Optical properties of Tb^{3+} doped tellurite glass

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The absorption and fluorescence spectra of Tb^{3+} in different lattices have been studied by several workers [1–5]. The ground state of Tb^{3+} is $^7F_6$ with its other components forming the low-lying excited states. Some of the other low lying excited states of Tb^{3+} are $^5D_{4,3,2,1}$, $^5L_{10}$, $^5G_6$, $^5L_9$, etc. It has been found that Tb^{3+}-doped samples show very poor absorption spectrum. However, they give an intense fluorescence in the green region. Tb^{3+} phosphors have been extensively utilized in display devices owing to their intense green emission caused by the $^5D_4$–$^7F_5$ transition [3–5]. Tb^{3+} is also known to have a blue emission, which competes with the green one.

The absorption bands of Tb^{3+} ions have been analyzed only for $\upsilon < 36\,000$ cm^{-1}, because at higher energies the 4f–4f transitions are superimposed on the more intense absorption bands due to the $4f^N$–$4f^{N-1}$ 5d transitions [6–8].

The energy transfer in different glass and crystal lattices doped with terbium ion has been studied by several workers [9–18]. The resonance energy transfer due to the electrostatic multipole and exchange interactions in systems in which many acceptors are randomly distributed around a donor has been investigated by Inokutti and Hirayama [9].

Several authors [10–13] have studied the fluorescence of Tb^{3+} in various hosts when another rare earth is also doped in the host. These studies have been used to identify the mechanism of energy transfer in Tb^{3+} codoped with other rare earths. It has been noted that the mechanism of energy transfer is different for different host lattices. With the increase in the concentration of Tb^{3+}ion in different host lattices, the cooperative energy transfer within Tb^{3+} ions itself has also been marked [14–16]. The fluorescence line widths and the excitation transfer in $Eu_{0.33}Tb_{0.66}P_5O_{14}$crystal have been studied by Laulicht *et al.* [17]. These workers used the rapid migration model to calculate the Tb^{3+} (donor)-Eu^{3+} (acceptor) dipole–dipole interaction parameters in the 45–250 K temperature range from the time decay curves of the $^5D_4$ manifold of Tb^{3+}. The diffusion limited energy transfer in $La_{1-x-y}Ce_xTb_yPO_4$ lattice has been studied by Bourecet *et al.* [18]. They found that the Tb^{3+} acts as the terminal site of the energy migration process.

Vedda *et al.* [19] have studied the optical absorption and thermoluminescence spectra of Tb^{3+}-doped phosphate scintillating glasses at room temperature both before and after x-ray irradiation. They proposed that after x-ray irradiation intrinsic defects created in the lattice and the Tb^{4+} ions are responsible for the optical absorption pattern. The recovery of the bands in the unexposed sample is explained as due to the de-trapping of the charge carriers from the defect-trapped states. They assumed that the de-trapping is followed by recombination at the activator and/or at defect sites and at radiation-induced centers responsible for absorption bands, which in this way return to their pre-irradiation configuration.

In this paper, we have examined the absorption and fluorescence spectra of Tb^{3+} ion doped in tellurite glass. The concentration-dependent fluorescence studies have also been made and the mechanism of quenching discussed. We have also measured the lifetime of the $^5D_4$ state at different concentrations of Tb^{3+}. A study of the effect of heating on the fluorescence intensity and the lifetime of the levels have also been made. The energy transfer in presence of Eu^{3+} has also been studied. The effect of γ-ray irradiation on the fluorescence yield of Tb^{3+} has been discussed.

Following compositions have been used to prepare the glass.

$$(80 - x)TeO_2 + 20Li_2\,CO_3 + xTb_2O_3.$$

where $x = 0.5$, 1.0, 2.0, and 3.0 mol% of Tb_2O_3.

