Chapter 2

Spectroscopic Characterization of \( \text{Sm}^{3+} \) Ions in PVA Film

Thick films of polyvinyl alcohol doped with samarium ions at different concentrations were prepared. The Judd-Ofelt intensity parameters were obtained from the absorption spectra and different radiative parameters like the transition probability, radiative life time, branching ratio and absorption cross-section, were calculated using the Judd-Ofelt parameters. The omega (\( \Omega \)) values obtained for PVA matrix were compared with that obtained from other matrices, and are in the range or more than that obtained for PMMA and inorganic glasses. The TGA/DTA was employed to analyse the thermal stability of the sample. The FTIR measurement gives different vibrational modes of the molecules present in the PVA film. The thickness and refractive index were measured using M-line spectroscopy. The transition \( ^4G_{7/2} \rightarrow ^6H_{11/2} \) is identified as a potential transition for optical application.
2.1 Introduction

Polymers are considered as good host materials because they can be designed to yield a variety of bulk physical properties and they normally exhibit long-term stability and possess flexible reprocessability. They can be processed easily, which is an advantage in the fabrication of optical devices [1]. Rare earth ions have been widely used in silica glass based lasers and optical amplifiers. However, in recent years, rare earth ions-containing polymers have attracted much attention for their potential applications for luminescence devices, laser systems and optical communication components [2–5]. Polymer hosts make it possible to incorporate rare earth ions, preventing concentration quenching at higher concentrations [6]. Further poly vinyl alcohol films can be used as a host matrix for transition metal elements, rare earth ions, dyes, nano particles etc., which can be used for wide range of applications in image storage, holography, laser applications, sensors, display applications, photovoltaic cells etc. [7-10]. In particular photo acoustic studies of Sm$^{3+}$ ions in poly vinyl alcohol have been reported [11]. Upconversion mechanisms are seen in Sm$^{3+}$ ions doped matrices and such a property can be used in storage devices and other photonic applications. The spectroscopic studies of Sm$^{3+}$ ions in the polymer PMMA matrix has been reported but such works are relatively limited in PVA matrix. In view of these factors we have attempted the spectroscopic studies of Sm$^{3+}$ ions in PVA matrix. The Judd–Ofelt theory has been widely used to estimate the radiative properties of the rare earth ions doped materials because the model provides reasonable
values on average. In this paper, optical properties of samarium ions doped PVA films were studied. The Judd–Ofelt phenomenological parameters, $\Omega_2$, $\Omega_4$ and $\Omega_6$ of doped material were obtained from the absorption spectrum. Based on the Judd–Ofelt theory [12, 13], the transition probabilities, fluorescence branching ratios and radiative lifetime of Sm$^{3+}$ doped PVA films were calculated. The investigation of radiative properties corresponding to the $^4\text{G}_{7/2} \rightarrow ^6\text{H}_{11/2}$ transition indicated that it is a potential transition for high optical amplification.

2.2 Experimental

2.2.1 Sample Preparation

Three samples A, B and C with samarium (1%, 3%, 5% by weight) respectively doped in polyvinyl alcohol (PVA) films were grown by slow evaporation at room temperature [14]. PVA was dissolved in double-distilled water and then heated on a hot plate for a few minutes. Subsequently the samarium chloride dissolved in water was mixed with the PVA solution. Following the procedure reported elsewhere Sm$^{3+}$ ions were added in their chloride form in solutions and it has been understood that the added amount would be intact in the matrix [15-17]. The solution cast into a polypropylene dish and was kept at $50^\circ$C for two days. The films were peeled off from the polypropylene dish. These films were used for spectral investigations.
2.3 Instrumental

2.3.1 Thermogravimetric Analysis

Thermal gravimetric/differential thermal analysis of the film was done by using Shimadzu DTG 60 system in nitrogen atmosphere. The temperature rate was $10^0\text{C/min}$. The thermal analyzer used for temperature control was TA 60 WS. The thermal stability of the PVA film can be found out from the curve obtained.

