Dysprosium doped silica matrices were prepared by sol-gel technique and the spectroscopic properties in dried gels and gel glasses were investigated. Judd-Ofelt (J-O) intensity parameters are derived from the optical absorption spectra. The calculated values of the J-O parameters are utilized in evaluating the various radiative parameters such as electric dipole line strengths ($S_{el}$), radiative transition probabilities ($A_{RAD}$), radiative lifetimes ($\tau_{RAD}$), fluorescence branching ratios ($\beta_{R}$) and the integrated absorption cross sections ($\alpha_{a}$) for stimulated emission from various excited states of the rare earth ion. The fluorescence properties of Dy$^{3+}$ ion are utilized to study the structural changes during the gel to glass transition of the silica xerogels. The fluorescence intensity ratio (yellow to blue, Y/B) is used as a measure of the symmetry of rare earth ion environment during the gel-glass conversion. The high value of the intensity ratio of gel heated to 1000°C showed that the rare earth ions are embedded in the glassy silica network with an asymmetric environment. Fluorescence study is also used to characterize the effect of metal cation co-dopants on the state of aggregation of rare earth ions in sol-gel silica. The addition of co-dopants inhibits the clustering of rare earth ions and promotes better dispersion. The inhibition of clustering is correlated with the generation of strong crystal field bonding sites for rare earth ions in the presence of co-dopants.
5.1 Introduction

Optical properties of rare earth ion doped glasses are widely investigated for potential applications in optical devices [1]. Rare earth ions have number of efficient and narrow emission lines in the visible and NIR wavelength region whose position is insensitive to their matrices due to the shielding effect of 5s and 5p electrons. Rare earth doped glasses, therefore, play an important role for optical applications such as glass lasers and optical fiber amplifiers and also hold promise for photochemical hole-burning memory, flat panel display etc [2]. The potential advantage of the sol-gel method for preparing optical materials includes obtaining new chemical compositions, better purity and more convenient processing conditions [3-4]. In addition to the conventional inorganic hybrid optical materials, inorganic-organic hybrid materials are currently receiving much attention [5]. The optical absorption and luminescence properties of several rare earth ions incorporated into sol-gel silica have been reported including Ce$^{3+}$[6], Sm$^{3+}$[7], Eu$^{3+}$[9-11], Er$^{3+}$[12], Tb$^{3+}$[15-17], Yb$^{3+}$[18], Pr$^{3+}$[19-22], and Nd$^{3+}$[23-28]. Compact and efficient all solid state lasers emitting in the visible spectral region are of great interest for a number of applications in medicine, biology, metrology, optical storage and display technology. With the ZBLAN material, laser oscillation has been observed in several rare earths such as trivalent praseodymium, neodymium, thulium, holmium and erbium [29,30]. However these laser materials donot cover the entire visible spectral range. Gaps especially exist in the yellow and blue range which cannot be filled by applying frequency doubled solid-state lasers. The dopant material dysprosium has the potential to fill these gaps due to the well known strong fluorescence in the visible spectral range around 575 and 480 nm [31].
Hydroxyl quenching and dopant clustering are the two complications that currently limit the luminescence efficiency of rare earth ions in sol-gel host materials [5]. Hydroxyl quenching is caused by residual water solvents and silanol groups present in sol-gel glasses, which leads to an enhancement of non-radiative pathways of rare earth ions. Dopant clustering refers to the tendency of a luminescent species to aggregate with itself through oxygen linkages. It leads to concentration quenching of luminescence through cross relaxation and energy transfer processes [32]. In numerous studies on the systems Eu$_2$O$_3$-SiO$_2$, Nd$_2$O$_3$-SiO$_2$, Er$_2$O$_3$-SiO$_2$, Pr$_2$O$_3$-SiO$_2$ and Tb$_2$O$_3$-SiO$_2$ prepared by sol-gel route, it was shown that this process cannot overcome the problem of cluster formation and phase separation [33]. Rare earth clustering has been inhibited by co-doping with Al$^{3+}$ and by using organic acid salts instead of mineral acid salts as rare earth precursors [24]. Recently Gijo et. al. have shown that the intensity of Eu$^{3+}$ emission in the silica matrix increased remarkably when it is co-doped with CdSe nano crystals[34]. Doped glasses obtained via thermal densification of the gels show similar properties with that of the melt route glasses [7]. Thermal treatment of the doped gels changes the local environment of the metal ions, which results changes in fluorescence spectra. Though this behavior is common for most of the modifier ions doped gels studied, a detailed study of the incorporation of Dy$^{3+}$ ions in sol-gel silica host is yet to be well established. In comparison with other rare earth ions like Eu$^{3+}$, Nd$^{3+}$ and Er$^{3+}$ the number studies on the Dy$^{3+}$ ions in silica gels and sol-gel glasses is rather limited. It is not clarified what structures the resultant materials have and how they are interconnected with their optical functionalities [35]. Since the optical properties of the doped silica systems depend on the local structure and bonding of the dopant cations [7], a detailed understanding of the structural evolution during the gel to glass conversion of Dy$^{3+}$doped silica gels is very important to fabricate the
material for optical applications. Development of such functional glasses requires
detailed microscopic information, especially on the local structures around the
rare earth ions. Further, systematic studies on the effect of –OH and clustering on
emission can have theoretical and practical significance in developing the
miniature of rare earth doped glass laser. In this context, it is worthwhile to
examine the structural evolution and changes in fluorescence properties of Dy$^{3+}$
in the gel to glass conversion. Here we report the results of a study on the
luminescence and structural properties of Dy$^{3+}$ doped silica xerogels. The yellow
to blue (Y/B) ratio is successfully used to study the asymmetries of the Dy$^{3+}$ sites
in glass hosts. We further used the fluorescence spectroscopy to characterize the
effect of several cation co-dopant on the clustering of Dy$^{3+}$ in sol-gel derived
silica.