The TeO_2 (Merck with 99.9% purity) acts as glass former and Li_2CO_3 (BDH with 99% purity) as glass modifier. All the chemicals were made into fine powder in a ceramic mortar and finally mixed properly. The homogeneously mixed sample was then heated up to 750 °C in a platinum crucible for 45 min. The melt was constantly stirred for homogeneous mixing and then suddenly poured into a steel cast kept at 400 °C, and then pressed with a flat disc to get flat glass about 1 mm thick. The absorption spectrum of Tb^{+3} (1.0 mol%) doped tellurite glass was recorded using a Lambda-19-UV-Vis-NIR double beam spectrophotometer in the region 400–2500 nm. For fluorescence spectrum we have used the 476.5 nm line with 130 mw power from a 10-watt (all line) Ar^+ laser, as the energy of this line is very close to the $^5D_4$ level of the Tb^{3+}. The spectra were recorded in the region of 500–744 nm. All these measurements were made at room temperature (30 °C).

The lifetime of the $^5D_4$ level has been measured for all the four samples (containing 0.5, 1.0, 2.0, and 3.0 mol% of Tb^{3+}) using 248 nm line from a K_rF excimer laser.

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Tb^{3+} ion gives very poor absorption spectrum in the 400–2500 nm region, though Tb^{3+} has several excited energy levels, which are expected to yield transitions in the visible region. Selvan *et al.* [20] observed no bands in the visible region in CsCl:Tb system but saw an intense absorption band at 360 nm, which they attribute to $^5D_3$–$^7F_6$ transition of Tb^{3+}. The same absorption band has been reported at 380 nm in $LaBr_3$:Tb^{3+} crystal by Joshi *et al.* [21]. This is outside the range of our observations. However, two bands are observed in the absorption spectrum at 1890.89 nm and 2234.89 nm here. These bands are attributed to $^7F_2 \leftarrow {}^7F_6$ and $^7F_3 \leftarrow {}^7F_6$ transitions.

Tb^{3+} ion doped in tellurite glass at room temperature (30 °C) shows an intense greenish fluorescence. There are four sharp bands at 545.2, 587.4, 624.4, and 653.4 nm. These bands arise due to $^5D_4 \rightarrow {}^7F_5$, $^5D_4 \rightarrow {}^7F_4$, $^5D_4 \rightarrow {}^7F_3$, and $^5D_4 \rightarrow {}^7F_2$ transitions, respectively. No bands due to $^5D_4 \rightarrow {}^7F_6$ or $^5D_4 \rightarrow {}^7F_{1,0}$ could be observed even at increased sensitivity. The fluorescence band at 545.2 nm is most intense and shows three components at 545.2, 547.6, and 548.9 nm due to Stark splitting.

As mentioned earlier we have prepared Tb^{3+}-doped tellurite glass with different concentrations of Tb viz. 0.5, 1.0, 2.0, and 3.0 mol% of Tb_2O_3. It is found that the fluorescence intensity of the bands increases from 0.50 mol% to 1.0 mol%, but as we move towards higher concentration it seems to decrease (Fig. 1). This is due to the energy transfer from the excited to unexcited Tb^{3+} ions in the glass matrix thereby reducing the fluorescence yield. If there is energy transfer, it affects the lifetime of the level also.