2.3.2 FTIR Analysis

The FTIR spectrum of the film in the region $4000-400\text{cm}^{-1}$ were recorded by using Shimadzu FTIR spectrometer 8400 S. The spectrum was taken with resolution of $8\text{ cm}^{-1}$ with about 15 scans. Different bending and stretching vibrations of the molecules present in the PVA film were obtained.

2.3.3 Thickness and Refractive Index Measurement

The refractive index and thickness of the PVA films were measured using a Prism Coupler (Metricon 2010) using 633nm wavelength. The experimental setup is given in Figure 2.1.

The sample to be measured is brought in contact with the base of the prism by means of a pneumatically-operated coupling head creating a small air gap between the film and the prism.
Laser light directed into the base of the prism will be totally reflected at the prism base until the angle of incidence $\theta$ becomes less than the critical angle $\theta_c$, where

$$\theta_c = \arcsin \left( \frac{n}{n_p} \right)$$  \hspace{1cm} (2.1)

$\theta_c$ is easily measured using the detector, $n$ and $n_p$ are refractive indices of the film and the prism respectively. The critical angle of the prism/film interface establishes an upper limit to the angle at which film propagation modes can occur. As the film with fixed index will become thicker, the angle at which the first propagation mode can occur and approaches the critical angle defined by the equation 3.1. As soon as two of the mode angles are found, film thickness and refractive index can be measured. The angular location of the first mode
determines the refractive index and the angular difference between the modes determines the film thickness. The thickness of the samples obtained were 16.8 µm, 17 µm and 17.2 µm and an average value of 17µm is taken. The refractive index has an average value of 1.49.

### 2.3.4 Spectral Studies

The absorption spectra of the films were taken using Shimadzu-UVPC 2401, at a wavelength range 190-900nm at a resolution of 0.1nm. The accuracy of wavelength measurements is ±0.3nm at slit width 0.2nm. The light source used here was deuterium lamp and Photomultiplier R-928 was used as detector. Shimadzu RFPC-5301 was used to record the fluorescence spectra. The wavelength scan range is from 220nm-900nm with wavelength accuracy of ±1.5nm. The light source used for measurements was 150W Xenon Lamp. The detectors used were photomultiplier tubes.

### 2.4. 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, 5p, 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 [18] method to calculate the Hamiltonian of the system. Hamiltonian of optically active electron is composed of several terms. The central field Hamiltonian \( H_0 \), 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

\[
H_{4f} = H_0 + H_c + H_{so} + H_{cf}
\]

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 labeled 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 basic energy levels of free ions are those of the configurations, which are \( 2(2l_1+1) \ 2(2l_2+1) \ ... \ 2(2l_n+1) \) degenerate, and have separation \( \sim 5 \times 10^4 \) cm\(^{-1}\). The detailed energy structure arises from the splitting of these levels by interaction between electrons. Here the interaction is between \( 4f \)-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

2.4.1 Judd-Ofelt Analysis

The theory of atomic spectra allows identification of definite \( J \) levels of \( 4f^5 \) in the \( \text{Sm}^{3+} \) ion. 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. The 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 [19].

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

The absorption properties of rare earth ions are best distinguished in the context of Judd-Ofelt theory [20]. In essence the \( 4f \rightarrow 4f \) transitions of a rare earth ion can be described as a simple linear combination of the so-called J-O 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
\[ f_{ed} = \frac{\nu}{(2J+1)} \left[ \frac{8\pi^2 mc (n^2 + 2)^2}{3h} \right] \sum_{\lambda=2,4,6} \Omega^\lambda \left< \psi J \right| U^\lambda \left| \psi' J' \right> ^2 \]

