

Stark splitting and energy transfer between Dy^{3+} – Ho^{3+} and between Tb^{3+} – Er^{3+} in calcium–lithium borate glass

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Abstract. Fluorescence spectrum of Dy^{3+} , Dy^{3+} – Ho^{3+} , Tb^{3+} and Tb^{3+} – Er^{3+} doped in calibo glass have been studied using Ar^+ and excimer lasers. Non-radiative energy transfer from trivalent dysprosium and terbium (donors) to holmium and erbium (acceptors) respectively has been observed on the basis of decrease in the life time of the levels and reduction in fluorescence intensity of Dy^{3+} and Tb^{3+} on increasing Ho and Er concentrations. The interaction mechanism of donor and acceptor ions is found to be dipole–dipole in both cases. Various parameters such as donor-acceptor distances, non-radiative energy transfer efficiency (η) and energy transfer probability (P_{da}) have been computed. Stark splitting have also been marked in several intense transition of the two.

Keywords. Fluorescence; non-radiative; dipole–dipole; transfer efficiency; Stark components.

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1. Introduction

The mechanism of donor-acceptor energy transfer is important in the study of phosphors and laser materials. The energy transfer may be through radiative or non-radiative processes. The non-radiative energy transfer processes are major factors in determining the long wavelength operating limits for the solid state lasers [1].

The non-radiative energy transfer has been studied by several authors [2–8] in different glasses with different rare-earth ions as dopant. A mechanism for energy transfer from donor to acceptor was first suggested by Forster [6] and then extended by Dexter [7]. This theory was however found inadequate to explain all concentration regimes of the acceptor. Fong and Diestler [8] developed a theory which takes into account the fact that for low acceptor concentrations there is usually a one-to-one correspondence between donor and acceptor while at higher acceptor concentrations one donor ion may interact with two or more neighbouring acceptor ions.

The non-radiative energy transfer from Dy^{3+} to Pr^{3+} in calibo and phosphate glasses has been reported by Joshi and coworkers [9, 10]. Similarly energy transfer from Tb^{3+} to Er^{3+} in sodium borate glass has also been studied by Joshi and Pandey [11]. At low acceptor concentration they found the transfer mechanism to be diffusion limited while at higher acceptor concentrations it involves electric dipole–dipole interaction. Nakazawa and Shionoya [12] have studied energy transfer between Tb^{3+} and several other rare earth

ions including Er^{3+} in calcium phosphate glass and the transfer mechanism was shown to involve an electric quadrupolar interaction. Energy transfer from Tb^{3+} to Nd^{3+} in borate glass lattice has been studied by Pant *et al* [13] and from Tb^{3+} to Er^{3+} in phosphate glass by Van Uitert [14] and a dipole–dipole transfer mechanism was reported.

In this paper we report the fluorescence spectra of Dy, Dy + Ho, Tb and Tb + Er doped in calibo glass host. We have been able to resolve the Stark components in the case of the intense transitions in Dy^{3+} and Tb^{3+} . We have also measured the life time of the fluorescing levels of the two in the presence and absence of the acceptor. A significant energy transfer from the excited Dy^{3+} (Tb^{3+}) to Ho^{3+} (Er^{3+}) was noticed from the weakening of the fluorescent lines and decrease in life time of Dy^{3+} (Tb^{3+}) level in the presence of Ho^{3+} (Er^{3+}) as acceptor. The mechanism was found to be dominated by dipole–dipole interaction. These changes have also been used to estimate the energy transfer efficiency (η) and transfer probability (P_{da}) in the two cases.

2. Experimental

The Dy^{3+} and $\text{Dy}^{3+} + \text{Ho}^{3+}$, Tb^{3+} and $\text{Tb}^{3+} + \text{Er}^{3+}$ doped glasses were prepared from the spectral grade reagents with 99% stated purity by mixing 20% CaO, 10% Li_2O_3 and 70% B_2O_3 . Keeping the Dy^{3+} concentration (1 wt%) fixed the concentration of Ho^{3+} was varied from 0.5 to 3 wt.%. Similarly the concentration of Tb^{3+} was held (2 wt.%) fixed and Er^{3+} concentration was varied from 0.5 to 5 wt.%. The mixture powder was melted in platinum crucible heated up to 1000°C in an electric furnace and the melt was poured into a suitable cast. The moulded glass was grinded and polished carefully to make it amenable to spectroscopic studies.

The density and refractive index were measured and other related physical properties were calculated following the procedure outlined in our previous paper [15] and

Table 1. Various physical parameters of Dy, Dy + Ho, Tb and Tb + Er in calibo glass.

