Chapter 5

The role of environment on the absorption and emission characteristics of Yb$^{3+}$ ions in lead aluminum silicate glasses

The glasses of the composition (40-x) PbO–(5+x) Al$_2$O$_3$–54 SiO$_2$– 1.0 Yb$_2$O$_3$ (in mol%) with x value ranging from 5 to 10 have been synthesized. The IR spectral studies of these glasses have indicated that there is a gradual transformation of Al$^{3+}$ ions from tetrahedral to octahedral with increase in the concentration of Al$_2$O$_3$ in the glass network. The optical absorption and luminescence spectra have exhibited bands due to $^2$F$_{7/2} \rightarrow ^2$F$_{5/2}$ and $^2$F$_{5/2} \rightarrow ^2$F$_{7/2}$ transitions, respectively. From these spectra, the absorption and emission cross-sections and fluorescence lifetime of Yb$^{3+}$ ions have been evaluated. Quantitative analysis of these data indicated a decreasing radiative trapping and increasing fluorescence lifetime of Yb$^{3+}$ ions with increase in the concentration of Al$_2$O$_3$. This has been explained in terms of structural variations in the vicinity of Yb$^{3+}$ ions due to variation in the concentration of Al$_2$O$_3$ in the glass network.
The role of environment on the absorption and emission characteristics of Yb$^{3+}$ ions in lead aluminum silicate glasses

5.1 Introduction

Aluminosilicate glasses possess higher values of glass transition temperatures, greater hardness and elastic moduli and chemical durability than many other glass systems [1, 2]. These glasses are being widely used as low cost optical connectors, dielectric and sealant materials for solid oxide fuel cells, in actinide immobilization as laser ion hosts in optical lenses, seals, and as in vivo radiation delivery vehicles [3-8].

In the glass network of aluminium silicates there is a possibility for the cross linking (like Al-O-Si) between Al tetrahedra and Si tetrahedra. The presence of such linkages improves the densification and mechanical strength of aluminosilicate glasses [9]. Depending up on the composition of the glass, aluminium ions may also participate in the glass network with AlO$_5$ and AlO$_6$ structural units and influence physical properties of aluminium silicate glasses to a large extent. The structural role of ions in aluminosilicate glasses is determined by the size (which controls their coordination number) and by the charge (which controls the strength of the bonds formed to the neighboring anions) of the constituents of the glass composition. The rare earth ions, depending on their size and the constituents of the glass network are found to
have co-ordination number 6-12. The bonds between rare earth ions and surrounding oxygens are relatively weaker in the glass network when compared to Al-O or Si-O bonds [4].

Yb$^{3+}$ doped laser materials are of interest in lasers for next generation nuclear fusion [10, 11]. These materials can be used as a gain media in the microchip laser at high doping levels [12]. The Yb$^{3+}$ energy level structure is particularly simple, consisting of a ground state manifold, $^2F_{7/2}$, Stark-split into four sublevels and an excited-state manifold, $^2F_{5/2}$, Stark split into three sublevels. Thus, excited state absorption at both the pump and signal wavelengths, is absent. The upper manifold lies approximately 10,500 cm$^{-1}$ above the ground level [13]. This large energy gap precludes significant multiphonon nonradiative decay [14] and the broad absorption spectrum of this ion due to Stark-splitting, permits a wide choice of pump wavelengths. Broad emission spectrum of Yb$^{3+}$ ion and its large saturation fluence permits lasing to be achieved over a wide range of wavelengths (1–1.2 µm) and makes it an attractive medium for the generation and amplification of ultrashort pulses [15, 16]. Further, these ions do not show excited state absorption, cross-relaxation process, upconversion or any other internal mechanism that can reduce the effective laser cross section. A considerable number of recent studies on emission properties Yb$^{3+}$ ions in different glass systems are available in the
literature [17, 18]. Additionally, the Yb\(^{3+}\) ion is also being used extensively as an effective sensitizer of energy transfer for infrared-to-visible up-conversion and infrared lasers [19].

In general, an efficient host material for laser operation should exhibit large emission cross section to provide high gain, long fluorescence lifetime to minimize pump losses incurred from spontaneous emission, large absorption cross section at the pump wavelength, good photothermal properties, absence of scattering centers and the possibility to incorporate high concentration of rare earth Yb\(^{3+}\) ions. The PbO–Al\(_2\)O\(_3\)–SiO\(_2\) glass materials possess relatively high refractive index and are transparent up to the far infrared wavelengths [20, 21] and allow incorporating the rare earth dopants in the desired site positions and offer suitable environment for hosting Yb\(^{3+}\) ion to give out high luminescence efficiency in the NIR region.