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 known as J-O intensity parameters. 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. [20]. In order to obtain the accuracy of the intensity parameters obtained, the root-mean-squared deviations (\(\delta_{rms}\)) are calculated using the relation \(\delta_{rms} = \sum \left[ \frac{(f_{exp} - f_{cal})^2}{N-M} \right] \left( \frac{1}{2} \right) \), where \(N\) is the number of levels fitted and \(M\) is the number of parameters determined. The bonding parameter (\(\bar{\delta}\)) defined as \(\delta = \left[ \frac{(1 - \bar{\beta})}{\bar{\beta}} \right] \times 100 \) where \(\bar{\beta} = \sum_{N} \beta / N\) and \(\beta = \frac{\nu_c}{\nu_a}\) (the nephelauxetic ratio), \(\nu_c\) and \(\nu_a\) 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 [19].

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 [18].

The position of $J$ levels of $4f^9$ in condensed matter is treated by the same techniques as for mono atomic entities, but the probabilities of absorption and emission between $J$ levels are entirely different. Radiative transition probabilities of the rare earths in polymers 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

$$A^{ed}_{JJ} = \frac{64\pi^2 e^2 \nu^3}{3h(2J+1)} \left[ \frac{n(n^2 + 2)^2}{9} \right] S_{ed} \quad 2.5$$

where

$$S_{ed} = \sum_{\lambda=2,4,6} \Omega_{\lambda} \langle \psi J | U^{\lambda} | \psi' J' \rangle^2 \quad 2.6$$

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

$$A^{ed}_{JJ'} = \tau^{-1}_{Rad} \quad 2.7$$

or

$$\tau_{rad} = \frac{1}{\sum_{JJ'} A_{JJ'}} \quad 2.8$$
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} (2.9)

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.

$$\sigma_a = \frac{A(\psi J)}{8\pi n^2 \nu^2}$$  \hspace{1cm} (2.10)

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

$$\sigma_E = \frac{\hat{\lambda}_p^4}{8\pi n^2 \Delta \lambda_{eff}} \cdot A(\psi J, \psi' J')$$  \hspace{1cm} (2.11)
where $\lambda_p$ is the peak wave length of the emission transition and $\Delta \lambda_{\text{eff}}$ is the effective band width of the emission transition.

2.5. Results and Discussion

2.5.1 Thermal Analysis

PVA films are highly transparent in the visible range of wavelength which may be utilized in transparent electronic devices.

![TGA/DTA curve of pure PVA](image)

Figure 2.2 TGA/DTA curve of pure PVA

The thermal property of the PVA film was obtained using TGA /DTA analysis. It was found that the degradation of the PVA film starts at around $300^\circ$C (Figure 2.2). Around 40% weight loss occurs at this temperature region. The degradation of polymers starts with free radical formations at weak bonds and/or chain ends, followed by their transfer to adjacent chains via interchain reactions. When the
temperature reached around 500°C approximately 80% weight of the sample is decomposed.

2.5.2 FTIR Spectrum

The FTIR spectrum of the pure PVA sample in the region 4000-500 cm\(^{-1}\) is shown in Figure 2.3. The spectrum exhibits band characteristics of stretching and bending vibrations of O-H, C-H and C=O groups. The IR band positions of the sample and their assignments are shown in Table 2.1. The FTIR spectrum clearly shows the large water content in the sample. Moreover the PVA sample has the tendency to absorb moisture from the atmosphere which will again add to the intrinsic water content.
Table 2.1 Band Assignments of the sample

<table>
<thead>
<tr>
<th>Vibrational frequency (cm(^{-1}))</th>
<th>Band assignment</th>
</tr>
</thead>
<tbody>
<tr>
<td>3344</td>
<td>OH (stretching)</td>
</tr>
<tr>
<td>2939</td>
<td>CH(_2) (stretching)</td>
</tr>
<tr>
<td>2167</td>
<td>CH+CC</td>
</tr>
<tr>
<td>1735</td>
<td>C=O (stretching)</td>
</tr>
<tr>
<td>1434</td>
<td>CH(_2) (bending)</td>
</tr>
<tr>
<td>1373</td>
<td>CH+OH</td>
</tr>
<tr>
<td>1326</td>
<td>CH+OH</td>
</tr>
<tr>
<td>1249</td>
<td>CH (stretching)</td>
</tr>
<tr>
<td>1095</td>
<td>C-O (stretching)</td>
</tr>
<tr>
<td>945</td>
<td>CC (stretching)</td>
</tr>
<tr>
<td>848</td>
<td>CH(_2) (stretching)</td>
</tr>
<tr>
<td>605</td>
<td>OH (stretching)</td>
</tr>
</tbody>
</table>