5.2 Theoretical analysis

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 ($\varepsilon$), and the energy of the
transition in wave number ($\nu$) by the relation [36].

$$f_{\text{exp}} = 4.32 \times 10^{-9} \int \varepsilon(\nu) d\nu$$

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. In essence the 4f→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.

According to J-O theory

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

(5.2)

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 \(U^{\lambda'}\)'s are parameters known as J-O intensity parameters. The values of the reduced matrix elements, \(\|U^\lambda\|\), have been evaluated for the Dy\(^{3+}\) ion using the relation

$$\langle f^N\alphaSLJ || U^\lambda || f^N f^N \alpha'S'L'J' \rangle = (-1)^{S+J+L'+\lambda}[2J+1](2J'+1)\xi_{SL}^{IJ,\lambda}$$

\[5.3\]

\[5.4\]

The matrix elements and the \(6j\) symbols required for the analysis have been taken from the literature [37]. The matrix elements were then transformed from the LS basis state to the physical coupling scheme prior to being used in the calculation. \(|\langle U^\lambda || \rangle|^2\) represents the square of the matrix elements of the unit tensor operator \(U^\lambda\) connecting the initial and final states. The matrix elements are calculated in the intermediate coupling approximation [38]. 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 Carnall et al. [39]. The reduced matrix elements \(|\langle L+2S || \rangle|\) for magnetic dipole transition are reported by Nielson and Koster [40].
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 [37]. For rare-earth ions, taking account of multiple terms splitting, its spontaneous radiative transition probability becomes

\[
A^{ed}_{JJ} = \frac{64\pi^2e^2v^3}{3h(2J+1)}\left[\frac{n(n^2+2)^2}{9}\right]S_{ed}
\]  
(5.4)

where

\[
S_{ed} = \sum_{\lambda=2,4,6} \Omega_\lambda \langle \psi_\lambda | U^{|J}| \psi'_J \rangle^2
\]  
(5.5)

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

\[
A^{ed}_{JJ} = \tau^{-1}_{Rad}
\]  
(5.6)

or

\[
\tau_{rad} = \sum_{JJ'} A_{JJ'}
\]  
(5.7)

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

\[
\beta_{JJ'} = \frac{A_{JJ'}}{\sum_{JJ'} A_{JJ'}}
\]  
(5.8)

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.
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

\[
\sigma_e = \frac{\lambda_p^4}{8\pi\nu^2 \Delta \lambda_{\text{eff}}} A(\nu J, \nu' J')
\]

where \( \lambda_p \) is the peak wavelength of the emission transition.

5.3 Experimental details

Silica sols containing 2 equivalent mol% Dy\textsubscript{2}O\textsubscript{3} were prepared by the method described in Chapter 4. The co-dopants were added in the form of their nitrates.

The following equations give the simplified mechanisms leading to the gelation of the precursor solution

\[
\begin{align*}
=\text{Si}-\text{OC}_2\text{H}_5 + \text{H}_2\text{O} & \rightarrow =\text{Si} - \text{OH} + \text{C}_2\text{H}_5\text{OH} \quad (1) \\
=\text{Si} - \text{OH} + \text{HO-Si} & \rightarrow =\text{Si} - \text{O-Si} = + \text{H}_2\text{O} \quad (2) \\
=\text{Si} - \text{OH} + \text{H}_5\text{C}_2\text{O-Si}= & \rightarrow =\text{Si} - \text{O-Si}= + \text{C}_2\text{H}_5\text{OH} \quad (3)
\end{align*}
\]