The main objective of this study is to synthesize PbO–Al\(_2\)O\(_3\)–SiO\(_2\): Yb\(_2\)O\(_3\) glasses with different contents of Al\(_2\)O\(_3\) and to investigate the influence of variation in the concentration of Al\(_2\)O\(_3\) on the fluorescence characteristics of Yb\(^{3+}\) ions in the glasses, which are important for the optical triggers and laser gain media. The study is further intended to evaluate the emission cross section of \(^2\!F_{5/2} \rightarrow ^2\!F_{7/2}\) luminescence transition of Yb\(^{3+}\) ions and to examine the influence of aluminium ions on this parameter. The IR spectral studies have
also been included so as to have some pre structural information on the glass network.

A particular composition (40-x) PbO–(5+x) Al₂O₃–54 SiO₂: 1.0 Yb₂O₃ (in mol %) with three values of x ranging from 0 to 5.0, is chosen for this study; the samples are labeled as AY₅ (x=0), AY₈ (x=3), AY₁₀ (x = 5).

5.2. Brief review of previous work on Yb³⁺ doped glasses

A brief review of recent studies on different glass systems doped with Yb³⁺ ions is presented here.

Fang et al. [22] have reported energy transfer and 1.8 µm emission in Yb³⁺/Tm³⁺ co-doped bismuth germanate glass. In this study it was reported that the energy transfer is assisted by energy migration among donor ions. Chen et al. [23] have reported the near infrared luminescence properties of Yb³⁺–Er³⁺ co-doped fluorophosphate glasses. In this study it was shown that the glass co-doped with 6 mol% YbF₃ and 2 mol% ErF₃ exhibited magnificent luminescence properties for telecommunication application. Kochanowicz et al. [24, 25] have reported the influence of temperature on upconversion luminescence in tellurite glass co-doped with Yb³⁺/Er³⁺ and Yb³⁺/Tm³⁺ and Nd³⁺/Yb³⁺. From this study it was concluded that the influence of temperature on FIR upconversion emission spectra of the thermally coupled Er³⁺: ⁶H₁₁/₂ and ⁴S₃/₂ levels enabled to achieve maximum sensitivity of 0.0036 °C⁻¹ at 225 °C. Lin et al. [26] have reported
spectroscopic and thermal properties of Yb$^{3+}$ doped TeO$_2$–Bi$_2$O$_3$–Nb$_2$O$_5$ based tellurite glasses. The results of these studies have showed that the glass with 15 mol% Nb$_2$O$_5$ possesses the largest emission cross-section of 1.36 pm$^2$, the longest fluorescence lifetime of 0.96 ms and the highest gain coefficient of 1.31 ms pm$^2$. Balaji et al. [27] have studied influence of Al$_2$O$_3$ on structural, elastic and thermal properties of Yb$^{3+}$doped Ba-La-Tellurite glass. The elastic properties of the glass revealed an improved rigidity of the glass network on addition of Al$_2$O$_3$. Yb$^{3+}$ fluorescence dynamics demonstrated that, Al$_2$O$_3$ inclusion helps in [28] restraining the detrimental radiation trapping of $\sim 1 \mu$ m emission. Zmojda et al. studied thermal and structural properties of germanate glasses co-doped with Yb$^{3+}$/Tb$^{3+}$ ions. Their studies indicated highest upconversion emission intensity in the germanate glass co-doped with 0.7Yb$_2$O$_3$/0.7Tb$_2$O$_3$.

Qiaoet et al. [29] have prepared Yb$^{3+}$ doped transparent glass ceramics containing cubic SrF$_2$ nanocrystals and studied near infrared emission characteristics. From the analysis of these results, the authors have suggested that Yb$^{3+}$ ion can be used as an efficient up-conversion sensitizer for other rare earth ions. Pan et al. [30] have fabricated Nd$^{3+}$/Yb$^{3+}$ co-doped TiO$_2$–La$_2$O$_3$ glasses modified by ZrO$_2$ by containerless method and studied the emission the energy transfer from Yb$^{3+}$ to Nd$^{3+}$ ions properties. From these studies the
authors have concluded that the up-conversion efficiency can be enhanced by increasing of ZrO$_2$ content in the glass matrix.

