glassy materials have attracted a great deal of attention for their wide variety of applications[11-13]. The red colour emitting rare earth ion namely Eu^{3+} ($4f^6$) ion has a lower lying exited level ($^5D_0$) to reveal intense and sharp emission transitions[12] with $^7F_6$ as the ground state. Similarly, the green colour emitting ion, namely Tb^{3+} ($4f^8$) ion could reveal more bright and line-like excitation and emission bands[14, 15] with $^7F_0$ as the ground state in the UV-Vis wavelength region. It has been found that the Cadmium lead boro tellurite glasses are promising materials because of their infrared properties. The emission lines of these glasses at wavelengths near 0.85 µm, 1.31 µm and 1.55 µm are frequently used in the fibre optics because of the local minima, optical attenuation and optical dispersion. 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 doped cadmium aluminum fluoro phospho boro tellurite glasses.

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.

$20TeO_2 – 49.5B_2O_3 – 10CdO – 10P_2O_5 – 10AlF_3$-0.5 Eu_2O_3
$20TeO_2 – 49.5B_2O_3 – 10CdO – 10\ P_2O_5 – 10AlF_3$-0.5 Tb_4O_7

All the chemicals were finely powdered and then mixed thoroughly. Each batch weighing 10g was melt by using alumina crucibles in an electric furnace at 950^0C, 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 200^0C for an hour in order to remove the thermal strains.

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

Powder X-ray diffraction (XRD) spectrum was obtained on a Shimadzu XD3A – diffractometer with a Ni-filter and CuKα (λ=1.542 A^0) radiation at an applied voltage of 30kv and 20mA anode current, calibrated with Si at the rate of 2^0/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 $20TeO_2 – 50B_2O_3 – 10CdO - 10\ P_2O_5- 10AlF_3$. Figs.2 shows the UV optical absorption spectra of reference glasses. From the absorption spectrum of $20TeO_2 – 50B_2O_3 – 10CdO - 10\ P_2O_5 –10AlF_3$ 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.

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

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, hν is given by the following relation.

$$\alpha = \text{Const}\ [h\nu - E_{opt}]^2/ h\nu \quad \text{----------> (2)}$$

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

$$(\alpha\ h\nu)^{1/2} = \text{Const}\ (h\nu - E_{opt}) \quad \text{----------> (3)}$$

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

The relation between 'α' and Urbach energy (ΔE) is given by the well known Urbach law and is given by

$$\alpha = \text{Const.}\ \exp(h\nu/\Delta E) \quad \text{----------> (4)}$$

ΔE is usually interpreted as the width of the tail of the localized states in the band gap.

The relation (4) can be rewritten as

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

Urbach plots are the plots where the natural logarithm of absorption coefficients, lnα is plotted against photon energy hν. In the present study, Urbach plot for a typical glass $20TeO_2 – 50B_2O_3 – 10CdO - 10P_2O_5– 10AlF_3$ is shown in Fig 4. The values of Urbach energy (ΔE) are calculated by determining the slopes of the linear regions of the curves and taking their reciprocals. The values of ΔE is found to be 0.25eV