Mechanism (1) represents hydrolysis reaction and mechanisms (2) and (3) represent condensation reactions. Simultaneously a cluster-cluster aggregation process takes place as the sol converts to gel. The rare earth and codopant nitrates become increasingly entangled and ultimately trapped within the growing clusters, which make the dopant ions disperse in the derived gel at a molecular level. TEM micrographs were taken using Hitachi H-600 electron microscope.
5.4 Results and Discussion

5.4.1 Optical absorption studies

The prepared gel samples were characterized at different stages of preparation using UV-VIS absorption spectroscopy to study the development of final local environment around the rare earth ions in the sol-gel process. Figure 5.1 shows the typical absorption spectra of 2mol% Dy₂O₃ doped silica gel fired at 200°C.

Figure 5.2 shows the energy level diagram of Dy³⁺ in silica matrix. All the spectra of rare earth ions arise from the intra-configuration transitions within the 4f shell [41]. In the free ion state, these transitions are prohibited by the parity rule of electric dipole transition [42]. However this prohibition can be avoided for ions embedded in a crystal field by non-centrally symmetric interactions of the ions with surrounding ions, which mix states of opposite parity and thus relax the parity restrictions. For Dy³⁺ ions, the transition occurs from the ⁶H₁₅/₂ levels to various excited levels [43]. It can be seen that the final position of the peak,
as it appears for the dense glass is more or less established when the heat treatment temperature has reached 200°C. It has been observed that the trend of the physical properties of Dy-doped sol-gel glass is rather similar to pure sol-gel silica. As the gels are gradually heated, the specific surface area and total pore volume decreased while the bulk density and shrinkage of the samples increased. From the phase transition occurring around 300°C these changes are gradual until the temperature reaches about 900°C and then changing much more quickly as pore closure occurs. It can be seen that this behaviour is also reflected in the increasing shifts of the absorption peak position around 700°C.
The electronic transitions of the trivalent lanthanides can be electric dipole, magnetic dipole or electric quadrupole in nature [44]. Electric dipole transitions between the states of the $4f^N$ configuration of an isolated trivalent rare earth ion are prohibited by the parity selection rule [42]. This prohibition can be more or less avoided due to the non-centrally symmetric interactions of the ions with its surroundings, which mix states of opposite parity and thus relaxing the parity restriction. Electric dipole transitions may also occur as a result of the symmetries produced by means of the vibronic coupling of the central ion with its ligands. In contrast to this parity restriction, electric quadrupole and magnetic dipole transitions are parity allowed [42]. Neglecting higher multipole mechanisms such as electric quadrupole transitions, oscillator strength ($f$) can be regarded as a sum of the electric dipole ($f_{ed}$) and magnetic dipole ($f_{md}$) contributions, i.e.,

$$f = f_{ed} + f_{md}$$

(5.11)

It is well known that for rare earth ions, the intermanifold line strength of magnetic dipole (md) transitions is much less than the line strength of electric dipole (ed) transitions ($S_{md}^{ij} \ll S_{ed}^{ij}$). Therefore in radiative intensity calculations the ed approximation is commonly used and md transitions are only taken into account if required [45]. The experimentally measured oscillator strengths of various absorption transitions of Dy$^{3+}$ ion in the present glassy systems are found to be in good agreement with that of other oxide systems. All the manifolds are crystal field split by the influence of the immediate environment (i.e. the first co-ordination sphere) of the rare earth ion, which consists of oxygen from the glass matrix. Owing to the absence of the long-range order in the glass, the micro symmetry around Dy$^{3+}$ ions differs slightly from site to site. And therefore the transitions are inhomogeneously broadened with typical half widths of about 200 cm$^{-1}$ for isolated bands. The overall appearance of the spectra does not change very much with glass composition.
Table 5.1 Oscillator strengths (10⁻⁴) and electric dipole line strengths (10⁻²⁰) of all the observed transitions of Dy⁺⁺ in silica matrices.

<table>
<thead>
<tr>
<th>Transitions from ⁶H₁₅/₂</th>
<th>Pure SiO₂</th>
<th>SiO₂ codoped with</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>f_mes</td>
<td>S_{ed}</td>
</tr>
<tr>
<td>⁶P₇/₂</td>
<td>2.94</td>
<td>1.31</td>
</tr>
<tr>
<td>⁵P₅/₂</td>
<td>2.31</td>
<td>1.06</td>
</tr>
<tr>
<td>⁴F₇/₂</td>
<td>0.984</td>
<td>0.484</td>
</tr>
<tr>
<td>⁴I₇/₂</td>
<td>0.622</td>
<td>0.355</td>
</tr>
<tr>
<td>⁵F₇/₂</td>
<td>1.13</td>
<td>1.08</td>
</tr>
<tr>
<td>⁶F₇/₂</td>
<td>6.27</td>
<td>6.41</td>
</tr>
</tbody>
</table>

