Phonon Sidebands and Local Vibrational Analysis of Eu$^{3+}$ Doped Glasses

The preparation and local vibrational analysis of Eu$^{3+}$ doped glassy hosts are discussed. The absorption and emission spectra of the Eu$^{3+}$ doped glasses show several inhomogeneously broadened bands due to $f$-$f$ transitions. The appearance of phonon side bands (PSBs) on the high-energy side of the zero phonon lines of the excitation transitions of Eu$^{3+}$ corresponds to vibrational transitions near the dopant ion. The PSBs provide useful information on the structural units present in the vicinity of the dopant ions. The average structure of the bulk glass is studied by means of Raman and FTIR spectroscopy. The appearance and features of the PSBs associated with the $^7F_0 \rightarrow ^5D_2$ transitions in sol-gel silica, borate and phosphate matrices have been discussed. An explanation for the extent of coupling between vibrational modes and electronic transitions is given by estimating the coupling constant. Further the nonradiative multiphonon relaxation processes have been investigated and discussed quantitatively.
4.1 Introduction

Rare earth ions possess optical transitions within the 4f level structure, which are critical for the development of optical amplifiers and phosphor materials. Both radiative and nonradiative processes that mediate the excited state decay within the 4f level are sensitive to the host material. A significant contribution to the measured emission lifetime, a key parameter of device performance, results from multiphonon nonradiative relaxation. The nonradiative relaxation rates depend on the highest energy of phonons available in the matrix. The optical absorption or excitation spectra of glasses containing rare earth ions often show weak vibronic features on the low energy side of the spectrum representing phonons created by the lattice vibrational modes. Intensity of these vibronic transitions is determined by the extent of electron phonon coupling. The relative intensities of the vibronic lines are of special interest as diagnostic probes for the rare earth-ligand interaction and crystal field dynamics.

The vibronic transition features or phonon sidebands (PSBs) for the $^3\text{H}_4\rightarrow^3\text{P}_0$ excitation transition of the Pr$^{3+}$ ion in La$_2$O$_2$S, Y$_2$O$_2$S, LiYF$_4$, LaF$_3$ were studied by Donega et. al. at low temperature. However the PSBs cannot be clearly observed for Pr$^{3+}$ doped glasses owing to the multiplet Stark splittings of its levels as well as inhomogeneous broadening of transition lines. Eu$^{3+}$ is widely used as a probe to investigate local structure because of its simple structure. In the excitation spectra of Eu$^{3+}$ the phonon sidebands associated with the $^5\text{D}_2\leftrightarrow^7\text{F}_0$ transition is clearly observed. From the measurement of PSB, the phonon energy $\hbar\omega$ coupled with nonradiative relaxation can be obtained. In rare earth doped glasses the nonradiative loss is dominated by highest energy phonons available in the matrix. Therefore it is important to select a host material for which the maximum phonon energy is as low as possible. In silicate and phosphate glasses this energy is found to be large, and it is quite low for chalocogenide glasses. Recently fluorozirconate glasses, zircon oxyhalide glasses, glass ceramics were investigated for lowering the phonon energy loss of rare earth fluorescence.
However these glasses lack many of the desirable features of silica based glasses such as mechanical strength and chemical durability. Silica glasses and modified silica glasses prepared by sol-gel method offers good host for rare earth doping.\textsuperscript{5,15,28} Fluorescent ions have been widely used as structural probes in conventional glass systems and recently in sol-gel systems.\textsuperscript{16} In sol-gel systems the Eu\textsuperscript{3+} fluorescence is a useful tool to probe the gel-glass transition and local site symmetry of rare earth ion in the matrix.\textsuperscript{17,18} Phonon sideband spectroscopy has been successfully employed for understanding phonon energy and local site symmetry in sol-gel systems with regard to persistent spectral hole burning(PSHB)\textsuperscript{20,21} and photochemical hole burning(PHB).\textsuperscript{16} Here we present the absorption, fluorescence and phonon sideband analysis of Eu\textsuperscript{3+} ions in sol-gel silica matrix to probe the gel to glass transition and the local structural evolution. Phonon sideband analysis is also done with Eu\textsuperscript{3+} ions for phosphate glasses and borate glasses and a comparative study has been performed. While PSBs provide information on the structural units, which are present in the vicinity of the dopant ion, the FTIR and Raman scattering spectral data provide average structure of the bulk glass and a near estimate of the maximum phonon energy.\textsuperscript{9,22,23} Thermogravimetric analysis (TGA) has also been done for the gel samples to study the removal of the counter ion and volatile components from the matrix through heat treatment up to 1100°C.

