Chapter 3
The de-clustering influence of aluminium ions on the emission features of Nd$^{3+}$ ions in PbO-SiO$_2$ glasses

Nd$^{3+}$ doped lead alunino silicate glasses with varying concentration of Al$_2$O$_3$ (from 5 to 10 mol%) have been synthesized. The IR and Raman spectral studies of these glasses have indicated that there is a gradual increase in the depolymerization of the glass network with increase in the concentration of Al$_2$O$_3$. The optical absorption, luminescence spectra and fluorescence decay curves of these glasses were recorded at room temperature. From these studies, the radiative parameters viz., spontaneous emission probability $A$, the total emission probability, the radiative lifetime $\tau$, the fluorescent branching ratio $\beta$ of different transitions originated from $^4F_{3/2}$ level of Nd$^{3+}$ ions have been evaluated. A clear increase in the quantum efficiency and luminescence emission of the two prominent NIR bands of Nd$^{3+}$ ions viz., $^4F_{3/2} \rightarrow ^4I_{11/2, 13/2}$, is observed with increase in the concentration of Al$_2$O$_3$. The increase has been attributed to the possible admixing of wavefunctions of opposite parities and due to the declusterization of Nd$^{3+}$ ions by Al$^{3+}$ ions in the glass network.
The de-clustering influence of aluminium ions on the emission features of Nd$^{3+}$ ions in PbO-SiO$_2$ glasses

3.1 Introduction

Aluminium containing silicate 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 because of their high mechanical strength, high electrical resistance and chemical durability [1-6]. Apart from these, it has been widely accepted that aluminum ions produce greater enhancement on fluorescence of all rare-earth ions embedded in the host material [7]; the enhancement is ascribed to the association of RE ions with Al$^{3+}$ ions in different ways. The traditional interpretation, is that rare-earth ions will be preferably partitioned by Al$^{3+}$, forming Al–O–RE bonds, rather than sitting together to form RE–O–RE bonds. Subsequently, the spacing among RE ions becomes larger in the alumina-doped silica host rather than in the non–alumina-containing host and facilitates for the enhancement of fluorescence [8].

Among various rare earth ions, Nd$^{3+}$ ions are known due to their significant emission transitions in NIR region. Out of three prominent emission transitions of Nd$^{3+}$ ions, the emission at 1.3 µm ($^{4}F_{3/2} \rightarrow ^{4}I_{13/2}$) is more important because of its significant impact on telecommunications. 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 ions. Aluminium silicate glasses meet all the above requirements and can therefore be considered as the most suitable glass for hosting Nd\(^{3+}\) ion with zero dispersion and low loss at 1.3 \(\mu\)m wavelength. Majority of the studies on 1.3 \(\mu\)m emission are devoted to Pr\(^{3+}\) doped glasses, whereas most of the studies on Nd\(^{3+}\) emission are concentrated upon 1.06 \(\mu\)m emission [9-11].

Normally neodymium oxide is immiscible in silica glass and forms aggregates or clusters in which cross relaxation can give rise to non-radiative de-excitation of neodymium, resulting in very short lifetimes [12]. Different research groups working in the field of luminescence have shown that the non-radiative de-excitation of neodymium ions can be minimized and enhancement of fluorescence is possible when Al is used as a co-dopant in the glasses because aluminium ions disperse RE clusters, reduce inter-ionic interactions and fluorescence quenching [7].

In this study we have synthesized PbO–Al\(_2\)O\(_3\)–SiO\(_2\): Nd\(_2\)O\(_3\) glasses with different contents of Al\(_2\)O\(_3\) and investigated the influence of variation of Al\(_2\)O\(_3\)
concentration on \(^{4}F_{3/2} \rightarrow ^{4}I_{11/2,13/2}\) fluorescence transitions and fluorescence time decays of Nd\(^{3+}\) ions in the titled glasses and evaluated the mechanism responsible for the variation in the intensity of above transition in terms of interactions between Al\(^{3+}\) ions and Nd\(^{3+}\) ions. The IR and Raman spectral studies have also been included so as to assess some pre-structural information on the glass network.

A particular composition (40-x) PbO–(5+x) Al\(_2\)O\(_3\)–54SiO\(_2\): 1.0 Nd\(_2\)O\(_3\) (in mol\%) with three values of x ranging from 0 to 5.0, is chosen for the present study.