2.5.3 Spectral Studies

2.5.3.1 Absorption Spectra

The absorption spectrum of pure PVA sample is shown in Figure 2.4. There is an absorption peak in the UV region for pure PVA sample.

Figure 2.4 Absorption spectrum of pure PVA sample
The major mechanism for transitions in rare earth ions is induced electric dipole arising from the very weak mixing of the order of magnitude of the ground state $4f^n$ wave function with functions of the opposite parity. The absorption spectra of doped PVA for different wt% of samarium ions follow a linear relationship with Sm$^{3+}$ concentrations. The ground state of the Sm$^{3+}$ ion is $^6H_{5/2}$ and the absorption bands arise due to transitions from this level to various excited levels. Spectral lines observed are assigned for different excited states $^4G_{7/2}$, $^4H_{9/2}$, $^4D_{3/2}$, $^6P_{7/2}$, $^6P_{3/2}$, $^6P_{5/2}$, $^4G_{9/2}$, $^6I_{13/2}$, $^6I_{11/2}$, [20] and is given in Figure 2.5.

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 polymer matrix. Experimentally determined oscillator strengths and the calculated oscillator strengths are tabulated in Table 2.2. 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 2.2** The oscillator strength of the different samples

<table>
<thead>
<tr>
<th>Transition from $^6H_{5/2}$</th>
<th>Sm1% $f_{mea} \times 10^{-6}$</th>
<th>Sm1% $f_{cal} \times 10^{-6}$</th>
<th>$\delta_{rms} \times 10^{-6}$</th>
<th>Sm3% $f_{mea} \times 10^{-6}$</th>
<th>Sm3% $f_{cal} \times 10^{-6}$</th>
<th>$\delta_{rms} \times 10^{-6}$</th>
<th>Sm5% $f_{mea} \times 10^{-6}$</th>
<th>Sm5% $f_{cal} \times 10^{-6}$</th>
<th>$\delta_{rms} \times 10^{-6}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$^4H_{9/2}$</td>
<td>0.17</td>
<td>0.08</td>
<td>0.29</td>
<td>0.18</td>
<td>0.27</td>
<td>0.21</td>
<td>0.61</td>
<td>0.66</td>
<td>0.66</td>
</tr>
<tr>
<td>$^4D_{3/2}$</td>
<td>0.17</td>
<td>0.26</td>
<td>0.46</td>
<td>0.57</td>
<td>0.61</td>
<td>0.66</td>
<td>0.52</td>
<td>0.66</td>
<td>0.66</td>
</tr>
<tr>
<td>$^4P_{7/2}$</td>
<td>0.23</td>
<td>0.27</td>
<td>0.51</td>
<td>0.63</td>
<td>0.61</td>
<td>0.66</td>
<td>0.52</td>
<td>0.66</td>
<td>0.66</td>
</tr>
<tr>
<td>$^4P_{3/2}$</td>
<td>1.14</td>
<td>1.12</td>
<td>2.43</td>
<td>2.41</td>
<td>0.40</td>
<td>2.79</td>
<td>2.78</td>
<td>0.41</td>
<td>2.78</td>
</tr>
<tr>
<td>$^6P_{5/2}$</td>
<td>0.14</td>
<td>0.17</td>
<td>0.36</td>
<td>0.36</td>
<td>0.42</td>
<td>0.42</td>
<td>0.31</td>
<td>0.20</td>
<td>0.31</td>
</tr>
<tr>
<td>$^4I_{13/2}$</td>
<td>0.11</td>
<td>0.08</td>
<td>0.25</td>
<td>0.18</td>
<td>0.31</td>
<td>0.20</td>
<td>0.31</td>
<td>0.20</td>
<td>0.31</td>
</tr>
<tr>
<td>$^4I_{11/2}$</td>
<td>0.19</td>
<td>0.009</td>
<td>0.58</td>
<td>0.02</td>
<td>0.66</td>
<td>0.02</td>
<td>0.66</td>
<td>0.02</td>
<td>0.66</td>
</tr>
</tbody>
</table>