4.2 Experimental Procedure

The sol-gel silica samples were prepared by the procedure similar to that described in the previous chapter. Silica sols containing 1wt\% of Eu\textsubscript{2}O\textsubscript{3} were prepared from tetraethyl orthosilicate (TEOS)(Merck), Eu\textsubscript{2}O\textsubscript{3} (IRE, India 99.9%), double distilled deionized water and high purity HCl. The desired amount of Eu\textsubscript{2}O\textsubscript{3} dissolved in HCl and water is poured into TEOS under vigorous stirring. The TEOS/H\textsubscript{2}O/HCl molar ratio was 1:14:0.01. The pH of the sol is adjusted between 2 and 3. The sols were then cast in polypropylene dishes and aged for one month at room temperature. The transparent crack free dried monoliths were obtained after drying them in air oven for 7 days at 50°C±2°C(dried gel). The
dried gels were heated at different temperatures ranging from 50 to 1000°C (gel glass) at a rate of 1°C/min. Heated samples were then cooled to room temperature. Phosphate glass doped with Eu₂O₃ (1wt%) was prepared following the procedure described in Chapter 2. Borate glass was prepared from pure boric acid (BDH, 99.9%) and sodium carbonate with Eu₂O₃ as dopant by conventional melt quenching method. The samples at different stages were characterized by UV-VIS spectroscopy (Shimadzu UV 2401PC) and FTIR spectroscopy (Nicolet AVTAR 360 ESP FTIR). Raman scattering measurements of the gel annealed at 1000°C was done with Dilor Z24 Laser Raman spectrometer. The fluorescence and phonon sideband spectra were recorded at room temperature with a spectrofluorophotometer (Shimadzu RF 5301PC). TGA of samples were recorded in the temperature range room temperature to 1100°C at a heating rate of 10°C/min under N₂ atmosphere on a Shimadzu Thermal Analyzer DT40. Different sample compositions used in the present study are given in Table 4.1.

Table 4.1 Composition of the prepared samples

<table>
<thead>
<tr>
<th>Composition</th>
<th>Composition</th>
</tr>
</thead>
<tbody>
<tr>
<td>EuSi 99SiO₂: 1Eu₂O₃ (wt%)</td>
<td>EuP 99NaH₂PO₄·2H₂O: 1Eu₂O₃ (wt%)</td>
</tr>
<tr>
<td>EuB 66.5B₂O₃: 22.5Na₂O: 1Eu₂O₃ (wt%)</td>
<td></td>
</tr>
</tbody>
</table>

4.3 Theoretical Background

It has been established that the variations of the radiative decay rate of rare earth ions with change of network modifier are different for various glassy hosts.¹⁰ The phonon sideband spectra provide useful experimental data to analyze and study the variations of the nonradiative decay rate of rare earth ions doped in different glassy matrices. The nonradiative multiphonon decay processes which are caused by the modulation of the crystal field by the network vibration can be understood with the help of a schematic energy level diagram of a rare earth ion (Figure 4.1). The generation of one phonon process is rapid for a small energy gap while a multiphonon relaxation process is expected for a larger energy gap. The total decay rate of an excited state is given by
\[ W = W_r + W_{nr} = \frac{1}{\tau_r} + \frac{1}{\tau_{nr}} \]  \hspace{1cm} (4.1)

where

\[ W_{nr} = W_{mp} + W_{ET} + W_{CR} + W_{OH} \]  \hspace{1cm} (4.2)

\( W_{mp}, W_{ET}, W_{CR} \) and \( W_{OH} \) are the rates of multiphonon decay, energy transfer, cross relaxation and decay due to water contained in the glasses respectively.

\[ \text{Excitation} \] \hspace{2cm} \[ \text{Emission} \] \hspace{2cm} \[ \text{MPR} \]