Table 5.1 contains the Russell-Saunders term symbols ²S+²L_J, oscillator strengths and electric dipole line strengths of all the observed transitions of Dy⁺⁺ in silica matrices. The position of the ²S+²L_J multiplets of the Dy⁺⁺ ion are determined by the Racah and spin orbit coupling parameters of the free ion. Changes of these positions in the glass arise from the nephelauxetic effect. Jorgensen proposed that the nephelauxetic effects result from an expansion of the partly filled f shell due to charge transfer from the liquids to the core of the central ion. It is therefore clear that the nephelauxetic effect may be used as a measure of the covalency of the bonding between the rare earth ion and the surrounding oxygens of the glass. The overlap with the ligands reduces the values of the free ion parameters and causes a contraction of the energy level structure of the ion in the glass. Consequently this leads to a shift of absorption and emission bands towards smaller energies.

5.4.2 Judd-Ofelt analysis and Radiative parameters

The Judd-Ofelt theoretical analysis [46,47] 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. The JO parameters are functions of crystal field parameters, intraconfigurational radial integral and energy separation of the \( 4f^n \) 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 \( \Omega_2<\Omega_4<\Omega_6 \). Jorgensen and Reisfeld [48] 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 [49] related the intensity parameter \( \Omega_4 \) for \( \text{Eu}^{3+} \) to the bulk properties of the glass host reflecting the covalency of the \( \text{Eu}-\text{O} \) 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 [50] 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.

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 [51]. 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. Table 5.2 shows the JO parameters of \( \text{Dy}^{3+} \) in silica matrices. 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 [52] 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 these 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.

Table 5.2 Judd-Ofelt parameters of Dy³⁺ in silica matrices.

<table>
<thead>
<tr>
<th>Matrix</th>
<th>JO parameters (10⁻²⁰ cm²)</th>
<th>Order</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Ω₂</td>
<td>Ω₄</td>
</tr>
<tr>
<td>SiO₂</td>
<td>7.07</td>
<td>5.08</td>
</tr>
<tr>
<td>Li-SiO₂</td>
<td>8.25</td>
<td>5.62</td>
</tr>
<tr>
<td>Na-SiO₂</td>
<td>5.86</td>
<td>4.44</td>
</tr>
<tr>
<td>K-SiO₂</td>
<td>5.78</td>
<td>6.36</td>
</tr>
<tr>
<td>Ag-SiO₂</td>
<td>6.21</td>
<td>3.24</td>
</tr>
</tbody>
</table>

Now once the Ω₂ quantities have been determined, they can subsequently be utilized to calculate the properties of transitions that have not been experimentally measured, including the radiative life time. The values of the radiative transition probability (A), total radiative transition probability (A₉), radiative life time (τ) fluorescence branching ratio (βᵣ) and the integrated absorption crosssection for stimulated emission are given in Table 5.3. From the table it is clear that the branching ratio and the stimulated absorption crosssection is maximum for the $⁴F_{9/2}→⁶H_{13/2}$ and $⁴F_{9/2}→⁶H_{15/2}$ transitions and these transitions can be utilized for optical amplification.
Table 5.3 Calculated radiative parameters of Dy$^{3+}$ ion in SiO$_2$ matrix