3.2.Eu^{3+}: glasses

The XRD pattern of the glass Eu^{3+} (0.5 mol %) : $20TeO_2 – 49.5B_2O_3 – 10CdO – 10\ P_2O_5\ -10AlF_3$is shown in Fig.5, which confirms 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 ($^7F_o \rightarrow {}^5D_4$), 379 nm ($^7F_0 \rightarrow {}^5G_6$), 392 nm ($^7F_0 \rightarrow {}^5L_6$) and 412 nm ($^7F_0 \rightarrow {}^5D_3$). Out of these, a prominent excitation band at 392 nm ($^7F_0 \rightarrow {}^5L_6$) 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 ($^5D_0 \rightarrow {}^7F_0$ nm), 591nm ($^5D_0 \rightarrow {}^7F_1$), 613 nm ($^5D_0 \rightarrow {}^7F_2$),652 nm ($^5D_0 \rightarrow {}^7F_3$) and 701 nm ($^5D_0 \rightarrow {}^7F_4$) 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 $^5D_0 \rightarrow {}^7F_2$ shows a strong red emission at a wavelength of 613 nm. Here, the $^5D_0 \rightarrow {}^7F_{2,4}$ transitions are electric dipole transitions and the red emission ($^5D_0 \rightarrow {}^7F_2$) is a hypersensitive transition which follows the selection rule of $\Delta J = \pm 2$. The transition $^5D_0 \rightarrow {}^7F_1$ is considered as a magnetic dipole transition with the selection rule $\Delta J = \pm 1$ [17]. 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 %): $30TeO_2 – 49.5B_2O_3- 10CdO-10\ P_2O_5$ 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 ($^7F_6 \rightarrow {}^5D_2$), 369 nm ($^7F_6 \rightarrow {}^5L_{10}$) and 376 nm ($^7F_6 \rightarrow {}^5G_6$) which are noted by the energy levels reported earlier [18,19]. The emission spectra of Tb^{3+}: glasses with λ_{exci} =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 ($^5D_4 \rightarrow {}^7F_6$), 543 nm ($^5D_4 \rightarrow {}^7F_5$), 584 nm ($^5D_4 \rightarrow {}^7F_4$) and 621 nm ($^5D_4 \rightarrow {}^7F_3$) are identified and are in good agreement with those reported in the literature[18-21]. Here, the intense green emission at 543 nm arises due to the Laporte-forbidden $^5D_4 \rightarrow {}^7F_5$ transition[18]. The transition $^5D_4 \rightarrow {}^7F_6$ at 489 nm is considered as the magnetic dipole transition which follows the selection rule of $\Delta J = \pm 1$ [22, 23].The emission mechanism in Tb^{3+}: glasses with λ_{exci}=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 $TeO_2 – B_2O_3 – P_2O_5 – CdO – AlF_3$glasses. From XRD the glass amorphous nature has been studued. 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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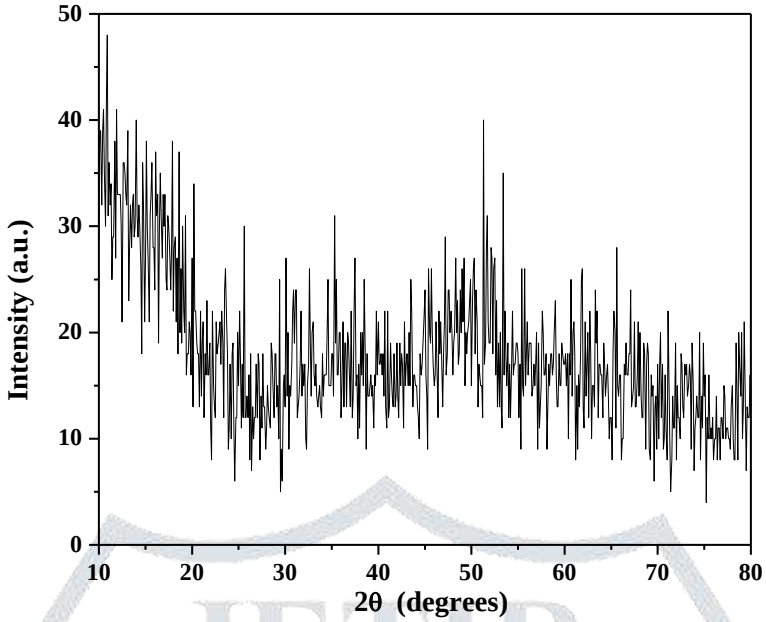

Figure.1. XRD profile of $20TeO_2 – 50B_2O_3 – 10CdO - 10\ P_2O_5$-$10AlF_3$ reference glass

