

Sensitizing Eu^{3+} by Dy^{3+} in zinc phosphate glass

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Enhancement of Eu^{3+} emission by non-radiative energy transfer from Dy^{3+} in zinc phosphate glass has been observed at room temperature. The variation of Dy^{3+} (donor) emission with varying Eu^{3+} concentration (acceptor) and the emission of Eu^{3+} emission in steady-state excitation have been studied. Various parameters necessary for the quantitative study e.g. energy transfer efficiencies, transfer probabilities, critical transfer distances have been computed.

[**Keywords:** Non radiative energy transfer, Zinc phosphate glass, Sensitizing Eu^{3+} by Dy^{3+}]

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1 Introduction

In recent past, the energy transfer from one rare earth ion (donor) to another rare earth (RE) ion (acceptor) has been studied extensively. Due to narrow emission lines, RE ions find wide application in lasers, optical communications etc. Dy^{3+} ions, due to their relatively long decay time ($^4\text{F}_{9/2}$ level) can be potential energy sensitizers. Uitert and Dearborn¹ have observed a non-radiative energy transfer from Dy^{3+} to Tb^{3+} in tungstates. Joshi and Joshi² have studied a diffusion limited energy transfer from Dy^{3+} to Nd^{3+} in calibo glass. Taking Dy^{3+} as energy donor Joshi *et al.*³ have reported non-radiative energy transfer from Dy^{3+} to Ho^{3+} and from Dy^{3+} to Er^{3+} in zinc phosphate glass. In the above studies, it was found that the interaction mechanism between donor and acceptor ions is mainly electric dipole in nature.

The red emission of Eu^{3+} doped phosphors has been extensively used in colour televisions and lasers⁴. To enhance the Eu^{3+} emission, many researchers have sensitized it by RE and other ions in various matrices. Reisfeld *et al.*⁵ have observed that the emission of Eu^{3+} is enhanced by two orders of magnitude due to non-radiative energy transfer from UO_2^{++} and from Bi^{3+} to Eu^{3+} in glasses. Joshi⁶ has also observed energy transfer from Tb^{3+} to Eu^{3+} in zinc phosphate glass. Keeping the above results in view, we have chosen the Dy^{3+} - Eu^{3+} system for energy transfer study in zinc phosphate glass.

2 Experimental Details

The glass matrix was prepared from a mixture of reagent grade sodium dihydrogen phosphate-2- hydrate ($\text{NaH}_2\text{PO}_4 \cdot 2\text{H}_2\text{O}$) (E Merck, India Ltd) and reagent grade zinc oxide (ZnO) (Ferak Berlin, Germany) in 3:1 ratio respectively by weight. Dysprosium oxide (Dy_2O_3 , 99.99%) and europium oxide (Eu_2O_3 , 99.99%)

were purchased from the Indian Rare Earth Limited Kerala. Glass pellets of almost the same size doped with Dy^{3+} and /or Eu^{3+} were prepared in an electric furnace (about 930°C) as described elsewhere².

The fluorescence spectra were recorded by exciting the samples with the 365 nm group of mercury lines. A grating monochromator (CEL, Model, HM104) with dispersion 3.3 nm/mm and Czerny-Turner mounting a photo-multiplier tube (RCA 1P21) connected to an electrometer (least count 1×10^{-9} amp) were used to scan the spectra at room temperature. For low light levels, the grating monochromator was replaced by a constant deviation prism monochromator.

3 Results and Discussion

The dysprosium and europium ions are in trivalent state in zinc phosphate glass as they emit from $^4\text{F}_{9/2}$ and $^5\text{D}_0$ states (Fig. 1) respectively to their ground multiplets. The energy level diagrams of Dy^{3+} and Eu^{3+} are shown in Fig. 1. Both types of ions emit in the visible region when excited by 365 nm group of mercury lines. Dy^{3+} ions rapidly de-excite to the emitting level ^4F and radiate energy at 482 nm ($^4\text{F}_{9/2} \rightarrow ^6\text{H}_{15/2}$) and 575 nm ($^4\text{F}_{9/2} \rightarrow ^6\text{H}_{13/2}$) apart from other lines. Europium ions show emission in the red region through $^5\text{D}_0 \rightarrow ^7\text{F}_0$ (577 nm) $^5\text{D}_0 \rightarrow ^7\text{F}_1$ (590 nm), and $^5\text{D}_0 \rightarrow ^7\text{F}_2$ (617 nm) transitions.