<table>
<thead>
<tr>
<th>Transition from $^{4}F_{9/2}$</th>
<th>Energy $\nu$ cm$^{-1}$</th>
<th>$S_{ed}$ (10$^{-22}$ cm$^{2}$)</th>
<th>$A$ s$^{-1}$</th>
<th>$A_T$ s$^{-1}$</th>
<th>$\tau_{rad}$ $\mu$s</th>
<th>$\beta$</th>
<th>$\sigma_a$ (10$^{-19}$ cm$^{2}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$^6F_{1/2}$</td>
<td>7283</td>
<td>0.203</td>
<td>1</td>
<td></td>
<td></td>
<td>0.001</td>
<td>0.091</td>
</tr>
<tr>
<td>$^6F_{3/2}$</td>
<td>7845</td>
<td>0.104</td>
<td>1</td>
<td></td>
<td></td>
<td>0.001</td>
<td>0.115</td>
</tr>
<tr>
<td>$^6F_{5/2}$</td>
<td>8649</td>
<td>5.144</td>
<td>8</td>
<td></td>
<td></td>
<td>0.006</td>
<td>0.647</td>
</tr>
<tr>
<td>$^6F_{7/2}$</td>
<td>10082</td>
<td>3.429</td>
<td>13</td>
<td></td>
<td></td>
<td>0.014</td>
<td>0.777</td>
</tr>
<tr>
<td>$^6H_{5/2}$</td>
<td>10892</td>
<td>2.293</td>
<td>7</td>
<td></td>
<td>1239</td>
<td>0.005</td>
<td>0.353</td>
</tr>
<tr>
<td>$^6H_{7/2}$</td>
<td>11955</td>
<td>7.285</td>
<td>34</td>
<td></td>
<td>807</td>
<td>0.027</td>
<td>1.431</td>
</tr>
<tr>
<td>$^6F_{9/2}$</td>
<td>12039</td>
<td>3.634</td>
<td>19</td>
<td></td>
<td></td>
<td>0.015</td>
<td>0.795</td>
</tr>
<tr>
<td>$^6F_{11/2}$</td>
<td>13361</td>
<td>5.133</td>
<td>48</td>
<td></td>
<td></td>
<td>0.038</td>
<td>1.625</td>
</tr>
<tr>
<td>$^6H_{9/2}$</td>
<td>13390</td>
<td>4.017</td>
<td>29</td>
<td></td>
<td></td>
<td>0.023</td>
<td>9.797</td>
</tr>
<tr>
<td>$^6H_{11/2}$</td>
<td>15269</td>
<td>9.03</td>
<td>78</td>
<td></td>
<td></td>
<td>0.069</td>
<td>2.02</td>
</tr>
<tr>
<td>$^6H_{13/2}$</td>
<td>17670</td>
<td>64.59</td>
<td>743</td>
<td></td>
<td></td>
<td>0.599</td>
<td>14.49</td>
</tr>
<tr>
<td>$^6H_{15/2}$</td>
<td>21140</td>
<td>12.94</td>
<td>258</td>
<td></td>
<td></td>
<td>0.208</td>
<td>3.498</td>
</tr>
</tbody>
</table>

5.4.3 Fluorescence studies

An important performance indicator for the samples to be useful for glass laser applications is its fluorescence properties. To determine the optical characteristics of the sample photoluminescence measurements were carried out. Figure 5.3 shows the excitation spectra for the 575nm emission of Dy$^{3+}$ doped silica gels heat-treated at various temperatures. The intensity and half bandwidth of the transitions increase with increasing heat treatment temperature. These results have a relation to the environment of Dy$^{3+}$ ions. Because the electrons of the 4f shells are screened by the outer shell electrons, the presence of the surrounding lattice has little effect on the f-f transitions, the silica network strengthens gradually, (Si-O)$_n$-Dy bonds form and Dy$^{3+}$ ions are coordinated by SiO$_4$ tetrahedra instead of H$_2$O as shown in Figure 5.4.
Figure 5.3. Excitation spectra of Dy$^{3+}$ in SiO$_2$ under various heat treatment temperatures

Figure 5.4. Structural change of Dy$^{3+}$ during gel to glass transition
Dy$^{3+}$ ion is situated in a distorted cube with eight non-bridging oxygens belonging to the corners of SiO$_4$ glass forming tetrahedral, each tetrahedron donating two oxygens.

Figure 5.5 shows the emission spectra of the xerogels heat treated at various temperatures. The fluorescence intensity increases remarkably, when the doped silica gel is heat treated in the range 60-1000°C. The result of the linear shrinkage of the gel versus heat treatment temperature shows that the shrinkage at room temperature – 500°C is much smaller than that at higher temperature. This indicates that the large increase in fluorescence intensity is not caused mainly by

![Figure 5.5 Emission spectra of Dy$^{3+}$ in silica matrix ($\lambda_{ex} = 355$nm)](image)

the increase in Dy$^{3+}$ ion concentration as a result of the decrease in sample volume [15]. The –OH groups which quench strongly the radiation transitions of Dy$^{3+}$ ion are from the coordination water rather than the physically absorbed water [15]. With increasing heat treatment temperature the silica network strengthens gradually and the coordination water molecules are substituted by
SiO$_4$ tetrahedron. After heating at 600°C, (Figure 5.6) the coordinated water molecules are almost removed by the formation of (Si-O)$_n$-Dy bonds. Increase in Dy$^{3+}$ ion concentration as a result of the decrease in sample's porosity and volume at elevated temperatures may lead to the enhancement of fluorescence.