Xia et al. [31] have demonstrated a novel method for preparing bulk Yb$^{3+}$-doped fused silica glass for high power laser by solution doping and high temperature melting technique. and studied the absorption and fluorescence emission spectra. At the end the authors have concluded that this glass is of interest as a new potential laser material serving as the core of photonic crystal fibers (PCF) for high power fiber laser applications. Sang et al. [32] have investigated the influence of Yb$^{3+}$ content on the luminescence emission in phosphate glasses. Their results have indicated that the optimal mole fraction of Yb$_2$O$_3$ is 4% for getting high luminescence efficiency. Tian et al. [33] have designed to achieve high-gain C-band waveguide amplifiers with integrated configuration, bent channel structures (S-, U-, and F-bend) based on buried Er$^{3+}$/Yb$^{3+}$ co-doped phosphate glass waveguide channel fabricated by field-assisted annealing (FAA). The simulation results of these studies have indicated that the bent structure designing is beneficial in obtaining high signal gain in buried Er$^{3+}$/Yb$^{3+}$ co-doped phosphate glass waveguides. Shyu et al. [34] have studied the effects of Er$_2$O$_3$ (0-8 mol%) doping and Er$_2$O$_3$ and Yb$_2$O$_3$ codoping (total 1-7 mol%) on the absorption cross-section, PL, and upconversion intensities of the SnO–P$_2$O$_5$ glass. They have concluded that an increase in the
Yb₂O₃ content caused the reduction of PL intensity and this they have explained in terms of the APTE upconversion effect. Sahar et al. [35] have reported detailed XRD and IR studies of Yb³⁺ doped tellurite glasses.

Hu et al. [36] have explored optical, thermal, and structural properties Yb³⁺ doped zinc aluminum silicate phosphate glasses. In their studies it was reported that maximum fluorescence can be obtained when the concentration of Yb₂O₃ is 7 mol%. Han et al. [37] have investigated the luminescence characteristics of Yb³⁺ and Al³⁺ co-doped silicate glasses. Their results have indicated that the co-doped silica-based glass has good thermal stability and large power threshold and found to be an ideal gain medium for large power photonic crystal fiber lasers. NengLi Dai et al. [38] have studied the spectroscopic properties of Yb³⁺ doped silicate glasses. Their results indicated that these glasses are potential materials for double cladding ytterbium fiber laser application. Sen et al. [39] have investigated the structural aspects of clustering of Yb³⁺ ions and the paramagnetic behavior in GeO₂ glasses doped Yb₂O₃ using time-domain electron paramagnetic resonance (EPR) spectroscopic techniques. Martin et al. [40] have studied the intense Tm³⁺ blue up-conversion emission in Tm³⁺–Yb³⁺ co-doped fluoroindate glasses under direct excitation into Tm³⁺ ions with a diode laser at 796 nm. The dependence of the intensity of this up-conversion emission on the Tm³⁺ and Yb³⁺
concentration has been studied in order to determine the optimum ion concentrations and the involved mechanisms. Plucinski et al. [41] have reported the luminescence and absorption at wavelengths 600–1000 nm from Yb$^{3+}$ ions embedded in PbO–Bi$_2$O$_3$–Ga$_2$O$_3$–BaO glass hosts at room and helium liquid temperatures. They found that excited pulsed XeII laser light ($\lambda = 714$ nm) gives substantial luminescence at 980 nm with efficiency up to 63.2%.

Liu et al. [42] have studied the effects of Al$_2$O$_3$, Yb$_2$O$_3$, Er$_2$O$_3$ and OH$^-$ on spectral properties of P$_2$O$_5$–Na$_2$O–SrO–Al$_2$O$_3$–Yb$_2$O$_3$–Er$_2$O$_3$ erbium phosphate glass. Mao et al. [43] have investigated absorption spectra and fluorescence spectra of Yb$^{3+}$ in phosphate glass between 8 and 300 K. Their results shown that there was an abnormal absorption line in absorption spectra at low temperatures, and the blue shift of the absorption peaks was discovered with the increase in temperature. Kassab et al. [44] have studied the spectroscopic properties of lead fluoroborate and heavy metal oxide glasses doped with Yb$^{3+}$ ions. Murata et al. [45] have investigated the matrix effect on local structure surrounding Yb$^{3+}$ ions and spontaneous emission probability in oxide glasses. Guinhos et al. [46] have studied the compositional dependence of up-conversion process in Tm$^{3+}$–Yb$^{3+}$ co-doped oxyfluoride glasses and glass-ceramics. Schaudel et al. [47] have observed emission centred around 500 nm under near infrared excitation in Yb$^{3+}$ doped borosilicate, aluminosilicate and
phosphate glasses. The lifetime measurements and convolution of infrared luminescence spectra confirm the cooperative nature of this visible emission. Jiang et al. [48] have determined the emission cross-section for the $^{2}F_{5/2} \rightarrow ^{2}F_{5/2}$ transition of Yb$^{3+}$ from absorption and emission measurements of tellurite glasses at room temperature. They have also determined the emission cross section for this ion in tellurogermanate glasses [49]. Tanabe et al. [50] have investigated the concentration and temperature dependences of lifetime of $^{2}F_{5/2}$ level in tellurite glasses doped with up to 6 mol% Yb$_2$O$_3$. Martin et al. [51] have analyzed the mechanisms and dynamics of the upconversion emissions in Yb$^{3+}$–Ho$^{3+}$-doped fluorindate glasses by exciting at 975 nm.