The detailed compositions are as follows:

AN\(_5\): 40 PbO–5Al\(_2\)O\(_3\)–54SiO\(_2\): 1.0 Nd\(_2\)O\(_3\)

AN\(_8\): 37 PbO–8Al\(_2\)O\(_3\)–54SiO\(_2\): 1.0 Nd\(_2\)O\(_3\)

AN\(_{10}\): 35 PbO–10Al\(_2\)O\(_3\)–54SiO\(_2\): 1.0 Nd\(_2\)O\(_3\)

3.2 A brief review on the spectroscopic studies of Nd\(^{3+}\) ions in various glass systems

The studies as such on spectroscopic properties of alumino silicate glasses are very few. However, a brief review on recent studies on luminescence properties of different other glass systems including some silicate glass systems is presented here.
Pérez-Rodríguez et al. [13] have studied relevance of radiative transfer processes on Nd\(^{3+}\) doped phosphate glasses for temperature sensing by means of the fluorescence intensity ratio technique. Their studies the reabsorption measurements in the samples with a higher Nd\(^{3+}\) content revealed that the reliability of the sensing performance is compromised with the doping concentration and the experimental conditions of the measurement. Pal et al. [14] have reported fluorescence and radiative properties of Nd\(^{3+}\) ions doped zinc bismuth silicate glasses. Their results have pointed out this glass system as good candidate to be used in the development of photonics devices operating in the near infrared spectral range. Sobczyk [15] has investigated temperature-dependent luminescence and temperature-stimulated NIR-to-VIS up-conversion in Nd\(^{3+}\)-doped La\(_2\)O\(_3\)–Na\(_2\)O–ZnO–TeO\(_2\) glasses. The results of this study indicated that the investigated glasses are potentially applicable as a 1063 nm laser host as well as an optical sensor for temperature measurements. Boetti et al. [16] reported the results of spectroscopic investigations of Nd\(^{3+}\) single doped and Eu\(^{3+}/Nd^{3+}\) co-doped phosphate glass for solar pumped lasers. This study has indicated that although energy transfer from Eu\(^{3+}\) to Nd\(^{3+}\)occured, a large Eu\(^{3+}\) concentration dependent quenching of Nd\(^{3+}\) fluorescence. This latter process reported to decrease the radiative quantum efficiency of Nd\(^{3+}:^{4}F_{3/2}\) emitting level. Gupta et al. [17] have studied the influence of bismuth on
structural, elastic and spectroscopic properties of Nd$^{3+}$ doped Zinc–Boro-Bismuthate glasses. These studies indicated that due to Bi$_2$O$_3$ incorporation reduced host phonon energy and its high optical basicity effect remarkably improved the Nd$^{3+}$ luminescence properties such as emission intensity, quantum yield and emission cross-section. Martin et al. [18] reported nanocrystal formation using laser irradiation on Nd$^{3+}$ doped barium titanium silicate glasses. Evidence of nanocrystal formation induced by laser irradiation was confirmed by optical spectroscopic, X-ray diffraction, scanning electron and atomic force microscopy. Lu et al. [19] reported crystallization, structure and fluorescence emission of Nd$^{3+}$- and Yb$^{3+}$-doped NCS transparent glass-ceramics. In this report it was said that there is strong fluorescence emission in the Nd$^{3+}$-and Yb$^{3+}$-doped NCS glass-ceramics when compared with the singly ion doped glasses. Sola et al. [20] studied the stress-induced buried waveguides in the 0.8CaSiO$_3$–0.2Ca$_3$(PO$_4$)$_2$ eutectic glass doped with Nd$^{3+}$ ions. The objective of this study was to characterize and to evaluate in what extent their optical properties could be modified by the waveguide fabrication process. Brahmachary et al. [21] have investigated spectroscopic properties of Nd$^{3+}$ doped zinc-alumino-sodium-phosphate (ZANP) glasses. Mahamuda et al. [22] have studied the spectroscopic properties and luminescence behavior of Nd$^{3+}$ doped zinc alumino bismuth borate glasses. From these studies it was
concluded that 1 mol% of Nd$^{3+}$ ion concentration is optimum for zinc alumino bismuth borate glasses to generate a strong laser emission at 1060 nm. Kawamura et al. [23] have reported the extraction of Nd$^{3+}$-doped LiYF$_4$ phosphor from sol–gel-derived oxyfluoride glass ceramics by hydrofluoric acid treatment. The photoluminescent (PL) properties were investigated for the sample before and after HF treatment. The results indicated that the Nd$^{3+}$ ions were predominantly incorporated in LiYF$_4$, and the extraction of LiYF$_4$ crystallites was successfully carried out without changing the PL properties of Nd$^{3+}$ ions. da Silva et al. [24] have investigated the frequency upconversion in Nd$^{3+}$ doped PbO–GeO$_2$ glasses containing silver nanoparticles. Their results indicated that the nucleation of silver NPs in Nd$^{3+}$-doped PGO glasses contributes to increase the UC efficiency. Fu et al. [25] have reported studies on single-mode waveguides generated in Nd$^{3+}$-doped silicate glass by nickel ion irradiation. Shanmugavelu et al. [26] have studied optical properties of Nd$^{3+}$ doped bismuth zinc borate glasses.