\textbf{Figure 4.1} Schematic diagram of multiphonon relaxation

The radiative decay rate is influenced by variations of the local crystal field symmetry at the rare earth site. The host matrix into which the ion is placed determines these variations. In addition to changes in field symmetry, the local vibrational density of states (DOS) of the host also provides a mechanism for depopulation of the excited state energy. Electron-phonon coupling allows an excited rare earth ion to decay nonradiatively via the production of lattice vibrations. Naturally, this nonradiative process from the upper level is unattractive for amplifying devices, which rely upon achieving and maintaining a population inversion. \( W_{ET} \) represents an additional nonradiative loss mechanism involving the transfer of excited state energy between rare earth ions that terminates when the energy counters a defect or trap. For low ion concentrations, this process is negligible. The \( W_{OH} \) component for the nonradiative decay can be neglected for water free glasses.
Determination of the intrinsic radiative decay rate $W_r$, was accomplished through a Judd-Ofelt\textsuperscript{24,25} analysis of the absorption spectra. The Judd-Ofelt theory allows one to estimate the radiative decay rate of all excited states as well as to predict oscillator strengths and branching ratios using the experimentally observed absorption curves. These oscillator strengths can be expressed under certain simplifying conditions as a linear sum of standard transition matrix elements involving the Judd-Ofelt parameters, $\Omega_\lambda$ ($\lambda=2,4,6$) whose values are directly influenced by the host matrix and provide a qualitative measure of the asymmetry of the local electrostatic field of the rare earth ion. Using the values of $W_r$ from the Judd-Ofelt analysis together with the experimentally observed excited state decay rate $W$, the nonradiative contribution $W_{nr}$, can be determined.

The non-radiative decay rate was estimated as

\[ W_{nr} = \frac{1}{\tau} - A_{rad} \]  \hspace{1cm} (4.3)

where $\tau$ is the measured lifetime and $A_{rad}$ transition probability obtained from Judd-Ofelt analysis. The probability for nonradiative processes, which arises out of the production of lattice vibrations (optical phonons), is determined by the strength of the electron-phonon coupling $g$.

According to Miyakawa and Dexter\textsuperscript{4}, the nonradiative decay rate due to the multiphonon relaxation process is given by

\[ W_{mp} = W_0 e^{-\alpha \Delta E} \]  \hspace{1cm} (4.4)

\[ \alpha = h\omega^{-1} \left[ \ln \left( \frac{p}{g(n+1)} \right) - 1 \right] \]  \hspace{1cm} (4.5)

\[ p = \frac{\Delta E}{h\omega} \]  \hspace{1cm} (4.6)

where $\Delta E$ is the energy gap, $h\omega$ is the phonon energy, $p$ is the phonon number, $g$ is the electron phonon coupling strength, $W_0$ is the experimental parameter corresponding to the decay rate at zero energy gap and zero phonon emission and
\[ n = \left( e^{\frac{\hbar \omega}{kT}} - 1 \right)^{-1} \]  

From these equations, it is quite evident that the larger the phonon energy and electron–phonon coupling strength, the larger the multiphonon decay rate. If \( W_0 \) is constant, the relative nonradiative decay due to the multiphonon relaxation process can be estimated from the phonon energy, electron–phonon coupling strength and energy gap. The electron phonon coupling strength (\( g \)) and phonon energy (\( \hbar \omega \)) can be determined from the phonon side band spectra. It is seen that the shape, mean energy and intensity of the sidebands vary with glass composition. Using the values obtained for \( g \) and \( \hbar \omega \) the host dependant parameter \( \alpha \) and the relative nonradiative decay rate \( W_{mp}/W_0 \) can be calculated.

4.4 Results and Discussion

Absorption spectra of the Eu\(^{3+}\) doped gel (50°C) and gel glass(1000°C) are shown in Figure 4.2. The absorption spectrum of the dried gel sample resembles with that of Eu\(^{3+}\) in solution. The most intense absorption peak occurs at 393nm

![Figure 4.2 Absorption spectra of EuSi dried at 50°C and 1000°C](image)
corresponding to the \( ^7F_0 \rightarrow ^5L_6 \) transition. The less intense absorption peaks observed at 374, 379 and 384nm corresponding to the \( ^7F_0 \rightarrow ^5G_6 \), \( ^7F_0 \rightarrow ^5G_3 \) and \( ^7F_1 \rightarrow ^5G_3 \) transitions respectively in the dried gel are replaced by a broad absorption band in the gel glass as expected. Another interesting feature of the absorption spectra is the appearance of strong absorption peak at 464nm.

![Excitation spectra of Eu³⁺ in different hosts](image)

**Figure 4.3** Excitation spectra of Eu³⁺ in different hosts

corresponding to the \( ^7F_1 \rightarrow ^5D_2 \) transition. This is also evident from the excitation spectra of the samples taken at different temperatures shown in Figure 4.3. The excitation spectrum is recorded in the wavelength range 350-600nm by monitoring the fluorescence at 613nm corresponding to the \( ^5D_0 \rightarrow ^7F_2 \) transition.
The spectra show the continuous evolution of silica network as the sol is converted to dried gel and then to gel glass. In the sol stage there is only a very weak excitation peak at 393nm corresponding to the $7F_0 \rightarrow 5L_6$ transition. More features begin to appear with appreciable intensity in the gel dried above 200°C.