Yin et al. [52] have studied the emission properties of Yb$^{3+}$ doped fluorophosphates glasses. They also determined the emission cross section of Yb$^{3+}$ in glasses by the reciprocity method [53]. Sampaio et al. [54] have studied the thermo-mechanical and optical properties of calcium aluminosilicate glasses doped with Er$^{3+}$ and Yb$^{3+}$. Santos et al. [55] have reported up-conversion luminescence and thermal effects in Pr$^{3+}$/ Yb$^{3+}$ and Er$^{3+}$/ Yb$^{3+}$ co-doped 60TeO$_2$–10GeO$_2$–10K$_2$O–10Li$_2$O–10Nb$_2$O$_5$ tellurite glasses excited by CW infrared radiation at 1.064 μm. Tanabe et al. [56] have studied the energy transfer and 1.3 μm emission in Pr$^{3+}$/ Yb$^{3+}$ co-doped tellurite glasses. Zhang et
al. [57] have evaluated the spectroscopic properties of Yb\(^{3+}\) in tetraphosphate glasses.

Zmojda et al. [58] have reported energy transfer in TeO\(_2\)–GeO\(_2\)–PbO–PbF\(_2\)–BaO–Nb\(_2\)O\(_5\)–LaF\(_3\) glass system doped with Yb\(^{3+}\)/Tm\(^{3+}\) ions. These authors have discussed process of non-resonant energy transfer mechanism based on up-conversion between Yb\(^{3+}\) and Tm\(^{3+}\) ions. Yu et al. [59] have reported enhancement of up-conversion luminescence properties in Yb\(^{3+}\)/Tm\(^{3+}\)/Er\(^{3+}\) tri-doped transparent oxyfluoride tellurite glass ceramics. In these studies the authors have observed that three-color up-conversion luminescence intensities by 980 nm pumping increases significantly due to the heat treatment. Zhang et al. [60] have reported abnormal up-conversion luminescence from Yb\(^{3+}\) doped and Tb\(^{3+}\)/Yb\(^{3+}\) co-doped high silica glasses induced by intrinsic optical bistability. Gong et al. [61] have reported up-conversion color tunability and white light generation in Tm\(^{3+}\)/Ho\(^{3+}\)/Yb\(^{3+}\) doped aluminum germanate glasses. Their studies have revealed that upconversion color tunability via pump power adjustment will promote the development of three-dimensional solid-state displays and upconversion illumination devices. Zhang et al. [62] have investigated temperature characteristics and splitting of photoluminescence spectra of Er\(^{3+}\)/Yb\(^{3+}\)/Tm\(^{3+}\) co-doped borosilicate glasses. Their studies have indicated that the photoluminescence spectra take on marked
splitting at room temperature, but the splitting become weaker at high temperature. Silva et al. [63] have reported highly efficient up-conversion emission and luminescence switching from Yb$^{3+}$/Tm$^{3+}$ co-doped water-free low silica calcium aluminosilicate glass. From these studies the authors have concluded that this switching mechanism could be used in the development of sensors and networks for optical processing and optical communications.

