Chapter - IV

Enrichment of orange emission of Er\(^{3+}\) ion with Sn\(^{4+}\) ion as sensitizer in lithium lead phosphate glass system

Lithium lead phosphate glasses doped with 1.0 mol\% of Er\(_2\)O\(_3\) and mixed with varying concentrations of SnO\(_2\) (from 0 to 7.0 mol\%) have been synthesized. Optical absorption and luminescence spectra of the prepared glasses were recorded at ambient temperature. The radiative life times were measured from the luminescence decay profiles recorded at room temperature. Similar studies have also been carried out for the SnO\(_2\) singly doped glasses. The absorption and luminescence spectra of Er\(^{3+}\) ions doped glasses were characterized using Judd-Ofelt theory. The radiative parameters viz., transition probability A, branching ratio \(\beta\) and the radiative life time \(\tau\) of principal emission transitions of these glasses have been evaluated. The energy transfer mechanism between Sn\(^{4+}\) and Er\(^{3+}\) in co-doped glasses has been explored as a function of SnO\(_2\) concentration with the help of rate equations. The results indicated a significant enhancement in the intensity of orange emission \(^4\)\(G_{11/2}\)\(\rightarrow\)\(^4\)\(I_{11/2}\) of Er\(^{3+}\) ions due to co-doping with SnO\(_2\). The results were further analyzed with IR spectral data and ac conductivity studies. The analysis pointed out that about 3.0 mol\% of SnO\(_2\) is the most favorable concentration for getting the highest quantum efficiency of orange emission and for the maximum energy transfer with low non-radiative transition probabilities.
Enrichment of orange emission of Er\(^{3+}\) ion with Sn\(^{4+}\) ion as sensitizer in lithium lead phosphate glass system

4.1 Introduction

Er\(^{3+}\) (4f\(^{11}\)) ion with \(^4\)I\(_{15/2}\) ground state gives rise to a large number of absorption and emission transitions in the ultraviolet, visible and near infrared regions. Erbium ion is an attractive candidate for pulsed solid state lasers both in NIR and visible regions. Many laser transitions have been identified for Er\(^{3+}\) ion in crystalline and amorphous hosts over a wide region [1, 2]. However, since erbium has only weak pumping bands, it is necessary to assist the pumping by resonant transfer donors like tin ions. Several detailed studies on absorption and emission spectra of Er\(^{3+}\) ion in borate, phosphate, germanate and tellurite glasses have been reported [3-5]. Normally, the transitions \(^4\)I\(_{15/2}\)\(\rightarrow\)\(^2\)H\(_{11/2}\) and \(^4\)I\(_{15/2}\)\(\rightarrow\)\(^4\)G\(_{11/2}\) of Er\(^{3+}\) in the absorption spectra are hypersensitive and their intensities are greatly influenced by the host matrices [6-9]. In some glass hosts the dopant concentration dependence of lifetime of \(^4\)S\(_{3/2}\) level that gives green emission has been reported [10]. The lifetime of this level in fact was reported to decrease with increasing concentration of the active ion and it was attributed to cross relaxation involving the levels \(^4\)G\(_{11/2}\), \(^4\)I\(_{15/2}\)\(\rightarrow\)\(^4\)F\(_{7/2}\), \(^4\)I\(_{13/2}\) and \(^2\)H\(_{11/2}\), \(^4\)S\(_{3/2}\), \(^4\)I\(_{15/2}\)\(\rightarrow\)\(^4\)I\(_{9/2}\), \(^4\)I\(_{13/2}\). Four level lasing involving \(^4\)S\(_{3/2}\)\(\rightarrow\) 4I\(_{15/2}\) transition has been reported for Er\(^{3+}\) at ambient temperatures in several hosts. This transition is of interest because of the existence of sensitive
photo detection at around 850 nm where the second harmonic of the above transition occurs. However, similar detailed studies on \( ^4G_{11/2} \rightarrow ^4I_{11/2} \) orange emission transition of Er\(^{3+}\) ions were less focused even though such laser sources are being widely used in geodesy. This particular beam is an ideal substitute of sodium derivative signal light source in astronomical telescope, also can be a copper vapor laser alternative. In medical field this laser source is highly useful in therapies such as photocoagulation in ophthalmology for the treatment of retinal disorders, removal of vascular lesions, in the treatment of acne and in skin rejuvenation.

Semiconducting tin oxide (SnO\(_2\)) mixed glasses are being widely used for optoelectronic devices and as photoconductors since this compound endows excellent optical and electrical properties to the host glass material [11-13]. Further, Sn\(^{4+}\) ions were reported to exhibit broad yellow-orange emission in the wavelength region 590-650 nm in different host materials [14]. Because of these reasons, Sn\(^{4+}\) ions are expected to act as a donor or alternatively as an energy transfer bridging ions for orange emission. Hence, efficient energy transfer processes from Sn\(^{4+}\) (S\(_1\)→S\(_0\)) to \( ^4G_{11/2} \rightarrow ^4I_{11/2} \) orange emission transition of Er\(^{3+}\) ion is possible and there by an intense orange emission is expected from the Sn\(^{4+}\) and Er\(^{3+}\) co-doped glasses. Further, as was reported in several studies there is a possibility for Sn\(^{4+}\) ions to get reduced to Sn\(^{2+}\) ions during the melting process of the glass [15]. These divalent tin ions may act as
modifiers and expected to bring the variations in the crystal field at the vicinity of rare earth ions in the glass host.

The host material chosen for this study is lithium lead phosphate glass. Lithium phosphate glasses though well known due to their applications in electrochemical devices such as high energy density batteries but these glasses are also equally suitable for hosting lasing rare earth ions. If PbO is added to the lithium phosphate glass system, it becomes more stable against devitrification and there will be an increase in the moisture resistant capability, density and refractive index of the system.

Thus the principal objective of this study is to report the influence of Sn$^{4+}$ ions on the emission features of Er$^{3+}$ ions (especially the orange emission band) in Li$_2$O–PbO–P$_2$O$_5$ glass system. The variation of SnO$_2$ content in the glass network not only inculcate the structural modifications and local field variations around Er$^{3+}$ ions embedded in the glass network but also contributes to the enrichment of orange emission of Er$^{3+}$ ions.

4.2 Brief review of the previous work on the glasses doped with Er$^{3+}$ ions:

Some of the recent studies on erbium ions doped glass systems have been briefly reviewed below:

Leal et al. [16] studied spectroscopic characterization of Er$^{3+}$/Yb$^{3+}$ co-doped tellurite glasses 70.8TeO$_2$–5Al$_2$O$_3$–13K$_2$O–(11–$x$)–BaO–0.2Er$_2$O$_3$–$x$Yb$_2$O$_3$, where $x$=0, 0.4, 0.8, 1.2 and 2 mol% through X-ray diffraction,
Raman, absorption and luminescence spectra. The Judd–Ofelt intensity parameters were calculated for 0.2 mol% Er\(^{3+}\)-doped glass and are used to evaluate radiative properties such as transition probabilities, branching ratios and radiative lifetime. The FWHM of the \(^4\text{I}_{13/2} \rightarrow ^4\text{I}_{15/2}\) transition as a function of Yb\(_2\)O\(_3\) mol% and distance (\(\delta\)) between the laser focusing point and the end-face of the glass has been reported. It was observed both, experimentally and numerically, a change in the FWHM with variations of \(\delta\) less than 8 mm. The latter was attributed to the radiation trapping effect.

