Optical absorption spectrum of the CdSe/Eu$^{3+}$ nanoparticles containing sol-gel glasses was recorded. From the measured absorption intensities of f-f transitions in europium codoped sol gel silica glass samples, the Judd-Ofelt (J-O) parameters $Ω_2$, $Ω_4$ and $Ω_6$ are evaluated. Judd-Ofelt theory is successfully applied to characterize the luminescence spectra of these glasses. The J-O parameters are found to vary with codopant CdSe nanocrystal. The various radiative properties like transition probability $A$, branching ratio $β$, the radiative life time $τ_R$ and the emission cross-section $σ_E^F$ for various levels of Eu$^{3+}$ ions in these glasses are also determined. These data are essential for the design and fabrication of optical devices such as lasers, color displays etc. The analysis predicts the fluorescence properties for the Eu$^{3+}$ ion in the present host. The size and size distribution of the CdSe nanocrystallites were determined by the UV-Visible absorption spectroscopy. In addition the absorption of light by the semiconductor nanoparticles resulting in the formation of exciton is discussed.
3.1. Introduction

Sol gel silica glasses are considered as very good materials for hosting rare earth ions along with semiconductor nanocrystals (quantum dots), as it allows incorporation at low temperatures with predetermined concentration and size\(^1\). The large pore volume fraction and the enormous surface area of the sol-gel glasses enable one to introduce materials in a phase-separated fashion, where the phase separation is in the nanometer range\(^2\). Sol gel method is useful in the preparation of quantum dots doped gel glasses with relatively high particle concentrations, small particle diameter and uniform size distribution\(^3\). 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\(^4\).

Optical transitions of rare earth ions, which are confined within the 4f level structure, have got crucial applications in optoelectronic technology\(^5\). Electron-electron and spin-orbit interactions dominate the electronic structure of the rare earth ions. Lanthanide ions have the fairly unique property of sharp spectral lines (4f-4f) in the solid phase\(^6,7\). 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\(^8\). Knowledge of the local structure of the rare earth in hosts is valuable in optical devices like upconversion laser and laser induced holographic gratings\(^9\). Semiconductor quantum dots in transparent media, especially in sol gel glasses, have received greater attention due to their promising applications in non-linear optics and optical switches\(^10,11\).

Semiconductor quantum dots possess a valence band with strong optical transitions to the conduction band and these transitions form the basis for application of nanocrystallites as laser emitters, storage devices, fluorescence markers and for many possible optical as well as photonic applications\(^12,13\). It has been experimentally proven that the fundamental properties of material
can become strongly size dependent on the size of the material below a certain threshold size. The development of new luminescent materials with complex composition is of interest for understanding the electronic excitation and relaxation phenomena with participation of two and more active centers. In view of these excellent properties of the semiconductor nanocrystallites and the rare earth ions, we tried to link their spectroscopic properties into a single sample.

3.2. Experimental details

The preparation of the sample is done as discussed in Chapter 2. The absorption spectrum is recorded using a spectrophotometer (Shimadzu–UVPC 2401). The excitation and luminescence spectra were taken using a spectrophotofluorimeter (Shimadzu-RFPC 5301) for samples heated to 500°C. All measurements were done at room temperature (~300K).

3.3. Theoretical analysis

The general property of rare earth is greatly determined by their 4f- electrons. The electrons at the inner shell are shielded by the 5s, p, d electrons. So the effect of ligand field becomes weak. The energy levels of rare earth ions depend on, firstly, the static electric interaction between electrons (H_e) and secondly on the interaction between spin and orbital (H_so). 4f^N electronic configuration forms the energy levels denoted with LSJ under the effect of the above two interactions. The energy levels of rare earth ions in glass are similar to those of free ions. Energy level of a system of state such as atom or ion is usually calculated by determining the Hamiltonian of the system. In many particle system like rare earths the most common method is to apply the central field approximation method to calculate the Hamiltonian of the system. Hamiltonian of optically active electron is composed of several terms. The central field Hamiltonian (H_o), which represents the interaction of electron with nucleus, the coulomb field (H_c), the interaction between the
electrons, the spin orbit field ($H_{so}$) represents the interaction between the spin and orbital motion of the electrons and the crystal field ($H_{cf}$) which represents the interaction of electron with the crystal field from the surrounding ion in the solid. Therefore the total Hamiltonian of the system can be written as