Acceptor	Ho^{3+}						Er^{3+}			
	0.0	0.5	1.0	1.5	2.0	3.0	1.0	2.0	3.0	5.0
Conc. (wt %)	0.0	0.5	1.0	1.5	2.0	3.0	1.0	2.0	3.0	5.0
Acceptor ion conc. ($N \times 10^{22}$ ions/cc)	–	0.45	0.86	1.02	1.56	2.22	0.92	1.56	2.91	4.5
Acceptor–acceptor separation	–	28.11	22.65	21.40	18.57	16.51	22.15	18.57	15.09	13.22
Acceptor ionic- radius (Å)	–	17.94	14.45	13.66	11.85	10.54	14.13	11.85	9.63	8.44
Ref. index	1.56	1.53	1.57	1.55	1.52	1.57	1.49	1.50	1.52	1.49
Density	3.12	2.95	3.00	3.11	3.10	2.86	2.91	2.87	3.23	3.51
Thickness	0.15	0.16	0.15	0.14	0.15	0.16	0.25	0.24	0.24	0.26
Dielectric const.	2.43	2.34	2.46	2.40	2.31	2.46	2.22	2.20	2.21	2.24
Reflection losses (R%)	4.59	4.37	4.90	4.63	4.22	4.90	3.90	3.82	3.84	3.98

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the results are presented in table 1. The average donor-acceptor distance in Dy–Ho system varies from 15.5 to 22.5 Å and for the Tb–Er system it varies from 12.3 to 17.2 Å

The fluorescence measurements were made at room temperature and at liquid N₂ temperature using Ar⁺ laser lines as exciting line. Ne emission lines from Fe–Ne hollow cathode lamp recorded simultaneously were used for wavelength calibration. It is interesting to note that the fluorescence intensity increases even up to 6 mol % of the Dy³⁺ and Tb³⁺ in the calibo glass host.

The life time measurements were made using excimer (XeCl) laser at 308 nm at 10 Hz repetition rate and a 5001 model EG&G box car averager with 5 ns gate width.

3. Results and discussion

The optical properties of trivalent Dy³⁺ and Tb³⁺ in glassy and other host matrices have been studied extensively [16–18]. From these studies it is well known that Dy³⁺ and Tb³⁺ give broad emissions in the visible region.

The fluorescence spectra of Dy³⁺, Dy³⁺ + Ho³⁺, Tb³⁺ and Tb³⁺ + Er³⁺ in calibo glass are shown in figures 1 and 2. Though both Dy³⁺ and Tb³⁺ ions show fluorescence at all the lines emitted by the Ar⁺ laser, the fluorescence yield is maximum at 488.0 nm

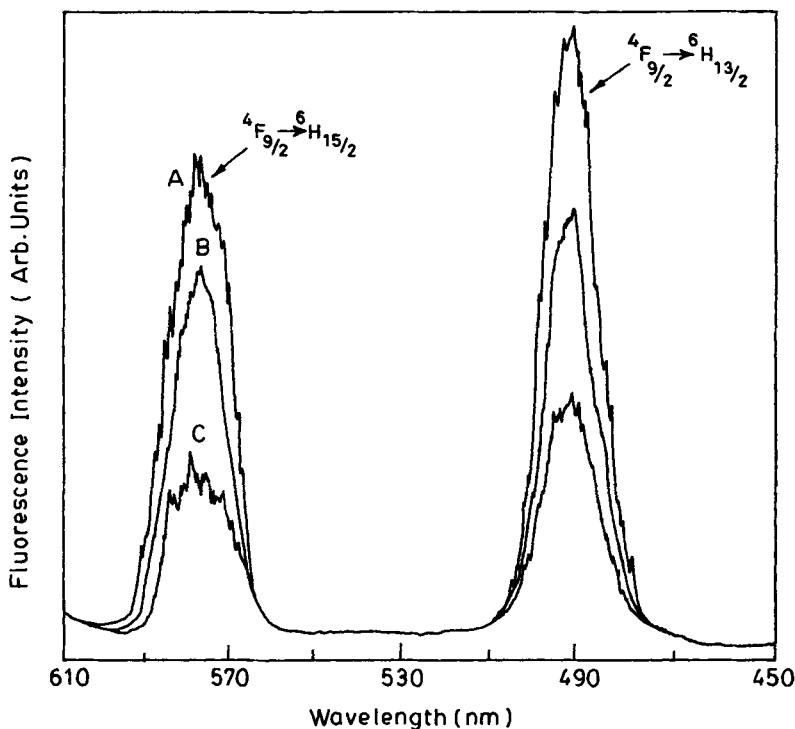


Figure 1. (A) Fluorescence spectra of Dy³⁺ (1 wt %), (B) Dy³⁺ (1 wt %) + Ho³⁺ (1 wt %) and (C) Dy³⁺ (1 wt %) + Ho³⁺ (3 wt %) in calibo glass at 300 K.