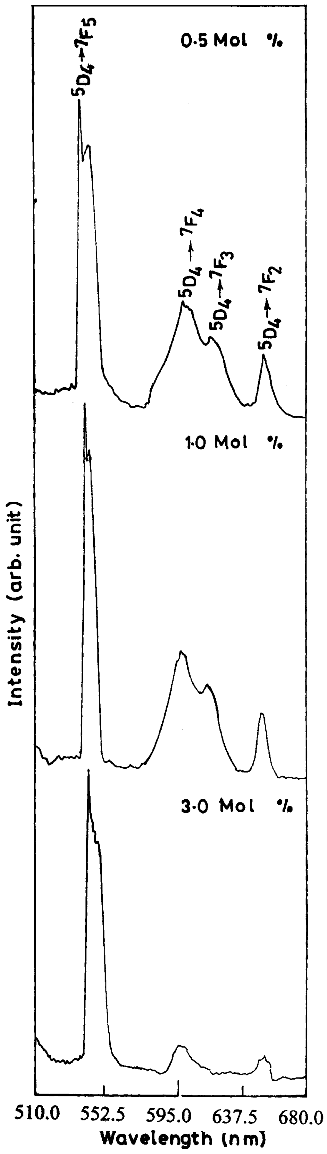

Figure 1 Effect of concentration of Tb^{3+} on the fluorescence intensity.

TABLE I Comparison of lifetime of $^5D_4$ level of Tb^{3+} in different host lattices

Host	Concentration of Tb^{3+}	Lifetime (ms)	Reference
TbF_3		0.18	[2]
Y_2O_3	0.001 wt%	2.8	[11]
Tb^{3+} phosphor	0.4 wt%	2.2	[25]
M_2O_2S:Eu^{3+}	1.0 wt%	0.58	[26]
Zinc phosphate glass	0.2 wt%	2.5	[12]
Borate glass	0.1 wt%	2.8	[27]
Oxyfluoroborate glass	0.5 mol%	1.73	[16]
	3.0 mol%	1.50	
	1.6 mol%	1.33	
	4.0 mol%	1.11	
	2.5 mol%	0.91	
Tellurite glass	0.5 mol%	1.00	[Present work]
	2.0 mol%	1.24	
	3.0 mol%	1.17	

In order to verify this we measured the lifetime of the $^5D_4$ level at different concentrations of Tb^{3+}. These values are given in Table I, which also lists the lifetime of the $^5D_4$ level in other lattices. It is noted that the lifetime of the $^5D_4$ level increases slightly when Tb_2O_3 concentration increases from 0.5 mol% to 1.0 mol% and then decreases at higher concentrations of Tb^{3+}. In order to understand the energy transfer mechanism we applied the Inokuti and Hirayama model [9]. According to this model the intensity of the band at the instant t is given as,

$$I(t) = I(0)\exp[-t/\tau_0 - \Gamma(1 - 3/S)C/C_0\,(t/\tau_0)^{3/S}] \tag{1}$$

where C_0 is the critical concentration and its value is found to be 1.49 mol% for this case. The critical transfer distance R_0 in this case is found to be 6.5 Å. This value is much larger than the critical distance for exchange interaction. Therefore, the energy transfer is dipolar. In this case the interaction is found to be of dipole–dipole type.

We measured fluorescence yield and the lifetime of the $^5D_4$ level at different temperatures from 276 to 523 K. It is found that the fluorescence yield and the lifetime of the $^5D_4$ level decrease as the temperature of the glass is increased. This is due to increase in lattice vibrations, which quenches the population of $^5D_4$ level. This can be understood as follows;

The rate of multiphonon relaxation at temperature T is affected by the population of the phonon mode $n(T)$.

The population of phonon mode at temperature T is given by [22] as,

$$n(T) = [\exp(h\omega/kT) - 1]^{-1}. \qquad (2)$$

The probability of creating "p" phonons in the relaxation process is proportional to $[n(T) + 1]^p$.

Therefore, the nonradiative decay rate due to multiphonon relaxation at temperature T is given by [23] as,

$$\begin{aligned} W_p(T) &= W_p(0)[n(T) + 1]^p \\ &= W_p(0)[1 - \exp(-h\omega/kT)]^{-p} \qquad (3) \end{aligned}$$

where $W_p(0)$ is the multiphonon decay rate at $T = 0$ K.

From Equation 3 it is clear that as the temperature of the glass (host material) increases, $W_p(T)$ increases. Therefore, with the increase in the temperature the nonradiative decay rate due to multiphonon relaxation will also increase. This causes the fluorescence yield and also the lifetime of the level to decrease with temperature. The temperature dependence of the fluorescence intensity and the lifetime of the $^5D_4$ level is shown in Figs 2 and 3.