Terra et al. [64] have reported the results of spectroscopic investigations of OH- influence on near-infrared fluorescence quenching of Yb$^{3+}$/Tm$^{3+}$ co-doped sodium-metaphosphate glasses. From these studies, the authors have concluded that samples prepared in nitrogen atmosphere exhibit higher fluorescence quantum efficiency than those prepared in air, and this feature is specially noted in the near-infrared region, where the interaction with the OH-radicals is more pronounced. Watekar et al. [65] have reported linear and non-linear optical properties of Yb$^{3+}$/Tm$^{3+}$ co-doped alumino-silicate glass prepared by sol-gel method. Qiu et al. [66] have investigated blue up-conversion luminescence and energy transfer process in Nd$^{3+}$–Yb$^{3+}$–Tm$^{3+}$ co-doped ZrF$_4$ based glasses. In their study it was demonstrated that the energy on the Tm$^{3+}$:1$^G_4$ level was back-transferred to Nd$^{3+}$ in the Nd$^{3+}$ high-concentration region, quenching the up-conversion luminescence.
5.3. Results

From the measured values of density $d$ and calculated average molecular weight $\overline{M}$, various physical parameters such as ytterbium ion concentration $N_i$ and mean ytterbium ion separation $r_i$ of these glasses are evaluated using the conventional formulae [67] and are presented in Table 5.1.

Table 5.1 Various physical parameters of PbO–Al$_2$O$_3$–SiO$_2$ glasses doped with Yb$_2$O$_3$.

<table>
<thead>
<tr>
<th>Property</th>
<th>Sample →</th>
<th>AY$_1$</th>
<th>AY$_2$</th>
<th>AY$_3$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Density $d$ (g/cm$^3$)</td>
<td></td>
<td>4.6302</td>
<td>4.6152</td>
<td>4.5699</td>
</tr>
<tr>
<td>Refractive index ($n_d$)</td>
<td></td>
<td>1.730</td>
<td>1.720</td>
<td>1.718</td>
</tr>
<tr>
<td>Yb$^{3+}$ ion conc. $N_i$ ($10^{20}$ ions/cm$^3$)</td>
<td></td>
<td>2.13</td>
<td>2.18</td>
<td>2.20</td>
</tr>
<tr>
<td>Polaron radius $r_p$ (Å)</td>
<td></td>
<td>6.74</td>
<td>6.69</td>
<td>6.67</td>
</tr>
<tr>
<td>Inter-ionic distance $r_i$ (Å)</td>
<td></td>
<td>16.74</td>
<td>16.60</td>
<td>16.55</td>
</tr>
<tr>
<td>Field strength $F_i$ ($10^{15}$ cm$^{-2}$)</td>
<td></td>
<td>0.66</td>
<td>0.67</td>
<td>0.675</td>
</tr>
<tr>
<td>Molar refraction ($R_m$)</td>
<td></td>
<td>11.27</td>
<td>10.88</td>
<td>10.76</td>
</tr>
<tr>
<td>Property</td>
<td>Sample →</td>
<td>AY$_1$</td>
<td>AY$_2$</td>
<td>AY$_3$</td>
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</table>
The Infrared spectra of PbO-Al₂O₃-SiO₂: Yb₂O₃ glasses (Fig. 5.1) exhibited prominent bands at about 1025 cm⁻¹ due to Si-O-Si asymmetric vibrations, 760 cm⁻¹ due to Si-O-Si symmetric vibrations and about 450 cm⁻¹ due to Si-O-Si rocking motion [68, 69]. With increase in the concentration of Al₂O₃, the intensity of the band due to Si-O-Si asymmetric vibrations and band due to Si-O-Si rocking motion increases, the intensity of the band due to Si-O-Si symmetric vibrations decreases. Incidentally, the vibrational frequency of Al-O stretching in AlO₄ structural units is found to exhibit band at about 750 cm⁻¹ and band due to AlO₆ structural units observed at 450 cm⁻¹ [70]. Hence, it is quite likely that tetrahedral Al ion to cross link with the neighbouring Si-O-Si structural units and form Al-O-Si linkages. The band due to the vibrations of PbO₄ structural units about 470 cm⁻¹ is also present in these glasses. The summary of the data on the positions of various bands observed in the IR spectra of PbO-Al₂O₃-SiO₂: Yb₂O₃ glasses is presented in Table 5.2.

