

## ENERGY TRANSFER STUDY BETWEEN $Dy^{3+}$ AND $Ho^{3+}$ IN $Dy^{3+}/Ho^{3+}$ CO-DOPED $Al(NO_3)_3$ - $SiO_2$ SOL-GEL GLASSES

P. Dutta

Laser and Spectroscopy laboratory, Department of Physics, Dibrugarh University, Assam, India

E-mail\*: [pankaj@dibru.ac.in](mailto:pankaj@dibru.ac.in)

### ABSTRACT

Fluorescence dynamics of the  ${}^4F_{9/2}$   $Dy^{3+}$  level in  $Al(NO_3)_3$ - $SiO_2$  glasses co-doped with  $Ho^{3+}$  have been experimentally investigated with the help of classical Forster- Dexter model for the energy transfer between  $Dy^{3+}$  (donor) and  $Ho^{3+}$  (acceptor). The energy transfer rates were calculated on the basis of fluorescence measurements. The study was carried out for the glass samples with fixed  $Dy^{3+}$  concentration at 0.01M while keeping the  $Ho^{3+}$  concentrations at 0M, 0.0025M, 0.005M, 0.0075M and 0.01M respectively. The study confirms the efficient energy transfer from the  ${}^4F_{9/2}$  Dysprosium level to  ${}^5F_3$  and  ${}^5F_2$   $Ho^{3+}$  levels via phonon assisted dipole-dipole interaction. The result indicates that  $Dy^{3+}$  can act as a potential sensitizer for  $Ho^{3+}$  lasing transitions in  $Al(NO_3)_3$ - $SiO_2$  sol-gel glasses.

KEYWORDS: Energy transfer, Gel glasses, radioactive properties,

### INTRODUCTION

The study of energy transfer phenomenon in different rare-earth (RE) combinations and in different hosts bear significant potential applications, because the radiative properties of ions embedded in host matrices are different from that of free ions due to local perturbations, including that caused by the electric field of the host ions. Similarly, if there are ions of the same or different types in the neighbourhood of the first, additional modifications may arise involving energy transfer between them. Such phenomena in different rare earth ion pairs, multi rare earth ions and rare earth ions and co-dopants of other species are extensively investigated in crystals and glasses by several authors to understand their role on efficiencies and tuning properties of lasers, amplifiers and up-converters. Excitation energy transfer from  $Yb^{3+}$  to  $Er^{3+}$  and  $Ce^{3+}$  to  $Er^{3+}$  has been utilized for effective pumping or  $Er^{3+}$  laser emissions in  $Yb^{3+}/Er^{3+}$  and  $Ce^{3+}/Er^{3+}$  fluorozirconate glass, making it a promising laser material.

In the  $Nd^{3+}/Cr^{3+}$  silicate glass the  ${}^4I_9$   $Nd^{3+}$  emission intensity in the presence of  $Cr^{3+}$  is largely enhanced as a result of energy transfer from  $Cr^{3+}$  to  $Nd^{3+}$ . With the use of three rare earths ( $Er^{3+}/Yb^{3+}/Tm^{3+}$ ) possibility for potential dual wavelength fiber-optic amplifiers to broaden the communication windows are predicted. But there are examples where energy transfer (cross relaxation type) can lead to unfruitful effects like reduction in gain and power efficiency. In the reported energy transfer between  $Tm^{3+}$  and  $Ho^{3+}$  or  $Tb^{3+}$  in Ge-Ga-As-S-CsBr glasses where  $Ho^{3+}$  or  $Tb^{3+}$  is introduced to achieve population inversion, the population of the  ${}^3F_4$   $Tm^{3+}$  levels was effectively quenched with  $Ho^{3+}$  or  $Tb^{3+}$  co-doping (Rai et al., 2008).