Energy transfer from Tb^{3+} to Eu^{3+} in a tellurite glass containing both the ions has also been studied. The fluorescence spectra of the tellurite glass doped with 1 mol% of Tb^{3+} and 1 mol% of Eu^{3+} have been studied separately as well as in a mixture of 1 mol% Tb^{3+} + 1 mol% Eu^{3+}; 1 mol% Tb^{3+} + 1.5 mol% Eu^{3+}; and 1 mol%Tb^{3+} + 2 mol% Eu^{3+} respectively. On excitation with 476.5 nm line Tb^{3+} glass shows fluorescence lines at 545.2 nm, 587.4 nm, 624.4 nm, and 653.6 nm as mentioned earlier. In the case of 1 mol% Eu^{3+}-doped TeO_2 glass excitation with 476.5 nm line with the same power gives lines of Eu^{3+} at 572.8 nm, 590.4 nm, 613.03 nm, 644.6 nm, and 700.6 nm as also reported by Akshaya *et al.* [24].

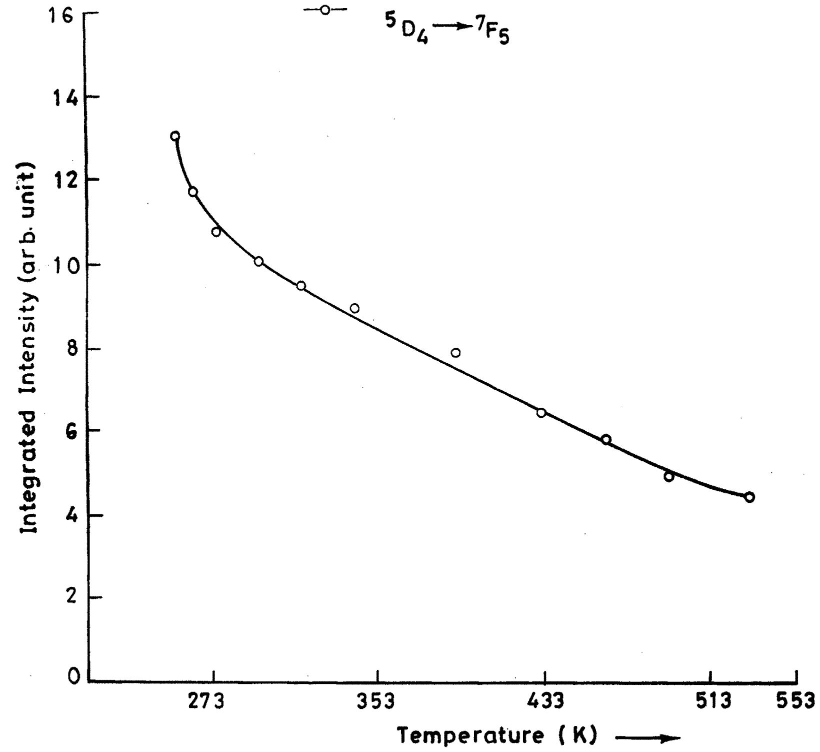

Figure 2 The temperature dependence of the fluorescence intensity of $^5D_4$–$^7F_5$ transition.