Table 5.2 Summary of data on band positions (cm⁻¹) in IR spectra of PbO-Al₂O₃-SiO₂: Yb₂O₃ glasses

<table>
<thead>
<tr>
<th>Glass</th>
<th>Si-O-Si asymmetric</th>
<th>Si-O-Si symmetric/AlO₄ units</th>
<th>Si-O-Si rocking/AlO₆ units</th>
<th>PbO₄ units</th>
</tr>
</thead>
<tbody>
<tr>
<td>AY₅</td>
<td>1022</td>
<td>760</td>
<td>457</td>
<td>473</td>
</tr>
<tr>
<td>AY₈</td>
<td>1006</td>
<td>772</td>
<td>454</td>
<td>479</td>
</tr>
<tr>
<td>AY₁₀</td>
<td>998</td>
<td>784</td>
<td>450</td>
<td>481</td>
</tr>
</tbody>
</table>
Fig. 5.1 IR spectra of PbO-Al₂O₃-SiO₂: Yb₂O₃ glasses.

The optical absorption spectra of PbO–Al₂O₃–SiO₂: Yb₂O₃ glasses (Fig. 5.2 and its inset) measured at room temperature in the spectral wavelength range 300-1200 nm have exhibited an absorption band corresponding to the transition [71]: $^2F_{7/2}$ (the ground state of Yb$^{3+}$ ion)$\rightarrow^2F_{5/2}$ with two distinct peaks between 950 to 1000 nm.
Fig. 5.2 Optical absorption spectra of PbO-Al\textsubscript{2}O\textsubscript{3}-SiO\textsubscript{2}: Yb\textsubscript{2}O\textsubscript{3} glasses (a) in the visible region (b) in the NIR region.

From the observed absorption edges, we have evaluated the optical band gaps ($E_0$) of these glasses by drawing Tauc plot between $(\alpha \ h \ \omega)^{1/2}$ and $h \ \omega$ as per the equation:

$$\alpha(\omega) \ h \ \omega = C \ (h \ \omega - E_0)^2$$  \hspace{1cm} (5.1)

Fig. 5.3 represents the Tau plots of all these glasses in which a considerable part of each curve is observed to be linear. From the extrapolation of the linear portion of these curves, the values of optical band gap ($E_0$) obtained for PbO–Al\textsubscript{2}O\textsubscript{3}–SiO\textsubscript{2}: Yb\textsubscript{2}O\textsubscript{3} glasses are presented in Table 5.1. The
value of optical band gap is found to decrease with increase in the concentration of Al$_2$O$_3$ (inset of Fig. 5.3).

Fig. 5.3 Tauc plot for PbO-Al$_2$O$_3$-SiO$_2$: Yb$_2$O$_3$ glasses and inset shows the variation of optical band gap with the concentration of Al$_2$O$_3$.

The emission spectra (Fig. 5.4) recorded at room temperature of PbO–Al$_2$O$_3$–SiO$_2$: Yb$_2$O$_3$ glasses (excited at 970 nm) have exhibited strong emission bands at 990 nm due to $^2F_{5/2} \rightarrow ^2F_{7/2}$ transition. The spectral intensity and also the stoke shift are found to increase with the content of Al$_2$O$_3$ in the samples.
Fig. 5.4 Emission spectra of PbO-Al$_2$O$_3$-SiO$_2$: Yb$_2$O$_3$ glasses

\[ ^{2}F_{5/2} \rightarrow ^{2}F_{7/2} \]
5.4. Discussion

Among various constituents of PbO-Al₂O₃-SiO₂: Yb₂O₃ glass system, SiO₂ is one of the most common glass formers and participates in the glass network with tetrahedral [SiO₄/2]⁰ units and all the four oxygens in SiO₄ tetrahedral are shared. Normally the modifier PbO, break the Si–O–Si linkage and cost to form Si–O termination. Thus, the structure is depolymerised or modified. The modification, results in the formation of metasilicates, pyrosilicates, and orthosilicates in the order: [SiO₄/2]⁰, [SiO₃/2]⁻, [SiO₂/2]²⁻, [SiO₁/2]³⁻, and [SiO⁴/2]⁴⁻ which are designated as Q⁴, Q³, Q², Q¹, and Q⁰, respectively [72]. Earlier nuclear magnetic resonance (NMR) studies on aluminum silicate glasses have indicated that aluminum ions occupy mainly tetrahedral (AlO₄) and octahedral (AlO₆) sites [73] as per the following relation: 2Al₂O₃ → [Al³⁺]ₙ + 3[AlO₄/2]ₜ. The AlO₄ tetrahedrons may enter the glass network and alternate with SiO₄ tetrahedrons.