$$H_{4f} = H_0 + H_c + H_{so} + H_{cf}$$  \hspace{1cm} (3.1)$$

Since the optical transition of interest in rare earth involves the $4f$-electrons, the magnitude of the different interaction terms is different in each rare earth ions. The other three terms give rise to a set of states labelled by total spin $S$, total orbital angular momentum $L$ and total angular momentum $J$. Spin-orbit interaction has considerable effect, so the resultant total angular momentum $'J'$ is considered to be a good quantum number in almost all circumstances.

The effect of other interactions such as those with nucleus or crystal fields is to lift the $(2J+1)$ degeneracy of the level and the small splitting produced may be treated as perturbation. The rare earth ion in a crystalline salt is situated in a potential $V(r)$ in the crystalline field, which arises from charge $Ze$ on neighboring ions at positive $R_i$ with a potential term of $V(r) = \sum_i eZ_i |r - R_i|$. This potential lifts the $(2J+1)$ degeneracy$^{15}$. From susceptibility measurements it is clear that these splittings due to $V(r)$ are much smaller than the multiplet separation. So that mixing of different multiplet can usually be neglected. In the absence of any magnetic field the levels of an ion with odd number of $4f$ electrons can at most be split into levels which are doubly

Figure 3.1. Schematic diagram of the splitting of energy levels of rare earth ions
degenerate. This is applied to rare earths with half-integral 'J' ground states e.g. Ce\(^{3+}\). The environment of an ion with a degenerate ground state spontaneously distorts to a lower symmetry so as to remove the degeneracy. It implies that ions with an even number of 4\(f\)-electrons always have singlet ground state e.g. Pr\(^{3+}\). This rule doesn't apply to excited state.

Riseberg and Weber \(^{16}\) describe the splitting of energy levels of rare earth in schematic fashion as shown in Figure 3.1. Typical separation due to coulomb interaction is \(\geq 10^4\) cm\(^{-1}\) and it is \(\approx 10^3\) cm\(^{-1}\) for spin-orbit interaction, which splits the 'L' terms into 'J' states. The crystal field interaction breaks the spherical symmetry of the Hamiltonian and remove (2J+1) degeneracy of the levels. The so-called Stark splitting is generally a few hundred cm\(^{-1}\) in magnitude. Radiative transition can occur from any Stark component of one \{L S J\} multiplet. As an example of the energy level splitting in rare earth, a schematic diagram of the splitting in 4\(f^6\) electronic configuration is given in

![Energy level splitting of 4f^6 configuration](image)

Figure 3.2. Energy level splitting of 4\(f^6\) configuration

Figure 3.2. Because of the extreme complexity of the splitting, only a part of the diagram is shown here. In crystal spectra, Zeeman and polarisation studies have made it possible to characterise the J manifolds to which many of the lower lying crystal levels belong. At higher levels this becomes more and more difficult \(^{17}\).

The basic energy levels of free ions are those of the configurations, which are \(2(2l_z+1)\) \(2(2l_z+1)\) \(\ldots\) \(2(2l_n+1)\) degenerate, and have separation \(\approx 5\times 10^4\) cm\(^{-1}\). The detailed energy structure arises from the splitting of these levels by interaction between electrons. Here the interaction is between 4\(f\)-electrons
involved and also between electrons and nucleus. In the case of rare earths three main interactions are dominant in order of magnitude.

(i) Coulomb repulsion between electrons

(ii) Spin orbit interaction

(iii) Nuclear hyperfine and quadrupole interaction

The advantages of glass lasers over crystal can be summarized as follows. The laser glass can be made in a variety of sizes and shapes, with excellent homogeneously and low birefringence; it is less expensive than crystals and it has good coupling to broad band pump sources such as flash lamps and is thus capable of high stored energy density. Glass by its nature has a variety of sites that differ from each other in the number and position of the surrounding anions. Thus transitions in glass are inhomogeneous and relatively broad. The broader emission lines and generally lower cross sections of glass are compensated by its broader absorption bands, which allow glass to couple more efficiently to broad band pump sources than do crystals. Laser glass can store large amounts of energy because it can be produced in large sizes and because of its low cross section. Laser glass has an additional advantage over laser crystals in lasers operating in the picosecond and femtosecond regime. The broad fluorescence line width of glass allows for shorter transform limited pulses. In addition to rare earth ions, the glass serves as a host for numerous other luminescent species. Solid state tunable dye lasers were developed by doping dye molecules in various sol-gel derived glasses and organically modified silicon (ORMOSILS). 18,19,20,21,22