Hence to understand the energy transfer mechanism in different rare earth combinations and also to study the energy transfer phenomenon in different hosts bears significant potential applications. The classic Forster-Dexter (Forster, 1948, Dexter, 1953) theory on energy transfer, a theory suggested by Forster and extended by Dexter is one of the most widely used theory amongst the many theories of energy transfer employed for RE and transition metal ions in dielectrics (Berberan-Santos *et al.*, 2004).

In this work, we have studied the energy transfer phenomena between  $Dy^{3+}$  and  $Ho^{3+}$  in  $Al(NO_3)_3$ - $SiO_2$  sol-gel glasses. We have investigated the energy transfer phenomena by keeping the donor ( $Dy^{3+}$ ) concentration fixed and varying the acceptor concentration ( $Ho^{3+}$ ).

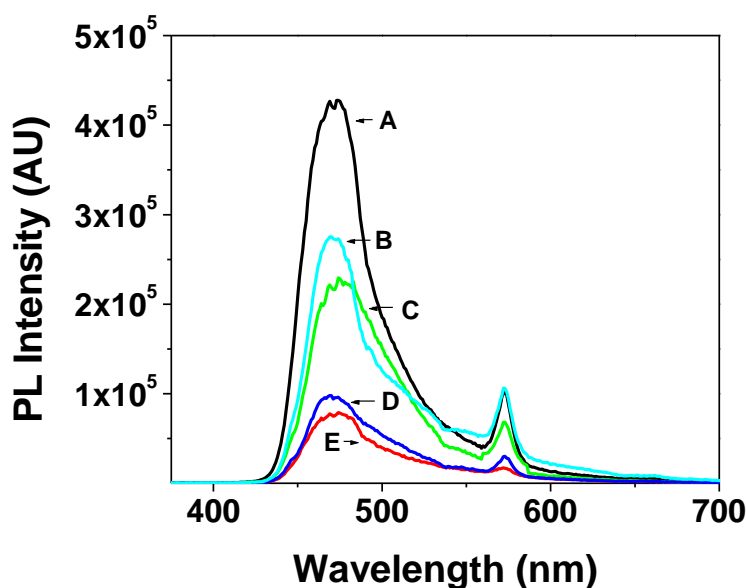
## EXPERIMENTAL

Glass samples for the present study were prepared by sol-gel route. The detail of the method of preparation is as explained in earlier paper (Dutta et al., 2011). The dopants were mixed with following concentrations.

- sample (A): Dy<sup>3+</sup> (.01M) + 0.03M Al(NO<sub>3</sub>)<sub>3</sub>-9H<sub>2</sub>O,  
 sample (B): Dy<sup>3+</sup> (.01M) + Ho<sup>3+</sup> (0.0025M) + 0.03M Al(NO<sub>3</sub>)<sub>3</sub>-9H<sub>2</sub>O,  
 sample (C): Dy<sup>3+</sup> (.01M) + Ho<sup>3+</sup> (0.005M) + 0.03M Al(NO<sub>3</sub>)<sub>3</sub>-9H<sub>2</sub>O  
 sample (D): Dy<sup>3+</sup> (.01M) + Ho<sup>3+</sup> (0.0075M) + 0.03M Al(NO<sub>3</sub>)<sub>3</sub>-9H<sub>2</sub>O.  
 sample (E): Dy<sup>3+</sup> (.01M) + Ho<sup>3+</sup> (0.01M) + 0.03M Al(NO<sub>3</sub>)<sub>3</sub>-9H<sub>2</sub>O.

Photoluminescence (PL) spectra for the samples were recorded by a Fluoromax 4P Spectrofluorimeter (with spectral resolution 1 nm). The measurements were done at room temperature.

## RESULTS AND DISCUSSIONS



**Figure 1:** PL spectra for Dy<sup>3+</sup>/Ho<sup>3+</sup> co-doped samples with varying Ho<sup>3+</sup> concentration.