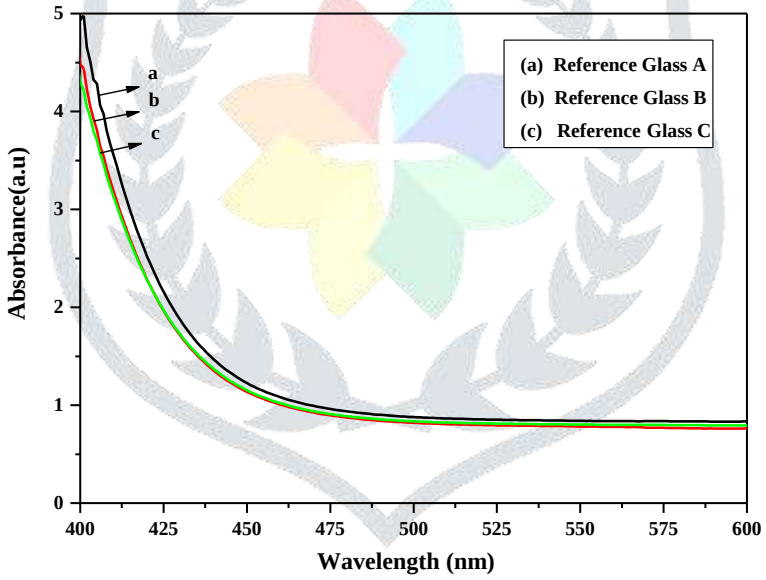

Figure.2. UV absorption spectra of $20TeO_2 – 49.5B_2O_3 – 10CdO - 10\ P_2O_5$-$10AlF_3$ glass

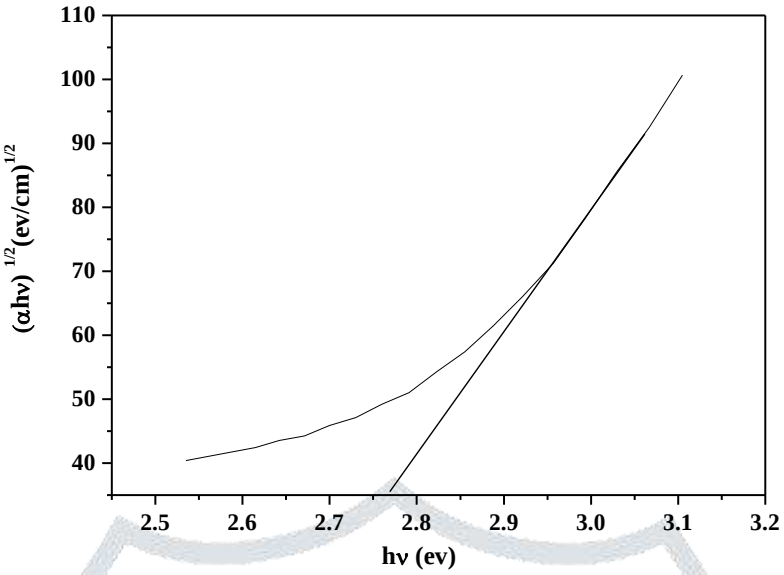

Figure.3. $(\alpha h\nu)^{1/2}$ as a function of photon energy hν for $30TeO_2 – 50B_2O_3 – 10CdO - 10 P_2O_5$ glass

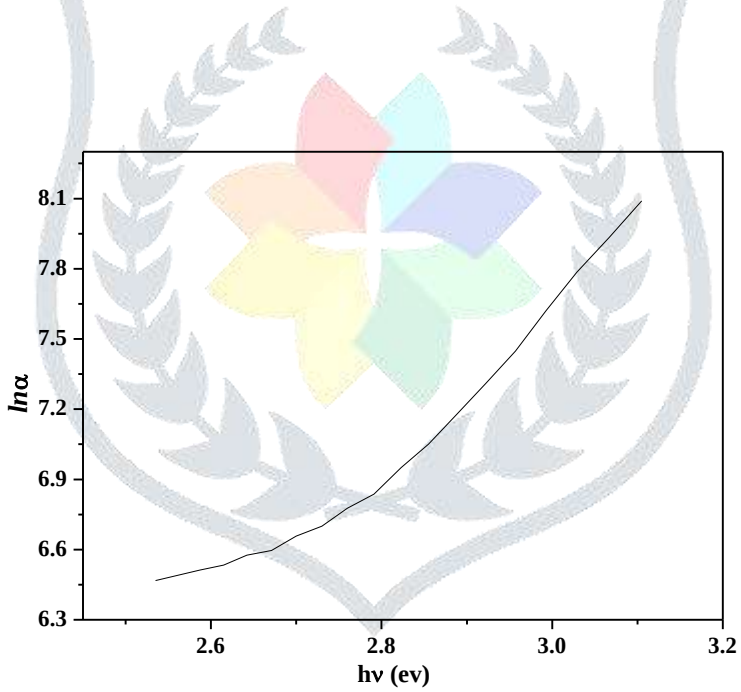

Figure.4. lnα plotted against photon energy hν for $30TeO_2 – 50B_2O_3 – 10CdO – 10 P_2O_5$ glass

