

Non-radiative energy transfer between Eu^{3+} and Er^{3+} ions in zinc phosphate glass

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A study of non-radiative energy transfer in Eu^{3+} - Er^{3+} has been done by observing the steady state emission of Eu^{3+} with varying concentration of Er^{3+} in zinc phosphate glass at room temperature. It has been observed that Eu^{3+} ion emission intensity decreases with increasing Er^{3+} concentration resulting in a non-radiative energy transfer from Eu^{3+} to Er^{3+} . The energy transfer mechanism for Eu-Er system is mainly found electric dipole-dipole in nature. Various parameters necessary for quantitative study e.g. energy transfer efficiencies, transfer probabilities etc. between Eu^{3+} and Er^{3+} have been computed.

Keywords: Zinc phosphate glass, Non-radiative energy transfer

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1 Introduction

The transfer of optical excitation energy from one ion/molecule (donor) to another ion/molecule (acceptor) has proved to be of potential importance in industrial applications apart from pedagogical and research uses e.g. fabrication of suitable lasers having their emission in desired wavelength region, optical fibre for communication, luminescent solar concentrators, upconverters etc.

The importance of Er^{3+} in infrared region is well known. Riesfeld *et al.*^{1,2} have studied and observed non-radiative energy transfer between Tm^{3+} and Er^{3+} ions in borate and phosphate and between Mn^{2+} to Er^{3+} in transition metal fluoride glasses. Joshi *et al.*³⁻⁵ have reported the transfer of energy from Mn^{2+} to Er^{3+} in phosphate glass.

2 Experimental Details

Reagent grade sodium dihydrogen phosphate 2-hydrate ($\text{NaH}_2\text{PO}_4 \cdot 2\text{H}_2\text{O}$) (E-Merck, India) and reagent grade zinc oxide (ZnO) (Ferak Berlin, Germany) were mixed in a proportion of 3:1 by weight respectively to prepare the host glass matrix. Europium oxide (Eu_2O_3 , 99.99% pure) was obtained from Indian Rare Earths Limited, Kerala, while erbium oxide (Er_2O_3 , 99.9% pure) from GTE, Sylvania.

Pure as well as rare earth doped glass pallets of almost equal geometry and surface area were prepared⁶ in an electric furnace at about 1213 K. The fluorescence spectra were taken by exciting the sample with the 365 nm group of mercury lines. A fluorometer using a grating monochromator (CEL Model, HM104) dispersion 3.3 nm mm^{-1} , czerny-turner mounting, with

a photomultiplier tube (RCA1P21) and a nanometer were used to scan the spectra. For low intensity emissions, the grating monochromator was replaced by a constant deviation prism monochromator. All spectra were taken at room temperature⁷ (20°C). Absorption spectra of erbium (1wt%) in zinc phosphate glass is taken by using EC double beam UV-VIS spectrometer (ECIL UVS 70455) at room temperature. For this we make the glass sample of size 1cm \times 1cm \times 3cm.

3 Results and Discussion

The emission spectra (uncorrected) of Eu^{3+} (1wt% fixed) and the mixture of Eu^{3+} and Er^{3+} are shown in curve A, B of Fig. 1, respectively. It indicates that europium ion is in trivalent state in zinc phosphate glass matrix⁸. The energy level diagram of Eu^{3+} and Er^{3+} are shown in Fig. 2. The two peaks in Eu^{3+} spectrum arise due to the transition ${}^5\text{D}_0 \rightarrow {}^7\text{F}_1$ (590 nm) and ${}^5\text{D}_0 \rightarrow {}^7\text{F}_2$ (617 nm) in the red region while erbium ions have unobservable emission in visible region in zinc phosphate glass by the excitation radiation (365 nm).

Fig. 3 shows the variation of Eu^{3+} emission (1 wt.%) with varying Er^{3+} concentrations at room temperature. The incorporation of erbium ions along with europium in zinc phosphate glass reduces the europium emission. The overall decrease in Eu^{3+} emission intensity is suggested to be due to non-radiative energy transfer⁹ of some of the excitation energy to erbium ion. Since the erbium ions have unobservable emission in visible region by the excitation radiation (365nm) possibility of back transfer of energy from Er^{3+} to Eu^{3+} is extremely low.

