

Excitation energy transfer between Eu^{3+} and Tm^{3+} ions in zinc phosphate glass

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Non-radiative energy transfer from Eu^{3+} to Tm^{3+} has been studied by observing the steady state emission of Eu^{3+} with varying concentration of Tm^{3+} in zinc phosphate glass. It has been observed that Eu^{3+} ion emission intensity decreases with increasing Tm^{3+} concentration resulting in a non-radiative energy transfer from Eu^{3+} to Tm^{3+} whereas energy transfer from Tm^{3+} to Eu^{3+} was not observed between donor and acceptor ions. This energy transfer has been explained on the basis of cross-relaxation of energy. The energy transfer mechanism and other parameters related to energy transfer between Eu^{3+} and Tm^{3+} have been computed.

Keywords: Excitation energy, Non-radiative energy transfer, Phosphate glass, Fluorescent spectra

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1 Introduction

Trivalent thulium ion can be used as a potential laser in some of its transitions. Besides others one most important transition of Tm^{3+} is ${}^3\text{F}_4 \rightarrow {}^3\text{H}_6$. Though the ${}^3\text{H}_6$ level is the ground level of Tm^{3+} , nevertheless, it can be used in continuous wave laser operations at low temperature and pulsed at room temperature¹. Instead of directly pumping the ${}^3\text{F}_4$ level of Tm^{3+} , it is advantageous to pump it indirectly via non-radiative energy transfer from some sensitizer ion.

Riesfeld *et al.*² have studied/observed non-radiative energy transfer between Tm^{3+} and Er^{3+} ions in phosphate and borate glasses and their results show a mutual migration of energy between Tm^{3+} and Er^{3+} ions. Joshi *et al.*³ have observed a non-radiative energy transfer from Tm^{3+} to Nd^{3+} and Ho^{3+} in phosphate glass. Keeping the above results in mind, we have taken Eu-Tm system for energy transfer study.

2 Experimental Details

Sodium dihydrogen phosphate 2-hydrate ($\text{NaH}_2\text{PO}_4 \cdot 2\text{H}_2\text{O}$) and zinc oxide (ZnO), both of reagent grades, were used in a proportion of 3:1 by weight to prepare glass matrix. Europium oxide (Eu_2O_3 , 99.99%) and thulium oxide (Tm_2O_3 , 99.9%) obtained from Indian Rare Earths Limited, Kerala, were used as dopants. Preparations of samples are described elsewhere⁴.

Emission spectra were taken by steady state excitation of the samples with the 365 nm group of

mercury lines obtained from a medium pressure mercury lamp having woods filter. A grating monochromator dispersion 3.3 nm mm^{-1} , Czerny turner mounting, with a photomultiplier tube RCA1P21 connected either to a current meter (least count $1 \times 10^{-9} \text{ A}$) or to a chart recorder⁵ were used to scan the spectra at room temperature (20°C).

3 Results and Discussion

The emission spectra of Tm^{3+} (1wt%) and Eu^{3+} (1wt%) in zinc phosphate glass are shown in Fig. 1. The two peaks in Tm^{3+} spectrum arise due to the transitions ${}^1\text{D}_2 \rightarrow {}^3\text{H}_4$ (454 nm) and ${}^1\text{G}_4 \rightarrow {}^3\text{H}_6$ (475 nm) and those in Eu^{3+} emission arise due to ${}^5\text{D}_0 \rightarrow {}^7\text{F}_1$ (590 nm) and ${}^5\text{D}_0 \rightarrow {}^7\text{F}_2$ (617 nm) transitions.

The fluorescent spectra (uncorrected) of Tm^{3+} and Eu^{3+} shown in Fig. 2 indicate that these ions are in trivalent state in zinc phosphate glass matrix⁶. The energy level diagram of these trivalent ions are shown in Fig. 3. The incident radiation (365 nm group of mercury lines) excites both types of ions to $27.39 \times 10^3 \text{ cm}^{-1}$ energy. The Eu^{3+} ions rapidly depopulate to ${}^5\text{D}_0$ level, where from emission is obtained via ${}^5\text{D}_0 \rightarrow {}^7\text{F}_1$ (590 nm) and ${}^5\text{D}_0 \rightarrow {}^7\text{F}_2$ (617 nm) transitions. The Tm^{3+} ions give emission via ${}^1\text{D}_2 \rightarrow {}^3\text{H}_4$ (454 nm) and ${}^1\text{G}_4 \rightarrow {}^3\text{H}_6$ (475 nm) transitions. Keeping Eu^{3+} ion concentration fixed and varying Tm^{3+} ion concentration results in a decrease in Eu^{3+} emission as shown in Fig. 2A. On the other hand, keeping Tm^{3+} ion concentration fixed and varying Eu^{3+} ion concentration, shows no change in Tm^{3+}

