Chapter 4

Spectral Analysis of Eu$^{3+}$ Ions in CdSe/ZnSe Nanocrystals Doped Silica Hosts

The phonon side band spectrum associated with the excitation transition $^5D_2 - ^7F_0$ of europium ions is used to analyze the local asymmetry of the rare earth ions in the glass host. The large inhomogeneous linewidth for the CdSe codoped samples indicates the wide distribution of the Eu$^{3+}$ ion in the matrix and is related to the flexibility of the local glass network. The fluorescence spectra reveal that the intensity of characteristic emission of europium increases considerably in the presence of CdSe particles. This phenomenon can be explained as due to the energy transfer resulting from electron–hole recombination in the CdSe to the rare earth ion. These zero-dimensional materials along with the effect of matrix incorporating europium ions are found to have increased the optical gain.
4.1 Introduction

Lanthanide ions have the fairly unique property of sharp spectral lines (4f-4f) in the solid phase have got crucial applications in opto-electronic technology\(^1\). Electron-electron and spin-orbit interaction, dominate the electronic structure of the rare earth ions. The spectral intensities of the trivalent lanthanide ions can be fine tuned by an appropriate choice of the medium in which the ion is embedded\(^2\). In glasses doped with rare earth ions, the local environment of the ion is widely distributed and narrow zero phonon lines are dominant in f-f transition of the rare earth ions so that inhomogeneous broadening plays a significant role\(^3\). Eu\(^{3+}\) is an excellent indicator of the site symmetry and chemical bonding in glasses since Eu\(^{3+}\) ions incorporated in low-symmetry sites exhibit enhanced f-f transition probabilities\(^4\). Recently nanoparticles have gained much attention due to their unique size dependent physical properties. Semiconductor nanocrystals possess a valence band with strong optical transitions to the conduction band and these transitions form the basis for application of quantum dots as laser emitters, storage devices and fluorescence markers and for many possible optical as well as photonic applications\(^5,\,\!^6\).

Clusters of semiconductor compounds such as CdSe often exhibit strongly size dependent electrical and optical properties. The band gap of nanoscale semiconductor structures increases as the size of the microstructure decreases, raising expectations for many possible optical and photonic applications\(^5,\,\!^7\). In the case of CdSe nanocrystals the valence band degeneracy completely modifies the selection rules and gives rise to substructure in the absorption and luminescence spectra\(^8\). The nanoparticles consists of large surface and interface areas, which influence the electronic properties of the materials\(^9\). Nanoparticles such as cadmium selenide are of great interest for sensing and electronic technologies due to their unique size dependent optical and electronic properties. The development of new luminescent materials with
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Complex composition is of interest for understanding the electronic excitation and relaxation phenomena with participation of two and more active centers. Complexation enhances the intensity of transition in the lanthanides 4f orbitals resulting in a free ion like spectra. The sol-gel process extends the conventional glass melting methods, as it allows incorporation of semiconductor nanocrystals along with rare earth elements at low temperatures with predetermined concentration and size. Sol-gel method is useful in the preparation of nanocrystallites doped gel glasses with relatively high particle concentrations, small particle diameter and uniform size distribution. Knowledge of the local structure of the rare earth in hosts is valuable in optical devices like upconversion laser and laser induced holographic gratings. In order to design the glass material with high efficiency it is better to select a glass matrix in which the maximum phonon energy is small i.e. the non-radiative loss due to multiphonon relaxation is small. Semiconductor nanocrystals in transparent media, especially in sol-gel glasses, have received greater attention due to their promising applications in non-linear optics and optical switches. The optical properties play a crucial role in applications like optical memory devices, lasers, fiber amplifiers, and fluorescence form the basis for these photonic applications.

We present the analysis of phonon sideband and fluorescence of Eu$^{3+}$ ions in sol gel silica matrix to probe the local structural evolution. We also report here the intensification of the fluorescence and resolution of excitation lines of the rare earth ions in the presence of cadmium selenide particles prepared by the sol-gel method.