Surendra Babu et al. [27] have recently reported the results of their studies on 1.06 µm emission in Nd$^{3+}$-doped alkali niobium zinc tellurite glasses. From this study they have concluded that $^4F_{3/2} \rightarrow ^4I_{11/2}$ is the probable lasing transition excited with low threshold power. Cankaya and Sennaroglu [28] have reported lasing emission of Nd$^{3+}$ ions in TeO$_2$–WO$_3$ glasses at 1.37 µm. In this
The authors have claimed to have measured the luminescence efficiency as much as 78%. Saleem et al. [29] have reported optical absorption and near infrared emission properties of Nd\(^{3+}\) ions in alkali lead tellurofluoroborate glasses. In this study the authors have evaluated total radiative transition probabilities (\(A_T\)), stimulated emission cross-sections (\(\sigma_E\)) and gain bandwidth parameters (\(\sigma_E \times \Delta \lambda P\)) and compared with the earlier reports. Zhong et al. [30] have reported 2.7 \(\mu\)m emissions of Nd\(^{3+}\), Er\(^{3+}\) codoped tellurite glass. In this study the authors have observed the enhanced mid infrared emission due to the co-doping. Verma et al. [31] have studied effect of modifiers (BaF\(_2\) BaCl\(_2\) and BaCO\(_3\)) and heat treatment on the fluorescence bands of Nd\(^{3+}\) ions in TeO\(_2\) glasses. Their study has indicated that the BaCl\(_2\) modified glass exhibits maximum upconversion intensity among the three modifiers. From the temperature dependent fluorescence studies of these glasses the authors have concluded that Nd\(^{3+}\) doped tellurite glass can be used as a temperature sensor.

Courrol et al. [32] have studied spectral properties of lead fluoroborate glasses doped with Nd\(^{3+}\). Wilhelm et al. [33] have reported the fluorescence lifetime enhancement of Nd\(^{3+}\)-doped sol–gel glasses by Al–codoping and CO\(_2\)-laser processing. Karthikeyan and Mohan [34] have reported the structural, optical and glass transition studies on Nd\(^{3+}\) doped lead bismuth borate glasses. Annapurna et al. [35] have investigated the NIR emission and upconversion
luminescence spectra of Nd\textsuperscript{3+}:ZnO–SiO\textsubscript{2}–B\textsubscript{2}O\textsubscript{3} glasses. Saisudha and Ramakrishna [36] have found large radiative transition probabilities in bismuth borate glasses doped with Nd\textsuperscript{3+} ions. Shen \textit{et al.} [37] have reported the compositional effects and spectroscopy of rare earths (Er\textsuperscript{3+}, Tm\textsuperscript{3+}, and Nd\textsuperscript{3+}) in tellurite glasses. Kumar \textit{et al.} [38] have explored the stimulated emission and radiative properties of Nd\textsuperscript{3+} ions in barium fluorophosphate glass containing sulphate. Chen \textit{et al.} [39] have studied ion-implanted waveguides in Nd\textsuperscript{3+} doped silicate glass and Er\textsuperscript{3+}/Yb\textsuperscript{3+} co-doped phosphate glass. Kam and Buddhudu [40] have studied luminescence enhancement in (Nd\textsuperscript{3+}+Ce\textsuperscript{3+}) doped SiO\textsubscript{2}: Al\textsubscript{2}O\textsubscript{3} sol-gel glasses. Rosa-Cruz \textit{et al.} [41] have reported the results of their study on spectroscopic characterization of Nd\textsuperscript{3+} ions on barium fluoroborophosphate glasses. Fernandez \textit{et al.} [42, 43] have evaluated the upconversion losses in Nd-doped fluoroarsenate glasses. Surana \textit{et al.} [44] have investigated the Laser action in neodymium-doped zinc chloride borophosphate glasses. Vijaya Prakash reported [45] his results of absorption spectral studies of Pr, Nd, Sm, Dy, Ho and Er ions doped in NASICON type phosphate glass, Na\textsubscript{4}AlZnP\textsubscript{3}O\textsubscript{12}. Rao \textit{et al.} [46] have reported luminescence properties of Nd\textsuperscript{3+}: TeO\textsubscript{2}–B\textsubscript{2}O\textsubscript{3}–P\textsubscript{2}O\textsubscript{5}–Li\textsubscript{2}O glass. Xiang \textit{et al.} [47] have studied the up-conversion emission in violet from yellow in Nd\textsuperscript{3+}: SiO\textsubscript{2}–TiO\textsubscript{2}–Al\textsubscript{2}O\textsubscript{3} sol-gel glasses. Bouderbala \textit{et al.} [48] have reported the results of their studies on infrared and visible room
temperature fluorescence induced by continuous laser excitation of new Nd$^{3+}$: phosphate glasses. Cassanjes et al. [49] have investigated Raman scattering, differential scanning calorimetry and Nd$^{3+}$ spectroscopy in alkali niobium tellurite glasses. Mehta et al. [50, 51] have investigated the spectroscopic properties including ESR of Nd$^{3+}$ doped phosphate and borate glasses. Kumar and Bhatnagar [52] have reported the effect of modifier ions on the covalency of Nd$^{3+}$ ions in cadmium borate glasses. Srinivasa Rao et al. [53] have reported the physical and absorption properties of Nd$^{3+}$ doped mixed alkali fluoro-borophosphate optical glasses. Ajit Kumar et al. [54] have reported the spectroscopic parameters of Nd$^{3+}$ ion in phosphate glasses. Joshi and Lohani [55] have investigated the non-radiative energy transfer from Tm$^{3+}$ to Ho$^{3+}$ and Nd$^{3+}$ in zinc phosphate glass. Dawar et al. [56] have studied the optical and acousto-optical properties of Nd: phosphate glasses. Ning Lei et al. [57] have fabricated Ti: sapphire laser pumped Nd: tellurite glass laser. Pozza et al. [58] have investigated the absorption and luminescence spectroscopy of Nd$^{3+}$ and Er$^{3+}$ in a zinc borate glass. Ratnakaran and Buddhudu [59] have reported the optical absorption spectra and laser analysis of Nd$^{3+}$ ions in fluoroborate glasses. Sen and Stebbins [60] have studied structural role of Nd$^{3+}$ in SiO$_2$ glass using NMR studies. Ebendorff et al. [61] have studied the spectroscopic properties of Nd$^{3+}$ ions in phosphate glasses.
3.3 Results and Discussion

