CHAPTER 7
ENERGY TRANSFER STUDIES BETWEEN TWO RARE EARTH IONS CODOPED WITH CdS NANOPARTICLES IN SOL-GEL SILICA GLASSES

7.1 Introduction

Energy transfer (ET) processes between rare earth (RE) ions in various crystal and glass hosts have generated great research interest and is the subject of continuing attention since they play an important role in many areas of Physics, Chemistry and Biology. The analysis of ET provides essential information to the applications of RE-doped materials. In such process, the excitation energy transfers from an excited (donor), to a nearby unexcited activator (acceptor). The ET processes are also important for solid state lasers, fluorescent lamps and displays, solar energy conversion cells, amplifier, up-converters, conformational analyses of proteins and investigations on the folding dynamics of DNA [1-7]. In addition, ET has got great interest for improving the efficiency of light sources, to reduce the energy consumption by down conversion.

In recently developed studies on this type of luminescence it has been recognize that the luminescences intensities of various trivalent RE ions are sometimes enhance or quench by the coexistence of other kinds of trivalent RE ions. For examples, the intensity of Eu$^{3+}$ emission in tungstates and molybdates is strengthed by energy transfer from Tb$^{3+}$ ions [8, 9] and the intensity of Tb$^{3+}$ emission is decreased by
energy transfer from \( \text{Tb}^{3+} \) to \( \text{Ho}^{3+} \) ions in phosphate glasses [10]. Interactions between trivalent RE ions, involves \( f-f \) transitions only, with enhanced emission from one species, have been reported for the following pairs: \( \text{Tb}^{3+} \rightarrow \text{Eu}^{3+} \) [11], \( \text{Dy}^{3+} \rightarrow \text{Tb}^{3+} \) [12], \( \text{Er}^{3+} \rightarrow \text{Tm}^{3+} \) or \( \text{Ho}^{3+} \) [13], \( \text{Nd}^{3+} \rightarrow \text{Yb}^{3+} \) [14], \( \text{Yb}^{3+} \rightarrow \text{Er}^{3+}, \text{Tm}^{3+}, \) or \( \text{Ho}^{3+} \) [15-17], \( \text{Gd}^{3+} \rightarrow \text{Tb}^{3+} \) or \( \text{Eu}^{3+} \) [18] and \( \text{Pr}^{3+} \rightarrow \text{Nd}^{3+} \) [19]. These phenomena have attracted the deep interest of a number of investigators; it has been concluded that these phenomena take place because of the nonradiative transfer of excitation energy from a RE ion which behaves as an energy donor or sensitizer to another RE ion behaving as an energy acceptor or activator. In addition, these phenomena have a significant applications to the research and development of laser materials. ET is one way to increase the lasing efficiency of RE ion by codoping with solid medium with ion that have broad, allowed absorption spectra in all UV or visible range and are capable of transferring the excitation energy efficiently to the lasing ion. ET can be radiative or non-radiative [20].

Many theories have been put forwards to give formulas for the rate of energy transfer by electric-dipole-dipole interaction, electric-dipole-quadrupole interaction, and the exchange interactions. While the former two of the interactions are electrostatic in origin, the last arises from requirement of the antisymmetry of the electronic wave function for the system consisting of a donor molecule and an acceptor molecule. These transfer mechanisms differ from one another in the dependence of the transfer rate on donor-acceptor distance, but common to all is the condition that an overlap between the donor emission spectrum and the acceptor absorption spectrum is essential for the transfer to occur. This is so even though we are
concerned with virtual, not real, photon emission and reabsorption in the transfer process. Experimental studies of resonance transfer in a condensed system have most frequently made through luminescence measurements: donor molecules are excited in the presence of acceptor molecules, and the luminescence yield of donor and/or acceptor and the decay time of donor luminescence are measure as functions of the acceptor concentration [21-24]. When one attempts to interpret an observed result, for instance, that of donor luminescence yield, it becomes necessary to have a theoretical relationship between the yield and the acceptor concentration.