4.2 Experimental details

Silica glasses with 3wt% of Europium concentration and varying CdSe concentrations were prepared by the sol-gel process from tetraethyl orthosilicate (TEOS) as precursor, cadmium acetate, selenic acid and europium nitrate in the presence of water and ethanol. The mixture (sol) is
poured into polypropylene containers, which is sealed and kept to form stiff gel. Variation in the annealing conditions resulted in stabilization of final products and provided a high mechanical strength of materials. The luminescence spectra were taken using a spectrophotofluorimeter (Shimadzu-RFPC 5301) and the absorption with UV-visible spectrophotometer (Shimadzu-UVPC2401) for all the samples heated to 500°C.

4.3 Results and Discussion

Photoluminescence, optical absorption, nonlinearity and many other properties of nanocrystals embedded in an amorphous matrix can be successfully studied only if the matrix is transparent in the region of the band and subband absorption of the nanocrystals.

4.3.1 Excitation spectra

The excitation spectra give the characteristic rare earth absorption lines corresponding to intraconfigurational 4fⁿ⁻⁴f⁰ transitions of the rare earth ions, but not the semiconductor host lattice excitation band. The excitation spectrum taken with an emission wavelength of 614nm gives a vivid picture of the different transitions associated with the Eu³⁺ ions and is given in Figure 4.1. The excitation spectrum also provides some information on the network

![Figure 4.1](image)

**Figure 4.1.** Excitation spectra of samples heated to 500°C (λ_{em} =614nm) taken at room temperature.
formation in gel matrices. The intense peak at 465nm is an indication of a rigid glassy network that is formed at comparatively low temperature in CdSe + Eu$^{3+}$ doped gel glass comparing to Eu$^{3+}$ doped one. Trivalent europium exhibits a vibration transition, phonon sidebands to a zero phonon line, which provides direct measurements of the phonon environment at the site of the emitter. This includes insights into the nature of nonradiative relaxations that limit the achievable quantum efficiency for luminescent emissions.

4.3.1.1 Phonon sideband Analysis

To investigate the local vibrational environment around rare earth ions, phonon sideband analysis is one of the most powerful tools. For the Eu$^{3+}$ ions, the multiphonon relaxation process is predominant between $^5\text{D}_j (j=0-3)$ levels and the radiative emission occurs from $^5\text{D}_0$ level. Therefore if the coordination ions are coupled with the Eu$^{3+}$ ions, the phonon sideband can be observed on the high energy side of the $^7\text{F}_0 - ^5\text{D}_j$ excitation$^{18,19}$. The Eu$^{3+}$ ion has a suitable transition $^5\text{D}_2\rightarrow^7\text{F}_0$ to measure phonon sidebands because fluorescence excitation band of the pure electronic transition is observed as a single peak and the energy gap to the next higher level is quite large$^{19}$.

Figure 4.2 shows the phonon side band (PSB) spectrum, which is observed at the high energy side of the zero phonon line (ZPL, $^7\text{F}_0\rightarrow^5\text{D}_2$) in the excitation spectrum. The phonon energy $\hbar\omega$ is obtained as the energy difference between the pure electronic state or ZPL and the phonon side band. The electron phonon coupling strength ‘g’ is estimated from the ratio of the area under PSB and the corresponding ZPL. According to Miyakawa and Dexter$^{20}$, the rate of multiphonon decay at temperature T can be expressed using the equation

$$W_p(T) = W_o(0)\exp \left[-\frac{\Delta E}{\hbar\omega} \ln \left(\frac{p}{g(n+1)}\right) - 1\right]$$

(4.1)
where $\Delta E$ is the energy gap between excited and ground state and ‘p’ the number of phonons consumed during multiphonon relaxation given by $p = \frac{\Delta E}{\hbar \omega}$. The Wo(0) is the transition probability extrapolated to zero energy gap which is independent of the electronic nature of the rare earth ion and ‘n’ is the Planck’s distribution function on the population of phonon as a function of temperature and phonon energy and is given by

$$n = \left(\exp\left(\frac{\hbar \omega}{kT}\right) - 1\right)^{-1} \quad (4.2)$$