Linganna et al. [17] prepared trivalent erbium (Er\(^{3+}\))-doped K–Sr–Al phosphate glasses and studied their spectroscopic properties as a function of Er\(_2\)O\(_3\) concentration. Judd–Ofelt analysis has been carried out for 1.0 mol% Er\(_2\)O\(_3\)-doped phosphate glass and in turn radiative properties have been evaluated for the excited levels of Er\(^{3+}\) ion. The radiative lifetime for the \(^4\text{I}_{13/2}\) level was found to be higher for the present glass when compared to other Er\(^{3+}\)-doped glasses. The emission cross-section spectrum for 1.0 mol% of Er\(_2\)O\(_3\)-doped glass has been evaluated using McCumber theory. The gain cross-section has been evaluated as a function of population inversion, which revealed that the lasing action would be achieved at 1.53 \(\mu\)m for a population inversion about 40%. Decay curves for the \(^4\text{I}_{13/2}\) level were measured and lifetimes have been determined for the studied glasses. Their results indicated that the present glasses could be useful for laser as well as optical amplifiers at 1.53 \(\mu\)m.
Miguel et al. [18] reported the near-infrared emission and upconversion of Er\(^{3+}\)–Tm\(^{3+}\) codoped fluorotellurite TeO\(_2\)–ZnO–ZnF\(_2\) glasses for different Tm\(^{3+}\) concentrations by using steady-state and time-resolved spectroscopy. A broad emission from 1350 to 1700 nm corresponding to the \(^3\)H\(_4\)→\(^3\)F\(_4\) (Tm\(^{3+}\)) and \(^4\)I\(_{13/2}\)→\(^4\)I\(_{15/2}\) (Er\(^{3+}\)) emissions which cover the complete telecommunication window of the wavelength-division-multiplexing transmission systems is observed. The addition of Tm\(^{3+}\) reduces the upconverted green emission due to Er\(^{3+}\)→Tm\(^{3+}\) energy transfer whereas the red emission is enhanced due to the cross-relaxation \(^3\)F\(_4\)→\(^3\)H\(_6\)(Tm\(^{3+}\);\(^4\)I\(_{11/2}\)→\(^4\)F\(_{9/2}\)(Er\(^{3+}\)) process. Fan et al. [19] investigated emissions at 2.7 μm from telluride glasses with various Er\(_2\)O\(_3\) doping concentrations. The prepared glasses have thermostability and high rare-earth solubility. Judd–Ofelt parameters are calculated based on the absorption spectra. A large emission cross section (1.12 × 10\(^{-20}\) cm\(^2\)) and a high spontaneous radiative coefficient (57.8 s\(^{-1}\)) are obtained at 2.7 μm. Strong upconversion emission caused by intense pump absorption is observed from the Er\(^{3+}\)-doped fiber under excitation by a 980 nm laser diode (LD).

Vijaya et al. [20] trivalent erbium doped zinc fluorophosphate glasses have been synthesized and their luminescence properties in the green visible range have been investigated as a function of temperature. The Judd–Ofelt theory has been used to predict the transition probabilities, branching ratios and lifetimes for the various excited states of Er\(^{3+}\) ions in 0.5 mol% of Er\(_2\)O\(_3\)-doped glass. The effect of Er\(^{3+}\) concentration on temperature dependent luminescence
has been studied for the wide temperature range from room temperature up to 773 K. The results revealed that the zinc fluorophosphate glass having relatively low concentration of Er$^{3+}$ ions can be useful as an optical temperature sensor due to their high sensitivity and the absence of radiative energy transfer processes. Guan et al. [21] studied 1.55 μm emission and upconversion luminescence of Er$^{3+}$-doped strontium borate glasses. The emission spectra, the luminescence decay curves and upconversion emission spectra were measured. Under the excitation of a 980 nm laser diode, 1.55 μm infrared fluorescence and efficient green and red upconversion fluorescence have been observed. The broad and intense emission positions centered at around 1550 nm show increasing red shift with the increase of Er$^{3+}$ ions concentration.

Desirena et al. [22] made comparative study of the spectroscopic properties of Yb$^{3+}$/Er$^{3+}$ codoped tellurite glasses modified with R$_2$O (R=Li, Na and K). The Judd–Ofelt parameters ($\Omega_i$), quantum efficiency in near infrared (1.55 μm) and visible up-conversion (546 and 660 nm) and quality factor spectroscopy ($\chi$) were calculated. Three up-conversion emission bands centered at 525, 546 and 660 nm were observed as maxima for glasses containing potassium. The energy transfer efficiency (ET) from Yb$^{3+}$ to Er$^{3+}$, ($^4F_{5/2}$)+($^4I_{15/2}$)$\rightarrow$($^4F_{7/2}$)+($^4I_{13/2}$), was calculated using the measured lifetimes of Yb$^{3+}$ with and without the presence of acceptor (Er$^{3+}$). The maximum calculated ET was 58% for 0.25 mol% of Er$^{3+}$ and 3 mol% of Yb$^{3+}$ for TeO$_2$–K$_2$O–ZnO–Ln$_2$O$_3$ glass composition. Sdiri et al. [23] investigated spectroscopic
properties of \( \text{Er}^{3+} \) and \( \text{Yb}^{3+} \) doped phosphate–borate glasses. The phenomenological Judd–Ofelt parameters \( \Omega_2, \Omega_4 \) and \( \Omega_6 \) are determined for both rare-earth ions together with their quality factors and compared to the equivalent parameters for other host glasses. Photoluminescence (PL) and its decay behaviour studies were carried out for the transition \( ^4I_{13/2} \rightarrow ^4I_{15/2} \).