The classical Förster-Dexter [25-27] theory, a theory suggested by Förster and extended by Dexter, on energy transfer is one of the most widely employed theory amongst the many theories of energy transfer employed for RE and transition metal ion in dielectrics. The theory assume random and uniform distribution of donors and acceptors where donor-donor interaction is taken to be absent. According to it, ET process depends strongly on the overlap of emission cross-section $\sigma_{em}^d$ and absorption cross-section $\sigma_{abs}^x$, expressed by the critical radius $R_{dx}$

$$R_{dx}^6 = \frac{3cT_d}{8\pi 4n^2} \int \sigma_{em}^d(\lambda)\sigma_{abs}^x(\lambda) d\lambda$$

(7.1)

where $d$ stands for donor, $x$ is either donor ($d$) or acceptor ($a$), $d$ in case of energy migration among donors and $a$, for acceptor (Sm$^{3+}$ in Tb$^{3+}$/Sm$^{3+}$ codoped system and Er$^{3+}$ in Tm$^{3+}$/Er$^{3+}$ codoped system) in case of ET from donor to acceptor.

A macroscopic statistical model, which takes into consideration the statistical distribution of the donor-acceptor separation; was developed by Inokuti and Hirayama [28]
In this chapter, the ET phenomenon between two pairs, viz. Tb$^{3+}$ + Sm$^{3+}$ and Tm$^{3+}$ + Er$^{3+}$ codoped with CdS nanoparticles in silica host has been studied. We have investigated the energy transfer phenomenon by keeping donor (Tb$^{3+}$ in Tb$^{3+}$ + Sm$^{3+}$ and in Tm$^{3+}$ in Tm$^{3+}$ + Er$^{3+}$) concentration fixed and varying acceptor concentration. The efficiency of the energy transfer phenomenon observed is analyzed in the light of Förster-Dexter theory.

7.2 Experimental details

Silica gels containing RE and CdS nanoparticles were prepared by sol-gel method with tetraethyl orthosilicate (TEOS) as precursor in the presence of methanol and water using nitric acid as catalyst, as described in details in chapter 2. The following set of samples were prepared and studied during this work:

a. Tb$^{3+}$ with varying concentration of Sm$^{3+}$ ions

b. Tm$^{3+}$ with varying the concentration of Er$^{3+}$ ions

7.3 Result and discussion

7.3.1 ET between Tb$^{3+}$ and Sm$^{3+}$ ions codoped with CdS nanoparticles in silica glasses

Fig. 7.1 shows the room temperature fluorescent spectra of Tb$^{3+}$/Sm$^{3+}$ ions in CdS nanoparticles doped sol-gel silica glasses under 370nm excitation. Four emission bands were observed belonging to the $^5D_4 \rightarrow ^7F_6$ (489nm), $^5D_4 \rightarrow ^7F_5$ (544nm), $^5D_4 \rightarrow ^7F_4$ (585nm) and $^5D_4 \rightarrow ^7F_3$ (621nm) transitions of Tb$^{3+}$ ions. From the it is observed that there is a significant reduction in the PL intensities of Tb$^{3+}$ ions due to
addition of Sm$^{3+}$ ions. These reveals that there is an efficient energy transfer from Tb$^{3+}$ to Sm$^{3+}$ ions in the studied host. The peak around 544nm due to the transition $^5D_4 \rightarrow ^7F_5$ was found to be most intense among all the transitions. Therefore, the qualitative analysis of ET between Tb$^{3+}$ and Sm$^{3+}$ ions were performed for this transition.

On excitation by 370nm excitation, the Tb$^{3+}$ ions in the Tb$^{3+}$/Sm$^{3+}$ codoped with CdS nanoparticles in sol-gel silica glasses are first excited to $^5D_3$ level. From which it further relaxed to $^5D_4$ level via nonradiative transition due to multi phonon relaxation. The energy difference between $^5D_4$ level of Tb$^{3+}$ (20,408cm$^{-1}$ from ground
state) and \(^4\text{I}_{11/2}\) level of Sm\(^{3+}\) (20, 920 cm\(^{-1}\) from ground state) are nearly equal, which permits an efficient resonant energy transfer from Tb\(^{3+}\) to Sm\(^{3+}\) ions. The small energy mismatch between \(^5\text{D}_4\) level of Tb\(^{3+}\) (20, 408 cm\(^{-1}\) from ground state) and \(^4\text{I}_{11/2}\) level of Sm\(^{3+}\) (20, 920 cm\(^{-1}\) from ground state) is compensated by the host lattice phonons [29, 30]. Moreover, the overlap of \(^6\text{H}_{5/2}\rightarrow^4\text{I}_{11/2}\) transition of Sm\(^{3+}\) absorption and \(^5\text{D}_4\rightarrow^7\text{F}_6\) transition of Tb\(^{3+}\) emission bands, shown in Fig. 7.2, reveal the efficient resonant ET from Tb\(^{3+}\) to Sm\(^{3+}\) ions. The nonradiative transfer depletes the population of \(^5\text{D}_4\) level of Tb\(^{3+}\) level and results in the quenching of \(^5\text{D}_4\rightarrow^7\text{F}_j\) (j = 3, 4, 5 and 6) levels of Tb\(^{3+}\) emission intensities. While the excited \(^4\text{I}_{11/2}\) level of Sm\(^{3+}\) level decays nonradiatively to the ground state of Sm\(^{3+}\) by exciting lattice vibration. The scheme of ET mechanism described here is illustrated in Fig. 7.3.