Figure 1 shows the room temperature PL spectra for Dy<sup>3+</sup>/Ho<sup>3+</sup> co-doped Al(NO<sub>3</sub>)<sub>3</sub>-SiO<sub>2</sub> sol-gel glasses under 350 nm excitation. The excitation wavelength was determined by studying the variation of emission intensity with simultaneous variation of excitation and emission wavelengths for Dy<sup>3+</sup> singly doped Al(NO<sub>3</sub>)<sub>3</sub>-SiO<sub>2</sub> glass. Two emission bands around 473 nm and 573 nm corresponding to <sup>4</sup>F<sub>9/2</sub> → <sup>6</sup>H<sub>15/2</sub> and <sup>4</sup>F<sub>9/2</sub> → <sup>6</sup>H<sub>13/2</sub> Dy<sup>3+</sup> transitions respectively were observed. The reduction in the Dy<sup>3+</sup> fluorescence intensity with the addition of Ho<sup>3+</sup> (shown in figure 2) confirms the efficient energy transfer from Dy<sup>3+</sup> to Ho<sup>3+</sup> ions. This decrease in intensity is attributed to the availability of more Ho<sup>3+</sup> ions around each Dy<sup>3+</sup> ion to accept the excitation energy. Moreover, the overlapping of the <sup>4</sup>F<sub>9/2</sub> → <sup>6</sup>H<sub>15/2</sub> Dy<sup>3+</sup> emission band with the <sup>5</sup>I<sub>8</sub> → <sup>3</sup>K<sub>8</sub> absorption band of Ho<sup>3+</sup> (shown in figure 3) enables efficient resonant energy transfer from Dy<sup>3+</sup> to Ho<sup>3+</sup> ions.

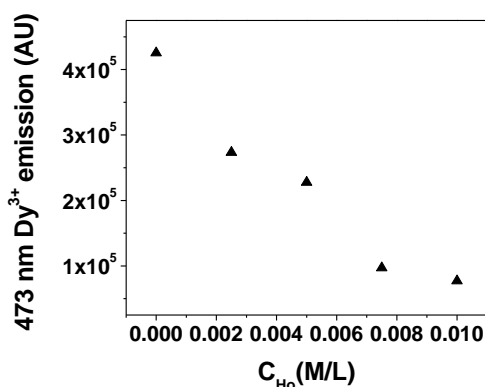


Figure 2: Intensity of  $Dy^{3+}$  (0.01 M) emission with varying  $Ho^{3+}$  concentration

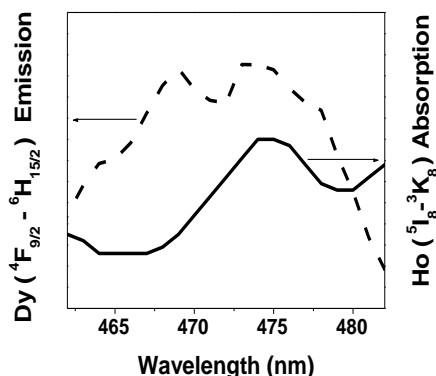


Figure 3: Figure depicting overlapping of  $Dy^{3+}$  emission with  $Ho^{3+}$  absorption

Based on the energy level diagram of  $Dy^{3+}$  and  $Ho^{3+}$  (shown in figure 4), we suggest that the energy from the  ${}^4F_{9/2}$  level of  $Dy^{3+}$  is being transferred to  ${}^5F_3$  and  ${}^5F_2$   $Ho^{3+}$  levels via electrostatic multipolar interactions (Joshi et al. 1995). Though  $Ho^{3+}$  ions also get excited via 350 nm excitation, energy transfer in the reverse direction i.e. from  $Ho^{3+}$  ion to the  ${}^4F_{9/2}$  level of  $Dy^{3+}$  is ruled out. This is because  $Ho^{3+}$  ion has close lying levels with small decay times as compared to  ${}^4F_{9/2}$  level of  $Dy^{3+}$  which have a larger decay time of 740  $\mu s$  (Joshi et al. 1995); hence the  $Ho^{3+}$  ions will relax internally quickly before they pass their energy to the  ${}^4F_{9/2}$  level of  $Dy^{3+}$ . The absorption spectrum of  $Ho^{3+}$  in glass lies in the visible region but falls outside the  $Dy^{3+}$  emission peaks; hence it excludes the possibility of radiative energy transfer from  $Dy^{3+}$  to  $Ho^{3+}$ .