Środa et al. [24] have studied optical properties of phosphate, borate, silicate and lead-silicate glasses. They showed that the integral intensity of the two main optical absorption transitions monotonically increases with the order: phosphate < borate < silicate < lead-silicate. Chilccej et al. [25] investigated the effects of \( \text{ZnF}_2 \) concentration on the optical and physical properties of \( \text{Er}^{3+} \)-doped oxy-fluoride tellurite glasses \( \text{Er}_2\text{O}_3-\text{TeO}_2-\text{ZnF}_2-\text{ZnO} \). They found that the \( \text{Er}^{3+} \) ion emission cross section spectrum at around 1550 nm of oxy-fluoride tellurite glass containing 30 mol% of \( \text{ZnF}_2 \) was very similar to those of Fluoride glasses. Bilir et al. [26] have investigated Judd-Ofelt analysis and near infrared emission properties of the \( \text{Er}^{3+} \) ions in tellurite glasses containing \( \text{WO}_3 \) and \( \text{CdO} \). They have determined the absorption and emission cross-section spectra and the Stark Levels splitting for the \( ^4I_{13/2} \) to \( ^4I_{15/2} \) transition of \( \text{Er}^{3+} \) centered at 1.5 \( \mu \text{m} \). Fang et al. [27] have carried out DSC measurements for \( \text{Na}_2\text{O}-\text{Li}_2\text{O}-\text{B}_2\text{O}_3-\text{Al}_2\text{O}_3-\text{BaO}-\text{P}_2\text{O}_5 \) glasses with different particle size. Two crystallization peaks appear on the DSC curves for sample sized 90-110\( \mu \text{m} \). They have also studied the effect of mixed alkali on glass thermal stability and evaluated the surface and bulk crystallization active energies. Feng et al. [28] investigated the
optimization of doping concentration in Er:tellurite glass based on heat analysis. Their results show that upconversion is an important heat-generation process and heat problem is serious especially at high Er$^{3+}$ doping level. Based on the heat analysis, the optimized doping concentration range of Erbium ions is about 0.5 mol% to 1.0 mol%. Rivera et al. [29] showed the annealing effect on silver and Erbium- doped tellurite glasses in the formation of nanoparticles (NPs) of silver, produced by the reduction of silver (Ag$^+\rightarrow$Ag$^0$), aiming to an fluorescence enhancement. Their observations demonstrated that the photoluminescence enhancement is due to the coupling of dipoles formed by NPs with the Er$^{3+}$I$_{13/2}\rightarrow$4I$_{15/2}$ transition.

Zhao et al. [30] investigated intense upconversion luminescence of Er$^{3+}$/Yb$^{3+}$ codoped oxyfluoride borosilicate glass containing Ba$_2$GdF$_7$ nanocrystals. Zhang et al. [31] have synthesized Er$^{3+}$ and Dy$^{3+}$ codoped tellurite glasses and observed five emission bands in the PL spectrum under 325 nm pumping. Their studies revealed that the intensity of Dy$^{3+}$ characteristic emission was enhanced as Er$^{3+}$ concentration increased while keeping Dy$^{3+}$ concentration constant. They claimed that these glasses with the controllable CIE coordinates might be a potential candidate for the widely realistic application such as solid-state white lighting and multicolor display. González-Órez et al. [32] investigated the control of the local devitrification on oxyfluoride glass doped with Er$^{3+}$ ions under diode laser irradiation. They have studied green upconversion emissions around 525 and 545 nm originated from
the thermalized $^2\text{H}_{11/2}$ and $^4\text{S}_{3/2}$ levels when the glass structure changes to glass ceramic (under 2300 mW and temperature around 783 K) of laser power during irradiation with a laser beam. Ichikawa et al. [33] investigated emission properties of Er$^{3+}$ in Ga$_2$S$_3$-GeS$_2$-Sb$_2$S$_3$ glasses at the mid-infrared region. They identified clear mid-infrared emissions were observed at 2750 and 4300 nm assigned to the $^4\text{I}_{11/2} \rightarrow ^4\text{I}_{13/2}$ and $^4\text{I}_{9/2} \rightarrow ^4\text{I}_{11/2}$ transitions, respectively. The lifetime of the initial level of the 4.3 μm emission, $^4\text{I}_{9/2}$, rapidly decreased with the Er$^{3+}$ concentration because of the cross relaxation of this level, which can take place even at considerably low Er$^{3+}$ concentration. Frej et al. [34] have reported photoluminescence properties of Er$^{3+}$ doped Ga$_{10}$Ge$_{25}$S$_{65}$ glasses excited at 980 and 532 nm. They have analyzed the PL temporal behavior through rate equations for the population densities and using the Inokuti-Hirayama model.

Huang et al. [35] have investigated mid-infrared spectral properties of Er$^{3+}$-doped GeS$_2$-Ga$_2$S$_3$-CsI glass-ceramics. Their results showed that the density and micro-hardness of the glass are significantly increases after heat treatment at 440°C for 14 h, while the infrared transmittance remains the same. The mid-infrared emission intensity at 2.8 μm corresponding to electronic transitions of $^4\text{I}_{11/2} \rightarrow ^4\text{I}_{13/2}$ in Er$^{3+}$ ions increased slightly. Qian et al. [36] have reported the spectroscopic properties of Er$^{3+}$-doped Na$_2$O–Sb$_2$O$_3$–B$_2$O$_3$–SiO$_2$ glasses. Haro-Gonzalez et al. [37] have reported optical properties of Er$^{3+}$-doped strontium barium niobate nanocrystals obtained by thermal treatment in
glass. Shixun Dai et al. [38] have reported the effect of OH\(^-\) content on emission properties in Er\(^{3+}\)-doped tellurite glasses. Padlyak et al. [39] have studied the optical spectroscopic properties of Er\(^{3+}\) doped CaO-Ga\(_2\)O\(_3\)-3GeO\(_2\) glasses. Chen et al. [40] have studied the spectroscopic properties of Er\(^{3+}\) doped tellurite glasses for 1.5 \(\mu\)m optical amplifier. Kassab et al. [41] have reported Er\(^{3+}\) laser transition in PbO-PbF\(_2\)-B\(_2\)O\(_3\) glasses. Yang et al. [42] have reported the results of their comparative investigations on energy transfer mechanisms between Er\(^{3+}\) and Ce\(^{3+}\) in tellurite glasses. Chena et al. [43] have reported the spectroscopic properties of Er\(^{3+}\) ions in bismuth borate glasses. Shih [44] reported the thermal, chemical and structural characteristics of Er\(^{3+}\) doped sodium phosphate glasses.

Yang et al. [45] investigated non-radiative \(^4\)I\(_{13/2}\)\(\rightarrow\)\(^4\)I\(_{11/2}\) transitions of Er\(^{3+}\) oxide glasses. Hood et al. [46] have reported the studies on Er\(^{3+}\) doped borotellurite glasses for 1.5 \(\mu\)m broadband amplification. Courrola and Kassab et al [47] reported the spectroscopic properties of heavy metal oxide glasses doped with erbium. Jose et al. [48] have fabricated active wave-guide Ag-Na ion exchange Er\(^{3+}\)-Yb\(^{3+}\) doped phosphate glasses. Marjanovica et al. [49] have reported the characterization of new Er\(^{3+}\) doped tellurite glass systems. Vermelho et al. [50] have reported the temperature investigation of infrared visible frequency upconversion in Er\(^{3+}\) doped tellurite glasses excited at 1540 nm. Chiodini et al. [51] studied the photo sensitiveness of Er\(^{3+}\) Tin-Silicate glasses. Ding et al. [52] have studied the spectral properties Er\(^{3+}\) doped lead
halo tellurite glasses for 1.5μm broadband amplification. Nii et al. [53] have reported the upconversion of Er$^{3+}$ and Yb$^{3+}$ doped TeO$_2$ based glasses. Tanebe et al. [54] have reported the compositional dependence of J-O parameters in Er$^{3+}$ ion alkali metal borate glasses.