In the presence of modifiers SiO₂ participates in the glass network with meta, pyro and ortho–silicates in the order: [SiO₄/2]⁰ (Q⁴), [SiO₃/2O]⁻ (Q³), [SiO₂/2O₂]²⁻(Q²), [SiO₁/2O₃]³⁻(Q¹) and [SiO₄]⁴⁻ (Q⁰) [62]. Earlier NMR studies on aluminium silicate glasses have indicated that aluminium ions occupy mainly tetrahedral (AlO₄) and octahedral (AlO₆) sites [63].

$$2\text{Al}_2\text{O}_3 \rightarrow [\text{Al}^{3+}]_o + 3[\text{AlO}_4/2]_t$$

The AlO₄ tetrahedrons enter the glass network and alternate with SiO₄ tetrahedrons, whereas octahedral Al³⁺ induce bonding defects in the glass network and participate in the declusterization of Nd³⁺ ions. Recently, it was demonstrated by Schmucker and Schneider [64] using NMR studies that the edge-sharing [AlO₄] tetrahedra also participate in inducing bonding defects in the silicate glass network. The oxygen triclusters of such units (oxygen ion bonded to two [AlO₄] and one [SiO₄] or one [AlO₄] and two [SiO₄]) take part in inducing bonding defects in the glass containing Al₂O₃ and SiO₂. PbO, normally in the concentration range used in the present study acts as a modifier and as a result Si-O-Si and Si-O-Al bonds are cleaved in succession. Such behaviour also lead to a de-polymerization of the glass network.
From the measured values of the density and average molecular weight $M$ of the samples, various other physical parameters such as Nd$^{3+}$ ion concentration $N_i$, mean Nd$^{3+}$ ion separation $R_i$ and molar volume for all the glass samples were evaluated and presented in Table 3.1. The dependence of density $d$ on the concentration of Al$_2$O$_3$ for all the titled glasses shows slight decrement with increasing Al$_2$O$_3$ content. The decrease of density can be understood due to the replacement of PbO by Al$_2$O$_3$.

Table 3.1 Physical parameters of PbO–Al$_2$O$_3$–SiO$_2$ glasses doped with different concentrations of Nd$_2$O$_3$.