Hence PbO-Al₂O₃-SiO₂ glass network is expected to be composed of three-dimensional aluminosilicate structural units. The lead ions insert in the cavities and act as charge balancers compensating for the negative charge due to the substitution of Si by Al. Owing to similarities in the nature of Si–O and Al–O bonds as well as close values of Al and Si atomic masses, the band due to Al–O (aluminium in tetrahedral coordination) and Si–O vibrations in the NIR
spectra are expected to be very close or may be merged. The ytterbium ion is expected to be coordinated by three such SiO$_4$/AlO$_4$ tetrahedral ligands as shown in the Fig.5.5.

Fig. 5.5 A structural fragment of cross linked Yb$^{3+}$ octahedron with SiO$_4$ and AlO$_4$ structural units.

In the IR spectra of all glasses the band due to AlO$_4$ structural units merged with band due to tetrahedral silicate groups and exhibited remarkable intensity. As the concentration of Al$_2$O$_3$ increases, the intensity of this band is observed to decrease. The band characteristic for the vibrations of Al–O bonds (aluminium in octahedral coordination) is found to be more intense in the spectrum of the glass mixed with 10 mol% of Al$_2$O$_3$. As the concentration of
Al₂O₃ is increased, the intensity of band due to Si-O-Si symmetric stretching vibrations is observed to decrease, whereas that of the bands due to Si–O–Si asymmetric vibrations, Si-O-Si rocking motions is increased. In other words the octahedral occupancy of aluminium ions increases gradually with increase in the concentration of Al₂O₃ in the glass network.

Thus we expect octahedrally coordinated Al³⁺ ions to weaken the glass network by breaking silicate chains similar to the role played by the conventional modifiers. Earlier NMR studies on aluminium silicate glasses have revealed that an oxygen triclusters (oxygen ion bonded to two [AlO₄] and one [SiO₄] or one [AlO₄] and two [SiO₄]) induce bonding defects in the glass containing Al₂O₃ and SiO₂ [74]. The edge-sharing [AlO₄] tetrahedra are observed to be associated with such oxygen triclusters. Thus the analysis of IR spectra points out that as the concentration of Al₂O₃ is raised in the glass matrix, there is in the structural depolymerization of the glass network. The decrease of optical band gap with the increase in the concentration of Al₂O₃ also supports this conclusion (inset of Fig.5.3).

The network of PbO-Al₂O₃-SiO₂: Yb₂O₃ glass containing different YbO₆ spheres can be assumed to be surrounded by aluminium of different cationic field strengths, polarizabilities. In view of this, the characteristics of Yb-O bond in the octahedral sphere are different for the glasses containing different
concentrations of $\text{Al}_2\text{O}_3$. In fact, we may expect strong distortion of the local structures in the vicinity of $\text{Yb}^{3+}$ ions in the glass containing high concentration of $\text{Al}_2\text{O}_3$, since the concentration of AlO$_6$ structural units is more in these glasses. Hence, the larger Stark splitting of $^2\!F_{5/2}$ and $^2\!F_{7/2}$ levels is expected in the absorption spectrum of these glasses.

The absorption band for the glass $\text{AY}_5$ seemed to be consisting of two distinct peaks at 954 nm and at 974 nm corresponding to the lowest sub-levels of $^2\!F_{7/2} \to ^2\!F_{5/2}$ transition; according to the crystal-field theory, the maximum allowed splitting number of $J = 5/2$ level is three hence we expect Stark splitting of $^2\!F_{5/2}$ level into three sublevels. In view of this absorption spectrum should be consisting of three broad spectral bands. Hence the weak broader band observed at shorter wavelength may be considered as a combination of two unresolved bands. Additionally, some disturbances caused by the interstitial embedding of the ions may also contribute to broadening of this band.

It is further notified that increasing concentration of $\text{Al}_2\text{O}_3$ in the glass matrix, the position of absorption band due to $^2\!F_{7/2} \to ^2\!F_{5/2}$ transition is shifted to slightly longer wavelengths and the absorption oscillator strength under given peak is found to be increased correlating to the $\text{Yb}^{3+}$ ion concentration. Such a red shift may indicate on a fact that the interaction between the ytterbium ions
and the surrounding ligand ions is weaker, leading a lower crystal-field splitting for $^2F_{7/2}$ and $^2F_{5/2}$ levels in these samples.