From the emission spectra of Dy$^{3+}$, the intensity ratio \((^4F_{9/2} \rightarrow ^6H_{15/2})/(^4F_{9/2} \rightarrow ^6H_{13/2})\) due to emissions in the yellow and blue regions designated as Y/B are calculated. The Y/B of Dy$^{3+}$ emission follows a trend parallel to red to orange (R/O) of Eu$^{3+}$, as these ratios are influenced by the site symmetry and electronegativity of the ligand atoms in a similar manner. The two prominent transitions are electric dipole in nature out of which \((^4F_{9/2} \rightarrow ^6H_{13/2})\) is hypersensitive. The intensity of the hypersensitive transition is affected by the metal ligand interactions. The ratio of their intensities is shown to be sensitive to the covalency of the ligand atoms and distortions from the cubic symmetry [50]. The larger the inequality of the emission intensities of these two transitions, the larger is the asymmetry and covalency effects. For the present case the Y/B ratio showed a marked increase, as the gel is heat treated (0.51 to 0.76). The high value
of the intensity ratio of the 1000°C heated gel showed that the Dy$^{3+}$ is embedded in the glassy network with an asymmetric environment.

5.4.4 Effect of co-doping

Figure 5.7 shows that the presence of a cation codopant has a strong influence on the fluorescence emission of Dy$^{3+}$ ion. Quantitatively the increase in fluorescence intensity varies with the cation codopant. The ability of the codopant to increase the fluorescence intensity increases as Li$^+\!>\!$Na$^+\!>\!$Ag$^+\!>\!$K. This behaviour can be explained by invoking the influence of the nonradiative rate, hydroxyl quenching and crossrelaxation on the radiative relaxation rate.

The total relaxation rate can be expressed as

$$\frac{1}{\tau} = \sum W_{NR} + \sum A + P_{CR}$$  \hspace{1cm} (5.12)

where $\sum A$ is the total radiative rate, $\sum W_{NR}$ is the nonradiative rate and $P_{CR}$ is the rate of cross-relaxation between adjacent ions.
The possible channels for non-radiative relaxation are discussed below

(a) Multiphonon relaxation involving phonons of energy $h\omega$ is described by

$$W_{NR} = A \exp(-Bp)$$  \hspace{1cm} (5.13)

where $A$ and $B$ are constants, $p$ is the number of phonons (excited lattice vibrations) and this can be calculated using the equation

$$p = \frac{\Delta E}{h\omega}$$  \hspace{1cm} (5.14)

where $\Delta E$ is the energy gap between emitting and terminal levels. For silica glass the phonon energy is $\sim 965$ cm$^{-1}$ due to the Si-O-Si stretching vibration. For codoped samples the phonon energy decreases and the number of phonons needed to bridge the excited and ground state increases. With increasing the number of phonons 'p', $W_{NR}$ decreased and as a result the quantum yield increased. Therefore the nonradiative rate is higher in R doped glasses.

(b) The hydroxyl quenching can be described by the relationship

$$\frac{1}{\tau_{em}} = \frac{1}{\tau_{rad}} + k_{OH} \alpha_{OH}$$  \hspace{1cm} (5.15)

where $\alpha_{OH}$ is the absorption coefficient of hydroxyl at 2700 nm ($\sim 40$ cm$^{-1}$) and $k_{OH}$ is the rate constant. The presence of hydroxyl band will also increase the non-radiative decay. From the FTIR spectra it was confirmed that a large amount of hydroxyl group was present in R doped glasses. The hydroxyl content in glasses processed at high temperature has been estimated from the IR spectra using the relationship

$$[OH](ppm) = (1000/t) \log(T_a/T_b)$$  \hspace{1cm} (5.16)

where $T_a$ and $T_b$ are the transmissions at 2.6 and 2.7 $\mu$m respectively and $t$ is the sample thickness (mm). Hydroxyl content around 4000 ppm was measured after the glass processed at 1000°C. This was explained to be the cause for the greater
nonradiative relaxation rate in codopant free rare earth doped glasses compared to codoped glasses.

(c) The cross relaxation may take place between the same lanthanides or between two different ions. This process between a pair of rare earth ions is graphically presented in Figure 5.8. When it is excited at 355nm in high-lying excited states of Dy$^{3+}$ several paths for self quenching by energy transfer between two similar neighbouring ions [54]. Eg. $[^4F_{9/2},^6H_{15/2}] \rightarrow [^6H_{5/2},^6H_{5/2}]$ or $[^4F_{9/2},^6H_{15/2}] \rightarrow [^6H_{9/2},^6F_{3/2}]$. In the first path there is a good resonance between the energy of the $[^4F_{9/2}\rightarrow ^6H_{5/2}$ and $[^6H_{9/2}\rightarrow ^6H_{5/2}$ transition. Cross relaxation occurs as follows.