The root mean square deviations in determining oscillator strength are also given in Table 2.2 and these values are comparable with other Sm$^{3+}$ systems [21, 22]. The measured and calculated values of electric dipole strengths for different absorption levels are tabulated.
in Table 2.3. The J-O parameters of Sm$^{3+}$ in PVA matrices for the three samples are given in Table 2.4.

<table>
<thead>
<tr>
<th>Transition from $^6H_{5/2}$</th>
<th>Sm1%</th>
<th>Sm3%</th>
<th>Sm5%</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$S_{\text{meas}}$</td>
<td>$S_{\text{cal}}$</td>
<td>$S_{\text{meas}}$</td>
</tr>
<tr>
<td>$^{9}H_{9/2}$</td>
<td>0.42</td>
<td>0.20</td>
<td>0.72</td>
</tr>
<tr>
<td>$^{4}D_{3/2}$</td>
<td>0.45</td>
<td>0.67</td>
<td>1.19</td>
</tr>
<tr>
<td>$^{4}P_{7/2}$</td>
<td>0.60</td>
<td>0.71</td>
<td>1.35</td>
</tr>
<tr>
<td>$^{4}P_{3/2}$</td>
<td>3.26</td>
<td>3.22</td>
<td>6.93</td>
</tr>
<tr>
<td>$^{6}P_{5/2}$</td>
<td>0.43</td>
<td>0.50</td>
<td>1.06</td>
</tr>
<tr>
<td>$^{4}I_{13/2}$</td>
<td>0.36</td>
<td>0.26</td>
<td>0.83</td>
</tr>
<tr>
<td>$^{4}I_{11/2}$</td>
<td>0.64</td>
<td>0.09</td>
<td>1.97</td>
</tr>
</tbody>
</table>

The value is found to be greater for Sm 5% sample. It has been well established that as the concentration of the rare earth ions increase in a matrix, the structural network gets modified with the result that the covalent bonding increases. The parameter has a direct relationship with the structural network which is reflected in the $\Omega_2$ values [23]. The transitions with a large value of $\Omega_2$ is called *hypersensitive pesudoquadrupolar* 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 JO parameters are functions of crystal field parameters, intraconfigurational radial integral and energy separation of the 4f and opposite parity configuration. Hence these parameters are dependent on the oscillator strengths and are found to vary from site to site. The increase in covalency (R-O covalency) is manifested directly in the increase of the parameter [24]. These parameters in turn determine the electric dipole and magnetic dipole line strengths of a transition. The bonding parameter (δ) obtained are also given in Table 2.4 and found to be positive which indicates the presence of covalent bonds.

Jorgensen and Reisfeld [25] related the intensity parameters Ω₄ and Ω₆ to the rigidity of various hosts such as crystals, glasses, solutions and vapours. Takebe et al. [26] suggested that the ionic packing ratio is related to the spontaneous emission probabilities which are determined by the intensity parameters Ω₄ and Ω₆ and it correlates with the rigidity of the polymer hosts and the covalency of the rare earth ion sites. The parameter Ω₂ is related to the covalency and/or structural changes in the vicinity of the Sm³⁺ ion (short range effect) and Ω₄ are related to the long range effects. Covalent bonding has the effect of lowering the electronic levels of the free ion due to the nephelauxetic effect and the value of Ω₂ gets strongly enhanced. A large value of Ω₃ intensity parameter is an indication of high covalence of the metal- ligand bonds and the values are found to be greater in PVA films than in inorganic glasses and aqueous solution. High
covalency provides greater $\Omega_2$ values, which indicates lower symmetry around the rare earth ion in the host.