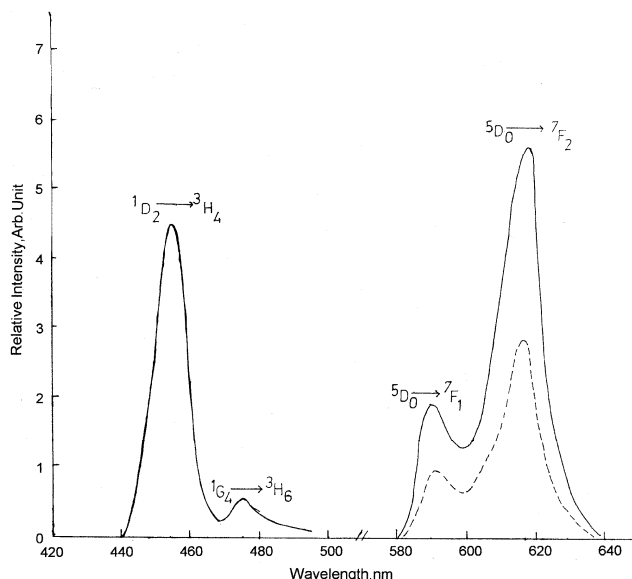


Fig. 1— Emission spectra (uncorrected) of (A) Tm^{3+} (1.0 wt. %) (B) Eu^{3+} (1.0 wt. %) and (C) Tm^{3+} (1.0 wt. %) + Eu^{3+} (1.0 wt. %)

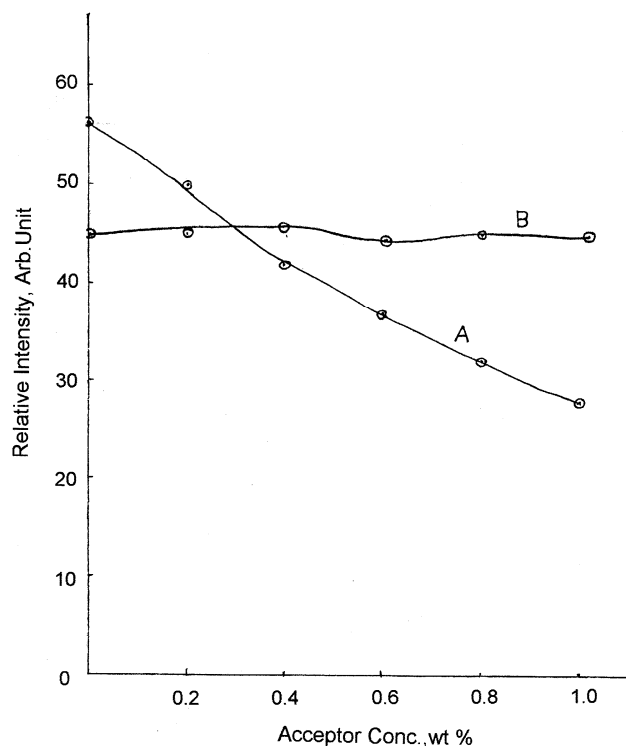


Fig. 2 — Emission intensity of Eu^{3+} (1.0 wt. %) in the presence of varying concentrations of Tm^{3+} (A) Tm^{3+} (1.0 wt. %) in the presence of varying concentrations of Eu^{3+} (B)

emission (violet blue emission) as shown in Fig. 2B. These observations clearly show that only in the former case the energy transfer is taking place. The overall decrease in Eu^{3+} emission, i.e. for all