![Spectral overlap of Tb\(^{3+}\) emission with Sm\(^{3+}\) absorption band in CdS nanoparticles doped silica glasses](image-url)
The Förster-Dexter theory on ET is used for quantitative analysis of ET in the present study. The Dexter’s model [27] for resonant energy transfer by dipole-dipole interaction defines transfer efficiency as
\[
\eta_T = \frac{P_{da} \tau_d}{1 + P_{da} \tau_d}
\]  

(7.2)

where linear dependence on total concentration for small concentration is assumed. In Eq. (7.2), \( P_{da} \) is donor-acceptor energy transfer probability defined as [31],

\[
P_{da} = \frac{1}{\tau_d} \frac{3h^4 c^4}{4 \pi n^4} \left( \frac{1}{R_{da}} \right)^6 \cdot \sigma_d \cdot \int \frac{f_d(E) F_a(E)}{E^4} \, dE
\]

\[
= \frac{1}{\tau_d} \left( \frac{R_0}{R_{da}} \right)^6
\]

(7.3)

where the critical interaction distance, \( R_0 \), on simplified terms is taken as the donor-acceptor distance at which energy transfer rate is one per second, \( \tau_d \) is the radiative lifetime of donor, \( n \) is the refractive index of host, \( R_{da} \) is the donor-acceptor separation, \( \sigma_d \) is the donor absorption cross-section, \( f_d(E) \) and \( F_a(E) \) are the normalized line shape function for the donor emission and acceptor absorption and other symbols have their usual meaning.

Förster [25, 26], alternatively, defined and related the transfer efficiency (\( \eta_T \)) to a change in the fluorescence yields in presence and absence of acceptor as,

\[
\eta_T = 1 - \frac{\eta}{\eta_0} = 1 - \frac{I}{I_0}
\]

(7.4)

where \( I \) and \( I_0 \) are the fluorescence intensities in presence and absence of acceptor, respectively. With Eqs. (7.2) and (7.4) the transition probability (\( P_{da} \)) for donor-acceptor concentration may be computed as

\[
P_{da} = \frac{1}{\tau_d} \left( \frac{\eta_0}{\eta} - 1 \right)
\]

(7.5)
Using Eqs. (7.4) and (7.5) ET probability ($P_{da}$), fluorescence yield ratio ($\eta/\eta_0$), transfer efficiency ($\eta_T$) are evaluated for $^5D_4 \rightarrow ^7F_5$ transition of Tb$^{3+}$ at three different Sm$^{3+}$ concentration and compile in the Table 7.1

Table 7.1

Transfer efficiency ($\eta_T$), ET probability ($P_{da}$), fluorescence yield ratio ($\eta/\eta_0$) between Tb$^{3+}$ and Sm$^{3+}$ at different concentration of Sm$^{3+}$ in Tb$^{3+}$/Sm$^{3+}$ codoped with CdS nanoparticles in sol-gel silica glasses for the $^5D_4 \rightarrow ^7F_5$ (545nm) transition of Tb$^{3+}$ at 370nm excitation

<table>
<thead>
<tr>
<th>Conc. Of Sm$^{3+}$ ($C_{Sm}$) (Mol.%)</th>
<th>Conc. Of Tb$^{3+}$ ($C_{Tb}$) (Mol.%)</th>
<th>$(C_{Sm} + C_{Tb})^2$</th>
<th>$\eta/\eta_0$</th>
<th>$\eta_T$</th>
<th>$P_{da}$ (s$^{-1}$)</th>
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<td>1</td>
<td></td>
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</tr>
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<td>0.335</td>
<td>180.96</td>
</tr>
<tr>
<td>5</td>
<td>1</td>
<td>36</td>
<td>0.557</td>
<td>0.443</td>
<td>283.46</td>
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</table>