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 [27]. 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.

Now once the $\Omega_\lambda$ quantities have been determined, they can subsequently be utilized to calculate the properties of fluorescent transitions from $^4G_{5/2}$, $^4G_{7/2}$, and $^4F_{3/2}$ levels that have not been experimentally measured, including the radiative lifetime. The values of the radiative transition probability ($A$), total radiative transition probability ($A_T$), radiative life time ($\tau_{\text{rad}}$) fluorescence branching ratio ($\beta_R$) and the integrated absorption cross-section for stimulated emission ($\sigma_A$) are given in Table 2.5.
Table 2.5 Radiative parameters for Sm$^{3+}$ doped PVA film

<table>
<thead>
<tr>
<th>Transition from $^4G_{5/2}$</th>
<th>Wave number $\text{cm}^{-1}$</th>
<th>$S_{\text{ed}} \times 10^{-22} \text{ cm}^2$</th>
<th>$A_s \text{s}^{-1}$</th>
<th>$A_T \text{s}^{-1}$</th>
<th>$\tau_{\text{rad}} \mu\text{s}$</th>
<th>$\beta(%)$</th>
<th>$\sigma_A \times 10^{-20} \text{ cm}^2$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$^4G_{5/2}$</td>
<td>2244</td>
<td>9.62</td>
<td>0.41</td>
<td></td>
<td>0.04</td>
<td>4.67</td>
<td></td>
</tr>
<tr>
<td>$^6F_{11/2}$</td>
<td>9095</td>
<td>5.08</td>
<td>7.21</td>
<td></td>
<td>0.78</td>
<td>5.01</td>
<td></td>
</tr>
<tr>
<td>$^6F_{9/2}$</td>
<td>10594</td>
<td>3.07</td>
<td>8.25</td>
<td></td>
<td>0.89</td>
<td>4.22</td>
<td></td>
</tr>
<tr>
<td>$^6F_{7/2}$</td>
<td>11881</td>
<td>40.63</td>
<td>192.73</td>
<td></td>
<td>20.96</td>
<td>78.42</td>
<td></td>
</tr>
<tr>
<td>$^6F_{5/2}$</td>
<td>12737</td>
<td>2.64</td>
<td>20.59</td>
<td></td>
<td>2.23</td>
<td>7.28</td>
<td></td>
</tr>
<tr>
<td>$^6F_{3/2}$</td>
<td>13260</td>
<td>12.74</td>
<td>168.09</td>
<td></td>
<td>18.28</td>
<td>54.91</td>
<td></td>
</tr>
<tr>
<td>$^6H_{15/2}$</td>
<td>13335</td>
<td>0.01</td>
<td>0.04</td>
<td></td>
<td>0.005</td>
<td>0.01</td>
<td></td>
</tr>
<tr>
<td>$^6H_{13/2}$</td>
<td>14822</td>
<td>0.31</td>
<td>1.66</td>
<td></td>
<td>0.18</td>
<td>0.43</td>
<td></td>
</tr>
<tr>
<td>$^6H_{11/2}$</td>
<td>16494</td>
<td>57.95</td>
<td>490.60</td>
<td></td>
<td>53.34</td>
<td>103.53</td>
<td></td>
</tr>
<tr>
<td>$^6H_{9/2}$</td>
<td>17640</td>
<td>1.07</td>
<td>13.33</td>
<td></td>
<td>1.45</td>
<td>2.46</td>
<td></td>
</tr>
<tr>
<td>$^6H_{7/2}$</td>
<td>18891</td>
<td>0.76</td>
<td>14.66</td>
<td></td>
<td>1.59</td>
<td>2.36</td>
<td></td>
</tr>
</tbody>
</table>