Low nonradiative losses and narrow line width are needed for stimulated and upconversion emission studies and these processes are governed by electron phonon coupling strength and crystal field distribution characteristics of the host matrix. In rare earth doped glasses the non-radiative loss is dominated by the highest energy phonon available in the matrix. Therefore it is important to select a host material for which the maximum phonon energy is as low as possible. The efficiency of rare earth activated glasses is greatly dependent on the multiphonon relaxation rate of the excited rare earth ions. The multiphonon relaxation rate exponentially increases with increasing maximum phonon energy of the host matrix. The lower phonon energy, multiphonon relaxation rate and low electron phonon coupling strength constitutes to the fluorescence enhancement observed in the CdSe/Eu$^{3+}$codoped sample. The quantitative estimate of these parameters are presented in Table 4.1.

For the relaxation of multiphonon emission by ion-phonon interaction is significant in nonradiative probabilities. The excited state relaxation process is governed by both radiative and nonradiative probabilities by the relation

$$\frac{1}{\tau} = \sum A + \sum W \quad (4.3)$$

The high energy transitions are observed if (i) phonon energy maxima for the parent matrices are low and (ii) electron-phonon coupling strengths are high.
Table 4.1 Phonon maxima (ħω), electron phonon coupling strength (g), Non radiative decay rates for $^5$D$_1$, $^5$D$_2$, $^5$D$_3$ transitions of Eu$^{3+}$ ion in Sample A (CdSe 7% Eu 3%) and Sample B (CdSe 0% Eu 3%)

<table>
<thead>
<tr>
<th>Sample</th>
<th>ħω (cm$^{-1}$)</th>
<th>g</th>
<th>Zero Phonon Line (cm$^{-1}$)</th>
<th>$W_P(T)/WO(0)$ from $^5$D$_1$ x(10$^{-6}$)</th>
<th>$W_P(T)/WO(0)$ from $^5$D$_2$ x(10$^{-6}$)</th>
<th>$W_P(T)/WO(0)$ from $^5$D$_3$ x(10$^{-6}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>694</td>
<td>0.00799</td>
<td>0.01456</td>
<td>21580</td>
<td>0.3556</td>
<td>74.805</td>
</tr>
<tr>
<td>B</td>
<td>757</td>
<td>0.01713</td>
<td>0.006984</td>
<td>21580</td>
<td>7.026</td>
<td>53.77</td>
</tr>
</tbody>
</table>
Figure 4.2. Phonon sideband spectra of samples heated to 500°C ($\lambda_{em}=614$nm) taken at room temperature.
The coupling strength between the electronic state of the rare earth ion and vibrational state of the ligand is estimated from the emission intensity of phonon sideband\textsuperscript{21}. In Sample A the phonon sideband clearly shows two shoulders at around 903 cm\textsuperscript{-1} and 694 cm\textsuperscript{-1}. The decrease of ħω is caused by the loosening of network due to the increase of non-bridging oxygens (NBO’s). In sample B the PSB shows two equally prominent peaks at \~1005 cm\textsuperscript{-1} and \~757 cm\textsuperscript{-1} in the deconvoluted spectrum (Figure 4.2). These shoulders can be assigned based on the vibrational transitions given by the FTIR studies on gel derived silica glasses\textsuperscript{22}. The peak around 1086 cm\textsuperscript{-1} corresponds to the Si-O-Si symmetric stretching in cyclic structures and it is found that in Sample B this is prominent. The peak at \~920 cm\textsuperscript{-1} is attributed to the non-bridging free broken Si-O bonds and by comparison with sample B we can see that it was generated in the host by the presence of CdSe. Vibrational energies of the SiO\textsubscript{4} unit in glasses range from 830 –1060 cm\textsuperscript{-1} depending upon the number of NBO’s in the tetrahedron\textsuperscript{23}. The CdSe acts as network modifiers at smaller concentrations, and this increases the NBO’s and the band gets shifted to lower energies. The transition at \~757 cm\textsuperscript{-1} is prominent in sample B which represents the SiO\textsubscript{4} asymmetric stretching and Si-O-Si bending in SiO\textsubscript{2} mode vibrations. The extent to which a particular vibrational mode is coupled to an electronic transition is usually described by the electron-phonon coupling strength ‘g’\textsuperscript{24}. The g value is higher in B for this phonon mode comparing the one at 962 cm\textsuperscript{-1} (Table 4.1). An increase in g with increase of CdSe is an indication of increasing covalency and/or a shortening of the Eu-O bond, and is observed as a shift of absorption band to smaller energies. The electron phonon coupling strength tends to increase, as the polarizability of oxygen increase and as the average interionic distance decrease. Larger Multiphonon relaxation rate \(W_p/W_0\) depends on the large ‘g’ and the higher phonon energy ħω. In the case of sample A the multiphonon relaxation rate (for example from \(^{5}D_1\)) is an order of magnitude greater than
that in sample B. The NBO’s would probably increase the phonon density of the high frequency mode around rare earth ions. This suggests higher nonradiative decay to the emitting level $^5D_0$ from the higher energy levels of the excited europium ion and nonradiative phonon assisted energy transfer from the CdSe to Eu in Sample A.