Using the Forster-Dexter theory, the energy transfer probability ( $P_{da}$ ), relative fluorescence yield ( $\eta/\eta_0$ ), transfer efficiency ( $\eta_T$ ) for  ${}^4F_{9/2} \rightarrow {}^6H_{15/2}$   $Dy^{3+}$  transition at four different  $Ho^{3+}$  concentrations have been evaluated using equations (Forster, 1948; Dexter, 1953)

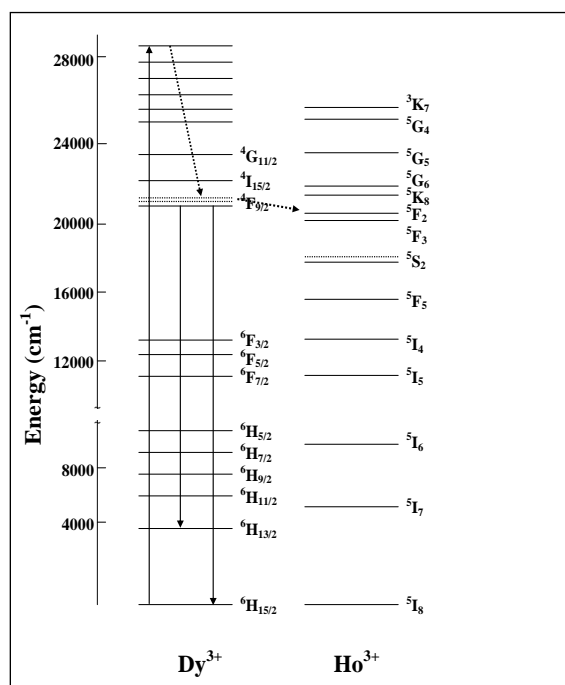
$$\eta_T = 1 - \frac{\eta}{\eta_0} = 1 - \frac{I}{I_0} \quad (1) \text{ and}$$

$$P_{da} = \frac{1}{\tau_d} \left( \frac{\eta_0}{\eta} - 1 \right) \quad (2). \text{ The results are presented in table 1.}$$

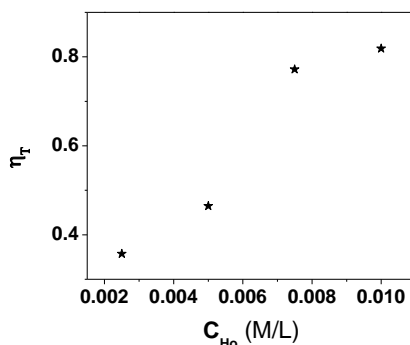
**Table 1:** Energy Transfer Efficiency, Transfer Probability, Fluorescence yield ratio between Dy<sup>3+</sup> and Ho<sup>3+</sup> at different concentrations of Ho<sup>3+</sup>

Conc. of Ho (C <sub>Ho</sub> )	Conc. of Dy (C <sub>Dy</sub> )	(C <sub>Ho</sub> +C <sub>Dy</sub> ) <sup>2</sup>	η/ η <sub>0</sub>	η <sub>T</sub>	P <sub>da</sub>
<b>0 M</b>	0.01 M	0.00015625			
<b>0.0025 M</b>	0.01 M	0.000225	0.642805	0.357195	<b>0.000745</b>
<b>0.005 M</b>	0.01 M	0.00030625	0.535416	0.464584	<b>0.001163</b>
<b>0.0075 M</b>	0.01 M	0.0004	0.227919	0.772081	<b>0.004541</b>
<b>0.01 M</b>	<b>0.01 M</b>	<b>0.00015625</b>	<b>0.181324</b>	<b>0.818676</b>	<b>0.006052</b>