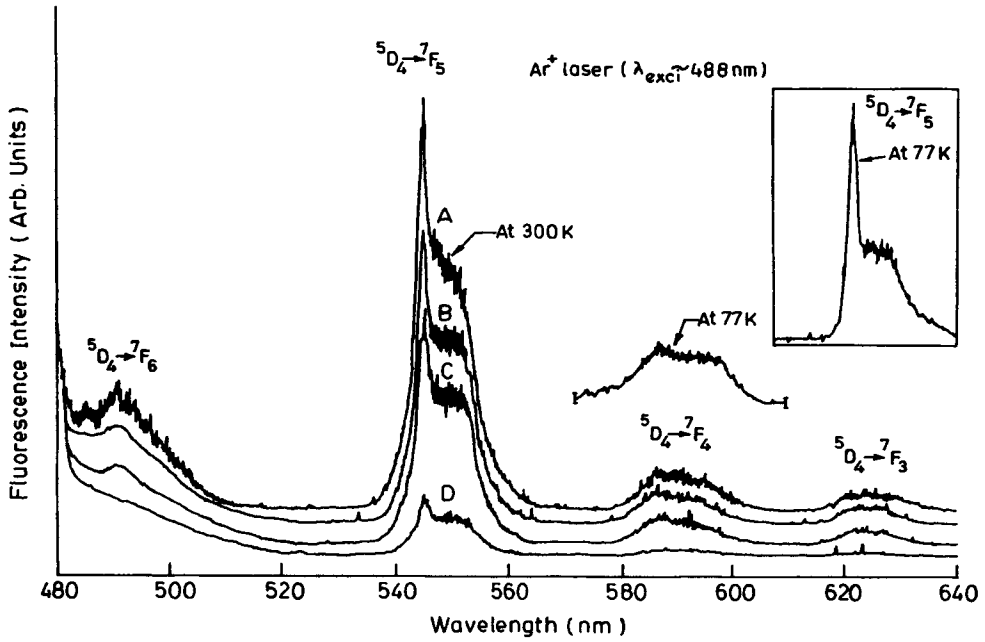


Figure 2. (A) Fluorescence spectrum of Tb^{3+} (2 wt %), (B) Tb^{3+} (2 wt %) + Er^{3+} (1 wt %), (C) Tb^{3+} (2 wt %) + Er^{3+} (2 wt %) and (D) Tb^{3+} (2 wt %) + Er^{3+} (5 wt %) doped in calibo glass at 300 K.

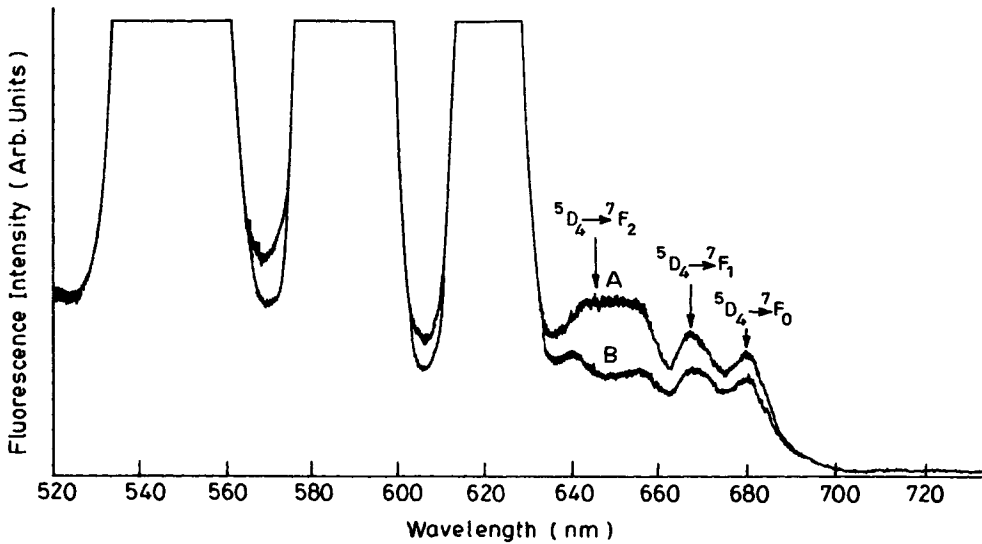


Figure 3. (A) Fluorescence spectrum of Tb^{3+} (2 wt %) and (B) Tb^{3+} (2 wt %) + Er^{3+} (5 wt %) at 50 mW laser power.

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Table 2. Fluorescence lines and their assignments in the spectrum of Dy, Dy + Ho; Tb and Tb + Er doped in calibo glass at 300 K.

Ion	Wavelength (Å)	Energy (cm ⁻¹)	Assignment	R.I.	FWHM (cm ⁻¹)	Ratio of int. of the peak at different conc. of Ho ³⁺ (wt %)		
						(1)	(2)	(3)
Dy ³⁺	5720	17477	⁴ F _{9/2} → ⁶ H _{13/2}	49	470	1	0.62	0.42
	4820	20741	⁴ F _{9/2} → ⁶ H _{15/2}	39	710	1	0.61	0.42
						At different conc. of Er ³⁺ (wt %)		
						(2)	(3)	(5)
Tb ³⁺	4911	20357	⁵ D ₄ → ⁷ F ₆	12	350	0.53	0.40	0.20
	5451	18340	⁵ D ₄ → ⁷ F ₅	30	290	0.52	0.39	0.19
	5881	17003	⁵ D ₄ → ⁷ F ₄	6.6	600	0.52	0.39	0.18
	6242	16015	⁵ D ₄ → ⁷ F ₃	5.3	500	0.53	0.40	0.20
	5609	15360	⁵ D ₄ → ⁷ F ₂	1.6	470	0.52	0.39	0.19
	6670	14988	⁵ D ₄ → ⁷ F ₁	1.3	140	0.53	0.39	0.20
	6788	14725	⁵ D ₄ → ⁷ F ₀	1.1	70	0.52	0.39	0.20