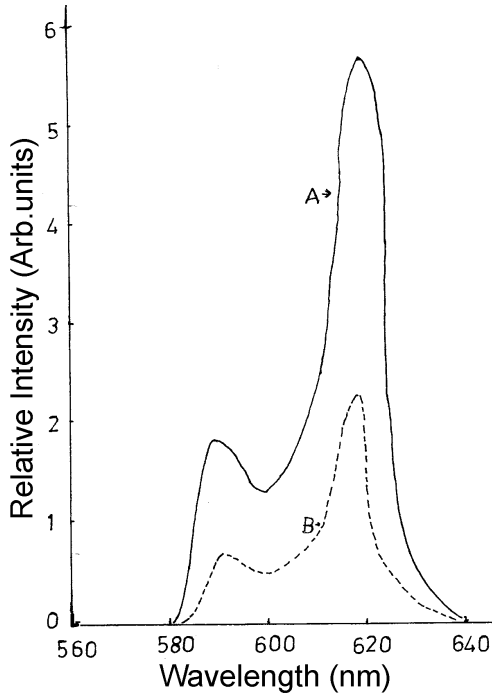


Fig. 1—Emission spectra (uncorrected) of (A) Eu³⁺(1.0 wt. % fixed) (B) Eu³⁺(1.0 wt. %) + Er³⁺(1.0 wt. %)

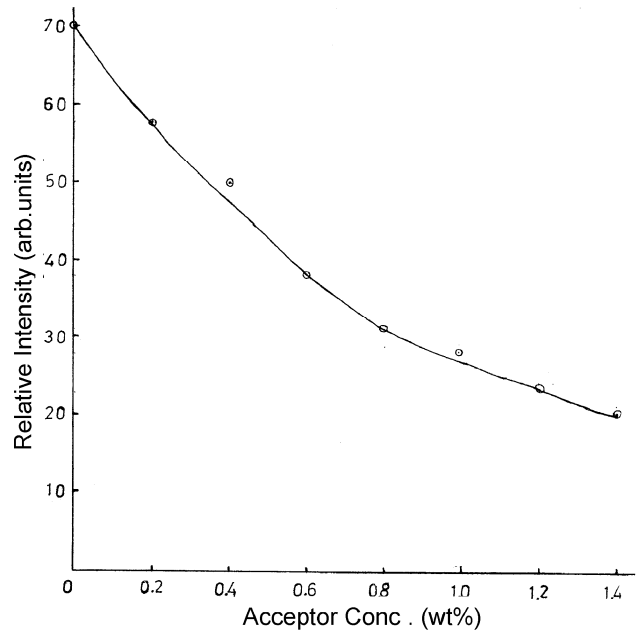


Fig. 3—Emission intensity of Eu³⁺(1.0 wt. %) in the presence of varying concentrations of Er³⁺