![Emission spectra of Eu$^{3+}$ in different hosts](image)

**Figure 4.4** Emission spectra of Eu$^{3+}$ in different hosts

It is observed that the peak at 415nm assigned to the $7F_0 \rightarrow 5D_3$ transition is the prominent one for the gel dried at 200°C. However, the peak at ~464nm($7F_0 \rightarrow 5D_2$) is still faint and becomes prominent only when the gel sample is annealed at 1000°C. The phonon sideband analysis is done with this excitation transition. Also a number of other excitations which contribute to the $5D_0 \rightarrow 7F_2$ emission transition are visible in the high temperature annealed gel glass quite similar to that observed in silicate glasses obtained by conventional methods.27
The excitation spectra of borate and phosphate glasses are also shown for comparison. They are almost similar to that of the gel glass, however for borate glass the most intense peak occurs at 464nm corresponding to the $^7F_0 \rightarrow ^5D_2$ transition. The features associated with the excitation spectra are due to the change in the chemical environment of the rare earth ion at various stages of the gel to glass transition. However the difference in chemical environment of Eu$^{3+}$ ions in dried gels and gel glasses did not have an important influence on the wavelength of the Eu$^{3+}$ emission bands. This is because the inner 4f electrons of the Eu$^{3+}$ ion are shielded by outer 5s, p, d electrons and are not strongly influenced by electrical action of the coordination polyhedron. The emission spectra of the Eu$^{3+}$ doped in the sol, sol-gel silica, phosphate and borate glasses are shown in Figure 4.4 in the wavelength range 525-700nm. All the spectra were recorded at room temperature with an excitation of 393nm to the $^5L_6$ state of the Eu$^{3+}$ ion. The emission lines are observed at the low energy side of the spectra corresponding to the $^5D_0 \rightarrow ^7F_j$ ($J=0, 1, 2, 3, 4$) transitions. The transition from the narrow profile (nonrigid environment of Eu$^{3+}$) of the spectrum for the sol sample (EuSi) to the typical inhomogeneously broadened profile (rigid environment of Eu$^{3+}$) shows a continuous evolution from gel to glass on thermal
treatment. Weak luminescence from higher excited states such as \( ^5D_1 \) is observed in the initial stages of the gel to glass transition in sol-gel silica corresponding to the \( ^5D_1 \to ^7F_0 \) (527nm), \( ^5D_1 \to ^7F_1 \) (535nm) and \( ^5D_1 \to ^7F_2 \) (556nm). The intensity of these peaks gradually decrease with thermal densification and disappears in the gel glass indicating a very efficient non-radiative relaxation from the \( ^5L_6 \) to \( ^5D_0 \) lower excited state. On the other hand, on the lower energy side the emission peaks corresponding to \( ^5D_1 \to ^7F_3 \) (652nm) and \( ^5D_1 \to ^7F_4 \) (700nm) transition gradually develops with densification of the gel. In Figure 4.5 relative intensities of these peaks shown magnified for the dried gel and gel glass.

**Table 4.2** Fluorescence intensity ratio for different hosts

<table>
<thead>
<tr>
<th>Sample</th>
<th>Fluorescence ratio ( ^7F_2(ED)/^7F_1(MD) )</th>
</tr>
</thead>
<tbody>
<tr>
<td>EuSi[Sol]</td>
<td>0.5924</td>
</tr>
<tr>
<td>EuSi[50°C]</td>
<td>0.7642</td>
</tr>
<tr>
<td>EuSi[200°C]</td>
<td>1.972</td>
</tr>
<tr>
<td>EuSi[1000°C]</td>
<td>2.332</td>
</tr>
<tr>
<td>EuB</td>
<td>2.892</td>
</tr>
<tr>
<td>EuP</td>
<td>1.977</td>
</tr>
</tbody>
</table>