3.4. Judd - Ofelt Analysis

The rare earths are usually doped into solid state host in the trivalent state. The theory of atomic spectra allows identification of definite J levels of 4f^n in the rare earth ion. The position of J levels of 4f^n in condensed matter is treated by the same techniques as monatomic entities, but the probabilities of
absorption and emission between J levels are entirely different. The observed spectra in the visible and infrared regions for the various rare earth ions involve transitions for the same f-electron configuration but for different values for the total spin S, orbital angular momentum L and total angular momentum J. The coulomb interaction between the electron and spin-orbit coupling are comparable. Judd and Ofelt calculated the total electric dipole transition probabilities between various values for ligand fields that lacked a center of symmetry. The transition probability would be zero for transitions between the same f-electron configuration. The special optical properties of trivalent rare earth ions results from the fact that the electrons of their partially filled 4f shell are shielded from the surrounding completely filled 5s and 5p shells. There is a finite electric dipole transition probability only when the ligand field allows mixing of a small amount of 5d or 5g electron configuration into the f-electron configuration. The resulting probabilities are considerably less than for allowed electric dipole transition $10^{-8}$ s to $10^{-9}$ s for spontaneous emission.

A measure of the strength of interaction with the ligand field is indicated by the splitting associated with the sublevels for a term with a given J value whereas the transition metal ions with partially filled 3d orbitals have ligand field splitting of the order of several thousand inverse centimeters, for rare earths the sublevel splitting for a given J value is only a few hundred inverse centimeters. Unlike crystals, in glasses there is much less structure in the absorption and fluorescent lines and the widths for any portion of the lines are a significant fraction of the total line width. Broadening of rare earth ion fluorescence and absorption bands in glasses is necessarily more complicated than that in crystals, since glasses have by definition a random structure, with each rare earth ion seeing a different electric field and having a different set of Stark levels. For a first approximation, it is considered that at room temperature, the broadening of the absorption and fluorescence bands of rare
earth doped glasses is homogeneous in nature. The Judd-Ofelt theory is developed based on this conclusion.

A convenient way of representing the intensity of an absorption band is to measure the oscillator strength of the transition, which is found to be proportional to the area under the absorption line shapes. Oscillator strength \( f \) can be expressed in terms of the molar extinction coefficient \( \epsilon \), and the energy of the transition in wave number \( \nu \) by the relation \(^{25}\)

\[
\begin{align*}
    f_{\text{exp}} &= \frac{2.303 \text{me}^2}{N\pi \epsilon^2} \int \epsilon(\nu) d\nu \\
    \text{or by substituting the standard values} \\
    f_{\text{exp}} &= 4.32 \times 10^{-9} \| \epsilon(\nu) d\nu 
\end{align*}
\]

The absorption properties of rare earth ions are best distinguished in the context of Judd-Ofelt theory. Since this type of analysis has been described many times we simply provide a qualitative outline here emphasizing the final results and their significance. The major mechanism for transitions is induced electric dipole arising from the very weak mixing of the order of magnitude of the ground state \( 4f^n \) wave function (being odd for \( n \) odd, and even for \( n \) even) with functions of the opposite parity. Two main kinds of external perturbations – (a) deviation from a local center of inversion of the distribution of nuclei of neighbour atoms, and (b) deviations due to vibrational motion of neighbour nuclei\(^{26}\).