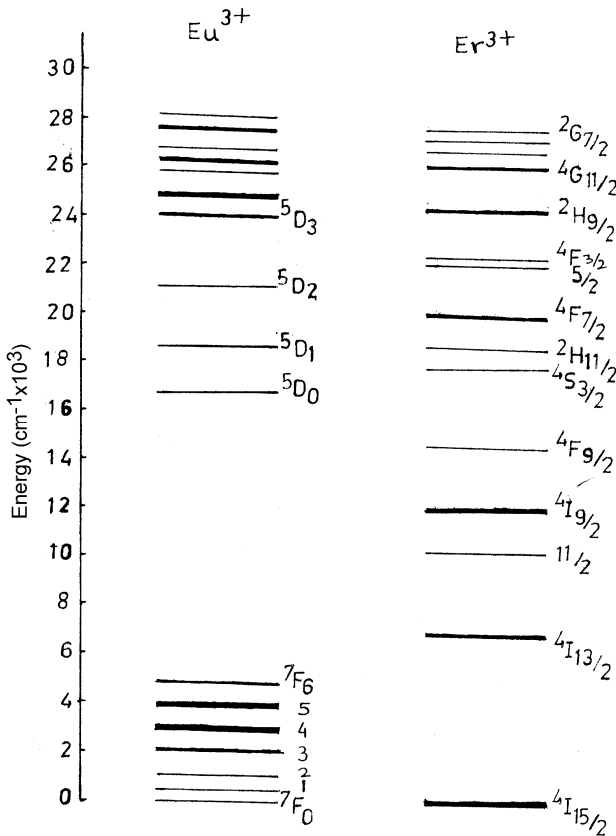


Fig. 2—Energy level diagrams of Eu³⁺ and Er³⁺

The energy level diagram of Eu³⁺ and Er³⁺(Fig. 2) shows that no energy level of Er³⁺ lies close to ⁵D₀ level of Eu³⁺. The ⁴F_{9/2} level of Er³⁺ is about 1000 cm⁻¹ below the ⁵D₀ level of Eu³⁺ hence, possibility of phonon assisted energy transfer is very less¹⁰. Therefore, we suggest that the only way of energy transfer from Eu³⁺ to Er³⁺ is ion pair resonance or cross-relaxation. This can be explained as follows:

The Eu³⁺ and Er³⁺ are randomly distributed in the glass matrix. When Eu³⁺ ion is excited by 365 nm groups of mercury lines, it is excited to 27.39 × 10³ cm⁻¹ energy. The Eu³⁺ ion rapidly depopulates to luminescent ⁵D₀ level and a nearby Er³⁺ ion is in its ground state ⁴I_{15/2}. As the energy gap between ⁵D₀ and ⁷F₆ level of Eu³⁺ matches the energy difference between ⁴I_{9/2} and ⁴I_{15/2} level of Er³⁺, this may cause the energy transfer from ⁵D₀ level of Eu³⁺ to ⁴I_{9/2} level of Er³⁺. This may be written symbolically as Eu³⁺ (⁵D₀ → ⁷F₆)-Er³⁺(⁴I_{15/2} → ⁴I_{9/2}) and shown in Fig. 4. Peterson and Bridenbaugh¹¹ 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. In the present case, this is plausible, since the decay time of the metastable state ⁵D₀ of Eu³⁺ is large (2.2 ms) hence, it has enough time to transfer its energy to ⁴I_{9/2} level of Er³⁺. Many other researchers^{2,11,12} also used cross-relaxation of energy to interpret their result of energy transfer.

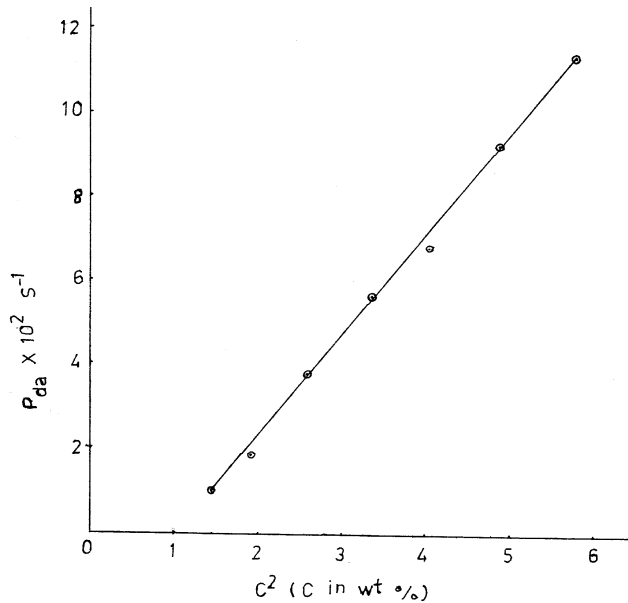


Fig. 4—Variation of energy transfer probability (P_{da}) with square of donor + acceptor concentration