4.3.1.2 $^5D_0$ - $^7F_0$ transition

The transition $^5D_0$ to $^7F_0$ is both spin and electric dipole forbidden. J is zero for the ground state $^7F_0$ and also for the principal emitting state $^5D_0$ and accordingly these states show no stark splitting. In Eu$^{3+}$, the spin selection rule is relaxed by the mixing of $^7F_0$ into $^5D_0$ by the spin-orbit interaction. The $^5D_0$ - $^7F_0$ transition is nondegenerate and not subject to crystal field splitting changes in the vicinity of the Eu$^{3+}$ ion. Therefore the position and line width of this 0 - 0 transition provide a measure of the local bonding environment and the coordination of the Eu$^{3+}$ ion

![Figure 4.3. $^5D_0$ - $^7F_0$ transition](image)

The $^5D_0$→$^7F_0$ transition is ideally suited for investigation of line broadening in glasses because a single transition between nondegenerate levels can be studied with no overlapping from neighbouring crystal field components. The $^5D_0$→$^7F_0$ transition is taken as a standard for inhomogeneous nature of the
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glass ($\Delta v_{hh}$) since both $^5D_0$ and $^7F_0$ states are non-degenerate. Factors like
local crystal fields, electron-phonon coupling and ion-ion interaction contribute to this broadening. Moreover the energy gap between $^5D_0$ state and the next lower $^7F_6$ state is about ten times the highest involved phonon energy. Therefore the probability of non-radiative deexcitation of the $^5D_0$ state by multiphonon process is very small. The $^5D_0 - ^7F_0$ line is asymmetric when the J mixing mechanism is dominant, while this line is nearly symmetric when other mechanisms are dominant. The inhomogeneous broadening of the $^5D_0 - ^7F_0$ transition is mainly determined by the energy fluctuation of the $^7F_0$ state among sites. This is because the crystal field potential causes mixing of the $^7F_2$ state with $^7F_0$, bringing about the lowering of the $^7F_0$ state, while for the $^5D_0$ state, the admixture of other states is much less than expected for the $^7F_0$ state.

When the inhomogeneous broadening is large, the energy transfer between the same electronic states encounter with a large energy mismatch. The inhomogeneous broadening of the $^5D_0 - ^7F_0$ line is mainly due to the value second order axial crystal –field parameter $B_{20}$ through J mixing. This is because Eu$^{3+}$ ion takes a wide variety of coordination number from 8 to 12 in oxide crystals and glasses is possible. The inhomogeneous broadening is dominant in this transition and since the absorption and emission line shapes coincide with each other (Figure 2.3). This line shape reflects the statistical distribution of the transition energy. Broadband width for the sample indicates the wide distribution of the Eu$^{3+}$ ions in the matrix. The observed $^5D_0 - ^7F_0$ emission is 17337 cm$^{-1}$ and 17316 cm$^{-1}$ for sample A and sample B respectively. The blue shift implies that the orbits of the rare earth valence electrons are contracted which might result from the differing coordination environment.