The uncorrected fluorescence spectra of Dy^{3+} (1wt% fixed); Eu^{3+} (1wt% fixed) and the mixture of dysprosium and europium are presented in Fig. A, B and C of Fig. 2 respectively. Fig. 3 depicts the variation of Dy^{3+} (1wt% fixed) emission intensity when co-doped with varying concentrations of Eu^{3+} and shows a decrease, in Dy^{3+} emission. The decrease of Dy^{3+} emission in overall

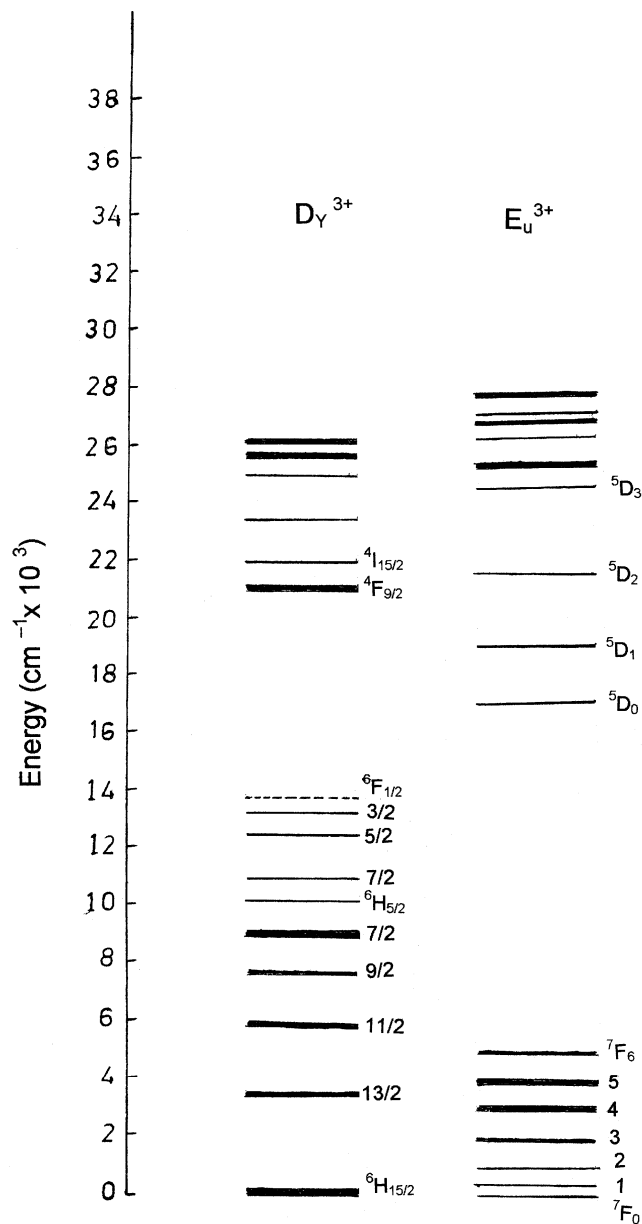
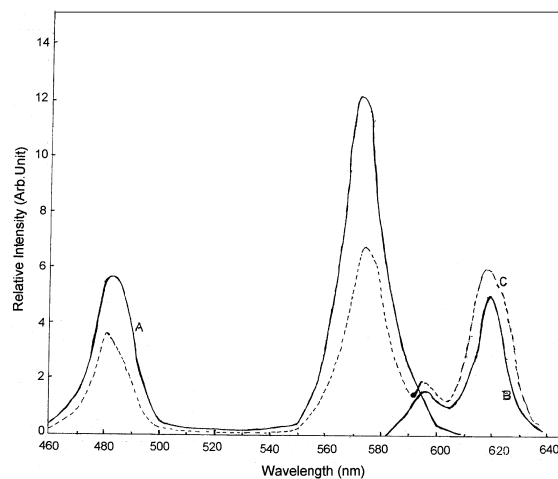
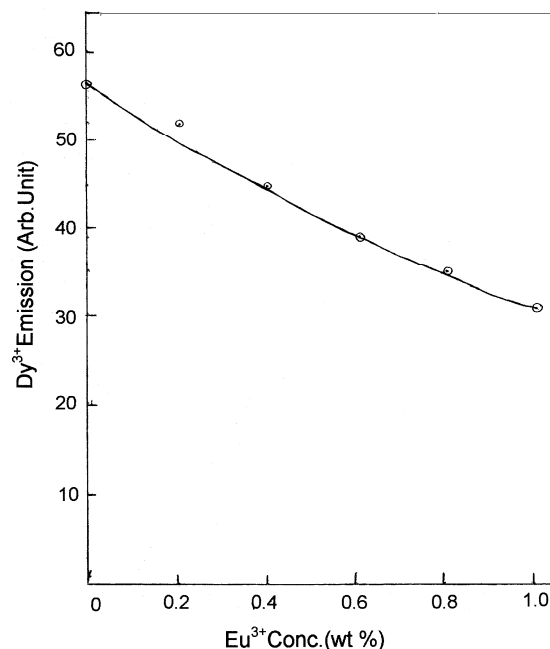
Fig. 1—Energy level diagrams of Dy³⁺ and Eu³⁺Fig. 2—Fluorescence spectra (uncorrected) of (A) Dy³⁺(1.0 wt. %) (B) Eu³⁺(1.0 wt%) and (C) Dy³⁺(1.0 wt. %) +Eu³⁺(1.0 wt%)Fig. 3—Fluorescence intensity of Dy³⁺(1.0 wt. %) in the presence of varying concentrations of Eu³⁺