<table>
<thead>
<tr>
<th>Physical parameter</th>
<th>Glass →</th>
<th>Nd$^{3+}$ series</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>AN$_5$</td>
<td>AN$_8$</td>
</tr>
<tr>
<td>Density $d$ (g/cm$^3$)</td>
<td>4.6218</td>
<td>4.4147</td>
</tr>
<tr>
<td>Refractive index</td>
<td>1.647</td>
<td>1.646</td>
</tr>
<tr>
<td>Nd$^{3+}$ ion conc. $N_i$ (x10$^{20}$ ions/cm$^3$)</td>
<td>2.14</td>
<td>2.10</td>
</tr>
<tr>
<td>Interionic distance $R_i$ (Å)</td>
<td>16.72</td>
<td>16.82</td>
</tr>
<tr>
<td>Polaron radius $R_p$ (Å)</td>
<td>6.74</td>
<td>6.78</td>
</tr>
<tr>
<td>Field Strength $F_i$ (10$^{14}$, cm$^{-2}$)</td>
<td>4.41</td>
<td>4.35</td>
</tr>
</tbody>
</table>
DSC studies on Nd$_2$O$_3$ doped PbO−Al$_2$O$_3$−SiO$_2$ glasses mixed with different concentrations of Al$_2$O$_3$ have been carried out. All DSC traces exhibit typical glass transition ($T_g$) with the inflection point between 850–870 K; the glass transition temperature decreases slightly with increasing Al$_2$O$_3$ content. At about 1240 °C, the process of crystallization begins and all the traces exhibited well defined exothermic peaks at $T_c$.

To observe the mass change effects during heating process, we have also recorded thermal gravimetric traces for all the samples; TG traces for two of the samples along with corresponding DSC traces are shown. The thermal gravimetric analysis for all the samples indicated that upto 1200 K virtually no change in the mass of the samples. In Fig. 3.1 DSC and TG traces for the glass AN$_5$ are presented. In the inset of Fig. 3.1 we have presented the variation of variation of $T_c$-$T_g$ (a parameter that gives the information on thermal stability of the glass) is found to be decreased slightly with the concentration of Al$_2$O$_3$. It may be noted here that DSC traces of all the three series of glasses viz., PbO−Al$_2$O$_3$−SiO$_2$:Nd$^{3+}$/Dy$^{3+}$/Yb$^{3+}$ exhibited a similar trend. In view of this, the DSC patterns PbO−Al$_2$O$_3$−SiO$_2$:Dy$^{3+}$/Yb$^{3+}$ were not presented in the subsequent chapters.
The optical absorption spectra of PbO–Al$_2$O$_3$–SiO$_2$: Nd$_2$O$_3$ glasses recorded at room temperature in the wavelength region 300-2000 nm exhibited conventional absorption bands corresponding to the following electronic transitions [65]

$$^4I_{9/2} \rightarrow ^2P_{1/2}, ^2D_{3/2}+^4G_{11/2}, ^4G_{9/2}+^4G_{7/2}, ^4G_{5/2}, ^2H_{11/2}, ^4F_{9/2}, ^4F_{7/2}, ^4F_{5/2} \text{ and } ^4F_{3/2}$$

The pattern of absorption spectra for all the three glasses remains the same; however, considerable variations in the peak positions and the intensity of these bands have been observed (Fig. 3.2).
Fig. 3.2 Optical absorption spectra of PbO-Al₂O₃-SiO₂: Nd₂O₃ glasses in the visible region (all transitions are from $^4I_{9/2}$).
The experimental oscillator strengths (OS) of the absorption transitions were estimated from the spectra for all the three rare earth ion doped glasses in terms of the area under absorption peaks. The procedure of fitting of the calculated OS to those evaluated from the experimental spectra is described in Ref.[66]. 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 $f_{\text{cal}}$ and observed $f_{\text{obs}}$ OS. The quality of fitting is determined by the root mean squared deviation (RMS) defined as [67], and presented in Table 3.2 for all the three glasses. The deviations indicate reasonably good fitting between theory and experiment, demonstrating the applicability of JO theory. The values of $\Omega_\lambda$ are found to be in the following order for the three glasses $\Omega_2 > \Omega_6 > \Omega_4$ and found to be consistent with the some recently reported values [68, 69]. For evaluating the JO parameters from the absorption spectra the baseline was drawn in such a way to remove the background in all absorption spectra, we mean to leave only those features corresponding to the 4f-4f transitions, which are clearly seen on the top of the background. Then such a baseline was subtracted from the spectrum, and the spectrum modified in this way was used for calculations of the experimental OS.

$\text{RMS} = \sqrt{\frac{\sum_{i=1}^{N}(f_{\text{obs}} - f_{\text{cal}})^2}{N-3}} \quad (3.1)$
Table 3.2 The absorption band energies, the oscillator strength for the transitions of Nd\(^{3+}\) ion PbO-Al\(_2\)O\(_3\)–SiO\(_2\) glasses. All transitions are from the ground state \(^{4}I_{9/2}\)