4.3.2. Fluorescence spectra

In Eu$^{3+}$ doped glass, the fluorescence is mainly due to the purely electronic
$^5D_0 \rightarrow 7F_{J=0,1,2,...}$ transitions although very weak $^5D_1 \rightarrow 7F_1$ lines as well as vibronic bands are also often observed. The $^5D_0 \rightarrow 7F_0$ and $^5D_0 \rightarrow 7F_2$ transitions are electric dipole and $^5D_0 \rightarrow 7F_1$ is magnetic dipole in nature. The strong excitation transition at 393nm hints at a possible enhancement in the principal emission line of Eu$^{3+}$ in the CdSe+Eu$^{3+}$ doped silica. Figure 4.4 depicts the fluorescence spectra of the samples heated to 500°C recorded at room temperature with an excitation of 393nm corresponding to the $^5L_6$ state of the Eu$^{3+}$ ion. It shows a considerable enhancement in the emission intensity corresponding to the $^5D_0 \rightarrow 7F_2$ transition for CdSe+Eu$^{3+}$ doped silica glass.

The structural features play a critical role on the fluorescent enhancement since the complex dielectric function of the composite medium depends directly on the structural features of the particles involved. In the case of Eu$^{3+}$, the main emission lines occur between the $^5D$ levels to the $^7F_J$ multiplets. The $^5D_0 \rightarrow 7F_2$ transition of Eu$^{3+}$ is hypersensitive to the chemical bond formed between Eu$^{3+}$ and its surrounding ligands. A larger transition probability of the $^5D_0 \rightarrow 7F_2$ hypersensitive transition may correspond to an increase of covalent

![Figure 4.4](image_url)

**Figure 4.4** Emission spectra of samples heated to 500°C ($\lambda_{ex} = 393$nm) taken at room temperature.
bonding induced by the presence of CdSe in the nearest neighbor coordination of the Eu$^{3+}$ which changes the geometrical atomic arrangement as well as the bond strength. The incorporation of CdSe to the first coordination shell of Eu$^{3+}$ provides a relative softening of the crystal field strength. However it also contributes to distort the anion symmetry around the rare earth and therefore promotes an enhancement of the transition rates. The fluorescence intensity ratio of $^5D_0 \rightarrow ^7F_2$ to $^5D_0 \rightarrow ^7F_1$ transition indicates the degree of asymmetry in the vicinity of Eu$^{3+}$ ions and Eu-O covalency which could be measured using the asymmetry ratio given as

$$\text{AS} = \frac{\int I_{0 \rightarrow 2} d\gamma}{\int I_{0 \rightarrow 1} d\gamma}$$

(4.4)

where $I_{0 \rightarrow j}$ denotes the intensity of $^5D_0 \rightarrow ^7F_j$ transition. This ratio is influenced by the site symmetry, electronegativity and covalency of the ligand atoms.

**Table 4.2.** Red to orange ratio (R/O), Energy & FWHM for $^5D_0 \rightarrow ^7F_0$ transition of Eu$^{3+}$ ion in Sample A (CdSe 7% Eu 3%) and Sample B (CdSe 0% Eu 3%)

<table>
<thead>
<tr>
<th>Sample</th>
<th>Asymmetry ratio R/O</th>
<th>$^5D_0 \rightarrow ^7F_0$ emission</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>Energy (cm$^{-1}$)</td>
</tr>
<tr>
<td>A</td>
<td>2.6915</td>
<td>17337</td>
</tr>
<tr>
<td>B</td>
<td>1.4539</td>
<td>17316</td>
</tr>
</tbody>
</table>