for Tb³⁺ and at 457.9 nm for Dy³⁺. We observed two emission lines for Dy³⁺ and four lines for Tb³⁺ at 25 mW of exciting laser power (see figures 1 and 2). However on increasing the laser power to 50 mW some additional lines are seen in the case of Tb³⁺ (see figure 3), but there is no such effect in Dy³⁺. From the recorded fluorescence profiles at two temperatures (300 and 77 K) in the two cases we notice that at liquid nitrogen temperature the peak fluorescence intensity is increased and the bands appear sharper. Fluorescence lines and their assignments in the two cases are presented in table 2.

Incorporating Ho³⁺ and Er³⁺ ions along with Dy³⁺ and Tb³⁺ respectively (in calibo glass) decreases the intensities of the Dy³⁺ and the Tb³⁺ emission peaks by different ratios (see figures 1 and 2).

3.1 Fluorescence spectra of Dy³⁺ and Dy³⁺ + Ho³⁺

The fluorescence spectra of Dy³⁺ and Dy³⁺ + Ho³⁺ in calibo glass excited by the 457.9 nm line of the Ar⁺ laser are shown in figure 1. The excited Dy³⁺ ion from ⁴I_{15/2} state decays rapidly to the ⁴F_{9/2} metastable state. The ⁴F_{9/2} level decays by fluorescence to the ground ⁶H_j multiplet (⁴F_{9/2} → ⁶H_{13/2} and ⁴F_{9/2} → ⁶H_{15/2}) giving emission lines at 572 nm and 482 nm respectively. The observed line widths are large probably owing to inhomogeneous local fields in the glass. One observes the same two lines in the fluorescence from other glasses doped with Dy though the observed wavelengths in calibo glass are slightly different than for the other glasses (borate, phosphate and heavy metal fluoride glasses [19]). It appears that the transition probability from ⁴F_{9/2} to other components of the ground levels are very small. A look at the fluorescence spectrum of the calibo glass containing both Dy and Ho with varying concentrations of Ho reveals that the intensity of the Dy fluorescence lines decreases

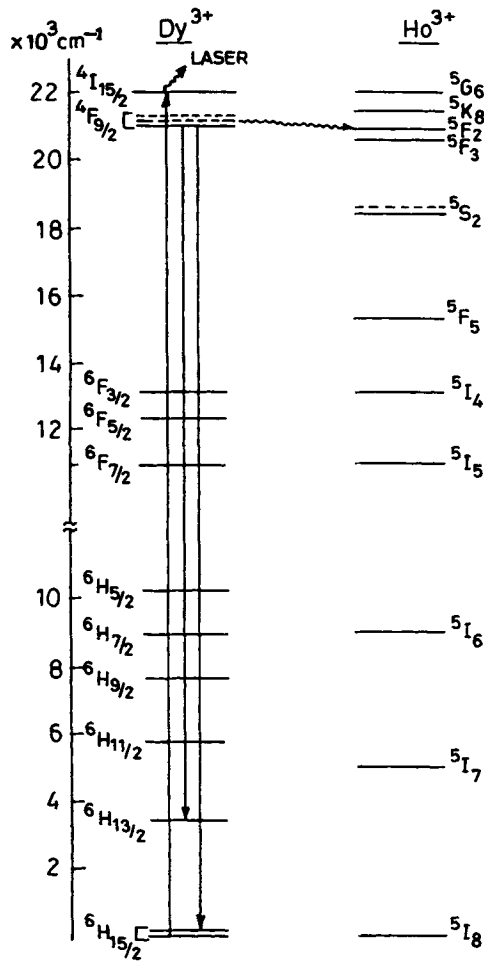


Figure 4. Energy level diagram and energy transfer scheme of Dy^{3+} and Ho^{3+} in calibo glass.

as the concentration of Ho increases. No fluorescence lines attributable to Ho are observed even up to 800 nm. This latter observation indicates that the Ho level being excited through energy transfer from Dy^{3+} decays non-radiatively. The energy separation between the ${}^4F_{9/2}$ level of Dy^{3+} and its ground state (21097 cm^{-1}) is almost the same as the height of the non-radiative level 5F_2 (21073 cm^{-1}) of Ho^{3+} over its ground state. So the energy can be transferred easily from the excited Dy^{3+} level to the Ho^{3+} level (see figure 4). There are a large number of other non-radiative levels in Ho^{3+} viz, 3K_8 , 5G_6 close to the 5F_2 state while the Ho^{3+} states known to decay radiatively have energies $18650\text{--}15550\text{ cm}^{-1}$ [19–21] above the Ho^{3+} ground state. Therefore, the presence of Ho ion in the same lattice as the Dy ion depletes the population of ${}^4F_{9/2}$ level of Dy^{3+} in a non-radiative manner. The depletion of the upper ${}^4F_{9/2}$ level of Dy^{3+} is established by the fact that the decrease in intensity is similar for both the fluorescence lines. The