<table>
<thead>
<tr>
<th>Transition</th>
<th>AN(_5)</th>
<th>AN(_8)</th>
<th>AN(_{10})</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Barycenter (cm(^{-1}))</td>
<td>(f_{\text{exp}}) ((\times 10^{-6}))</td>
<td>(f_{\text{cal}}) ((\times 10^{-6}))</td>
</tr>
<tr>
<td>(^{4}I_{9/2}) → (^{4}F_{3/2})</td>
<td>11358</td>
<td>3.2433</td>
<td>2.5644</td>
</tr>
<tr>
<td>(^{4}F_{5/2})</td>
<td>12381</td>
<td>13.6470</td>
<td>11.7574</td>
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<td>(^{4}F_{7/2})</td>
<td>13403</td>
<td>11.3087</td>
<td>12.3779</td>
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<td>(^{4}F_{9/2})</td>
<td>14622</td>
<td>0.8325</td>
<td>1.6259</td>
</tr>
<tr>
<td>(^{2}H_{11/2})</td>
<td>15735</td>
<td>0.55</td>
<td>0.3541</td>
</tr>
<tr>
<td>(^{4}G_{5/2})</td>
<td>17113</td>
<td>34.7772</td>
<td>34.6050</td>
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<td>(^{4}G_{7/2})</td>
<td>18911</td>
<td>3.7539</td>
<td>5.9892</td>
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<tr>
<td>(^{4}G_{9/2})</td>
<td>19575</td>
<td>1.1836</td>
<td>2.3194</td>
</tr>
<tr>
<td>(^{2}P_{1/2},^{2}D_{3/2},^{4}G_{11/2}^{\prime},^{4}G_{9/2})</td>
<td>21091</td>
<td>1.6681</td>
<td>1.4947</td>
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<tr>
<td>(^{2}P_{1/2},^{2}D_{5/2})</td>
<td>23141</td>
<td>1.0995</td>
<td>0.5657</td>
</tr>
<tr>
<td><strong>rms deviation</strong></td>
<td>(+1.3349)</td>
<td>(+1.7984)</td>
<td>(+0.6150)</td>
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<table>
<thead>
<tr>
<th>JO parameters</th>
<th>(\Omega_2)</th>
<th>(\Omega_4)</th>
<th>(\Omega_6)</th>
<th>(\Omega_2)</th>
<th>(\Omega_4)</th>
<th>(\Omega_6)</th>
<th>(\Omega_2)</th>
<th>(\Omega_4)</th>
<th>(\Omega_6)</th>
</tr>
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<tbody>
<tr>
<td>((\times 10^{20}), cm(^2))</td>
<td>13.94</td>
<td>3.37</td>
<td>13.58</td>
<td>12.16</td>
<td>2.81</td>
<td>12.08</td>
<td>9.36</td>
<td>0.56</td>
<td>8.42</td>
</tr>
</tbody>
</table>
According to the Judd–Ofelt theory, crystal field parameter that determines the symmetry and distortion related to the structural change in the vicinity of Nd$^{3+}$ ions. In the present context, this may be understood as follows: the larger the degree of disorder or depolymerization in the glass network, the larger is the average distance between Si–O–Si, Si–O–Pb chains causing the average Nd–O distance to increase. Such increase in the bond lengths produces weaker field around Nd$^{3+}$ ions leading to a low value of $\Omega_2$ for the glass mixed with 10.0 mol% of Al$_2$O$_3$ [68]. Additionally the variations in the concentration of silicate groups with different number of non-bridging oxygens, as discussed before, also play an important role in the variation of value of $\Omega_2$.

The luminescence spectra of Nd$^{3+}$ doped glasses excited at 582 nm recorded at room temperature in the spectral range 0.95 to 1.6 $\mu$m region are shown in Fig. 3.3; the spectra exhibited bands due to $^4F_{3/2} \rightarrow ^4I_{13/2}$ (at 1.06 $\mu$m) and $^4F_{3/2} \rightarrow ^4I_{11/2}$ (at 1.3 $\mu$m) transitions. Further a gradual growth of these bands is clearly observed with increase in the concentration of Al$_2$O$_3$. From these spectra, various radiative parameters viz., spontaneous emission probability, $A$, the total emission probability, $A_T$, the radiative lifetime $\tau$, the fluorescent branching ratio $\beta$ of different transitions originated from $^4F_{3/2}$ level of Nd$^{3+}$ ions have been evaluated and presented in Table 3.3.

The fluorescence decay curve of the $^4F_{3/2}$ excited level of Nd$^{3+}$ doped glasses is shown in Fig. 3.4; the curves viewed to be double exponential with a smaller ($\sim$ 20%) and a larger ($\sim$ 80%) fast decay component ($\tau_{fd}$). The evaluated lifetimes with possible errors
are presented in Table 3.4. The lifetimes, both experimental and calculated, were found to be in the increasing order with increase in the concentration of \( \text{Al}_2\text{O}_3 \).