In essence the \( 4f \rightarrow 4f \) transitions of a rare earth ion can be described as a simple linear combination of the so-called JO parameters \( \Omega_\lambda \) (\( \lambda = 2, 4, 6 \)). The coefficients of each linear combination of \( \Omega_\lambda \) are independent of the host and are determined by the fundamental nature of the \( 4f \) wave functions and the particular transitions at hand. Judd-Ofelt analysis is accurate to 10-15% and is particularly valuable for obtaining strengths of transitions for which direct measurements are difficult or impossible. For bulk samples it is usually the
Spectroscopic parameters of CdSe/Eu\(^{3+}\) Ions ----- Silica Matrix Hosts

Absorption cross sections are measured, since these are straightforward to obtain if the ion concentration is known. JO intensity parameters can then be extracted from the absorption data, enabling one to calculate the strength of the emission transition and thereby scale a measured emission spectrum.

According to J-O theory

\[
f_{ed} = \frac{\nu}{(2J+1)} \left[ \frac{8\pi^2 mc}{3h} \right] \frac{(n^2 + 2)^2}{9n} \sum_{\lambda=2,4,6} \Omega_{\lambda} \left( \langle \psi' J' \| U^J \| \psi J \rangle \right)^2
\]

(3.2)

where \((2J+1)\) is the degeneracy of the ground state, \(\nu\) is the mean energy of the \(|\psi J\rangle \rightarrow |\psi' J'\rangle\) transition, \(U^\lambda\) is a unit tensor operator of rank \(\lambda\) and \(\Omega_{\lambda}\)'s are parameters known as J-O intensity parameters. The values of the reduced matrix elements, \(\|U^\lambda\|^2\), have been evaluated for the Eu\(^{3+}\) ion using the relation

\[
\langle f^N \alpha SL \| U^\lambda \| f^N \alpha' S' L' J' \rangle = (-1)^{S+J+L+\lambda} \left[ (2J+1)(2J'+1) \right] \frac{\Omega_{J\lambda}}{L\lambda S \lambda S} \times \langle f^N \alpha SL \| U \| f^N \alpha' S' L' \rangle
\]

(3.3)

The matrix elements and the 6j symbols required for the analysis have been taken from the literature\(^{27}\). The matrix elements were then transformed from the LS basis state to the physical coupling scheme prior to being used in the calculation. \(|\langle U \| \rangle|^2\) represents the square of the matrix elements of the unit tensor operator \(U^I\) connecting the initial and final states. The matrix elements are calculated in the intermediate coupling approximation\(^{28}\). Because of the electrostatic shielding of the 4f electrons by the closed 5p shell electrons the matrix elements of the unit tensor operator between two energy manifolds in a given rare earth ion do not vary significantly when it is incorporated in different hosts. Therefore, the matrix element computed for the free ion may be used for further calculations in different media and are reported by Carnal et al.\(^{29}\). The reduced matrix elements \(<\langle L+2S\rangle\>\) for magnetic dipole transition are reported by Nielson and Koster\(^{30}\).
For Eu$^{3+}$ ion the ground term $^7F_0$ is very close to the next excited $^7F_1$ level and therefore both levels are populated at room temperature and absorption takes place from both the levels to the excited states. The fractional thermal population $C_J/C_0$ of any excited level $^{2S+1}L_J$ is given by

$$C_J/C_0 = \left[ \frac{g_J}{g_0} \right] \exp \left( \frac{(-E_J - E_0)}{kT} \right)$$  \hspace{1cm} (3.4)$$

where $C_0, g_0$ and $E_0$ refer to the population, degeneracy and energy respectively of the ground state and the subscript ‘$J$’ refers to the excited state$^{29}$. This expression corrects the thermalisation effect and allows to determine the exact oscillator strength and can be applied for the correctness of the spectroscopic parameters determined.

The bonding parameter ($\delta$) defined as

$$\delta = \left[ \left( 1 - \frac{1}{\bar{\beta}} \right) \right] \times 100$$  \hspace{1cm} (3.5)$$

where $\bar{\beta} = \sum_{N} \frac{\beta}{N}$ and $\beta = \frac{v_c}{v_a}$ (the nephelauxetic ratio ), $v_c$ and $v_a$ are the energies of the corresponding transitions in the complex and aqua ion respectively, and $N$ refers to the number of levels used to compute $\bar{\beta}$ values. Depending upon the environmental field, $\delta$ may be positive or negative indicating covalent or ionic bonding respectively.