The radiative lifetime of the $^5D_4 \rightarrow ^7F_5$ (545nm) transition of Tb$^{3+}$ was experimentally measured for the glass samples containing (0.01M Tb$^{3+}$ + 0.0M Sm$^{3+}$), which is found to be 0.3738ms, shown in Fig. 7.4, and this radiative lifetime is used in these calculation. The transfer efficiency ($\eta_T$) and nonradiative ET probability ($P_{da}$), both, are seen to increase with acceptor concentration ($C_{Sm}$).
Fig. 7.4 Experimentally measured radiative lifetime of donor, i.e. Tb\(^{3+}\) in absence of acceptor.

To determine the nature of transfer mechanism involved, ET probability (\(P_{da}\)) and relative fluorescence yield (\(\eta_0/\eta\)) variation with the square of the total concentration (\(C_{Sm} + C_{Tb}\))^2 are studied. Both \(P_{da}\) and \(\eta_0/\eta\) are linear with (\(C_{Sm} + C_{Tb}\))^2, shown in Fig. 7.5 and 7.6, respectively. Their linear behavior suggests the transfer rate is proportional to the inverse sixth power of donor-acceptor distance [32, 33] confirming the involvement of dipole-dipole interaction in excitation ET.
Fig. 7.5 Variation of ET probability ($P_{da}$) with square of donor-acceptor concentration ($C_{Sm} + C_{Tb})^2$.  

Fig. 7.6 Variation of relative fluorescence yield ($\eta_0/\eta$) with square of donor and acceptor concentration ($C_{Sm} + C_{Tb})^2$.  

155
7.3.2 ET between Tm$^{3+}$ and Er$^{3+}$ ions codoped with CdS nanoparticles in silica glasses

The decrease in the relative upconversion (UC) fluorescence intensities of $^1D_4 \rightarrow ^3H_4$ and $^1G_4 \rightarrow ^3H_6$ transition of Tm$^{3+}$ in the presence of Er$^{3+}$ in the Tm$^{3+}$/Er$^{3+}$ codoped with CdS nanoparticles in sol-gel silica glasses is an evidence of excitation energy transfer from Tm$^{3+}$ (donor) to unexcited Er$^{3+}$(acceptor) under 650nm excitation, as shown in Fig. 7.7. Moreover, the increased reduction in Tm$^{3+}$ UC fluorescence intensities with Er$^{3+}$ concentration is indicative of ET rate dependence on Er$^{3+}$ (acceptor) concentration.

![Fig. 7.7 UC spectra of Tm$^{3+}$/Er$^{3+}$ codoped sample under 650nm excitation](image)

Fig. 7.7 UC spectra of Tm$^{3+}$/Er$^{3+}$ codoped sample under 650nm excitation
Also, the overlapping of the Tm$^{3+}$ (donor) ions emission with the absorption bands of the Er$^{3+}$(acceptor) ions enables an efficient resonant ET from Tm$^{3+}$ to Er$^{3+}$ ions, shown in Fig. 7.8.

Fig. 7.8 Figure depicting the overlapping of Tm$^{3+}$ emission with Er$^{3+}$ absorption band in CdS doped silica glasses
Based on the energy level diagram of Tm$^{3+}$ and Er$^{3+}$, shown in Fig. 7.9, we suggest the possible ET from Tm$^{3+}$ to Er$^{3+}$ ions.

Fig. 7.9 Energy level diagram and ET scheme of Tm$^{3+}$ and Er$^{3+}$ in CdS doped silica glasses
The thulium ion (donor ions) is excited by 650nm in presence of Er$^{3+}$ (acceptor ions), having transition of $^3H_4$→$^3F_2$ is quenched from Tm$^{3+}$ ($^3F_4$) level to the Er$^{3+}$ ($^4I_{9/2}$) level by energy transfer,
\[
\text{Er}^{3+} (^4I_{15/2}) + \text{Tm}^{3+} (^3F_4) \rightarrow \text{Er}^{3+} (^4I_{9/2}) + \text{Tm}^{3+} (^3H_6)
\]
after a rapid multiphonon relaxation. As a result, it depopulate the Tm$^{3+}$:$^3F_4$ level, the initial level of Tm$^{3+}$ ($^1D_2$←$^3F_4$) excited state absorption (ESA), which result in the quenching of Tm$^{3+}$ (415, 452nm) upconversion luminescence, i.e. $^1D_4$→$^3H_4$ transition. As the mean lifetime of $^3H_4$ is high ($\approx 6$ms) [34], it act as a metastable state. Before $^3H_4$→$^1G_4$ transition takes place, the $^3H_4$ level has to be populated first by emission from $^1D_2$ level. Moreover, the ion in the $^3F_4$ level may also relax to the $^3H_4$ level via nonradiative transition or cross-relaxation process. If ion is in the $^3H_4$ level and second excited photon is absorbed, which populate $^1G_4$ level from which another blue emission due to transition from $^1G_4$→$^3H_6$ level, centered at 470, 484 and 493nm are observed.