![Photoluminescence spectra of PbO-Al\(_2\)O\(_3\)-SiO\(_2\): Nd\(_2\)O\(_3\) glasses in the NIR region excited at 582 nm.](image)

Fig. 3.3 Photoluminescence spectra of PbO-Al\(_2\)O\(_3\)-SiO\(_2\): Nd\(_2\)O\(_3\) glasses in the NIR region excited at 582 nm.
Table 3.3 Various radiative properties of transitions of Nd$^{3+}$ ions in PbO–Al$_2$O$_3$–SiO$_2$ glasses

<table>
<thead>
<tr>
<th>Transition</th>
<th>$AN_5$</th>
<th>$AN_8$</th>
<th>$AN_{10}$</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$A$ (s$^{-1}$)</td>
<td>$\beta$ (%)</td>
<td>$A$ (s$^{-1}$)</td>
</tr>
<tr>
<td>$^{4}F_{3/2} \rightarrow ^{4}I_{9/2}$</td>
<td>1796</td>
<td>29.38</td>
<td>1634</td>
</tr>
<tr>
<td>$\rightarrow ^{4}I_{11/2}$</td>
<td>3499</td>
<td>57.26</td>
<td>3538</td>
</tr>
<tr>
<td>$\rightarrow ^{4}I_{13/2}$</td>
<td>774</td>
<td>12.67</td>
<td>768</td>
</tr>
<tr>
<td>$\rightarrow ^{4}I_{15/2}$</td>
<td>42</td>
<td>0.69</td>
<td>47</td>
</tr>
<tr>
<td>$\tau$</td>
<td>164 $\mu$s</td>
<td>167 $\mu$s</td>
<td>169 $\mu$s</td>
</tr>
</tbody>
</table>

Table 3.4 Summary of the data on life measurements of $^{4}F_{3/2}$ excited level

<table>
<thead>
<tr>
<th>Glasses</th>
<th>Life time Nd doped samples; $\lambda_{\text{excitation}} = 582$ nm and $\lambda_{\text{emission}} = 1064$nm</th>
<th>Quantum efficiency $\eta$%</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>measured ($\mu$s)</td>
<td>Calculated ($\mu$s)</td>
</tr>
<tr>
<td>$AN_5$</td>
<td>$\tau_{\text{fd}}$</td>
<td>$\tau_{\text{sd}}$</td>
</tr>
<tr>
<td>$AN_8$</td>
<td>67 (21%)</td>
<td>171 (79%)</td>
</tr>
<tr>
<td>$AN_{10}$</td>
<td>69 (21%)</td>
<td>187 (79%)</td>
</tr>
</tbody>
</table>

The Infrared spectra of PbO–Al$_2$O$_3$–SiO$_2$: Nd$_2$O$_3$ glasses (Fig. 3.5) exhibited conventional bands at about 1025 cm$^{-1}$ due to Si-O-Si asymmetric vibrations, 760 cm$^{-1}$ due to Si-O-Si symmetric vibrations and at about 450 cm$^{-1}$ due to Si-O-Si rocking motion [62, 70]. Incidentally, the vibrational frequency of Al–O stretching in AlO$_4$ structural units is found to exhibit band at about 750 cm$^{-1}$ and band due to AlO$_6$ structural units lie
Fig. 3.4 Decay curves of Nd$^{3+}$ ($^4F_{3/2} \rightarrow ^4I_{11/2}$) doped PbO–Al$_2$O$_3$–SiO$_2$ glasses recorded at room temperature excited at 582 nm.