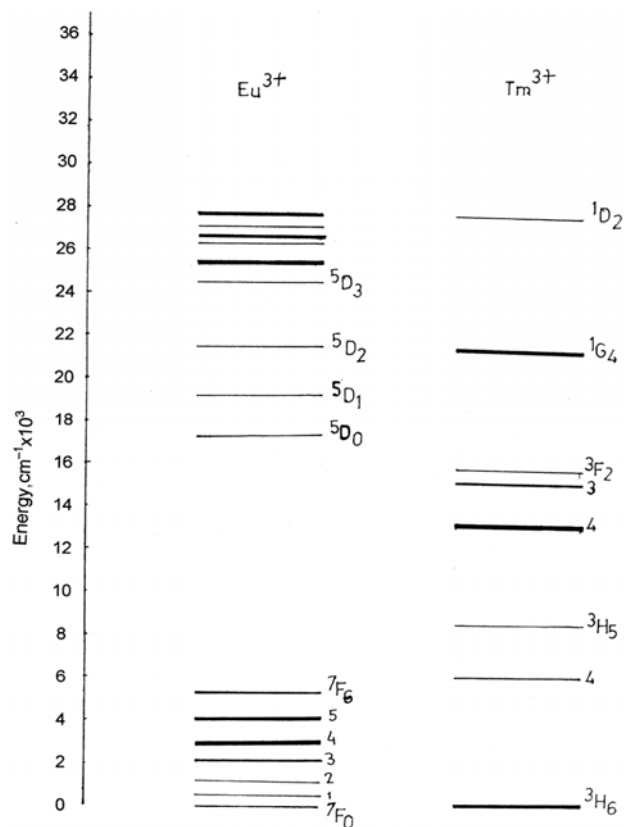


Fig. 3— Energy level diagrams of Eu^{3+} and Tm^{3+}

transitions originating from $^5\text{D}_0$ level of Eu^{3+} , suggest that the energy transfer is non-radiative¹². Careful observation of energy level diagram of Eu^{3+} and Tm^{3+} in Fig. 3 shows that there is no energy level of Tm^{3+} in energy equal to the $^5\text{D}_0$ level of Eu^{3+} . Moreover, the $^3\text{F}_2$ level of Tm^{3+} is more than 2500 cm^{-1} below the $^5\text{D}_0$ level of Eu^{3+} hence phonon assisted energy transfer is less possible⁷. Therefore, we suggest that the only way of energy transfer from Eu^{3+} to Tm^{3+} is the ion pair resonance or cross-relaxation. This can be explained as follows. The Eu^{3+} and Tm^{3+} are randomly distributed in the glass matrix. Suppose the Eu^{3+} ion after de-excitation from higher levels come to the luminescent $^5\text{D}_0$ level and a nearby Tm^{3+} ion is in its ground state $^3\text{H}_6$. As the energy gap between $^5\text{D}_0$ and $^7\text{F}_6$ level of Eu^{3+} matches the energy difference between $^3\text{F}_4$ and $^3\text{H}_6$ level of Tm^{3+} , this may cause the energy transfer from $^5\text{D}_0$ level of Eu^{3+} to $^3\text{F}_4$ level of Tm^{3+} . This may be written symbolically as $\text{Eu}^{3+} (^5\text{D}_0 \rightarrow ^7\text{F}_6) - \text{Tm}^{3+} (^3\text{H}_6 \rightarrow ^3\text{F}_4)$. This is plausible, since the decay time of the metastable state $^5\text{D}_0$ of Eu^{3+} is large (2.2 ms) in comparison with the decay time¹ τ_d of $^3\text{F}_4$ level of Tm^{3+} (0.86 ms). Peterson and Bridenbaugh⁸ also interpreted their experimental data of energy

transfer by cross-relaxation of energy. They suggested that such processes become appreciable if energy is leaving the long-lived metastable state. van Uitert *et al.*⁹ interpreted their result of self-quenching of Sm^{3+} by cross-relaxation of energy. Reisfeld *et al.*² also used this process to explain their result of energy transfer in Tm-Er system. Back transfer of energy from $^3\text{F}_4$ level of Tm^{3+} to $^5\text{D}_0$ level of Eu^{3+} is hardly possible as the decay time of $^3\text{F}_4$ level is very small compared with that of $^5\text{D}_0$ level.