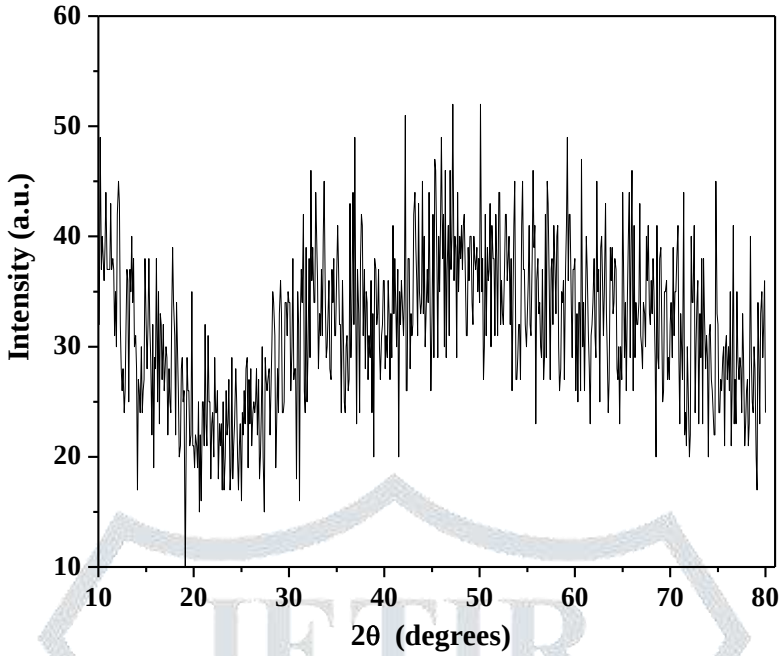

Figure.5. XRD profile of Eu^{3+}: $30TeO_2 – 50B_2O_3 – 10CdO - 10\ P_2O_5$ glass

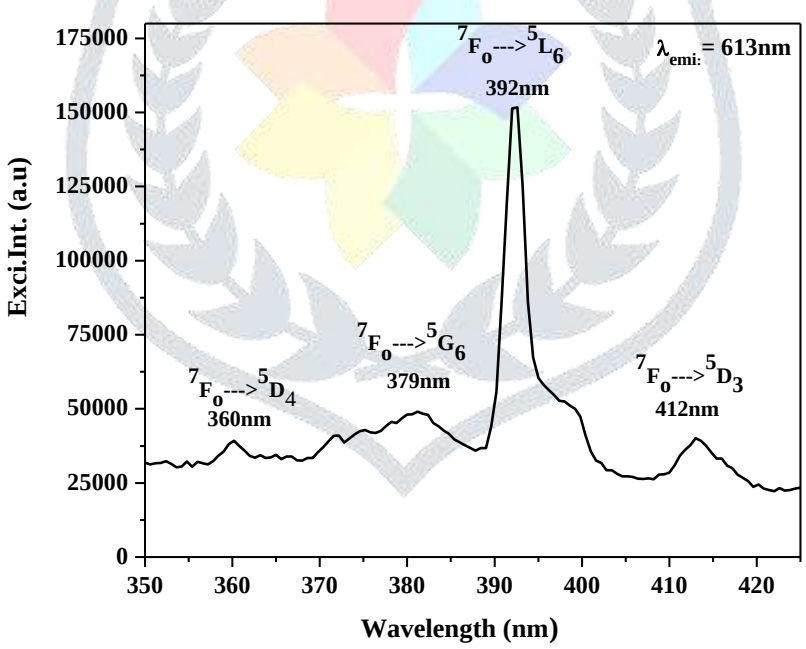

Figure.6. Excitation spectrum of Eu^{3+}: $20TeO_2 – 49.5B_2O_3 – 10CdO - 10\ P_2O_5$-$10AlF_3$ glass