### 4.3 Results

The details of the composition of the glasses chosen for the present study are:

- **S$_1$**: 20Li$_2$O–20PbO–59P$_2$O$_5$: 1.0 SnO$_2$
- **S$_3$**: 20Li$_2$O–20PbO–57P$_2$O$_5$: 3.0 SnO$_2$
- **S$_5$**: 20Li$_2$O–20PbO–55P$_2$O$_5$: 5.0 SnO$_2$
- **S$_7$**: 20Li$_2$O–20PbO–53P$_2$O$_5$: 7.0 SnO$_2$
- **S$_1$E**: 20Li$_2$O–20PbO–58P$_2$O$_5$–1.0 Er$_2$O$_3$: 1.0 SnO$_2$
- **S$_3$E**: 20Li$_2$O–20PbO–56P$_2$O$_5$–1.0 Er$_2$O$_3$: 3.0 SnO$_2$
- **S$_5$E**: 20Li$_2$O–20PbO–54P$_2$O$_5$–1.0 Er$_2$O$_3$: 5.0 SnO$_2$
- **S$_7$E**: 20Li$_2$O–20PbO–52P$_2$O$_5$–1.0 Er$_2$O$_3$: 7.0 SnO$_2$

From the measured values of density $d$ and calculated average molecular weight $\bar{M}$ of Li$_2$O–PbO–P$_2$O$_5$–Er$_2$O$_3$–SnO$_2$ glasses, various physical parameters such as Er$^{3+}$ ion concentration $N_i$ and mean Er$^{3+}$ ion separation $r_i$ are evaluated using the conventional formulae and are presented in Table 4.1.
Table 4.1. Physical parameters of Li$_2$O–PbO–P$_2$O$_5$–SnO$_2$–Er$_2$O$_3$ glasses.

<table>
<thead>
<tr>
<th>Glass</th>
<th>Density (g/cm$^3$)</th>
<th>$N_i$ ($10^{22}$ ions/cm$^3$)</th>
<th>$R_i$ (Å)</th>
<th>Refractive Index (n)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$S_0$</td>
<td>3.224</td>
<td>-</td>
<td>-</td>
<td>1.647</td>
</tr>
<tr>
<td>$S_1E$</td>
<td>3.288</td>
<td>1.43</td>
<td>4.12</td>
<td>1.649</td>
</tr>
<tr>
<td>$S_3E$</td>
<td>3.397</td>
<td>1.48</td>
<td>4.07</td>
<td>1.650</td>
</tr>
<tr>
<td>$S_5E$</td>
<td>3.460</td>
<td>1.50</td>
<td>4.05</td>
<td>1.651</td>
</tr>
<tr>
<td>$S_7E$</td>
<td>3.603</td>
<td>1.56</td>
<td>3.99</td>
<td>1.652</td>
</tr>
</tbody>
</table>

The optical absorption spectra of Er$^{3+}$ glasses recorded at room temperature in the visible and NIR regions (Fig. 4.1) exhibited the following absorption bands:

$^4$I$_{15/2}$ $\rightarrow$ $^4$G$_{9/2}$, $^4$G$_{11/2}$, $^2$H$_{9/2}$, $^4$F$_{5/2}$, $^4$F$_{7/2}$, $^2$H$_{11/2}$, $^4$S$_{3/2}$, $^4$F$_{9/2}$, $^4$I$_{9/2}$, $^4$I$_{11/2}$, $^4$I$_{13/2}$.

With the increase in the concentration of SnO$_2$ up to 3.0 mol%, a significant increase in the intensity of absorption bands is observed and beyond this concentration a considerable decrement in the absorption under the absorption peaks is noticed. Further, slight shifts in the peak positions of the absorption bands are also noticed with increase in the concentration of SnO$_2$. It may be noted here that in the region of $^4$I$_{15/2}$ $\rightarrow$ $^4$F$_{5/2}$ there is an absorption band corresponding to $S_0$$\rightarrow$S$_2$ transition of Sn$^{4+}$ ion. Similarly, in the region of $^4$I$_{15/2}$ $\rightarrow$ $^4$S$_{3/2}$ the absorption band corresponding to $S_0$$\rightarrow$S$_1$ transition does exist [55].
The experimental oscillator strengths (OS) of the absorption transitions are estimated from the absorption spectra in terms of the area under an absorption peak. The numerical values of the OS are evaluated using the conventional expression, \( f = 4.319 \times 10^{-9} \int \varepsilon(\nu) d\nu \), where \( \varepsilon(\nu) \) is the molar absorptivity at frequency \( \nu \) (in cm\(^{-1}\)) and is equal to \( \frac{1}{LC} \log(I_0/I) \) with \( C \) being the rare earth ion concentration (in mol %), \( L \) the optical path length (thickness) in cm and \( \log(I_0/I) \) the optical density. The OS of the electric dipole transition between two states have been calculated using the JO theory, with the standard Eq. (1.21).
Fig. 4.1 Optical absorption spectra of Li$_2$O–PbO–P$_2$O$_5$–SnO$_2$ glasses doped with Er$^{3+}$ recorded at room temperature. All transitions are from the ground state $^4$I$_{15/2}$. 

Absorbance (arb. units)
A set of matrix equations (which includes the $U_2$, $U_4$, and $U_6$ matrices, the matrices of the experimental OS and the energies of the corresponding transitions) have been solved to minimize the difference between the calculated $f_{\text{calc}}$ and observed $f_{\text{exp}}$ OS. The quality of fitting is determined by the root mean squared deviation and presented in Table 4.2. The deviation indicates reasonably good fitting between theory and experiment demonstrating the applicability of JO theory. The summary of the JO parameters $\Omega_\lambda$ for Er$^{3+}$ doped Li$_2$O–PbO–P$_2$O$_5$–SnO$_2$ glasses is presented in Table 4.3. The values of $\Omega_\lambda$ are found to be in the following order: $\Omega_2 > \Omega_4 > \Omega_6$ and further the values were found to be the highest for the glass mixed with 3.0 mol% of SnO$_2$.

The luminescence spectra of Li$_2$O–PbO–P$_2$O$_5$–Er$_2$O$_3$–SnO$_2$ glasses recorded at room temperature in the visible region exhibited emission bands (Fig. 4.2) corresponding to the following transitions:

Er$^{3+}$ glass ($\lambda_{\text{exc}} = 380$ nm): $^2H_{9/2} \rightarrow ^4I_{15/2}, ^4F_{5/2} \rightarrow ^4I_{11/2}, ^4F_{7/2} \rightarrow ^4I_{13/2}, ^2H_{11/2} \rightarrow ^4I_{15/2},$

$^4S_{3/2} \rightarrow ^4I_{15/2}, ^2G_{9/2} \rightarrow ^4I_{13/2}, ^4G_{11/2} \rightarrow ^4I_{11/2}, ^4F_{3/2} \rightarrow ^4I_{15/2},$

$^4F_{5/2} \rightarrow ^4I_{13/2}, ^4F_{9/2} \rightarrow ^4I_{15/2}, ^2G_{9/2} \rightarrow ^4I_{11/2} \text{ and } ^4F_{3/2} \rightarrow ^4I_{11/2}.$

Among various emission bands, the band due to $^4G_{11/2} \rightarrow ^4I_{11/2}$ transition is found to have remarkable intensity. For the sake of comparison the luminescence spectrum of SnO$_2$ free glass is also recorded under the same conditions ($S_0E$) and the same is presented in Fig. 4.2. The comparison clearly indicates a significant enhancement of $^4G_{11/2} \rightarrow ^4I_{11/2}$ emission transition due to co-doping.
Table 4.2. The absorption band energies (cm$^{-1}$), the experimental ($f_{\text{exp}}$) and calculated ($f_{\text{cal}}$) oscillator strengths ($\times 10^6$) for the absorption transitions of Er$^{3+}$ doped Li$_2$O–PbO–P$_2$O$_5$–SnO$_2$ glasses.