In the present work, the average donor acceptor distance along with energy transfer probabilities and transfer efficiencies are presented in Table 1. The average separation between donor (Eu^{3+}) and acceptor (Tm^{3+}) ions varies between 2.37 nm and 1.91 nm (Table 1) which is in the range of electric dipole-dipole interaction between donor and acceptor in accordance with Forster's¹⁰ and Dexter's¹¹ theories of multipolar interactions. This is further corroborated by the graph shown in Fig. 4, between energy transfer probabilities (P_{da}) and square of the concentrations (donor + acceptor) which gives a straight line¹². The critical transfer distance (R_0), at which the energy transfer probability is equal to the radiative transition probability, in our system is 1.91 nm. This value can be compared with those obtained by Eyal *et al.*¹³ $R_0=2.1$ nm in Mn-Tm system in metal fluoride glass and by Joshi *et al.*¹⁴ 2.50 nm in Sm- UO_2^{3+} system in zinc phosphate glass for electric dipole-dipole interactions.

In the present study, the energy transfer by exchange mechanism is not possible which needs a donor-acceptor ion separation of about 0.3-0.4 nm with considerable overlap of wavefunctions. Also, radiative energy transfer between Eu-Tm system is ruled out as no particular wavelength emission of Eu

Table 1—Energy transfer efficiencies and probabilities between donor (Eu^{3+}) and acceptor (Tm^{3+})

C_{donor} (wt%)	C_{acceptor} (wt%)	D_{D-A} (nm, ± 0.1)	I_{di} (± 1)	η (± 0.05)	$P_{da} \times 10^4$ ($S^{-1} \pm 0.05$)
1.0	0.0	2.37	56(I_{do})	—	—
	0.2	2.24	50	0.11	5.45
	0.4	2.13	42	0.25	15.15
	0.6	2.05	37	0.34	23.34
	0.8	1.97	32	0.43	34.09
	1.0	1.91	28	0.50	45.45

where C_{donor} , donor concentration; C_{acceptor} , acceptor concentration; D_{D-A} , average donor-acceptor distance; I_{di} , donor intensity in presence of acceptor; I_{do} , donor intensity in the absence of acceptor; η , energy transfer efficiency = $(1 - I_{\text{di}}/I_{\text{do}})$; P_{da} , energy transfer probability = $1/\tau_{\text{d}}(I_{\text{do}}/I_{\text{di}} - 1)$.

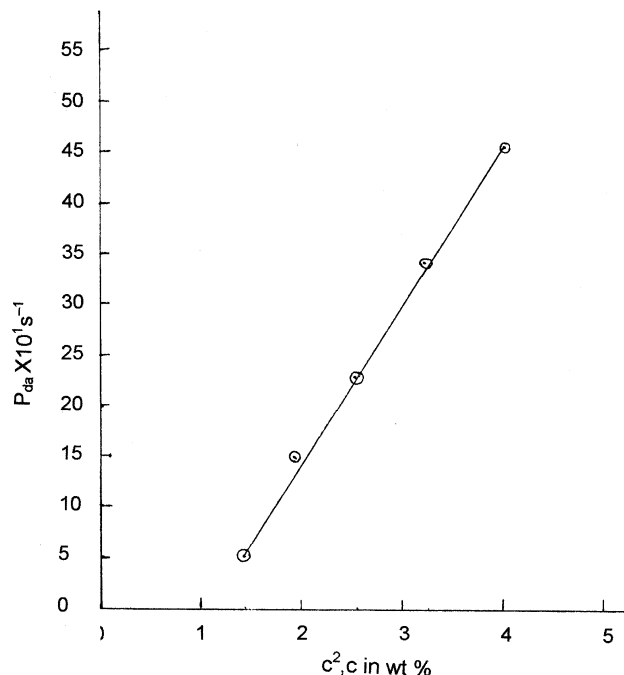


Fig. 4—Variation of energy transfer probability (P_{da}) with square of donor + acceptor concentration

or Tm is absorbed by either of the ions in visible region of spectra.

4 Conclusion

Non-radiative energy transfer from Eu^{3+} to Tm^{3+} occurs in zinc phosphate glass. The emission intensity of $^3\text{F}_2$ to $^3\text{H}_4$ transition of Tm^{3+} can be enhanced by the energy transfer, which can be used as a laser material.

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