As is evident from the Figure 4.4 the thermal treatment progressively develops line broadening. As for the intensities in the free ion all the \( ^7F_6 \) intraconfigurational transitions are electric dipole forbidden and also spin forbidden. Some transitions such as \( ^5D_0 \to ^7F_1 \) becomes weakly magnetic dipole (MD) allowed and by spin orbit mixing with other states since the magnetic dipole transitions are regulated by the selection rule \( \Delta l=0 \) and \( \Delta J=0, \pm 1 \) (except \( 0 \to 0 \)). The \( ^5D_0 \to ^7F_1 \) emission around 590nm is allowed by magnetic dipole considerations and hence relatively indifferent to the local symmetry. However the lowering of the inversion symmetry leads to the mixing of different parity states and produces weakly allowed electric dipole (ED) transitions which are otherwise forbidden in principle by Laporte’s selection rule (\( \Delta l= \pm 1 \) and \( \Delta J\leq2l \) with \( l=3 \)). Consequently their intensity depends on the degree of mixed...
parity, which arises from the lack of centre of symmetry. Therefore the emission at 613 nm ($^5D_0 \rightarrow ^7F_2$) is particularly dependent on the local site symmetry around the rare earth ion. Accordingly the intensities of ED transitions with respect to MD transition gives a measure of the cistortion from the inversion symmetry at the Eu$^{3+}$ site. The ratio of the emission intensities of the $^5D_0 \rightarrow ^7F_2$ and $^5D_0 \rightarrow ^7F_1$ transitions are given in Table 4.2.

The observed increase in intensity of the ED transition($^5D_0 \rightarrow ^7F_2$) with respect to the MD($^5D_0 \rightarrow ^7F_1$) transition on heat treatment of the gel indicates a progressive distortion of the coordination sphere of Eu$^{3+}$ ion. Moreover, the Stark splitting of the transitions increases with heat treatment and this effect is evident for the $^5D_0 \rightarrow ^7F_1$ transition centered at ~590 nm for gel glass. Such a splitting arises due to the complete lifting of the degeneracy, which is indicative of the $C_{2v}$, or low symmetry of the ion sites.\textsuperscript{28, 29, 30} The small peak at 578 nm ($^5D_0 \rightarrow ^7F_0$) on the triplet structure at the higher energy side appearing in the range 570-580 nm is characteristic of the coordination of the Eu$^{3+}$ ion.\textsuperscript{31, 32, 33} This suggests 8-9 coordination for Eu$^{3+}$ ion in the investigated glass systems. In phosphate and borate glasses the most intense band corresponds to the electric dipole allowed $^5D_0 \rightarrow ^7F_2$ transition which is similar to that observed in gel glass. The dominance of the $^5D_0 \rightarrow ^7F_2$ indicates a lack of an inversion centre for the local symmetry of the Eu$^{3+}$ ion in these glasses.

Thermogravimetric analysis (TGA) curves of the three gel samples, [A] (aged and dried at 50°C), [B](aged at room temperature for one month), [C] (aged and dried sol-gel silica samples)

\begin{figure}
\centering
\includegraphics[width=\textwidth]{figure4.6}
\caption{TGA traces of aged and dried sol-gel silica samples}
\end{figure}
[C] (aged at room temperature for one week) are shown in Figure 4.6 for comparison. Major part of the weight loss occurs between room temperature and 200°C, owing to the vaporization of the adsorbed water and residual organic molecules. (Table 4.3). A substantial amount of water and other organics present in the dried gel are removed below 550°C. The weight loss and the shrinkage of the gel are rapid during this period hence a controlled heating is required below this temperature to avoid cracking. The small weight loss at higher temperatures is attributed to the removal of trapped residual hydroxyls in single step acid catalyzed gels.34

**Table 4.3** TGA data for various temperature ranges (T<sub>1</sub> - T<sub>f</sub>)

<table>
<thead>
<tr>
<th>Sample</th>
<th>T&lt;sub&gt;1&lt;/sub&gt; - T&lt;sub&gt;f&lt;/sub&gt; (°C)</th>
<th>Wt.loss (%)</th>
<th>T&lt;sub&gt;1&lt;/sub&gt; - T&lt;sub&gt;f&lt;/sub&gt; (°C)</th>
<th>Wt. loss (%)</th>
<th>T&lt;sub&gt;1&lt;/sub&gt; - T&lt;sub&gt;f&lt;/sub&gt; (°C)</th>
<th>Wt. loss (%)</th>
<th>Total wt. loss</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>27.1 - 110.3</td>
<td>24.07</td>
<td>110.3 - 544.4</td>
<td>11.45</td>
<td>544.4 - 1098</td>
<td>1.75</td>
<td>37.28</td>
</tr>
<tr>
<td>B</td>
<td>26.2 - 110.4</td>
<td>32.01</td>
<td>110.4 - 456.7</td>
<td>16.82</td>
<td>456.7 - 1099.5</td>
<td>1.715</td>
<td>50.55</td>
</tr>
<tr>
<td>C</td>
<td>27 - 110.6</td>
<td>51.6</td>
<td>110.6 - 544.7</td>
<td>12.61</td>
<td>544.7 - 1099.2</td>
<td>0.6548</td>
<td>64.27</td>
</tr>
</tbody>
</table>