2.5.3.2 Emission Spectra

The emission spectra of the three samples are given in Figure 2.6. The main peak is at 595nm, similar to Sm$^{3+}$ ions. The main peak due to Sm$^{2+}$ ions is at around 700nm [28-30]. Therefore the appearance of emission spectra due to Sm$^{2+}$ ion is ruled out. From the emission spectra, branching ratio for each level is calculated using the standard procedure [31]. Using the relation 2.11 the stimulated emission cross-section for the levels is calculated. These values are tabulated in Table 2.6.
Spectroscopic Characterization…..Sm$^{3+}$ ions in PVA Film

Table 2.6 Emission parameters for Sm$^{3+}$ doped PVA film

<table>
<thead>
<tr>
<th>Transition</th>
<th>$\lambda_p$ nm</th>
<th>$\Delta \lambda_{\text{eff}}$ nm</th>
<th>$\beta$ %</th>
<th>$\sigma_e$ cm$^2$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$^4G_{7/2} \rightarrow ^6H_{9/2}$</td>
<td>559</td>
<td>11</td>
<td>22.34</td>
<td>6.79x10$^{-23}$</td>
</tr>
<tr>
<td>$^4G_{7/2} \rightarrow ^6H_{11/2}$</td>
<td>595</td>
<td>12.7</td>
<td>65.54</td>
<td>2.9x10$^{-21}$</td>
</tr>
<tr>
<td>$^4G_{7/2} \rightarrow ^6H_{13/2}$</td>
<td>642</td>
<td>13.49</td>
<td>11.99</td>
<td>1.2x10$^{-23}$</td>
</tr>
</tbody>
</table>

From the table it is clear that the transition $^4G_{7/2} \rightarrow ^6H_{11/2}$ shows the highest stimulated emission cross-section and hence it has high optical gain. This is in agreement with the theoretical obtained branching ratio and integrated absorption cross-section for the transition $^4G_{7/2} \rightarrow ^6H_{11/2}$. The branching ratio and integrated absorption cross-section are higher for the transition $^4G_{7/2} \rightarrow ^6H_{11/2}$ in PVA films than in Zinc Borosulphate (ZnBS) glasses ($\beta=4.4, \sigma_\lambda=2.5x10^{-20}$ cm$^2$).
In alkali fluoroborate glasses this transition has a higher value of branching ratio ($\beta=67$) and can be used for optical amplification [32].

Hence we can conclude that the transition $^4G_{7/2}\rightarrow^6H_{11/2}$ can be utilized for optical amplification in Sm$^{3+}$ doped PVA films. Some of the major advantages attributed to polymers in the context of polymers doped with rare earth ions are (i) the rare earth ions doped polymer matrix shows higher covalent bonding, (ii) such systems are ideal candidates for optical image storage, (iii) a hologram could be written easily at a wavelength corresponding to the absorption peaks of the rare earth ions and (iv) they can be processed easily and exhibit better long term photostability.

2.6 Conclusion

The optical properties of Sm$^{3+}$ doped PVA films were studied. The various important spectral parameters were obtained from the absorption spectrum such as radiative lifetime, transition probability, branching ratio and absorption cross-section. The transition $^4G_{7/2}\rightarrow^6H_{11/2}$ has been identified as the one which yields the maximum fluorescence emission. The evaluation of the radiative properties indicate that Sm$^{3+}$ doped PVA is promising for making polymer optical active devices. The thermal analysis shows that the degradation of the sample starts at 300$^\circ$C. The FTIR analysis has been employed to ascertain the various molecular vibrations of the sample. It shows the presence of large water content within the sample. Even at 300$^\circ$C or above it is extremely difficult to remove all the residual OH content which acts as fluorescence quenchers. Heat treatment at high temperature may reduce the water content but on the other hand it may result in the complete degradation of the sample.
References