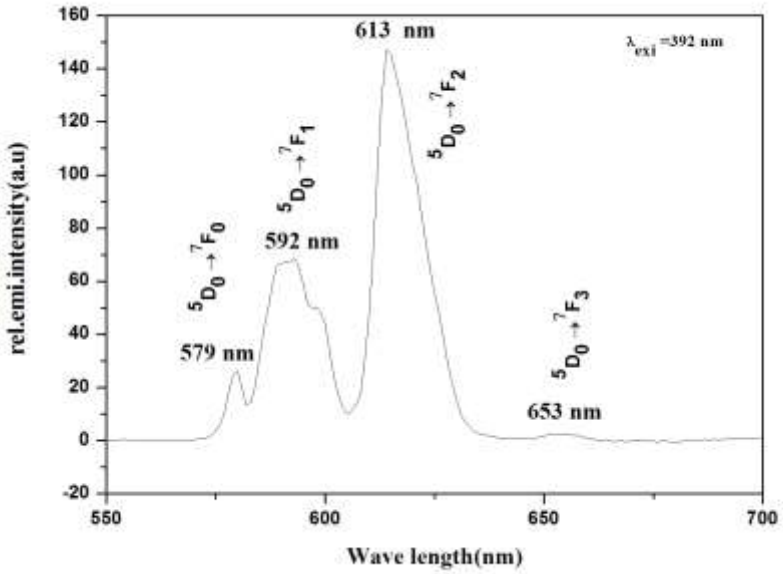

Figure.7. Emission spectra of Eu^{3+}: $20TeO_2 – 49.5B_2O_3 – 10CdO - 10\ P_2O_5$-$10AlF_3$ glass

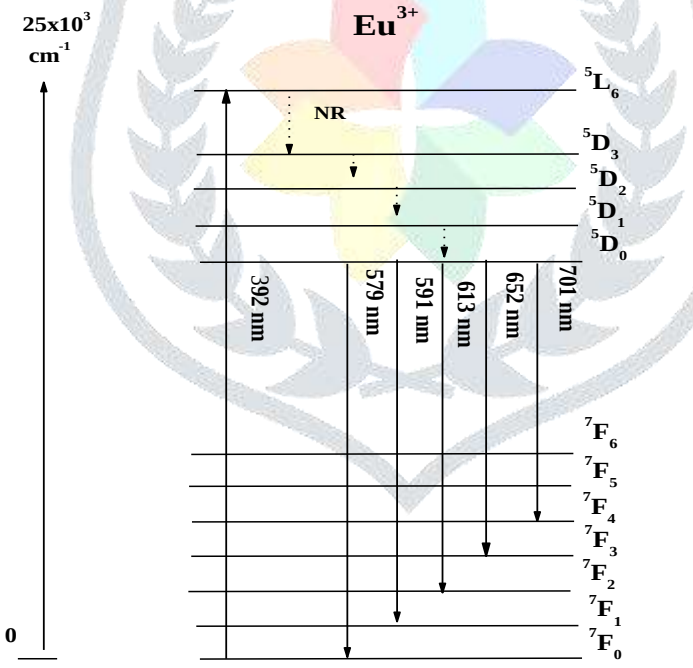

Figure.8. Energy level scheme for emission process in Eu^{3+}: $20TeO_2 – 49.5B_2O_3 – 10CdO - 10\ P_2O_5$-$10AlF_3$ glass

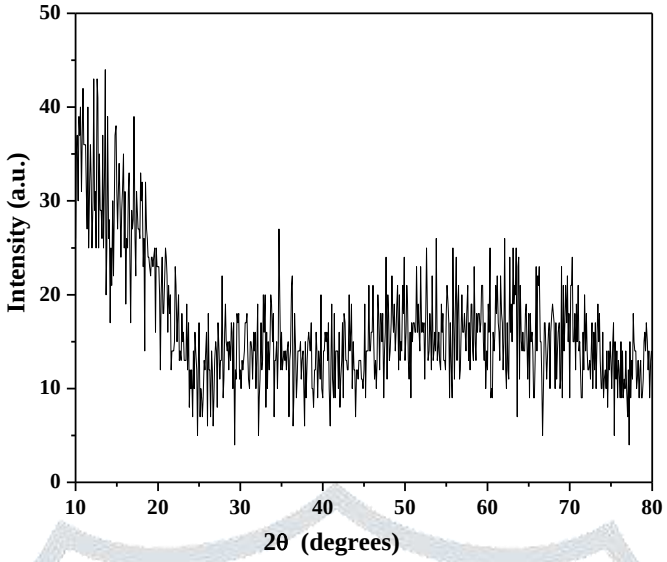

Figure.9. XRD profile of Tb^{3+}: $20TeO_2 – 49.5B_2O_3 – 10CdO - 10\ P_2O_5$-$10AlF_3$ glass