The complimentary nature of IR and Raman spectra is apparent from the IR and Raman spectra obtained after gel consolidation at 1000°C (Figure 4.7). Major features of the IR spectra change little above 200°C and hence little information is obtainable concerning the evolution of silica network. A comparison of the gel dried at 50°C and 1000°C give some useful information to support the removal of organics. The gel dried at 50°C show sharp absorption bands characteristic of the \( \delta_{3} \text{CH}_{3} \) (~1380 cm<sup>-1</sup>) symmetric vibration, Si-OH stretching vibration (bands at 1645 cm<sup>-1</sup> and 3000-3800 cm<sup>-1</sup> not shown). It is observed that the intensity of these bands show substantial decrease above 200°C and have got negligible intensity in the high temperature heat treated gel confirming the removal of a substantial portion of the water and residual organic molecules in dried silica gels. Since the gel often bloats or cracks into pieces when water and residual
organic molecules vaporize rapidly, careful heat treatment around this temperature is required if bulk gel glass is to be obtained. Moreover the intensity of the Si-OH and SiO-H stretching band of terminal silanol groups which occur at 955 cm\(^{-1}\) decreases with heat treatment indicating the gradual strengthening of silica network through cross-linking. The 460 cm\(^{-1}\) band is assigned to network Si-O-Si bending mode and the 800 cm\(^{-1}\) band to symmetric Si-O-Si stretching. The most intense absorption at 1085 cm\(^{-1}\) is assigned to the TO mode of the Si-O-Si asymmetric bond stretching vibration while the shoulder at ~1200 cm\(^{-1}\) represents LO mode of Si-O-Si asymmetric bond stretching vibration.\(^{35}\) It is also observed that the most intense band at 1085 cm\(^{-1}\) in dried gel shifts to 1100 cm\(^{-1}\) in gel glass. This reflects the relaxation of internal stress increase in the degree of connectivity of the system on the structural level.\(^{36}\)

The Raman measurements also provide an average picture of the vibration density of states in the gel glass, which coincide to a large extent to the IR observations. The state of polymerization of the silica framework of the glass can be assessed with Raman bands on the basis of relative concentrations of silicon Q\(^n\) species obtained from Si-NMR studies.\(^{37}\) In Q\(^n\), \(n\) refers to the number of bridging oxygens bonded to the silicon. Thus a Q\(^4\) species corresponds to a fully polymerized silicon atom and a Q\(^0\)species refers to an unpolymerized orthosilicate unit. Each Q\(^n\) species has a characteristic Raman band associated with it. The principal Raman features in the undoped silica
annealed at 1000°C and their assignments are \(-1050\text{ cm}^{-1}(Q^2)\), \(-970\text{ cm}^{-1}(Q^2)\), \(-800\text{ cm}^{-1}\) (motion of Si in a tetrahedral oxygen cage), \(-600\text{ cm}^{-1}\) (Si-O-Si defect) and \(<500\text{ cm}^{-1}\) (Si-O-Si modes). Thus the Si-OH stretching vibration (\(-980\text{ cm}^{-1}\)) is observed in the Raman spectrum with weak intensity confirming the presence of residual hydroxyl group. Depending on the local bonding environment of the rare earth ion within the glass matrix some of these vibration modes may or may not be coupled to electronic excited states.

The phonon sidebands which are present at the high energy side of the Eu\(^{3+}\) excitation spectra provides useful information on the electron-phonon coupling in the rare earth doped glasses. The partial energy level diagram of Eu\(^{3+}\) with the phonon sideband process is schematically shown in Figure 4.8. The phonon sideband arises due to the presence of sideband energy levels close to the \(^{5}D_2\) level. The phonon sideband spectra are obtained for Eu\(^{3+}\) doped gel silica, phosphate and borate glasses by recording the excitation spectra in the

\[\text{Figure 4.8 Partial energy level diagram of Eu}^{3+}\text{ ion. Schematic of the phonon sideband process is also shown magnified.}\]
430-480nm range while monitoring the fluorescence at 613nm($^5D_0 \rightarrow ^7F_2$).