Radiative transition parameters such as total radiative transition probability ($A_T$), radiative lifetime ($\tau_{RAD}$), and the fluorescence branching ratio ($\beta_R$) are calculated using the known expressions$^{27}$. Radiative transition probabilities of the rare earths in glasses are composed mainly of the electric dipole contribution and to a much lesser extent by the magnetic dipole contribution. For rare-earth ions, taking account of multiple terms splitting, its spontaneous radiative transition probability becomes
Spectroscopic parameters of CdSe/Eu$^{3+}$ Ions — Silica Matrix Hosts

\[ A_{edJJ}^{ed} = \frac{64\pi^4 n^3}{3hc^3(2J+1)} \left[ \frac{n(n^2+2)^2}{9} \right] S_{ed} \]  \hspace{1cm} (3.6)

where \[ S_{ed} = \sum_{J=2,4,6} \Omega_{ed} \langle \psi J | J' | \psi J' \rangle^2 \] \hspace{1cm} (3.7)

As the coefficients for spontaneous emission equal the reciprocal radiative relaxation time, we have

\[ A_{edJJ}^{ed} = \tau_{rad}^{-1} \] \hspace{1cm} (3.8)

or

\[ \tau_{rad} = \frac{1}{\sum_J A_{JJ'}} \] \hspace{1cm} (3.9)

The position of the lines in absorption or emission spectra seems to be independent of the surroundings. Their intensity ratios vary strongly, indicating certain selection rules, which are reflected by the branching ratio. The relative amplitudes of the fluorescence transitions or fluorescence branching ratio is given by

\[ \beta_{JJ'} = \frac{A_{JJ'}}{\sum_J A_{JJ'}} \] \hspace{1cm} (3.10)

Branching ratio is the ratio of the radiative transition probability to the total radiative relaxation rate. It measures the percentage of emission for a given transition from a state with respect to all other transitions from this state. The integrated absorption cross-section or effective cross-section (\(\sigma_a\)) for stimulated emission is estimated using the Fuchtbauer–Landenberg equation.

\[ \sigma_a = \frac{A(\psi J)}{8\pi c n^2 c^2} \] \hspace{1cm} (3.11)

The effective cross-section, which is the stimulated cross-section integrated over the total band gives a measure of the peak stimulated emission cross-section for transitions under the assumption that the bands do not contain
sharp emission peaks. Knowing the radiative transition probability and effective fluorescence line width the stimulated emission cross section ($\sigma_e$) can be calculated using the equation

$$\sigma_e = \frac{\lambda_p^4}{8\pi c n^2 \Delta \lambda_{\text{eff}}} A(\psi J, \psi' J') \quad (3.12)$$

where $\lambda_p$ is the peak wavelength of the emission transition, and $\Delta \lambda_{\text{eff}}$ is the effective line width of the transition in nm.

3.5. Absorption studies

The optical absorption spectra of Eu$^{3+}$ doped and CdSe + Eu$^{3+}$ doped glassy matrices heat treated at 800°C are shown in Figure 3.3. The absorption spectrum shows splitting of the weak absorption bands and appearance of new peaks which are characteristic of Eu$^{3+}$ ions in the presence of CdSe nanocrystallites. The peaks are assigned to each transitions, as $^7F_0 \rightarrow ^5L_6$ (393nm) the most prominent one followed by $^7F_1 \rightarrow ^5G_3$ (380nm), $^7F_0 \rightarrow ^5D_4$ (361nm) and $^7F_0 \rightarrow ^5H_0$ (318nm) based on the free ion energy level structure. The most intense $^7F_0 \rightarrow ^5L_6$ is forbidden by the $\Delta S$ and $\Delta L$ selection rules but
allowed by $\Delta J$ selection rule. The transitions reveal that the absorption takes place from two thermally populated ground and next excited states $^7F_0$ and $^7F_1$, as they are closely spaced ($\sim 250 \text{ cm}^{-1}$).

### 3.5.1 Judd-Ofelt analysis and Radiative parameters

Europium is the only trivalent lanthanide in which the ground term has $J = 0$. But the absorption spectrum includes transitions arising from $^7F_1$ and $^7F_2$ levels, since these levels are thermally populated at room temperature. For most practical purposes the oscillator strengths and the connected radiative transition probabilities obtained from the absorption spectra correspond to some average values due to the total number of sites. A small shift of the free ion levels to lower energies can be observed as a result of the covalency between the rare earth and the matrix in certain glasses.