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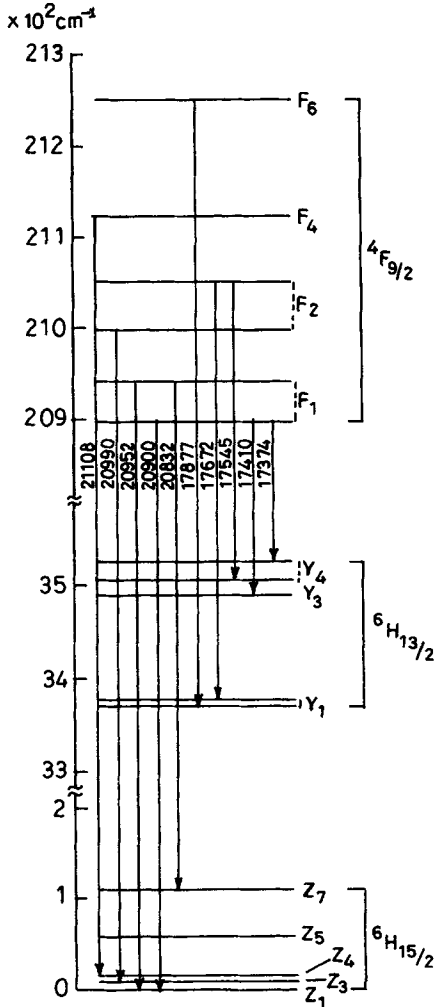


Figure 5. Stark splitting in different energy levels and observed transitions in Dy³⁺ doped in calibo glass.

fact that in our study no additional fluorescence lines due to the presence of Ho are observed is probably due to

- (i) no direct excitation of the Ho ions as the exciting line is far removed in energy from suitable Ho³⁺ levels
- (ii) Absorption of the emitted radiation from the Dy³⁺ ions is not possible as Ho³⁺ absorption lines are far removed in energy

Joshi and coworkers [9, 10] also could not detect any radiative part in the energy transfer from Dy³⁺ to Pr³⁺ in calibo and phosphate glasses doped simultaneously with both rare earths. Self-quenching of Dy³⁺ fluorescence (via exchange interactions) has

Table 3. Assignment of Stark components of ${}^4F_{9/2} \rightarrow {}^6H_{15/2,13/2}$ transitions of Dy^{3+} and ${}^5D_4 \rightarrow {}^7F_{5,4}$ transitions of Tb^{3+} in calibo glass.

${}^4F_{9/2} \rightarrow {}^6H_{15/2}$	${}^4F_{9/2} \rightarrow {}^6H_{13/2}$	${}^5D_4 \rightarrow {}^7F_5$	${}^5D_4 \rightarrow {}^7F_4$
20694 –	17374 ($F_1 - Y_4$)	18440 ($A_4 - X_1$)	17265 ($A_6 - Y_1$)
20832 ($F_1 - Z_7$)	17410 ($F_1 - Y_3$)	18400 ($A_1 - X_1$)	17143 ($A_1 - Y_2$)
20900]	17545 ($Y_2 - Y_4$)	18388 ($A_3 - X_2$)	17100 –
20952] ($F_1 - Z_1$)	17672 ($F_2 - Y_1$)	18310 ($A_3 - X_5$)	
20990 ($F_2 - Z_3$)	17877 ($F_6 - Y_1$)	18290 ($A_4 - X_7$)	
21108 ($F_4 - Z_4$)	17980 –		

been observed at considerably high Dy concentrations in various crystalline and glassy [20] hosts. The Dy concentration in our case is probably too small to cause any self-quenching.

The two observed fluorescence lines are seen to split into several Stark components when the slit width of the spectrometer is reduced and the laser power is increased. The spectral peaks observed at 482 nm and at 572 nm show five components each. The individual components could be assigned on the basis of the energy level data from Dieke [21] and they are shown in figure 5. Their assignments are given in table 3.