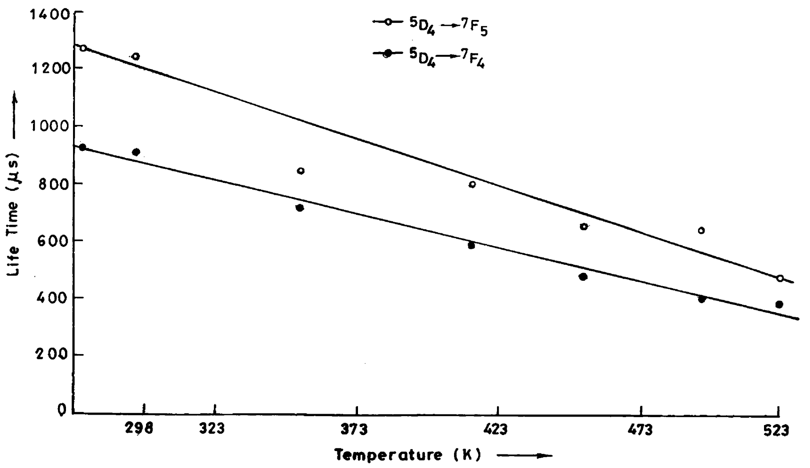

Figure 3 The temperature dependence of the lifetime of $^5D_4$ level in $^5D_4$–$^7F_5$ and $^5D_4$–$^7F_4$ transitions.

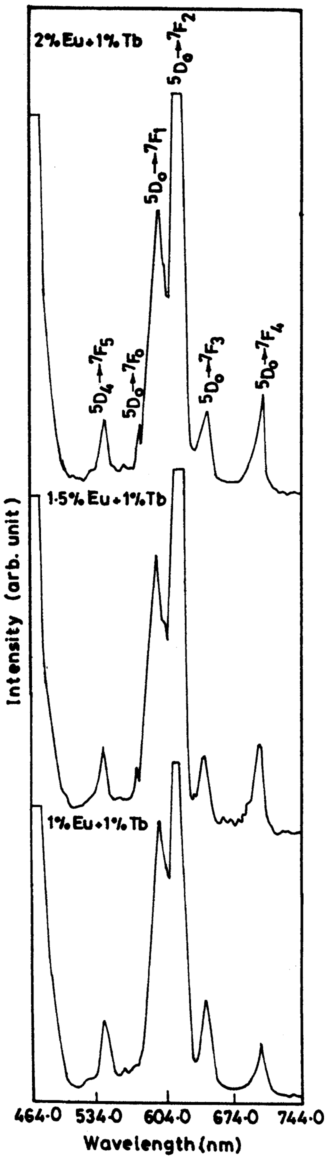

Figure 4 The mechanism of the energy transfer from Tb^{3+} to Eu^{3+} in Tb^{3+} + Eu^{3+} codoped tellurite glass.

Again if we excite the glass containing 1 mol% Tb^{3+} + 1 mol% Eu^{3+} with the same line with the same power keeping all the other parameters unchanged, spectral lines corresponding to both the rare earth ions are seen. However, the fluorescence intensity of the lines due to Tb^{3+} ion is greatly reduced as compared to their intensity in the glass containing 1 mol% Tb^{3+} only. On the other hand the fluorescence intensity of Eu^{3+} ion ($^5D_0 \rightarrow {}^7F_2$) in the co-doped glass is increased enormously compared to the fluorescence intensity in the glass doped only with 1 mol% Eu^{3+}.

It appears that $^5D_4 \rightarrow {}^7F_5$ transition of Tb^{3+} emitting at 545.2 nm is reabsorbed by Eu^{3+} ion in its ground state $^7F_0$ and excites it to $^5D_0$ level. The branching ratio for $^5D_0 \rightarrow {}^7F_2$ transition in Eu^{3+} being large, it fluoresces strongly at this transition. The mechanism is presented in the Fig. 4.

For glass hosts containing 1 mol% Tb^{3+} + 1.5 mol% Eu^{3+} and 1 mol% Tb^{3+} + 2.0 mol% Eu^{3+}, the fluorescence intensity of Eu^{3+} ($^5D_0 \rightarrow {}^7F_2$) appears to be further enhanced, while the fluorescence intensity of Tb^{3+} in the co-doped glass is reduced (but not in the same proportion as in 1:1 case).