The Er$^{3+}$ ions excited by strong absorption via the transition $^4F_{9/2}$←$^4I_{15/2}$, relax to the $^4I_{13/2}$ level and the ET occur to the Tm$^{3+}$ ($^3H_4$) level
\[
\text{Tm}^{3+} (^3H_6) + \text{Er}^{3+} (^4I_{13/2}) \rightarrow \text{Tm}^{3+} (^3H_4) + \text{Er}^{3+} (^4I_{15/2})
\]
which is the initial level of Tm$^{3+}$ ($^1G_4$←$^3H_4$) (ESA). Similar result has been reported by J. F. Johnson et. al in a crystal of CaMoO$_4$ [35]. They showed that this ET is due to the resonant interaction process and that the observed probabilities indicate a dipole-dipole interaction. R. Reisfeld & Y. Eckstein in borate and phosphate glasses [31] and S. Tanabe et. al in Tellurite glasses [36] also observed similar result and reported the mechanism of mutual ET process.
Using the Forster-Dexter theory, we evaluated the transfer efficiency ($\eta_T$), ET probability ($P_{da}$), fluorescence yield ratio ($\eta/\eta_0$) between Tm$^{3+}$ and Er$^{3+}$ at different concentration of Er$^{3+}$ in Tm$^{3+}$/Er$^{3+}$ codoped with CdS nanoparticles in sol-gel silica glasses for the $^1G_4\rightarrow^3H_6$ (789nm) transition of Tm$^{3+}$, using Eqs (7.3) and (7.4). The evaluated values are compiled in the Table 7.2.

<table>
<thead>
<tr>
<th>Conc. Of Er$^{3+}$ ($C_{Er}$) (Mol.%)</th>
<th>Conc. Of Tm$^{3+}$ ($C_{Tm}$) (Mol.%)</th>
<th>$(C_{Er} + C_{Tm})^2$</th>
<th>$\eta/\eta_0$</th>
<th>$\eta_T$</th>
<th>$P_{da}$ (s$^{-1}$)</th>
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<td>0.638</td>
<td>0.362</td>
<td>1494.74</td>
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</tbody>
</table>

The radiative lifetime of the $^1G_4$ Tm$^{3+}$ level is assumed as 0.38ms [37] in these calculation. The transfer efficiency ($\eta_T$) and nonradiative ET probability ($P_{da}$), both, are seen to increase with acceptor concentration ($C_{Er}$).

### 7.4 Conclusion

From the above study, the non-radiative ET from Tb$^{3+}$ to Sm$^{3+}$ and from Tm$^{3+}$ to Er$^{3+}$ ions in Tb$^{3+}$/Sm$^{3+}$ and Tm$^{3+}$/Er$^{3+}$ codoped with CdS nanoparticles in sol-gel
silica glasses under 370 and 650nm excitation, respectively; has been observed. The transfer efficiency is found to be 0.203 to 0.443 for Tb$^{3+}$/Sm$^{3+}$ and 0.040 to 0.362 in Tm$^{3+}$/Er$^{3+}$ doped glasses. The results were quantitatively analyzed using Förster-Dexter model which confirms the involvement of dipole-dipole interaction for the excitation energy transfer from donors to the acceptors.

The results indicates that Tb$^{3+}$ can act as a potential sensitizer for Sm$^{3+}$ lasing transition while Tm$^{3+}$ can do the same for Er$^{3+}$ transition in CdS nanoparticles doped sol-gel glasses.

7.5 References


15. E. Snitzer and R. Woodcock, Appl. Phys. Lett. 6 (1965) 45


34. E.W.J. L. Oomen, J. Lumin. 50 (1992) 317