3.2 Fluorescence spectra of Tb^{3+} and $\text{Tb}^{3+} - \text{Er}^{3+}$

The fluorescence spectra of Tb^{3+} doped calibo glass recorded at room and at liquid nitrogen temperature show seven emission lines at 491.1, 545.1, 588.1, 624.2, 654.0, 667.0 and 678.8 nm corresponding to all the seven components of 7F_j which is rare. They are assigned to ${}^5D_4 \rightarrow {}^7F_j$ ($j = 6, 5, 4, \dots, 0$) transitions of Tb^{3+} and are shown in figures 2 and 3. The fluorescence spectrum at liquid nitrogen temperature is sharper than the one at room temperature thereby emphasizing the role of the host matrix lattice vibrations in causing the line broadening. The fluorescence yield in Tb^{3+} is maximum for an excitation wavelength of 488.0 nm because the energy of the 5D_4 ($\sim 20462 \text{ cm}^{-1}$) level of Tb^{3+} above its ground state is closed to the exciting photon energy ($\sim 20491 \text{ cm}^{-1}$).

Addition of Er^{3+} reduces the intensity of the fluorescence lines of Tb^{3+} . At 5 mol % of Er^{3+} , the ${}^5D_4 \rightarrow {}^7F_2$ peak of Tb^{3+} which appears as a single broad peak at lower Er^{3+} concentrations split into two well defined peaks. Though ${}^4F_{7/2}$ level of Er^{3+} lie very close to the 5D_4 level of Tb^{3+} , it is difficult to say that the extra peak is due to transition from ${}^4F_{7/2}$ level of Er^{3+} to its lower level. The near equality of the energy difference between the 5D_4 level ($\sim 20462 \text{ cm}^{-1}$) of Tb^{3+} from its ground state to that of the ${}^4F_{7/2}$ level of the Er^{3+} (see figure 6), permits efficient energy transfer from Tb^{3+} to Er^{3+} . The slight mismatch in the two energy differences may be compensated for by the host lattice phonons. The ${}^4F_{7/2}$ level of Er^{3+} is a fluorescing level but it is surprising that it does not give any line due to its de-excitation in the spectral region 480–740 nm in calibo host. Joshi and Joshi [22] and Joshi *et al* [23] have made a similar study for energy transfer from Eu^{3+} to Er^{3+} and from Tb^{3+} to Er^{3+} in calibo and sodium phosphate glasses respectively. In these cases also the excitation energy is transferred from 4D_0 level of Eu^{3+} and 5D_4 level of Tb^{3+} to the level ${}^4F_{7/2}$ of Er^{3+} but no extra line due to Er^{3+} is

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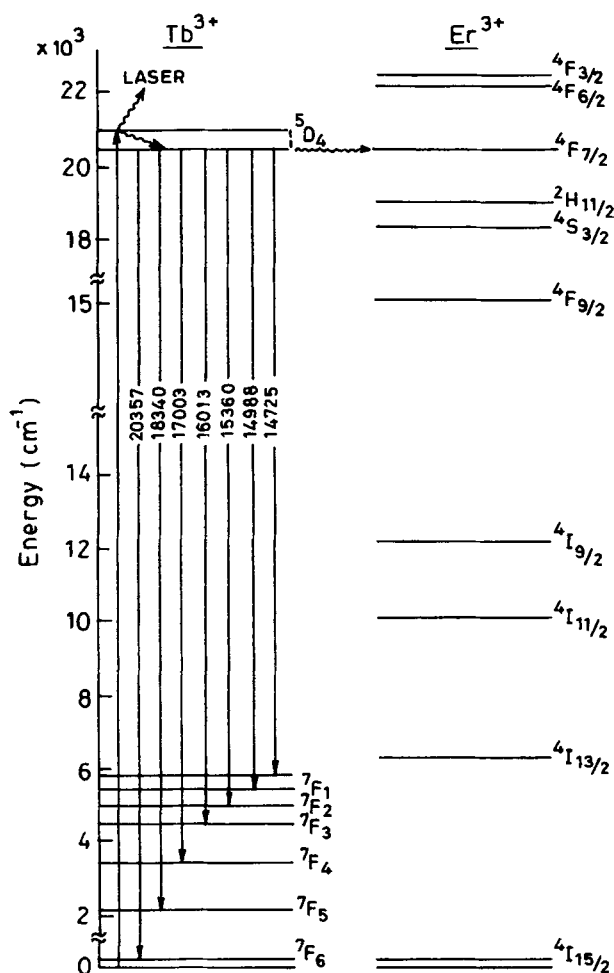


Figure 6. Energy transfer scheme of Tb³⁺ and Er³⁺ in calibo glass.

observed. It appears that Er³⁺ in the ⁴F_{7/2} level relaxes rapidly to the ⁴I_{13/2} level (metastable state) which then decays through the transition ⁴I_{13/2} → ⁴I_{15/2} at 1.5 μm in the IR region which is a lasing transition. The energy levels of Tb³⁺ and Er³⁺ are shown in figure 6.

The spectral peak observed at 545.1 nm ascribed to the transition ⁵D₄ → ⁷F₅ of Tb³⁺ is very intense and we have succeeded in recording Stark splittings in it by increasing the input laser power and by reducing the slit width of the monochromator. Five Stark components are seen in this line while for the other ⁵D₄ → ⁷F₄ transition two lines are seen at 583.3 nm and 579.2 nm. Assignments of the observed Stark splitted components, have been made on the basis of the known energy levels of the triply ionized rare earth ions [21] and are given in table 4. The energy levels are shown in figure 7.