<table>
<thead>
<tr>
<th>Transition</th>
<th>Energy</th>
<th>$S_{1}E$</th>
<th>$S_{3}E$</th>
<th>$S_{5}E$</th>
<th>$S_{7}E$</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$f_{\text{exp}}$</td>
<td>$f_{\text{cal}}$</td>
<td>$f_{\text{exp}}$</td>
<td>$f_{\text{cal}}$</td>
<td>$f_{\text{exp}}$</td>
</tr>
<tr>
<td>$^{4}I_{15/2}\rightarrow^{4}I_{13/2}$</td>
<td>6536</td>
<td>2.72</td>
<td>2.64</td>
<td>2.84</td>
<td>2.62</td>
</tr>
<tr>
<td>$\rightarrow^{4}I_{11/2}$</td>
<td>10288</td>
<td>1.11</td>
<td>1.21</td>
<td>1.35</td>
<td>1.33</td>
</tr>
<tr>
<td>$\rightarrow^{4}I_{9/2}$</td>
<td>12594</td>
<td>0.39</td>
<td>0.34</td>
<td>0.83</td>
<td>0.64</td>
</tr>
<tr>
<td>$\rightarrow^{4}F_{9/2}$</td>
<td>15408</td>
<td>3.05</td>
<td>3.09</td>
<td>3.38</td>
<td>3.27</td>
</tr>
<tr>
<td>$\rightarrow^{4}S_{3/2}$</td>
<td>18484</td>
<td>0.19</td>
<td>0.16</td>
<td>0.51</td>
<td>0.57</td>
</tr>
<tr>
<td>$\rightarrow^{2}H_{11/2}$</td>
<td>19230</td>
<td>10.38</td>
<td>10.31</td>
<td>12.87</td>
<td>12.82</td>
</tr>
<tr>
<td>$\rightarrow^{4}F_{7/2}$</td>
<td>20618</td>
<td>2.61</td>
<td>2.59</td>
<td>2.75</td>
<td>2.64</td>
</tr>
<tr>
<td>$\rightarrow^{4}F_{5/2}$</td>
<td>22371</td>
<td>0.90</td>
<td>0.91</td>
<td>1.49</td>
<td>1.46</td>
</tr>
<tr>
<td>$\rightarrow^{2}H_{9/2}$</td>
<td>24813</td>
<td>0.27</td>
<td>0.25</td>
<td>0.72</td>
<td>0.70</td>
</tr>
<tr>
<td>$\rightarrow^{4}G_{9/2}$</td>
<td>27701</td>
<td>2.54</td>
<td>2.51</td>
<td>2.66</td>
<td>2.68</td>
</tr>
</tbody>
</table>

rms deviation $\pm0.050$ $\pm0.084$ $\pm0.078$ $\pm0.107$
Fig. 4.2 Emission spectra of Li$_2$O–PbO–P$_2$O$_5$–SnO$_2$–Er$_2$O$_3$ glasses with varying concentrations of SnO$_2$ ($\lambda_{\text{exc}}$=380 nm). Dotted line indicates emission spectrum of SnO$_2$ free glass (S$_0$E).
The increase in the content of SnO$_2$ up to 3.0 mol% in the glasses caused slight red shift in the band positions and enhanced the intensity of emission bands. For further increase of SnO$_2$ content, a decrement in the intensity of these bands could be visualized. In addition, the spectra have also exhibited bands at about 480 nm and a doublet in the range 599-630 nm and these have been identified as being due to $S_2\rightarrow S_0$ and $S_1\rightarrow S_0$ transitions of Sn$^{4+}$ ions [56] respectively.

The luminescence spectra of SnO$_2$ doped glasses (without rare earth ion) are presented in Fig. 4.3. The spectra exhibited bands at about 480 and a doublet spread over 595-630 nm assigned to $S_2\rightarrow S_0$ and $S_1\rightarrow S_0$ transitions of Sn$^{4+}$ ions, respectively. With increase in SnO$_2$ content up to 3.0 mol% a clear increase in the intensity of these bands is observed. For further increase of SnO$_2$ a slight decrement in the intensity of these bands is visualized.

For having some pre-structural understanding over the influence of tin ions on Li$_2$O–PbO–P$_2$O$_5$ glass network we have studied IR spectra of these glasses. In Fig. 4.4 the IR spectrum of Li$_2$O–PbO–P$_2$O$_5$–SnO$_2$ glasses doped with 3.0 mol% SnO$_2$ is presented. The spectrum exhibited vibrational band at about 1270 cm$^{-1}$ identified as being due to anti-symmetrical vibrations of PO$_2^-$ groups/P=O stretching vibrations. The band due to symmetric stretching vibrations of PO$_4^{3-}$ units is observed at about 1080 cm$^{-1}$, whereas the band due to P–O–P asymmetric stretching vibrations is detected at about 910 cm$^{-1}$ [57–59].
Fig. 4.3  Emission spectra of Li$_2$O–PbO–P$_2$O$_5$–SnO$_2$ glasses with varying concentration of SnO$_2$ ($\lambda_{exc}=380$ nm). Inset shows the variation of ac conductivity of these glasses with concentration of SnO$_2$. 
Fig. 4.4  IR spectra of Li$_2$O–PbO–P$_2$O$_5$–SnO$_2$–Er$_2$O$_3$ glass doped with 3.0 mol% of SnO$_2$ recorded at room temperature. Inset shows the variation of intensities of asymmetrical and symmetrical bands.
The details of other bands observed in the spectrum are mentioned in the Fig. 4.4. With the gradual introduction of SnO$_2$ up to 3.0 mol%, the intensity of asymmetrical bands of the phosphate groups is observed to increase and beyond this concentration the symmetrical bands are observed to grow at expense of asymmetrical bands. To understand this more clearly, we have shown in the inset of the same figure, the variation of the intensity of PO$_4^{3-}$ symmetrical and P–O–P asymmetric stretching vibrational bands with the concentration of SnO$_2$ is presented. The figure clearly shows at about 3.0 mol% of SnO$_2$ the intensity of asymmetrical band is the maximum, whereas that of symmetrical bands is the minimum.

4.4 Discussion

As mentioned in the previous chapter Li$_2$O–PbO–P$_2$O$_5$–SnO$_2$ glass network is mainly built up of PO$_4$ structural clusters. Sn ions do exist in both Sn$^{2+}$ and Sn$^{4+}$ states [60, 61]. The divalent tin ions participate in the phosphate glass network with trigonal SnO$_3$ pyramids with electron lone pair at the apex [62, 63]. The maximum intensity of asymmetrical bands observed in IR spectrum of S$_3$E glass suggests higher degree of disorder or depolymerization of the network of this glass.