Finally, we have also studied the fluorescence of the glass containing 1.5 mol% Tb^{3+} + 1 mol% Eu^{3+}, 2 mol% Tb^{3+} + 1 mol% Eu^{3+}. We noted that the fluorescence intensity (after excitation with 476.5 nm line, same power) for both the rare earth ions is reduced compared to the singly doped rare earth glass. It seems that the concentration of Tb^{3+} ion is large enough to initiate a self-quenching.

We also studied the effect on the fluorescence of Tb^{3+} doped glass by irradiating the glass with different doses (150 CGy, 300 CGy, and 600 CGy) of γ-rays. Irradiation of the glass with γ-rays creates defects in the lattice and changes the ionization state of the rare earth present in the host. We monitored the infrared (IR) absorption as well as the laser fluorescence spectra of the irradiated glasses at different time intervals. The unexposed

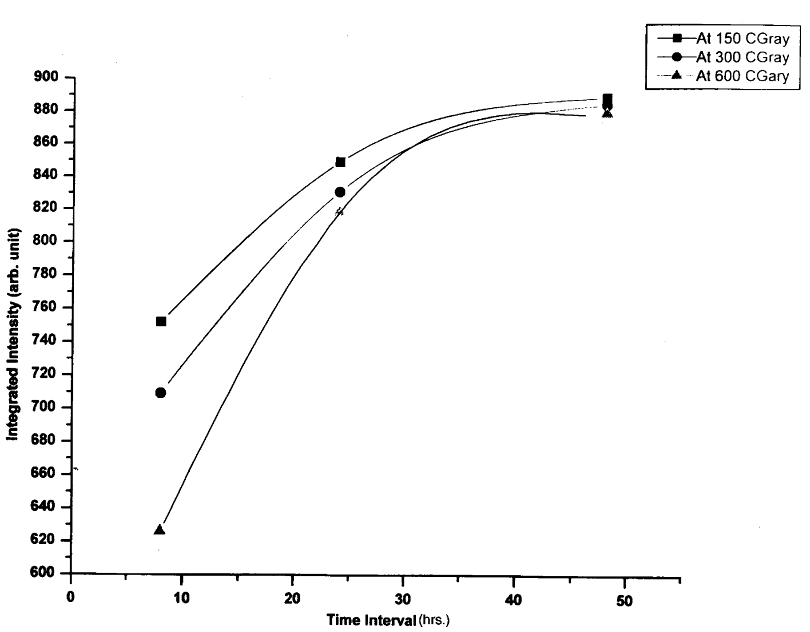

Figure 5 Recovery of the fluorescence intensity after different time intervals.

glass in its IR spectrum shows an absorption band near 650 cm^{-1} and strong transmission at 950 cm^{-1}. The infrared (IR) spectra of the exposed glasses show an overall increase in background absorption, and the peak at 650 cm^{-1} becomes broad and weak. These changes are directly proportional to the dose of the γ-ray. The infrared (IR) spectra do not show any substantial change in the structure with time. It seems that γ-ray radiation disrupts the lattice, breaks Te—O bonds, and this effect is dependent on the γ-ray dose.

The fluorescence spectra of the glasses before and immediately after irradiation as well as after a lapse of 24, 48, and 56 hr were recorded. We noted that the fluorescence intensity of the Tb^{3+} in the irradiated glass is less than that for the unexposed glass and this decreases further as the dose of γ-ray increases. However, the fluorescence intensity increases with time as the Tb^{3+} regains its original state. This has been explained as follows.

As the dose of γ-rays increases, an increasing number of defects are created in the host. The ionization state of Tb^{3+} is also changed. Thus the number of Tb^{3+} giving fluorescence is reduced. Due to the loosening of Te—O bonds the defects thus formed behave as killer sites, reducing the overall fluorescence intensity. However, with time the host lattice tries to regain its original configuration, restoring the fluorescence intensity. Overall recovery takes 56 hr (Fig. 5).

Acknowledgments

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