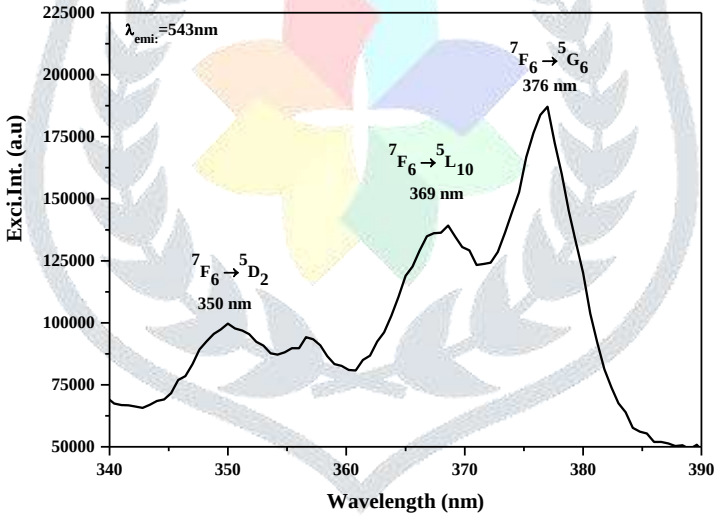

Figure.10. Excitation spectrum of Tb^{3+}: $20TeO_2 – 49.5B_2O_3 – 10CdO - 10\ P_2O_5$-$10AlF_3$ glass

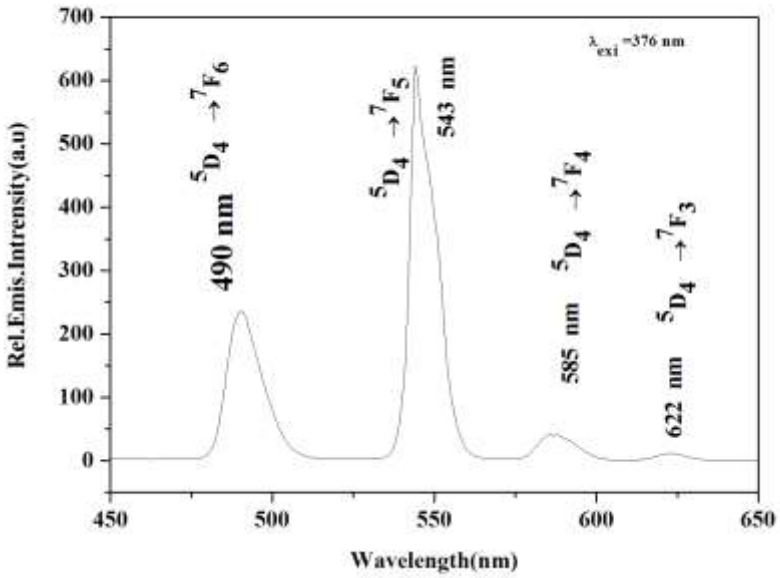

Figure.11. Emission spectra of Tb^{3+}: $20TeO_2 – 49.5B_2O_3 – 10CdO - 10\ P_2O_5$-$10AlF_3$ glass

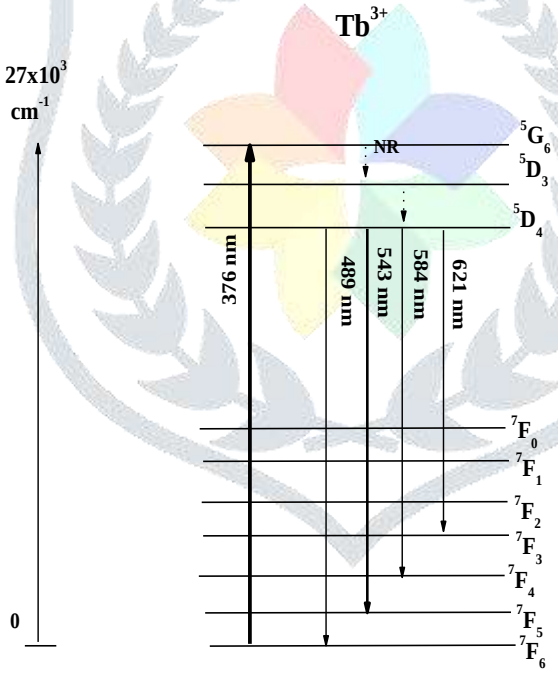

Figure.12. Energy level scheme for emission process in Tb^{3+}: $20TeO_2 – 49.5B_2O_3 – 10CdO - 10\ P_2O_5$-$10AlF_3$ glass