Normally, most of the rare earth ions (other than Yb$^{3+}$ ion) occupy different coordination sites (with 8-12 co-ordination number) with non-centro symmetric potential. The value of J-O parameter $\Omega_2$ depends upon the degree of non-uniformity of the potential around rare earth ion [64, 65]. Further, even for
the rare earth ions having similar coordination number, the disparity in the
distortion at the ion sites may cause dissimilarities in the crystal field. All such
type of structural changes in the neighborhood of Er\(^{3+}\) (short-range effect) ions
lead to bring variations in the value of \(\Omega_2\). The other two J-O parameters \textit{viz.},
\(\Omega_4\) and \(\Omega_6\) are strongly dependent on the vibrational energy levels of central
rare earth ions bonded to the ligand atoms.

The close look at the values of \(\Omega_2\) parameters obtained for the studied
glasses (Table 4.3) indicates the lowest value for the glass S\(_3\)E. According to
the Judd–Ofelt theory this parameter, as said above, depends on distortion
related to the structural change in the vicinity of rare earth ions. It appears that
there is a possibility for the existence of tin ions in divalent state (probably in
large proportions in the glass S\(_3\)E) in addition to Sn\(^{4+}\) state; these divalent ions
act as modifiers and increase the average distance between P–O–P chains and
cause to increase the average Er–O distance. As a result, there will be weaker
field around Er\(^{3+}\) and contributes to the decrease of \(\Omega_2\) value.

Table 4.3. The summary of J-O parameters \(\Omega_\lambda\) (x \(10^{-20}\) cm\(^2\)).

<table>
<thead>
<tr>
<th>Conc. of SnO(_2) (mol %)</th>
<th>Er(^{3+}) doped glasses</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>(\Omega_2)</td>
</tr>
<tr>
<td>1.0</td>
<td>5.23</td>
</tr>
<tr>
<td>3.0</td>
<td>3.26</td>
</tr>
<tr>
<td>5.0</td>
<td>3.92</td>
</tr>
<tr>
<td>7.0</td>
<td>5.16</td>
</tr>
</tbody>
</table>
To further strengthen our argument on existence of a portion of tin ions in Sn\(^{2+}\) state, we have measured ac conductivity (\(\sigma_{ac}\)) as a function of SnO\(_2\) concentration. Inset of Fig. 4.3 represents \(\sigma_{ac}\) measured at 300 K at a frequency of 100 Hz. The conductivity is found to be the maximum at about 3.0 mol\% of SnO\(_2\). The main contribution to the electrical conductivity is from the polaron hoping between Sn\(^{2+}\)–Sn\(^{4+}\) pairs. The maximum electrical conductivity at 3.0 mol\% of SnO\(_2\) clearly suggests the maximum concentration of such Sn\(^{2+}\)–Sn\(^{4+}\) pairs.

Branching ratio \(\beta\) that represents the luminescence efficiency of the transition for blue, green, orange and red emission levels of Er\(^{3+}\) ions for the glasses mixed with different concentrations of SnO\(_2\) are presented in Table 4.4.

Table 4.4. Transition probability and branching ratios of Er\(^{3+}\) doped Li\(_2\)O–PbO–P\(_2\)O\(_5\)–SnO\(_2\) glasses.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Blue emission</th>
<th>Green emission</th>
<th>Orange emission</th>
<th>Red emission</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>(A \text{ (s}^{-1})</td>
<td>(\beta)%</td>
<td>(A \text{ (s}^{-1})</td>
<td>(\beta)%</td>
</tr>
<tr>
<td>(4^F_{7/2} \rightarrow 4^I_{15/2}) v=21277 cm(^{-1})</td>
<td>11861.25</td>
<td>82.34</td>
<td>5138.46</td>
<td>67.68</td>
</tr>
<tr>
<td>(4^S_{3/2} \rightarrow 4^I_{15/2}) v=17953 cm(^{-1})</td>
<td>11957.87</td>
<td>83.01</td>
<td>5152.13</td>
<td>68.50</td>
</tr>
<tr>
<td>(4^G_{11/2} \rightarrow 4^I_{11/2}) v=16921 cm(^{-1})</td>
<td>11877.34</td>
<td>82.45</td>
<td>5145.84</td>
<td>68.12</td>
</tr>
<tr>
<td>(4^F_{9/2} \rightarrow 4^I_{15/2}) v=15923 cm(^{-1})</td>
<td>11828.67</td>
<td>82.12</td>
<td>5127.91</td>
<td>67.06</td>
</tr>
</tbody>
</table>

The comparison of \(\beta\) values indicated the largest value for the glass mixed with 3.0 mol\% of SnO\(_2\) indicating that these glasses exhibit better lasing action among all other Er\(^{3+}\) doped glasses. Further, among all the emission
transitions, the intensity of the band corresponding to $^4G_{11/2} \rightarrow ^4I_{11/2}$ (orange emission) is found to be the highest and its branching ratio $\beta$ is also observed to be the largest.

The luminescence decay curve of $^4G_{11/2} \rightarrow ^4I_{11/2}$ transition of Er$^{3+}$ doped glasses mixed with different concentrations of SnO$_2$ are presented in Fig. 4.5. The curves observed to be single exponential and fluorescence lifetimes $\tau_{exp}$ evaluated from these graphs are presented in Table 4.5. The value of $\tau_{exp}$ is found to be the largest for the glass $S_3E$ among all the glasses studied. Further, the values $\tau_{exp}$ are found to be smaller when compared to those evaluated life times from the J–O theory (Table 4.5). The highest value of $\tau_{exp}$ observed for the glass $S_3E$ suggests low phonon losses in this glass network. The decay profiles of $S_1 \rightarrow S_0$ transitions of Sn$^{4+}$ ions singly doped glasses are presented in Fig. 4.6. The curves exhibited single exponential up to about 400 $\mu$s. The life times evaluated from these curves were plotted as a function of SnO$_2$ concentration and presented as the inset of Fig. 4.6. The curve exhibited maximum at 3.0 mol% of SnO$_2$.

Table 4.5. Radiative lifetimes of Er$^{3+}$ doped Li$_2$O–PbO–P$_2$O$_5$–SnO$_2$ glasses.