Figure 4.9 shows the zero phonon line (ZPL) corresponding to $^7F_0 \rightarrow ^5D_2$ transition with the sidebands at the higher energy side. In the inset, the phonon sidebands are shown magnified by 100 times. In the gel glass the phonon sideband occurs at a mean energy shift of 945cm$^{-1}$ from the pure electronic transition (ZPL) peaked at $\sim$21570cm$^{-1}$. The value of PSB energy obtained in the present study supports the assignment of the PSB band to Si-O vibrations. This is very close to the energy values (950cm$^{-1}$) reported for SiO$_2$-PbF$_2$ glass.

![Figure 4.9](image)

**Figure 4.9** Phonon sideband associated with the $^7F_0 \rightarrow ^5D_2$(ZPL) transition of Eu$^{3+}$ for a. EuB, b. EuSi, c. EuP. Inset shows the PSB's magnified by 100 times.

ceramics$^{14}$ and in sol-gel aluminosilicate$^{16}$ glasses. In the figure the largest phonon sideband peak of the sodium borate glass is at an energy shift of 1387cm$^{-1}$ from ZPL and the second largest peak is at 1033cm$^{-1}$ from the ZPL. The peak at higher energy side is attributed to the vibration modes of bridging oxygen (BO) and non-bridging oxygen (NBO) which are usually created when non-glass forming oxides such as Na$_2$O is incorporated in the borate glass network. The formation of BOs and NBOs has already been discussed in Chapter 1. The peak
on the lower energy side of the PSB (1033 cm\(^{-1}\)) is produced by the presence of diborate and tetraborate groups.\(^{38,39}\) The \(h\omega\) value (1084 cm\(^{-1}\)) obtained from the PSB for the phosphate glass is comparable to that of the infrared absorption maximum (1200 cm\(^{-1}\), Chapter 2) corresponding to the out of chain PO\(_2\) stretching vibration.\(^{40}\) The PSB peaks, which correspond to the highest energy phonon available in the glass matrix, are found to be shifted to lower values in all the glass hosts studied. It has been argued that due to the large effective mass of the rare earth ion, peak frequencies in the PSB spectrum will be shifted to lower energies in comparison with IR and Raman measurements of the ion-free glass.\(^{841}\) This means that there are some differences in the phonon energy between the local structure around the rare earth ions and the glass matrix. Brecher and Riseberg\(^{42}\) proposed a structural model for the behaviour of the first coordination shell of the Eu\(^{3+}\) ion in the glassy matrix based on laser induced fluorescence line narrowing (FLN) studies. This model involves a gradual change from eight fold to nine-fold coordination in the immediate environment of the Eu\(^{3+}\) ion, while maintaining an overall C\(_{2v}\) symmetry throughout. So the phonon energy obtained from the PSB measurements clearly gives the local vibration environment around rare earth ion, which corresponds to the strongest one among several local variations that contributes to multiphonon relaxation.

A quantitative estimate of the parameters of multiphonon relaxation in the investigated glasses has been made and are summarised in Table 4.4. The values of \(\alpha\) and \(W_{mp}/W_0\) are determined using Eqs.4.4 \& 4.5 with known values of the energy gap \(\Delta E\) for \(^5D_1\), \(^5D_2\) and \(^5D_3\) of Eu\(^{3+}\) ion. The electron-phonon coupling strength is estimated as the ratio of the integrated intensity of phonon sideband to that of pure electronic transition. The phonon energy corresponds to the mean energy difference between pure electronic transition and the phonon sideband.

The phonon energy and electron phonon coupling strength in phosphate glass are larger than those in silica glass. According to the Eq.4.5, these results lead to a larger nonradiative decay rate due to the multiphonon relaxation process in phosphate glasses than that in silica glasses. The g value is found to be higher for
EuP as compared to EuSi and EuB. This is due to the strong covalent bonding of rare earth ion with the local site and higher nonradiative decay as expected in this glass system, and the present results (Table 4.4) support this argument. In gel glass even though the phonon energy is comparatively less, the coupling strength is found to be close to that of the phosphate glass. The relative multiphonon relaxation rate is high enough to quench the fluorescence from $^1D_2$ level. The emission transitions from the $^5D_1$ level in the high energy region of borate and phosphate glasses are very weak. In borate glass the phonon energy maximum is high (1387 cm$^{-1}$) irrespective of the coupling strengths. This high phonon energy is primarily responsible for the quenching of the fluorescence transitions in the high energy region which is actually observed in the spectrum of the borate glass (Figure 4.4). In the phosphate glass the phonon energy maximum has intermediate value but the electron-phonon coupling strength $g$ is quite high and therefore the high energy transitions although weak are observed. The comparatively low values of phonon energy and coupling strengths explain the appearance of weak fluorescence transitions in the higher energy side as discussed earlier. It can also be noted that the radiative efficiency from the