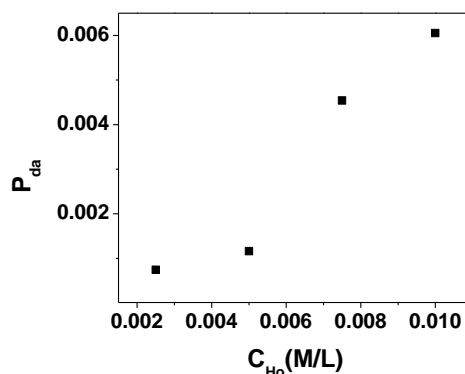
The radiative lifetime of <sup>4</sup>F<sub>9/2</sub> Dy<sup>3+</sup> level is assumed as 740 μs (Hoogschagen, et al. 1948, Banks et al., 1956) in these calculations. η/η<sub>0</sub> for different concentrations were determined from measured relative fluorescence intensities of the <sup>4</sup>F<sub>9/2</sub> → <sup>6</sup>H<sub>15/2</sub> Dy<sup>3+</sup> transition. The transfer efficiency (η<sub>T</sub>) and non radiative transition probability (P<sub>da</sub>), both are seen to increase with Ho<sup>3+</sup> (acceptor) concentration, the results are shown in figures 5 and 6.



**Figure 4:** Energy level diagram and energy transfer scheme of Dy<sup>3+</sup> and Ho<sup>3+</sup> in Al(NO<sub>3</sub>)<sub>3</sub> - SiO<sub>2</sub> sol-gel glass

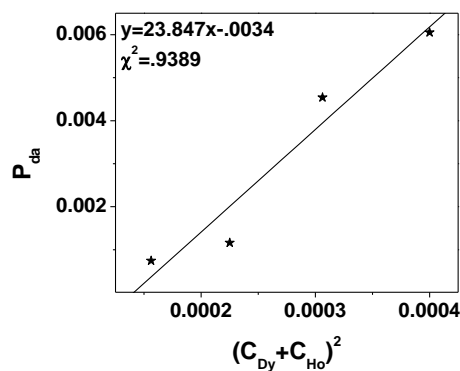


**Figure 5:** Variation of transfer efficiency ( $\eta_T$ ) with acceptor concentration ( $C_{Ho}$ )

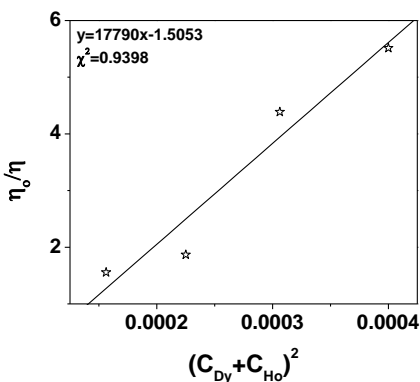


**Figure 6:** Variation of Energy transfer probability ( $P_{da}$ ) with acceptor concentration ( $C_{Ho}$ )

In order to determine the kind of multipolar interaction responsible for the energy transfer, the variation of  $P_{da}$  and  $\eta_o/\eta$  with the square of the total concentration  $(C_{Dy} + C_{Ho})^2$  are plotted and are shown in figures 7 and 8.



**Figure 7:** Variation of energy transfer probability ( $P_{da}$ ) with square of donor and acceptor concentration  $(C_{Dy} + C_{Ho})^2$



**Figure 8:** Variation of relative fluorescence yield ( $\eta_0/\eta$ ) with square of donor and acceptor concentration  $(C_{Dy} + C_{Ho})^2$

Both these parameters are found to be nearly linear in  $(C_{Dy} + C_{Ho})^2$ . Their linear behaviour suggests that the transfer rate is inversely proportional to the sixth power of the donor-acceptor distance [7, 8], which confirms the involvement of dipole –dipole interaction in excitation energy transfer.

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