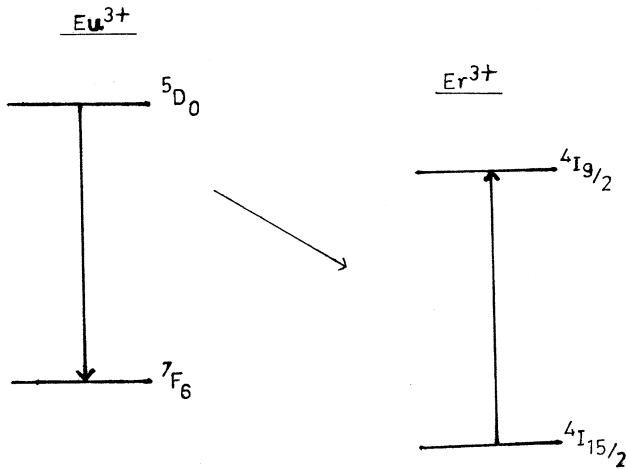


Fig. 5—Schematic representation of cross-relaxation between Eu^{3+} and Er^{3+}

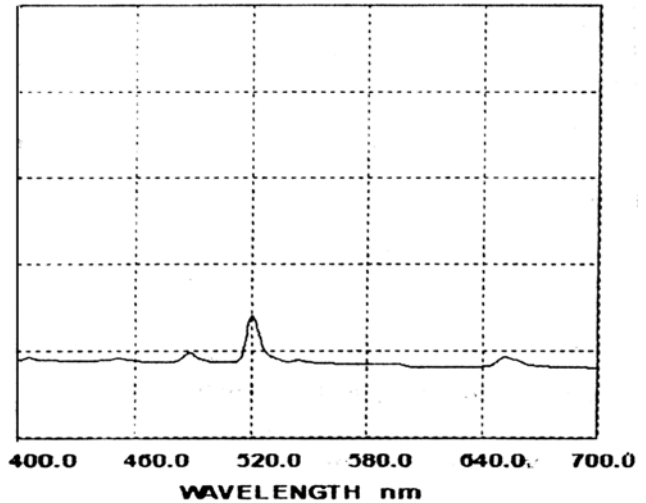


Fig. 6—Absorption spectra of Eu^{3+} (1.0 wt %) in zinc phosphate glass

In order to find out the multipolar term responsible for the energy transfer, probabilities (P_{da}) were plotted against the square of the donor + acceptor concentrations (Fig. 5) which gives a straight line. It shows the R^{-6} dependence of transfer probability, therefore, it shows that the mechanism of energy transfer between Eu^{3+} and Er^{3+} is electric dipole-dipole in nature⁹. Moreover, the average donor-acceptor separation, which varies between 1.66 to 2.03 nm and falls in the range of electric dipole interaction between donor and acceptor, is in accordance with Forster¹³ and Dexter¹⁴ theory of multipolar interaction. In the present work, the average donor acceptor distance along with energy transfer probabilities and transfer efficiencies are presented in Table 1.

The critical transfer distance (R_0), at which the energy transfer probability is equal to the radiative transition probability, in our system is 2.01 nm which

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

C_{donor} (wt%)	C_{acceptor} (wt%)	D_{D-A} (nm, ± 0.1)	I_{di} (± 1)	η (± 0.05)	$P_{da} \times 10^2$ ($S^{-1} \pm 0.05$)
1.0	0.0	2.26	70(I_{do})	—	—
	0.2	2.14	58	0.17	0.94
	0.4	2.04	50	0.29	1.82
	0.6	1.95	38	0.46	3.83
	0.8	1.88	31	0.56	5.72
	1.0	1.82	28	0.60	6.82
	1.2	1.76	23	0.67	9.29
	1.4	1.71	20	0.71	11.36

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

can be compared with those obtained by Eyal *et al*¹⁵. $R_0=2.1$ nm in Mn-Tm system in metal fluoride glass and by Joshi *et al*^{16,17}. 2.50 nm in Sm^{3+} - UO_2^{++} system and 1.91 nm in Dy^{3+} - Ho^{3+} in zinc phosphate glass for electric dipole-dipole interactions.

Energy transfer by exchange process is ruled out in this case because it needs a donor-acceptor ion separation of about 0.3-0.4 nm with considerable overlap of wave functions. Also as no particular wavelength emission of Eu is absorbed in visible range, hence, radiative transfer is negligible (Fig. 6).

4 Conclusion

It is concluded that energy transfer occurs from Eu^{3+} to Er^{3+} in zinc phosphate glass and the transfer is mainly electric dipole-dipole in nature.

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