Table 1—Energy transfer efficiencies, probabilities and average donor-acceptor distances

C_{donor} (wt%)	C_{acceptor} (wt%)	$D_{\text{D-A}}$ (nm \pm 0.1)	I_{do} (± 1)	I_{d} (± 1)	η (± 0.05)	$P_{\text{da}} \times 10^2$ ($s^{-1} \pm 0.05$)
1.0	0.2	2.27	56	52	0.07	1.34
	0.4	2.15		45	0.20	4.29
	0.6	2.05		39	0.30	7.65
	0.8	1.97		35	0.38	10.53
	1.0	1.90		31	0.45	14.15

where C_{donor} is the donor concentration; C_{acceptor} is the acceptor concentration; $D_{\text{D-A}}$ is the average donor – acceptor distance; I_{do} is the donor intensity in the absence of acceptor; I_{d} is the donor intensity in the presence of acceptor; η is the energy transfer efficiency ($=1 - I_{\text{d}}/I_{\text{do}}$); and P_{da} is the energy transfer probability [$= (1/\tau_0) (I_{\text{do}}/I_{\text{d}} - 1)$].

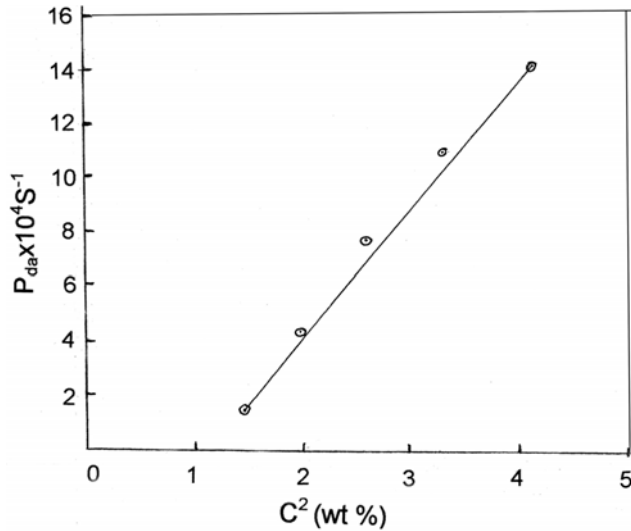


Fig. 4—Variation of transfer probability with the square of the donor + acceptor concentrations

indicates that there is non-radiative energy transfer from ${}^4F_{9/2}$ level of Dy^{3+} to Eu^{3+} ions as shown in B of Fig. 2. Close observation of Fig.1 indicates that the energy level of Eu^{3+} close to ${}^4F_{9/2}$ level of Dy^{3+} in 5D_2 reveals that the excitation energy of Dy^{3+} ion (${}^4F_{9/2}$ level) is transferred to 5D_2 level of Eu^{3+} and is subsequently transferred to 5D_0 level of Eu^{3+} by phonon emission. It causes an enhancement in the europium emission. The decay time of ${}^4F_{9/2}$ level of Dy^{3+} is quite large ($\tau=570 \mu\text{s}$) and hence this level has enough time to transfer its energy to 5D_2 level of Eu^{3+} . Fig. 2 clearly shows that the emission of 1wt% Dy^{3+} decreases when 1wt% of Eu^{3+} is co-doped with Dy^{3+} ions and enhances the europium (1wt%) 5D_0 emission.

The donor to acceptor average distance varies from 1.9 to 2.3 nm in our experiments (Table 1) which is in the range of electric dipole-dipole interaction between donor and acceptor ions^{9,10}. This distance is comparable with that obtained by Joshi *et al*^{6,11}. (1.7

to 2.04 nm) in Dy-Er system in zinc phosphate glass.

The energy transfer by exchange is ruled out in this case since this process requires a separation between donor-acceptor ions not more than 0.3-0.4 nm Dy ions emission with considerable overlap. Eu^{3+} ions absorption do not overlap in visible range and hence radiative transfer is negligible.

A plot between energy transfer probability (P_{da}) and C^2 (C is the sum of donor and acceptor concentration) resulted a straight line suggesting that the mechanism of energy transfer is largely electric dipole – dipole in nature (Fig. 4).

4 Conclusion

Non-radiative energy transfer from Dy^{3+} to Eu^{3+} has been observed in zinc phosphate glass. The emission intensity of Eu^{3+} increases when Dy^{3+} is doped with Eu^{3+} . Energy transfer parameters have been calculated which show that the transfer is mainly electric dipole-dipole in nature.

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