Deexcitation of one Dy$^{3+}$ from $[^4F_{9/2}$ level to a $^6H_{5/2}$ manifold ($[^4F_{9/2}\rightarrow ^6H_{5/2}$) and energy transfer to another Dy$^{3+}$ ion $[^6H_{15/2}\rightarrow ^6H_{5/2}$ follows by energy dissipation in the silica glass. There are more than six cross-relaxation paths originating from the $[^4F_{9/2}$ emitting level and even more when all the excited states are taken into account [54]. By this process the original system loses the energy ($E_2-E_1$) by obtaining the lower state $E_2$ (which may also be the ground state $E_1$) and another system acquires the energy by going to a higher state $E_2$[21]. The two energy gaps may be equal or can be balanced by one or two phonons. It is a dominating factor at high concentrations. In the present case a small amount of codopant prevented the aggregation resulting in the circumvention of the cross relaxation process.
5.4.5 Structural studies

The incorporation of rare earth ions into melt prepared silicate glass is problematic because of the tendency of phase separation to occur due to the low solubility of the rare earth oxides in silica [5]. The sol-gel process represents an alternative route to rare earth doped glasses and offers the potential to achieve the higher doping concentrations desired for many applications. To realize this potential however it is necessary to prepare sol-gel glasses with a uniform distribution for rare earth dopants. Recent work has demonstrated the tendency of rare earth (and other metal) ions to form clusters in sol-gel silica [55-57]. Further understanding of the factors that govern metal ion clustering is needed in order to constructively control the spatial distribution of dopants in sol-gel glasses. Clustering is also significant even at low concentrations.

Since Dy$_2$O$_3$ is immiscible in silica glass in the composition range from 2 mol% and above [15], it forms aggregates or clusters in which cross relaxation can give rise to non-radiative de-excitation of dysprosium resulting in very weak fluorescence. The TEM micrograph of the xerogel heat treated at 1000°C shown in Figure 5.9 confirms the formation of clusters and the clustering resulted in quenching of luminescence [58]. The average size is found to be
Dopant clustering refers to the tendency of luminescent species to aggregate with itself through oxygen linkages and it leads to concentration quenching of luminescence through cross relaxation and energy transfer processes [5]. The tendency to cluster can also lead to phase separation at high dopant concentrations normally desired for luminescence and lasing applications. Greaves [59] proposed that modifying cations are not distributed randomly in glass but rather that they have a tendency to aggregate locally with some degree of ordering. The overall structure of the glass is proposed to consist of randomly distributed modifier rich regions and modifier-deficient domains. The modifier rich domains are largely ionic while the modifier deficient regions are largely covalent and comprised predominantly of network forming species.

The aforesaid picture is consistent with the spectral results obtained for the present sample doped with Dy$^{3+}$. The lack of visually observable phase separation suggests that the clustering occurs locally and that distinct, isolated clusters are distributed throughout the glass. Inhomogeneous broadening occurs because of the disorder within the clusters (which will likely vary with clusters) and differences in the interaction of individual clusters with the network former-rich regions of the glass. The microscopic clustering of Dy$^{3+}$ is caused by its large field strength which causes the large liquid immiscibility dome in the R$_2$O$_3$-SiO$_2$ system [57]. When a lanthanide rare earth ion is introduced into the silica network, it needs to be co-ordinated to a higher number of non-bridging oxygens to screen the electronic charge of the cation. The addition of Dy$_2$O$_3$ generates only a limited number of non-bridging oxygens to ensure electrical neutrality. Therefore dysprosium ions cluster to share the number-limited non-bridging oxygens.

The TEM results shows that the rare earth ions aggregate inside the silica matrix and crystallize in the form of small R$_2$O$_3$ clusters during glass sintering at high
temperature. This phenomenon will appear all the more pronounced as the rare earth content in the glass is greater. This can be a serious drawback in terms of photoluminescence efficiency of the doped glass, as it is well known that clusterisation effect impedes the rare earth photoluminescence. When the rare earth ions are concentrated in the form of clusters, there is a dramatic decrease in the photoluminescence efficiency as energy transfer between ions increases. An ideal configuration to get a good photoluminescence response is an amorphous matrix in which the dispersion of rare earth ions would be in the atomic unit scale [60]. Depending on the nature of the host matrix, there is a maximum concentration (quenching concentration) that allows one to obtain a homogeneous distribution of rare earth cations without luminescence quenching due to the clusterisation. It is known that in general rare earth cations have a poor affinity for silica host matrices and easily tend to clusterise in the form of R₂O₃ precipitates, which limits drastically the quenching concentration value. It has been shown from the TEM data that even for weak doping level of 1%, R³⁺ ions are found to form clusters [5].