<table>
<thead>
<tr>
<th>Glass</th>
<th>$h\omega$ (cm$^{-1}$)</th>
<th>$^5D_1$</th>
<th>$^5D_2$</th>
<th>$^5D_3$</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$\alpha (x10^{-5})$</td>
<td>$W_{mp}/W_0$</td>
<td>$\alpha (x10^{-5})$</td>
<td>$W_{mp}/W_0$</td>
</tr>
<tr>
<td>EuSi</td>
<td>0.0121 945</td>
<td>3.6</td>
<td>183</td>
<td>4.33</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>EuP</td>
<td>0.0178 1084</td>
<td>2.78</td>
<td>776</td>
<td>3.43</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>EuB</td>
<td>0.0055 1387</td>
<td>3.02</td>
<td>498</td>
<td>3.02</td>
</tr>
<tr>
<td></td>
<td>0.0046 1033</td>
<td>4.28</td>
<td>56</td>
<td>4.91</td>
</tr>
</tbody>
</table>

$\Delta E$ for $^5D_1$=1750 cm$^{-1}$, $^5D_2$=2500 cm$^{-1}$, $^5D_3$=2800 cm$^{-1}$ and T=300K

Table 4.4 Parameters of multiphonon relaxation in different glass hosts

Table 4.5 Comparison of $W_{mp}$ of Pr$^{3+}$ in phosphate glass

<table>
<thead>
<tr>
<th>Level</th>
<th>$\Delta E$ (cm$^{-1}$)</th>
<th>$\tau_{RAD}$ (µs)</th>
<th>$\tau$ (µs)</th>
<th>$W_{mp}$ (s$^{-1}$)</th>
<th>$\alpha (x10^{-3})$</th>
<th>$W_{mp}$ (s$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$^1D_2$</td>
<td>7220</td>
<td>216</td>
<td>120</td>
<td>3.7$\times10^3$</td>
<td>4.44</td>
<td>1.7$\times10^1$</td>
</tr>
<tr>
<td>$^3P_0$</td>
<td>3987</td>
<td>86</td>
<td>40</td>
<td>1.3$\times10^4$</td>
<td>3.79</td>
<td>1.4$\times10^6$</td>
</tr>
</tbody>
</table>

For phosphate glass $W_0=5.4x10^{12}$s$^{-1}$
higher \( ^5D_J \) levels \( (J=1, 2, 3) \) is greatly influenced by the nonradiative decay rate due to their smaller energy gap as compared to the \( ^5D_0 \) level. In order to check the correlation of the PSB analysis to modified J-O analysis we have effected the calculations to Pr\(^{3+}\) in phosphate glass (Glass A, Chapter 3). As expected, the \( W_{mp} \) value is found to be less for the \( ^1D_2 \) level obtained from the PSB analysis. The discrepancy between J-O and PSB analysis for the \( W_{mp} \) value is attributed to nonradiative decay due to cross relaxation and the higher energy gap. On the contrary, the \( ^3P_0 \) level shows a reverse trend suggesting less probability for cross-relaxation and an inherent uncertainty in the estimation of the radiative decay rate based on the J-O theory in phosphate glasses.

4.5 Conclusions

Bulk Eu\(^{3+}\) ion doped silica glasses can be obtained by careful thermal treatment of dried gel. Owing to the difference in local environment of Eu\(^{3+}\) ions, the ratio of the emission intensities of the \( ^5D_0 \rightarrow ^7F_2 \) and \( ^5D_0 \rightarrow ^7F_1 \) transition in gel glasses is different from that in dried gels and is comparable to that of phosphate and borate hosts. Phonon sideband measurements elucidate the local vibration density of states that is comparable to the average structure obtained from FTIR and Raman measurements. But the measurements show some distinctive differences. In particular it was found that \( \hbar \omega \) is not in agreement with the IR active maximum phonon energy of the glass matrix. This lack of agreement is attributed to the difference in the phonon mode between the glass matrix and the local structure around the rare earth ions. The nonradiative decay rate due to multiphonon relaxation process was estimated on the basis of the Miyakawa-Dexter's theory with the electron phonon coupling strength and phonon energy determined from phonon sideband measurements. These results were then compared with the one obtained from the J-O analysis and lifetime measurements for the \( ^1D_2 \) and \( ^3P_0 \) levels of Pr\(^{3+}\) ions in phosphate glass. The observed differences were ascribed to nonradiative processes such as cross relaxation, energy transfer and the inherent error in the calculation of the radiative lifetime theoretically.
References