<table>
<thead>
<tr>
<th>SnO$_2$ conc. (mol%)</th>
<th>Orange emission</th>
<th>Quantum efficiency</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$\tau_c$ ($\mu$s)</td>
<td>$\tau_m$ ($\mu$s)</td>
</tr>
<tr>
<td>1.0</td>
<td>95.73</td>
<td>65.14</td>
</tr>
<tr>
<td>3.0</td>
<td>116.80</td>
<td>104.66</td>
</tr>
<tr>
<td>5.0</td>
<td>109.52</td>
<td>89.90</td>
</tr>
<tr>
<td>7.0</td>
<td>88.83</td>
<td>74.70</td>
</tr>
</tbody>
</table>
**Fig. 4.5** Fluorescence decay curve of Li$_2$O–PbO–P$_2$O$_5$–SnO$_2$–Er$_2$O$_3$ glasses recorded at room temperature corresponding to the emission line $^4G_{11/2}$→$^4I_{11/2}$ at 599 nm and inset (a) shows the variation of decay time with SnO$_2$ concentration and inset (b) represents the variation of energy transfer efficiency with the concentration of SnO$_2$. 
Fluorescence decay curve of Li$_2$O–PbO–P$_2$O$_5$–SnO$_2$ glasses recorded at room temperature corresponding to the emission line $S_1 \rightarrow S_0$ ($\lambda = 596$ nm). Inset shows the variation of decay time with the concentration of SnO$_2$. 
When Er$^{3+}$ and Sn$^{4+}$ are present together in the glass, the incident radiation 380 nm excites both the ions. The emission spectra of Sn$^{4+}$ ions individually doped glasses exhibited bands corresponding to $S_2\rightarrow S_0$ and $S_1\rightarrow S_0$ transitions. $S_1\rightarrow S_0$ transition energy is nearly equal to that of $^4G_{11/2}\rightarrow ^4I_{11/2}$ and $^4G_{9/2}\rightarrow ^4I_{9/2}$ transitions of Er$^{3+}$ ions. Similarly, $S_2\rightarrow S_0$ transition energy is equal to that of $^4G_{11/2}\rightarrow ^4I_{13/2}$ transition. Hence $^4G_{11/2}$ is populated not only through the excitation from $^4I_{15/2}$ but also due to excitation from $^4I_{9/2}$ and $^4I_{11/2}$ levels due to the energy transfer from $S_1\rightarrow S_0$ transition. $S_2\rightarrow S_0$ transition also contributes to the population of $^4G_{11/2}$ by exciting Er$^{3+}$ ions from $^4I_{13/2}$ to $^4G_{11/2}$. In view of these contributions $^4G_{11/2}\rightarrow ^4I_{11/2}$ transition is reinforced and strong orange emission is expected as observed. In addition the other two transitions viz., $^4F_{3/2}\rightarrow ^4I_{13/2}$ and $^4F_{5/2}\rightarrow ^4I_{13/2}$ also give near orange emission.

As can be seen from the emission spectra of tin ions doped glasses, the bands corresponding to both the transitions viz., $S_1\rightarrow S_0$ and $S_2\rightarrow S_0$ are found to be more intense in the glass mixed with 3.0 mol% of SnO$_2$. As has been mentioned earlier there is a possibility for the tin ions to exist both in Sn$^{2+}$ and Sn$^{4+}$ valance states in the glass network. The divalent ions normally act as modifiers, whereas Sn$^{4+}$ ions do participate in the network. As the concentration increases beyond 3.0 mol%, the concentration of Sn$^{4+}$ ions that take part network forming positions prevail over the Sn$^{2+}$ ions. The increase of intensity of symmetrical bands of phosphate structural units in the IR spectra of the glasses S$_5$E and S$_7$E, in fact supports this view point.
Fig. 4.7 Energy level diagram of Li₂O–PbO–P₂O₅–SnO₂–Er₂O₃ glass with 3.0 mol% of SnO₂.
The Sn\textsuperscript{4+} ions (with simultaneous presence of low proportions of Sn\textsuperscript{2+} modifying ions) mostly interlocked with PO\textsubscript{4}\textsuperscript{3-} units and thereby there is a possibility for the increase of non-radiative emission transitions of Sn\textsuperscript{4+} ions. This may be the reason why there is a decrease in the intensity of orange emission either in the SnO\textsubscript{2} singly doped or co-doped with Er\textsuperscript{3+} ions when the concentration of SnO\textsubscript{2} is increased beyond 3.0 mol% of SnO\textsubscript{2}.

To throw more light in understanding energy transfer from Sn\textsuperscript{4+} to Er\textsuperscript{3+} for getting intense orange emission as shown in energy level diagram (Fig. 4.7), we have presented the rate equations of emission probabilities for various emission levels.

For Er\textsuperscript{3+} energy levels:

\[
\frac{dN_1}{dt} = \omega_{0,1}N_0 + \omega_{9,1}N_9 + \omega_{10,1}N_{10} + \varphi \sigma_{3,1}N_3 - \varphi \sigma_{1,1}N_1 - (q_1 + \tau_1^{-1})N_1
\]  
(4.1)

\[
\frac{dN_2}{dt} = \omega_{9,2}N_9 + \omega_{10,2}N_{10} + \omega_{11,2}N_{11} + \varphi \sigma_{2,2}N_2 - \varphi \sigma_{2,1}N_2 - (q_2 + \tau_2^{-1})N_2
\]  
(4.2)

\[
\frac{dN_3}{dt} = \varphi \sigma_{1,3}N_1 - \varphi \sigma_{3,1}N_3 - (q_3 + \tau_3^{-1})N_3
\]  
(4.3)

\[
\frac{dN_4}{dt} = \omega_{11,4}N_{11} - \omega_{4,4}N_4 - (q_4 + \tau_4^{-1})N_4
\]  
(4.4)

\[
\frac{dN_5}{dt} = \omega_{11,5}N_{11} - \omega_{5,0}N_5 - (q_5 + \tau_5^{-1})N_5
\]  
(4.5)

\[
\frac{dN_6}{dt} = \omega_{11,6}N_{11} - \omega_{6,0}N_6 - (q_6 + \tau_6^{-1})N_6
\]  
(4.6)
\[
\frac{dN_7}{dt} = \omega_{1,7}N_{11} - \omega_{7,0}N_7 - (q_7 + \tau_7^{-1})N_7 \quad (4.7)
\]
\[
\frac{dN_8}{dt} = \omega_{1,8}N_{11} - \omega_{8,0}N_8 - \omega_{8,1}N_8 - (q_8 + \tau_8^{-1})N_8 \quad (4.8)
\]
\[
\frac{dN_9}{dt} = \omega_{1,9}N_{11} - \omega_{9,1}N_9 - \omega_{9,2}N_9 - (q_9 + \tau_9^{-1})N_9 \quad (4.9)
\]
\[
\frac{dN_{10}}{dt} = \omega_{1,10}N_{11} - \omega_{10,0}N_{10} - \omega_{10,1}N_{10} - \omega_{10,2}N_{10} - (q_{10} + \tau_{10}^{-1})N_{10} \quad (4.10)
\]
\[
\frac{dN_{11}}{dt} = \varphi\sigma_{0,11}N_0 + \varphi\sigma_{1,11}N_1 + \varphi\sigma_{2,11}N_2 + \omega_{12,11}N_{12} - \omega_{11,2}N_{11} - (q_{11} + \tau_{11}^{-1})N_{11} - \omega_{1,10}N_{11} - \omega_{1,9}N_{11} - \omega_{1,8}N_{11} - \omega_{1,7}N_{11} - \omega_{1,6}N_{11} - \omega_{1,5}N_{11} - \omega_{1,4}N_{11} \quad (4.11)
\]
\[
\frac{dN_{12}}{dt} = \varphi\sigma_{3,12}N_3 - \varphi\sigma_{12,11}N_{12} - (q_{12} + \tau_{12}^{-1})N_{12} \quad (4.12)
\]