Table 3.1 Oscillator strengths of all the observed transitions of Eu$^{3+}$ in silica matrices along with the bonding parameter.

<table>
<thead>
<tr>
<th>Transition from $^7F_0$</th>
<th>Pure SiO$_2$ ($x 10^{-7}$)</th>
<th>SiO$_2$ codoped with CdSe ($x 10^{-7}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$f_{\text{meas}}$</td>
<td>$f_{\text{cor}}$</td>
</tr>
<tr>
<td>$^5L_6$</td>
<td>117.07</td>
<td>70.387</td>
</tr>
<tr>
<td>$^5G_2$</td>
<td>4.75</td>
<td>2.857</td>
</tr>
<tr>
<td>$^5D_4$</td>
<td>9.5</td>
<td>5.714</td>
</tr>
<tr>
<td>$^7F_1$-$^5L_7$</td>
<td>3.024</td>
<td>1.818</td>
</tr>
</tbody>
</table>

The oscillator strengths for the observed transitions are calculated using the equation 3.1 by measuring their integrated areas and are tabulated in Table 3.1. Oscillator strengths are approximately one for fully allowed electric dipole transitions and roughly seven orders of magnitude weaker for magnetic dipole transitions. These are corrected for thermal population at room temperature by multiplying by a factor 0.6012 determined using equation 3.4.
The $f_{\text{meas}}$ values are corrected for thermal population of the $^7F_1$ level and are given in Table 3.1 along with calculated values. The bonding parameter $\delta$ determined for each glasses shows correlation but an increased value for the CdSe doped sample indicates less covalent environment for the Eu$^{3+}$ ions.

The Judd-Ofelt theoretical analysis of the absorption spectra yielded the J-O parameters. According to the JO theory the oscillator strengths are found to be functions of the three JO parameters ($\Omega_2, \Omega_4, \Omega_6$) and can be represented as a linear combination of these parameters. These parameters in turn determine the electric dipole and magnetic dipole line strengths of a transition. Table 3.2 shows the JO parameters of Eu$^{3+}$ in silica matrices.

**Table 3.2 Judd-Ofelt parameters of Eu$^{3+}$ in silica matrices**

<table>
<thead>
<tr>
<th>Matrix</th>
<th>JO parameters (10$^{-20}$ cm$^2$)</th>
<th>Q-factor</th>
<th>Order</th>
</tr>
</thead>
<tbody>
<tr>
<td>SiO$_2$</td>
<td>$\Omega_2$: 12.815 $\quad \Omega_4$: 17.96 $\quad \Omega_6$: 5.45</td>
<td>3.295</td>
<td>$\Omega_4$$\gg$$\Omega_2$$&gt;$$\Omega_6$</td>
</tr>
<tr>
<td>CdSe-SiO$_2$</td>
<td>$\Omega_2$: 8.155 $\quad \Omega_4$: 18.434 $\quad \Omega_6$: 5.324</td>
<td>3.462</td>
<td>$\Omega_4$$\gg$$\Omega_2$$&gt;$$\Omega_6$</td>
</tr>
</tbody>
</table>

The transitions with a large value of $\Omega_2$ is called *hypersensitive pseudoquadrupolar* in the sense that they have the same absolute selection rules and numerical relative size. Most plausible explanation for high $\Omega_2$ is based on an inhomogeneous dielectric constant resulting from the strong covalent bonding (ligand field). The large value of $\Omega_2$ support the more ionic nature or less covalency for the undoped sample. The JO parameters are functions of crystal field parameters, intraconfigurational radial integral and energy separation of the $4t^N$ and opposite parity configuration. Hence these parameters are dependent on the oscillator strengths and are found to vary from site to site. In most of the hosts these parameters show the general tendency $\Omega_4$$>$$\Omega_2$$>$$\Omega_6$.