Improved efficient luminescence was obtained in Eu/CdSe codoped silica glass due to the reduction of concentration quenching (more dispersion of Eu ions) compared to Eu single doped samples. This clearly indicates that the presence of the nanocrystallites is responsible for an increase of both the covalency and the polarization of the local vicinities of the Eu$^{3+}$ cations. A greater ratio corresponds to a more distorted or asymmetric local cation environment. This difference can be attributed to the change in chemical environment of Eu$^{3+}$ in different media. The latter transition is magnetic dipole allowed and its strength is not very site dependent. On the contrary
$^5\text{D}_0 \rightarrow ^7\text{F}_2$ transition is forbidden and becomes electric dipole allowed in an odd field. The intensity ratio of the $^5\text{D}_0 - ^7\text{F}_0$ to the $^5\text{D}_0 - ^7\text{F}_1$ fluorescence increases linearly with $^5\text{D}_0 - ^7\text{F}_0$ energy, which indicates that the $^5\text{D}_0 - ^7\text{F}_0$ transition probability increases linearly with the transition energy.

The intensity of fluorescence from Eu$^{3+}$ in sol-gel glass is highly dependent on the preparation, drying procedure and also varies as a function of time and temperature of dehydration of the gel. The polycondensation of the gel, and its concomitant densification prevents the oxidation of the crystallites. Thermal treatment allows to improve the crystalline quality of the clusters and to narrow their characteristic optical features. As a result of finite size, continuous bands of energy are replaced by molecule-like discrete energy levels. As the particle size increases the energy spacing between the states decreases. In nanoparticles, most ions at the surface are nonsaturated in coordination. Electrons and holes may be easily excited and escape from the ion. Much more carriers trapped at the surface states or defect sites are released by photoexcitation as excitonic or trapped luminescence. Quantum confinement enhances the allowed energies resulting in from an increase in binding energy of shallow impurity. Heat treatment leads to an increase in the inhomogeneities of the local environment owing to the crosslinking between silica chains and consequent shrinkage. As the densification continues, clustering of Eu$^{3+}$ induces strong energy transfer even at lower concentrations. The low fluorescent intensity of the gels was due to electron-phonon coupling with C-H and O-H groups.

The intensity of $^5\text{D}_0 \rightarrow ^7\text{F}_2$ emission relative to the $^5\text{D}_0 \rightarrow ^7\text{F}_1$ emission is increased with CdSe adsorption. By exciting at 393nm the energy from the nonradiative recombination of electron-hole pairs of the CdSe nanoparticles can be transferred to the higher energy levels of the Eu$^{3+}$ ion. This will increase the population of the emitting levels and thereby increasing the fluorescence from the rare earth ion. Larger the inequality of the emission
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intensities of the Eu$^{3+}$ larger is the asymmetry and covalency effects. The J splitting becomes more apparent as the Eu$^{3+}$ environment becomes more asymmetric.

4.4 Conclusions

Sol-gel process has been employed to prepare Eu$^{3+}$ ions along with small sized CdSe crystallites doped in silica matrices. The absorption spectra reveals the formation of CdSe + Eu$^{3+}$ sites in the gel matrix and the excitation spectra on the other hand confirms the densification of the gel and presence of strong excitation bands with the codoping. The excitation spectrum of Eu$^{3+}$ gives rise to phonon assisted sidebands for $^7F_0\rightarrow^5D_2$ transition at higher energy side with a lower phonon energy maximum ($h\omega$) and electron phonon coupling strength ($g$) with codoping. The emission intensities of the europium ions are found to be considerably increased by codoping with nanoparticles of CdSe. This observed stronger fluorescence could be correlated to the low phonon energy observed in the matrix containing CdSe nanocrystallites. The adsorption of the semiconductor nanoparticles on to the SiO$_2$ matrix provides local field enhancement, and the photogenerated electron trapped in the CdSe strongly interact with Eu$^{3+}$ ion located close to the nanocrystallites in the SiO$_2$ matrix. The nonradiative energy transfer from the electron-hole recombination of the CdSe nanoparticles to the rare earth ion will result in the observed fluorescence enhancement.
References