Table 4. Energy transfer efficiency (n_r) and the energy transfer probability P_{da} between donor and acceptor.

Donor (%)	Acceptor (%)	Donor-acceptor			Intensity (I_d)	n_r	$P_{da} \times 10^{-3} \text{ sec}^{-1}$
		Average distance (A)	Lifetime (τ) ms				
Dy ³⁺ 1	Ho ³⁺ 0	—	1.012	39 (I_{d0})			
	1	19.8	0.726	28	0.28	0.389	
	2	17.2	15.5	20	0.48	0.814	
	3	15.5	0.427	16	0.58	1.354	
Tb ³⁺ 2	Er ³⁺ 0	—	1.4825	27 (I_{d0})			
	1	17.27	1.24	19	0.29	0.155	
	2	15.70	1.01	19	0.35	0.317	
	3	13.65	0.820	15	0.45	0.546	
	5	12.32	0.510	4.2	0.85	1.766	

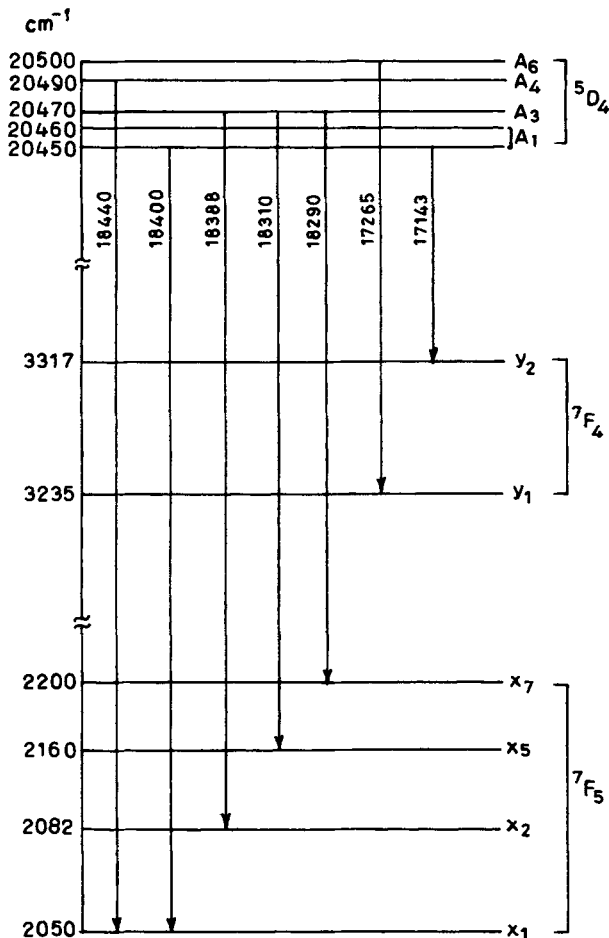


Figure 7. Energy level of Stark component observed in Tb³⁺ doped in calibo glass.

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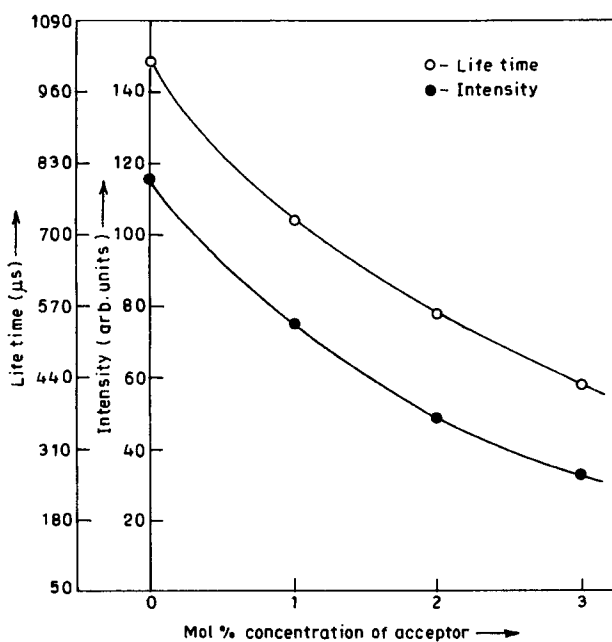


Figure 8a. Variation of life time and intensity with acceptor concentration for the ${}^4F_{9/2} - {}^4I_{13/2}$ transition of Dy^{3+} (with Dy^{3+} concentration 1% fixed).