at about 450 cm$^{-1}$ [71]. 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. Hence the band observed at 760 cm$^{-1}$ may be considered as the band due to Si-O-Al linkages. The band due to the vibrations of PbO$_4$ structural units about 470 cm$^{-1}$ is also present in these glasses. With increase in the concentration of Al$_2$O$_3$, the intensity of the bands due to Si-O-Si asymmetric vibrations and Si-O-Si rocking motion increases at the expense of band due to Si-O-Si/ Si-O-Al symmetric vibrations. A visible increase in the intensity of the band due to AlO$_6$ structural units is also observed with the increase in the concentration of Al$_2$O$_3$. Such features of the spectra indicate an increasing concentration of Al$^{3+}$ ions that act as modifiers with increasing content of Al$_2$O$_3$ in the glass matrix.
Fig. 3.5 IR spectra of PbO-Al₂O₃ -SiO₂: Nd₂O₃ glasses.
The Raman spectra of PbO–Al₂O₃–SiO₂:Nd₂O₃ glasses (Fig. 3.6) exhibited bands at 1050 cm⁻¹ and at 815 cm⁻¹ due to Si–O–Si asymmetric modes and symmetric vibrations of SiO₄ tetrahedra respectively. In the region of Si-O-Si symmetric modes, Al–O stretching vibrations of Al tetrahedral coordination are also possible. The spectra also exhibited a band at 550 cm⁻¹ attributed to the bridging oxygen breathing mode in (Si, Al) three-membered rings and another band at 475 cm⁻¹ due to Si-O-Si rocking vibrations [72]. The spectra also exhibited a weak envelope at about 330 cm⁻¹ due to the vibrations of PbO₄ units [73]. As the concentration of Al₂O₃ increases a noticeable enhancement in the intensity of the bands due to Si–O–Si asymmetric modes and Si-O-Si rocking vibrations of SiO₄ tetrahedra is observed at the expense of the band due to symmetric vibrations of SiO₄. Such changes clearly indicate an increasing disorder in the glass network with increasing content of Al₂O₃. Thus both IR and Raman spectra of the studied glasses suggests that there is an increase in the concentration of Al³⁺ ions that act as modifiers (which may de-cluster Nd³⁺ ions) with increase in the concentration of Al₂O₃ in the glass network.
Neodymium oxide normally exhibits immiscible tendency in silica glass and as a result it forms aggregates or clusters in which cross relaxation can give rise to non-radiative de-excitation of neodymium, resulting in very short lifetimes. Comparatively weak fluorescence intensity and short emission lifetime observed for glass AN$_5$ indicates possible formation of more concentration of Nd$^{3+}$ clusters that are responsible for luminescence quenching in this glass matrix [9]. The observed increase of PL peak intensity with increase in the Al$_2$O$_3$ concentration clearly suggests that Al increases PL
output indicating the possibility of admixing of wavefunctions of opposite parities which lead to increase the radiative probabilities of all the f-f transitions [74]. Among the two life time components observed from the decay curves, the value of $\tau_{fd}$ is found to be virtually invariant while $\tau_{sd}$ is found to increase significantly with increase in the concentration of $\text{Al}_2\text{O}_3$. The fast decay component is obviously due to the emission from clusterized $\text{Nd}^{3+}$ ions which cross relax (concentration quenching) and give rise to non-radiative de-excitation of neodymium ions. The slow decay component can be attributed to the emission from $\text{Nd}^{3+}$ ions that are uniformly dispersed in the silica matrix; the increasing value of this component with increase in the concentration of $\text{Al}_2\text{O}_3$ indicates aluminum ions gradually disperse $\text{Nd}^{3+}$ ions uniformly in the glass matrix and reduces fluorescence quenching due to cross-relaxation. Branching ratio ‘$\beta$’ (that defines the luminescence efficiency of the transition) of the orange emission due to $^4\text{F}_{3/2} \rightarrow ^4\text{I}_{11/2}$ transition, among various transitions originated from $^4\text{F}_{3/2}$, is found to be the highest (∼63%) for the glass AN$_{10}$ and it is ∼ 57% for the glass AN$_5$.

The quantum efficiency ($\eta = \tau_{exp}/\tau_{cal}$), defined as the radiative portion of the total relaxation rate of a given energy level is found to be increasing (Table 3.3) with increase in the concentration of $\text{Al}_2\text{O}_3$ ($\tau_{exp}$ is taken as an average of two components). As has been discussed earlier, the degree of dispersion of $\text{Nd}^{3+}$ ions is higher in the glass containing higher concentration of $\text{Al}_2\text{O}_3$ which lead to high non–radiative losses causing higher value of $\eta$. 
3.4 Conclusions

Lead alumino silicate glasses of the composition (40-x) PbO–(5+x) Al$_2$O$_3$–54SiO$_2$: 1.0 Nd$_2$O$_3$ (in mol%) with three values of x ranging from 0 to 5.0 were prepared. IR, Raman, optical absorption, photoluminescence and luminescence decay have been studied.

(i) The IR and Raman spectral studies have indicated that there is a gradual depolymerization of the glass network with increase in the concentration of Al$_2$O$_3$.

(ii) The optical absorption spectra of these glasses exhibited bands due to $^4$I$_{9/2}$ → $^2$P$_{1/2}$, $^2$D$_{3/2}$+$^4$G$_{11/2}$, $^4$G$_{9/2}$+$^4$G$_{7/2}$, $^4$G$_{5/2}$, $^2$H$_{11/2}$, $^4$F$_{9/2}$, $^4$F$_{7/2}$, $^4$F$_{5/2}$ and $^4$F$_{3/2}$ transitions. The spectra have been characterized by JO theory and a reasonable matching between experimental and theoretical oscillator strengths could be achieved.

(iii) The luminescence spectra of these glasses excited at 582 nm exhibited two prominent transitions viz., $^4$F$_{3/2}$→$^4$I$_{11/2}$+$^4$I$_{13/2}$ in the spectral region 950 to 1600 nm. An increase in the PL output of these transitions is observed with increase in the concentration of Al$_2$O$_3$.

(iv) The quantitative analysis of these results has revealed that the Al$^{3+}$ ions cause declustering of Nd$^{3+}$ ions and thereby decrease the luminescence quenching due to cross relaxation.
References