For \( \text{Sn}^{4+} \) energy levels:
\[
\frac{dN_{1'}}{dt} = \omega_{1,1'}N_{11} - \varphi\sigma_{1',1}N_{1'} - \omega_{1',0}N_{1'} - (q_{1'} + \tau_{1'}^{-1})N_{1'} \quad (4.13)
\]
\[
\frac{dN_{2'}}{dt} = \omega_{1,2'}N_{11} - \varphi\sigma_{2',2}N_{2'} - \omega_{2',0}N_{2'} - (q_{2'} + \tau_{2'}^{-1})N_{2'} \quad (4.14)
\]
\[
\frac{dN_{3'}}{dt} = \omega_{1,3'}N_{11} - \varphi\sigma_{3',3}N_{3'} - \omega_{3',0}N_{3'} - (q_{3'} + \tau_{3'}^{-1})N_{3'} \quad (4.15)
\]

In the Eqs. (4.1) to (4.15) \( N_i \) represents the population of \( i^{th} \) excited level, \( \omega_{i,j} \) represents \( i \rightarrow j \) transition probability, \( \tau_i \) and \( q_i \) respresent life time
and quenching rates of \(i^{th}\) level, respectively. Pumping flux is denoted by \(\varphi\), whereas the absorption cross-section is symbolized by \(\sigma_{ij}\).

To evaluate the intensity of orange emission of \(\text{Er}^{3+}\) ions from the levels \(^4\text{G}_{11/2}, ^4\text{F}_{3/2}\) and \(^4\text{F}_{5/2}\) the equations are solved under the steady state conditions, by assuming depopulation rate of an intermediate level is negligible with respect to the spontaneous and non-radiative emission from the level under consideration. With this we obtain

\[
N_{11} = \frac{\varphi^4 \sigma_{0,11} \sigma_{1,11} \sigma_{2,11} \sigma_{3,12} \omega_{2,11} N_0 N_1 N_2 N_3}{(q_{12} + \tau_{12}^{-1})(q_{11} + \tau_{11}^{-1})(q_3 + \tau_3^{-1})(q_2 + \tau_2^{-1})(q_1 + \tau_1^{-1})} \tag{4.16}
\]

\[
N_{9} = \frac{\varphi^4 \sigma_{0,11} \sigma_{1,11} \sigma_{2,11} \sigma_{3,12} \omega_{1,19} N_0 N_1 N_2 N_3}{(q_{11} + \tau_{11}^{-1})(q_9 + \tau_9^{-1})(q_3 + \tau_3^{-1})(q_2 + \tau_2^{-1})(q_1 + \tau_1^{-1})} \tag{4.17}
\]

\[
N_{8} = \frac{\varphi^4 \sigma_{0,11} \sigma_{1,11} \sigma_{2,11} \sigma_{3,12} \omega_{1,19} N_0 N_1 N_2 N_3}{(q_{11} + \tau_{11}^{-1})(q_8 + \tau_8^{-1})(q_3 + \tau_3^{-1})(q_2 + \tau_2^{-1})(q_1 + \tau_1^{-1})} \tag{4.18}
\]

Then the intensities three probable orange emission transitions viz., \(^4\text{G}_{11/2} \rightarrow ^4\text{I}_{11/2}, ^4\text{F}_{3/2} \rightarrow ^4\text{I}_{13/2}\) and \(^4\text{F}_{5/2} \rightarrow ^4\text{I}_{13/2}\) are:

\[
I_{11} = \frac{\hbar \omega_{12} \varphi^4 \sigma_{0,11} \sigma_{1,11} \sigma_{2,11} \sigma_{3,12} \omega_{1,12} N_0 N_1 N_2 N_3}{(q_{12} + \tau_{12}^{-1})(q_{11} + \tau_{11}^{-1})(q_3 + \tau_3^{-1})(q_2 + \tau_2^{-1})(q_1 + \tau_1^{-1})} \tag{4.19}
\]

\[
I_{9} = \frac{\hbar \omega_{19} \varphi^4 \sigma_{0,11} \sigma_{1,11} \sigma_{2,11} \sigma_{3,12} \omega_{1,9} N_0 N_1 N_2 N_3}{(q_{11} + \tau_{11}^{-1})(q_9 + \tau_9^{-1})(q_3 + \tau_3^{-1})(q_2 + \tau_2^{-1})(q_1 + \tau_1^{-1})} \tag{4.20}
\]

\[
I_{8} = \frac{\hbar \omega_{19} \varphi^4 \sigma_{0,11} \sigma_{1,11} \sigma_{2,11} \sigma_{3,12} \omega_{1,9} N_0 N_1 N_2 N_3}{(q_{11} + \tau_{11}^{-1})(q_8 + \tau_8^{-1})(q_3 + \tau_3^{-1})(q_2 + \tau_2^{-1})(q_1 + \tau_1^{-1})} \tag{4.21}
\]

Similarly expressions for the intensities of \(\text{Sn}^{4+}\) ion \(S_1 \rightarrow S_0\) emissions can be written as
From the Eqs. (4.19) to (4.23), it is clear that the intensities of all possible orange emission lines are proportional to the radiative life times of the upper levels. The life time $\tau$ for $^4G_{11/2}$ level (either calculated or measured) is the largest for the glass $S_3E$ (Table 4.5); hence the intensity of the orange emission is expected to be the highest for this glass.

As has been discussed above the intensity of orange emission is strongly dependent on the energy transfer efficiency ($\eta_{\text{eff}}$) from Sn$^{4+} \rightarrow$Er$^{3+}$ which can be expressed as [66].

$$\eta_{\text{eff}} = 1 - \frac{\tau_{\text{Sn+Er}}}{\tau_{\text{Sn}}}$$  \hspace{1cm} (4.26)

The obtained values of $\eta_{\text{eff}}$ for the orange emission ($^4G_{11/2} \rightarrow ^4I_{11/2}$) were plotted as a function of SnO$_2$ concentration (inset of Fig. 4.5). The plot exhibits the maximum at 3.0 mol% of SnO$_2$. This observation suggests maximum
energy transfer efficiency possibility for getting intense orange emission for the glass mixed with 3.0 mol% of SnO$_2$.

4.5 Conclusions

The luminescence characteristics of Er$^{3+}$ and Sn$^{4+}$ ions co-doped Li$_2$O–PbO–P$_2$O$_5$ glasses have been investigated as a function of SnO$_2$ concentration. A significant enhancement in the intensity of orange emission corresponding to $^4G_{11/2} \rightarrow ^4I_{11/2}$ has been observed due to co-doping and about 3.0 mol% of SnO$_2$ is found to be the optimal concentration for the enrichment of this emission. The reasons for this enhancement have been analyzed in the light of varying environment of rare earth ions due to the variations in the content of SnO$_2$. The energy transfer mechanism from Sn$^{4+}$ ($S_1 \rightarrow S_0$) to Er$^{3+}$ ($^4G_{11/2} \rightarrow ^4I_{11/2}$) is quantitatively discussed with the rate equations.
References