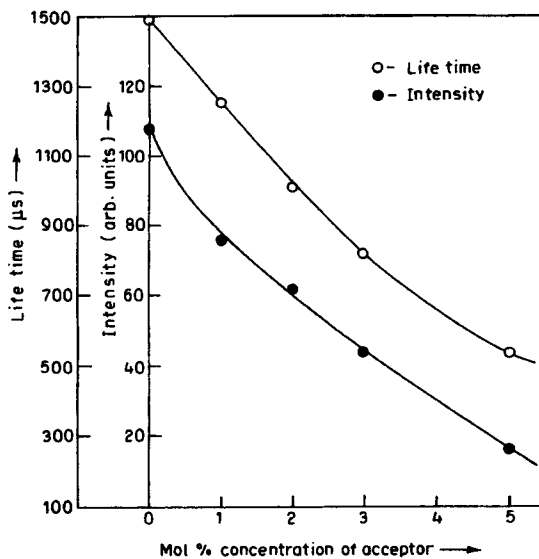


Figure 8b. Variation of life time and intensity with acceptor concentration for the ${}^5D_4 - {}^7F_5$ transition of Tb^{3+} (with Tb^{3+} concentration 2% fixed).

4. Energy transfer and life time of the levels

The life time of ${}^4F_{9/2}$ level of Dy^{3+} and 5D_4 level of Tb^{3+} were measured in the presence and absence of acceptor ions Ho^{3+} and Er^{3+} respectively. The life time of ${}^4F_{9/2}$ level of Dy^{3+} were found to be 1.012 ms and of 5D_4 level of Tb^{3+} 1.485 ms in the absence of acceptors. The life time of these levels were found to decrease in the presence of the acceptor. The life time decreases rapidly on increasing the acceptor concentrations. The variation of intensity and life time with acceptor concentration are shown in figures 8a and 8b. The absence of any line due to acceptor in the spectra indicates that the energy transfer is non radiative.

The energy transfer probabilities (P_{da}) and energy transfer efficiencies (η_T) have been calculated employing the formula given by Reisfeld [24]

$$P_{da} = 1/\tau_d((\eta_{d0}/\eta_d) - 1) = 1/\tau_d((I_{d0}/I_d) - 1) = (1/\tau_d - 1/\tau_{d0})$$

$$\eta_T = 1 - (\eta_d/\eta_{d0}) = 1 - (I_d/I_{d0})$$

where η_d and η_{d0} are the donor fluorescence quantum efficiencies in the presence and absence of the acceptor respectively (for the same donor concentration) and I_d , I_{d0} are the corresponding fluorescence intensities. τ_d and τ_{d0} are the measured decay time of the donor fluorescence in the presence and absence of the acceptor. The measured values are given in table 4. The calculated values for the energy transfer efficiencies and energy transfer probabilities are also given in the same table.

The mechanism responsible for energy transfer from donor to acceptor may be identified by plotting energy transfer probability (P_{da}) against the square of the donor + acceptor concentration ($C_d + C_a$)². This type of plot in the two cases are given in figure 9.

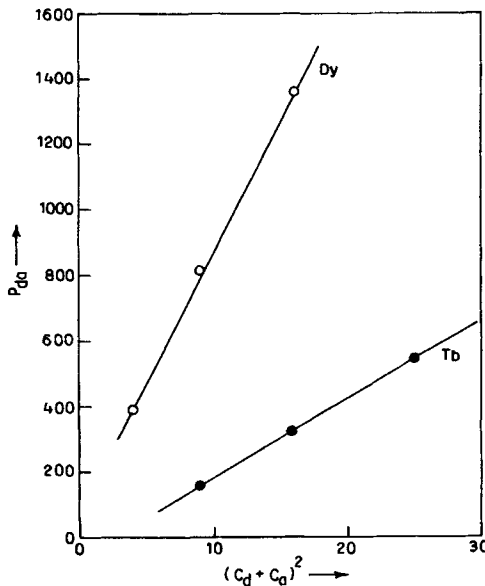


Figure 9. A plot of energy transfer probability versus concentration².

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The curves are straight line. This linear dependence suggest that the rate constant is proportional to inverse sixth power of the ion distance (i.e. $C^S/3 = C^{6/3} \sim 1/R^6$). The value of $S = 6$ indicates that electric dipole–dipole coupling is the predominant interaction mechanism for energy transfer. At very large concentration of acceptor a deviation from the linearity is marked. Such a deviation may be due to some other mechanism which has started taking place in the glass with the larger acceptor concentration. This is also supported by an abrupt decrease in fluorescence intensity of Tb^{3+} when the concentration of Er^{3+} is 5%.

5. Conclusion

Fluorescence spectra of Dy^{3+} , $Dy^{3+} + Ho^{3+}$, Tb^{3+} and $Tb^{3+} + Er^{3+}$ have been studied at different concentration of Ho^{3+} and Er^{3+} . From the variation in intensity of the spectral lines it is concluded that Dy^{3+} and Tb^{3+} are good sensitizers for Ho^{3+} and Er^{3+} ions in calibo glass hosts. The lifetime of the ${}^4F_{9/2}$ level of Dy^{3+} and 5D_4 level of Tb^{3+} in presence and absence of acceptor Ho^{3+} and Er^{3+} respectively have been measured. From this it is concluded that a non-radiative energy transfer is taking place and the mechanism is electric dipole–dipole. Stark splitting have been marked in some of the strong transitions of the two.

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