Jorgensen and Reisfeld$^{32}$ related the intensity parameters $\Omega_4$ and $\Omega_6$ to the rigidity of various hosts such as crystals, glasses, solutions and vapours.
Oomen and Dongen\textsuperscript{33} related the intensity parameter $\Omega_4$ for Eu\textsuperscript{3+} to the bulk properties of the glass host reflecting the covalency of the Eu-O bond. They did not however demonstrate the properties involved. Also in various glass systems similar variations of $\Omega_4$ and $\Omega_6$ with compositions were observed. Takebe et al\textsuperscript{34} suggested that ionic packing ratio is related to the spontaneous emission probabilities which are determined by the intensity parameters $\Omega_4$ and $\Omega_6$ and it correlates with the rigidity of the glass hosts and the covalency of the rare earth ion sites. The Judd-Ofelt parameters ($\Omega_2, \Omega_4, \Omega_6$) contain the crystal field parameters $A_{tp}$ related to the symmetry in the environment of rare earth ion, and $\Sigma (t, \lambda = 2, 4, 6)$ the radial part of 4f wave functions and the energy denominator between 4f and admixing levels which measures the covalency rate of the rare earth ligand bond.

According to the Judd-Ofelt theory the JO parameters and spontaneous emission probability are affected by the structural change around rare earth ions and/or the covalency of the rare earth sites\textsuperscript{35}. Especially, the spontaneous emission probability which is determined by the value of the $\Omega_4$ and $\Omega_6$ are affected by the covalency of the rare earth ion sites. The greater quality factor Q observed for the CdSe codoped sample suggests an increase in fluorescence for the sample.

A correlation between the intensity of the f-f transitions and the chemical nature of the lanthanide complex is more difficult to establish than a correlation between spectroscopic and structural properties for d group transition metal complexes, because f-orbitals are much better shielded from the environment than the d-orbitals. Binnemans et al\textsuperscript{36} suggested that small compositional changes of a few percent significantly change the physical and optical properties. These changes can in general be only small variations in the intensity parameters and the changes are only within the experimental uncertainties. In our case we believe that the variations observed in the JO
parameters are due to the difference in glass composition and also due to the errors inherent for these parameters.

Once the $\Omega_\lambda$ quantities have been determined, they can subsequently be utilized to calculate the various radiative properties that have not been experimentally measured, including the radiative life time. The values of the radiative transition probability ($A$), total radiative transition probability ($A_T$), radiative life time ($\tau$) fluorescence branching ratio ($\beta_R$) and the integrated absorption cross section for stimulated emission are given in Table 3.3(a) and (b). Radiative lifetimes for fully allowed electric-dipole transitions are roughly $10^{-8}$s. The increased total radiative decay rate is determined by the asymmetry and covalency of the ligand field. Large $A_T$ for the Eu$^{3+}$ ion alone is due to the large asymmetry connected with the chain structure. Branching ratio, which influence the performance of a device has a significant impact on the threshold of a laser and the efficiency of an amplifier.

Table 3.3(a) Calculated radiative parameters of Eu$^{3+}$ ion alone in SiO$_2$ matrix

<table>
<thead>
<tr>
<th>Transition from $^5D_0$</th>
<th>Energy $\nu$ cm$^{-1}$</th>
<th>$S_{ed}$ (10$^{-20}$)</th>
<th>$A$ s$^{-1}$</th>
<th>$A_T$ s$^{-1}$</th>
<th>$\tau_{rad}$ ms</th>
<th>$\beta$ (%)</th>
<th>$\sigma_A$ (10$^{-20}$ cm$^2$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$^7F_2$</td>
<td>16270</td>
<td>.0423</td>
<td>151.6</td>
<td></td>
<td></td>
<td>58.94</td>
<td>35.64</td>
</tr>
<tr>
<td>$^7F_4$</td>
<td>14420</td>
<td>.0413</td>
<td>103.09</td>
<td>257.169</td>
<td>3.89</td>
<td>40.09</td>
<td>30.86</td>
</tr>
<tr>
<td>$^7F_6$</td>
<td>12260</td>
<td>.001635</td>
<td>2.507</td>
<td></td>
<td></td>
<td>0.975</td>
<td>1.386</td>
</tr>
</tbody>
</table>

Table 3.3(b) Calculated radiative parameters of Eu$^{3+}$ ion in CdSe containing SiO$_2$ matrix