Emission cross section is evaluated from the absorption spectra using the relation [75, 76]:

$$\sigma_{em}(\lambda) = \sigma_{abs}(\lambda) \frac{Z_1}{Z_2} \exp\left(\frac{\epsilon - hc\lambda^{-1}}{kT}\right)$$  \hspace{1cm} (5.2)

where

$$\sigma_{abs}(\lambda) = 2.303 \frac{\log(I_0/I)}{NL} ,$$

h is the Planck’s constant, c is the speed of light, k is Boltzmann’s constant, L is the thickness of the sample, N is the concentration of Yb$^{3+}$ expressed as ion/cm$^3$, log(I$_0$/I) is the optical density, $\sigma_{abs}(\lambda)$ is the absorption cross section at wavelength $\lambda$, $\epsilon$ is the zero line energy (defined as the energy separation between the lowest crystal field levels of the upper and lower manifolds determined from the most intense absorption peak of Yb$^{3+}$), $Z_1$ and $Z_2$ represent the partition functions of the lower and upper levels respectively. For Yb$^{3+}$ in glasses, $Z_1/Z_2 \sim 1.2$ [77]. The values of $\sigma_{em}$ obtained for the samples under investigation are given in Table 5.3. The emission cross sections are found to be increasing with the increase in the concentration of Al$_2$O$_3$. 
Table 5.3 The spectroscopic parameters of PbO-Al₂O₃-SiO₂: Yb₂O₃ glasses

<table>
<thead>
<tr>
<th>Glass</th>
<th>λₚ (nm)</th>
<th>λₑ (nm)</th>
<th>σ_{abs} (λₚ) (10^{-19} cm²)</th>
<th>σ_{em} (λₑ) (10^{-18} cm²)</th>
<th>τᵣ (ms)</th>
<th>β_{min}</th>
</tr>
</thead>
<tbody>
<tr>
<td>AY₅</td>
<td>977</td>
<td>981</td>
<td>4.92</td>
<td>2.39</td>
<td>0.11</td>
<td>0.15</td>
</tr>
<tr>
<td>AY₈</td>
<td>980</td>
<td>987</td>
<td>2.86</td>
<td>1.39</td>
<td>0.22</td>
<td>0.17</td>
</tr>
<tr>
<td>AY₁₀</td>
<td>983</td>
<td>992</td>
<td>2.34</td>
<td>1.02</td>
<td>0.29</td>
<td>0.18</td>
</tr>
</tbody>
</table>

The shape of measured fluorescence spectrum of Yb³⁺ ions is strongly affected by radiation trapping [77, 78]. Hence, a large discrepancy between measured life time from fluorescence spectra and the intrinsic radiative lifetime is predicted. The calculated lifetime may therefore be considered as a reference in determining the true value of measured lifetime [78]. The error originated from the radiation trapping can be suppressed by evaluating radiative lifetime using [6]:

\[
\tau_r = \frac{\Lambda^4}{8 \pi cn^2 \int \sigma_{em}(\lambda) d\lambda},
\]

where \( \Lambda^4 = \int \lambda^4 g(\lambda) d\lambda \).

The calculated lifetimes of the studied glasses indicated gradual increase with increase in the concentration of Al₂O₃ (Table 3). The increasing Stokes shift observed with the increase in the content of Al₂O₃ indicates that there is a
decreasing radiative trapping; such decrease leads to an increase of radiative lifetime as observed.

The near coexistence of the absorption and emission indicates the possible reabsorption; the effect of the resonant absorption loss is indicated by the parameter $\beta_{\text{min}} (= \sigma_{\text{abs}}/(\sigma_{\text{abs}}+\sigma_{\text{em}}))$ which represents the minimum fraction of Yb ions that must be excited to balance the gain exactly with the ground-state absorption. The value of $\beta_{\text{min}}$ obtained for the studied glasses exhibited an increasing trend (Table 3) with the concentration of Al$_2$O$_3$; such trend indicates a gradual decrease of absorption loss with the increase in the concentration of Al$_2$O$_3$.

5.5 Conclusions

Optical absorption and luminescence spectra of Yb$^{3+}$ in PbO-Al$_2$O$_3$–SiO$_2$ as a function Al$_2$O$_3$ concentration have been investigated. From these spectra, the absorption and emission cross-sections and fluorescence lifetime of Yb$^{3+}$ ions have been evaluated. Quantitative analysis of these results has indicated a decreasing radiative trapping and increasing fluorescence lifetime of Yb$^{3+}$ ions in with increase in the concentration of Al$_2$O$_3$. This has been explained in terms of structural variations in the vicinity of Yb$^{3+}$ ions due to variation in the concentration of Al$_2$O$_3$ in the glass network.
References