Alumina addition was found to improve the dissolution of rare earths in glasses prepared by vapour phase deposition or melting. Recent studies indicate that addition of alumina is also effective in dispersing SiO₂ glasses prepared by sol-gel process [33]. It is known that the analysis of the emission properties of rare earth ions can give information on the clustering in glasses. In order to confirm these arguments we have studied the effect of codopants on the fluorescence properties of Dy³⁺ ion in SiO₂ matrix. From the fluorescence spectra (Figure 5.7) it is clear that the presence of a cation codopant has a strong influence on the local bonding environment of the R³⁺. All the codopants lead to the fluorescence enhancement. We attribute the effect to the ability of codopants to penetrate R³⁺ clusters or to inhibit their formation. According to the crystal chemistry
approach [61] multiple cation modifiers will co-exist in the modifier rich regions. This implies that when a codopant is added to $\text{R}^{3+}$ doped sample, it will penetrate the $\text{R}^{3+}$ clusters and promote inter dispersion. The interdispersion occurs because of the formation of R-O-M linkages where M is a codopant. The net effect is increased separation and reduced energy transfer between the $\text{R}^{3+}$ ions. The field strength of the codopant will influence the covalency of the R-O bond [62,63]. Higher field strength codopants in linkages will form stronger, more covalent bonds with oxygen. This in turn leads to weaker, less covalent R-O bonds in the linkage. In effect, there is a competition between $\text{R}^{3+}$ and the codopant for the electron density associated with oxygen and the higher field strength cation exerts the controlling effect. As a result, the intensity increases remarkably. In either case the average R-R distance increases and as a result the energy transfer decreases thereby increasing the fluorescence intensity.

Table 5.4 Ionic radii, charge densities and field strengths of the codopants.

<table>
<thead>
<tr>
<th>Cation</th>
<th>Ion radius $r$ (Å)</th>
<th>Charge density $Z/r$ (Å⁻¹)</th>
<th>Field strength $Z/r$ (Å²)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\text{Li}^+$</td>
<td>0.68</td>
<td>1.47</td>
<td>2.16</td>
</tr>
<tr>
<td>$\text{Na}^+$</td>
<td>0.95</td>
<td>1.05</td>
<td>1.1</td>
</tr>
<tr>
<td>$\text{K}^+$</td>
<td>1.33</td>
<td>0.751</td>
<td>0.564</td>
</tr>
<tr>
<td>$\text{Ag}^+$</td>
<td>1.26</td>
<td>0.793</td>
<td>0.629</td>
</tr>
</tbody>
</table>

This observation suggests that the ability of the codopants to inhibit $\text{R}^{3+}$ clustering decreases as $\text{Li}^+ > \text{Na}^+ > \text{Ag}^+ > \text{K}^+$. This ordering is significant because it parallels the trend observed for the field strength ($Z/r^2$) cation codopant (or charge density $Z/r$) of the cation codopant (Table 5.4). This suggests that high field strength cation codopants are more effective at $\text{R}^{3+}$ clustering and promoting more uniform distribution of $\text{R}^{3+}$ ions than low field strength codopants. The
comparison with Al$^{3+}$ is complicated by the fact, however that Al$^{3+}$ will act as a network former whereas Li$^+$, Na$^+$, K$^+$ and Ag$^+$ are expected to act as a network modifiers. It is possible that the charge density effect saturates for modifier and that the network forming capability rather than the charge density governs the effect of Al$^{3+}$ on the clustering of R$^{3+}$. It is also possible that smaller concentrations of high charge density modifiers are as effective at inhibiting R$^{3+}$ clustering as larger concentrations of lower charge density modifiers [5].

5.5 Conclusion

Dy$^{3+}$ doped silica matrices were prepared by sol-gel process and the spectroscopic properties in dried gels and gel glasses were studied. Using the Judd-Ofelt parameters various radiative parameters were evaluated. Fluorescence properties were utilized to study the structural changes during the gel to glass transition of the silica xerogels. The increase in the fluorescence intensity ratio suggests that the Dy$^{3+}$ ion is embedded in a highly asymmetric environment. TEM data clearly shows the clustering of Dy$^{3+}$ ion with distinct and isolated distribution throughout the glass. The addition of cation codopants promotes the dispersion of rare earth ions. The cation codopants penetrate these clusters and interdisperse with Dy$^{3+}$. This effect leads to larger Dy$^{3+}$-Dy$^{3+}$ separations and better isolation of Dy$^{3+}$ ions. This study indicates that the state of aggregation of a dopant ion sol-gel glasses can be controlled to a certain extent by the addition a cation codopants.
References

    271(1992)63
17. Itoh K, Kamata N, Shimazu T, Satoh C, Tonooka K, Yamada K., J. Lumin,
    87(2000)676
40. Neilson C W, Koster G F, Spectroscopic Coefficients for p and f configurations, MIT. Cambridge MA (1964)
60. Langlet M, Coutier C, Meffre W, Maudier, Fick J., RimetJ, Jacquier B
   *J. Lumin.*, 96(2002)295