<table>
<thead>
<tr>
<th>Transition from $^5D_0$</th>
<th>Energy $\nu$ cm$^{-1}$</th>
<th>$S_{ed}$ (10$^{-20}$)</th>
<th>$A$ s$^{-1}$</th>
<th>$A_T$ s$^{-1}$</th>
<th>$\tau_{rad}$ ms</th>
<th>$\beta$ (%)</th>
<th>$\sigma_A$ (10$^{-20}$ cm$^2$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$^7F_2$</td>
<td>16270</td>
<td>.0269</td>
<td>96.454</td>
<td></td>
<td></td>
<td>71.189</td>
<td>22.68</td>
</tr>
<tr>
<td>$^7F_4$</td>
<td>14420</td>
<td>.01224</td>
<td>30.56</td>
<td>135.491</td>
<td>7.381</td>
<td>22.552</td>
<td>9.148</td>
</tr>
<tr>
<td>$^7F_6$</td>
<td>12260</td>
<td>.00553</td>
<td>8.481</td>
<td></td>
<td></td>
<td>6.259</td>
<td>3.512</td>
</tr>
</tbody>
</table>
The predicted lifetime ($\tau_{\text{rad}}$) of $^5D_0$ level for CdSe containing glass is found to be greater than that without CdSe. Higher the radiative lifetime, lower the presence of higher vibrational frequencies leading to high nonradiative losses. From the radiative lifetimes it is also evident that the interaction of Eu$^{3+}$ ion with the glass network is much lower for glass containing CdSe. From the table it is clear that the branching ratio and the stimulated absorption cross section is maximum for the $^5D_0 \rightarrow ^7F_2$ transition and this transition can be utilized for optical amplification.

Stimulated emission cross-section $\sigma_E$ is the most important laser parameter. Its value signifies the rate of energy extraction from the laser material. The values of $\sigma_E$ for different observed transitions are given in Table 3.4.

**Table 3.4. Stimulated emission parameters**

<table>
<thead>
<tr>
<th>Matrix</th>
<th>$\lambda_p$(nm)</th>
<th>$\Delta\lambda_{\text{effe}}$(nm)</th>
<th>$\sigma_E$(10$^{-21}$cm$^2$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>SiO$_2$</td>
<td>612.2</td>
<td>12.208</td>
<td>1.086</td>
</tr>
<tr>
<td></td>
<td>651</td>
<td>4.325</td>
<td>2.665</td>
</tr>
<tr>
<td>CdSe-SiO$_2$</td>
<td>612</td>
<td>11.72</td>
<td>7.246</td>
</tr>
<tr>
<td></td>
<td>650.6</td>
<td>3.804</td>
<td>9.631</td>
</tr>
</tbody>
</table>

The high value for the transition $^5D_0 \rightarrow ^7F_2$ suggests that this could be used as a laser transition.

### 3.6. Conclusions

The emission intensity of the transitions $^5D_0 \rightarrow ^7F_2$ and $^5D_0 \rightarrow ^7F_1$ depend on the Judd-Ofelt parameters $\Omega_2$ and $\Omega_4$ respectively. The intensity of the emission $^5D_0 \rightarrow ^7F_2$ depend on the $\Omega_2$ parameter and the value of $\Omega_6$ depend mainly on long range effects related to the bulk properties of the glasses. The values of $\Omega_4$ and $\Omega_6$ depend strongly on the vibrational frequencies of the Eu$^{3+}$ ions linked to the ligand atoms. The emission intensity of $^5D_0 \rightarrow ^7F_2$ transition(RED) is subjected to local symmetry (electric dipole) but $^5D_0 \rightarrow ^7F_1$ (ORANGE) is independent of local symmetry (magnetic dipole). The observed increase in
the intensity ratio (R/O), $\Omega_2$ and the bonding parameter is due to increase of covalency between the Eu$^{3+}$ ion and the ligands. The branching ratio of the luminescence transitions originating from the $^5D_0$ level characterizes the lasing power and $\beta_R$ with a value greater than 50% becomes a potential laser emission. From the radiative lifetimes it is evident that the interaction of Eu$^{3+}$ ion with the glass network is much lower for glass A.
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