Chapter 3

ABSORPTION AND FLUORESCENCE FEATURES OF Pr$^{3+}$ ION IN LITHIUM-FLUORO-BORATE GLASS-INFLUENCE OF MODIFIER OXIDES
3.1 Introduction

Rare-earth ions doped glasses with efficient frequency up conversion, have received considerable attention due to the possibilities of achieving efficient solid state lasers emitting in the blue–green region of the optical spectrum. Pr$^{3+}$ systems are interesting as short-wavelength up conversion laser materials [1-4]. Among the various rare-earth ions, Pr$^{3+}$ is an attractive optical activator, because its energy level spectrum contains several meta-stable multiples, $^3P_{0,1,2}$, $^1D_2$ and $^1G_4$ that offer the possibility of emission in the blue, green, orange and red wavelengths [5]. In recent years, studies on luminescence features of trivalent praseodymium ions have become more popular because of its 4f$^2$ configuration, which possess 91 fold degeneracy [6].

Pr$^{3+}$-doped glasses finds potential applications as UV–vis–NIR lasers, upconverters, optical fibers and optical amplifiers [7]. Studies on Pr$^{3+}$ ion are ideal for the comparison of different relaxation processes such as multiphonon relaxation and cross relaxation due to numerous energy levels [8]. Over the past few years, there has been a considerable interest in the study of borate based glasses due to their structural and optical properties. Luminescence of RE ions depends more on the nature of the host and the ambient temperature [9]. An interesting characteristic of borate glass is the appearance of variations in its structural properties when different modifier oxides (MgO, CaO, CdO and PbO) are introduced. The fluoride compounds (BaF$_2$ and NaF) are usually used as a minor addition to enhance the luminescence properties. The differences in spectroscopic investigations depend upon the introduction of modifier oxides. The addition of alkali earth oxides (MgO and CaO) into the glass structure leads to disruption of the glass network and promotes the formation of non-bridging oxygen groups [10]. In contrast to alkaline earth oxides, PbO has the ability to form stable glasses due to its dual role, one as modifier (if Pb–O is ionic) and the other as glass former (if Pb–O is covalent) depending upon the structural units [11]. It is well established that the radiative parameters associated with luminescence transitions of Ln$^{3+}$ ions in glass lattice are highly sensitive even for small changes in the chemical environment. The transition probabilities of emission transitions of Ln$^{3+}$ ions are expected to increase with increase in covalency that depends upon the network forming ions. Network modifiers also change
the local environment of Ln$^{3+}$ ions to some extent [12, 13]. It is for this reason the author has chosen PbO which acts both as network former and modifier instead of conventional alkali oxide as the modifying component.

The objective of this work is to investigate the structural changes that take place due to the introduction of modifier oxides into the Li$_2$B$_4$O$_7$-BaF$_2$-NaF-MO (where M=Mg, Ca, Cd and Pb) glass network by applying the J-O theory and the role of modifier ions in this process. However, it is well known that the application of J–O theory to Pr$^{3+}$ ion presents some problems due to the small energy difference between the ground configuration 4f$^2$ and the first- excited state configuration 4f$^4$5d$^1$ [14]. This manifests itself both as a large deviation between the measured and calculated oscillator strengths and as such the difficulty experienced to fit the $^3$H$_4$→$^3$P$_2$ hypersensitive transition [15]. The obtained results were analyzed with the support of data from FT-IR, optical absorption and photoluminescence studies. The Judd–Ofelt parameters obtained from VIS–NIR absorption spectra along with the measured luminescence data have been used to evaluate the transition probabilities ($A_R$), branching ratios ($\beta_R$), radiative lifetimes ($\tau_R$) and stimulated emission cross-sections ($\sigma_p$) for different emission transitions of Pr$^{3+}$ ions in lithium fluoro-boratae glasses.

**Review of literature**

Rare earth ions doped glasses with efficient frequency upconversion, have received considerable attention due to the possibilities of achieving efficient solid state lasers emitting in the blue-green region of the optical spectrum. Kaushal kumar et al [16] reported UV/visible upconversion and energy transfer between Nd$^{3+}$ and Pr$^{3+}$ ions in co-doped tellurite glass. Visible upconversion emissions in Pr$^{3+}$-doped TeO$_2$–ZnO glass were studied by Rai [17]. The luminescence properties of Pr$^{3+}$-doped transparent oxyfluoride glass-ceramics containing BaYF$_5$ nano crystals were studied by Mu Gu et al. [18]. Hu et al [19]. reported the synthesis and efficient near-infrared quantum cutting of Pr$^{3+}$/Yb$^{3+}$ codoped LiYF$_4$ single crystals. The luminescence of rare-earth ions in glass–ceramics has been intensively investigated by Wang et al [20]. In 2009, the photoluminescence of Pr$^{3+}$-doped SiO$_2$–Al$_2$O$_3$–BaF$_2$–GdF$_3$ glasses [21] and the photo-
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Luminescence of Pr$^{3+}$ in glass ceramic containing LiGdF$_4$ were reported [22]. Rai et al [23] analyzed optical properties and upconversion in Pr$^{3+}$ doped in aluminum, barium, calcium fluoride glass. Spectral properties and dynamics of luminescent states of Pr$^{3+}$ and Tm$^{3+}$ in lead borate glasses modified by PbF$_2$ were analyzed by Dominiak-Dzik et al [24]. Upconversion in Pr$^{3+}$ doped tellurite glass was emphasized by Rai et al [25].

Recently Zhang et al [26] were emphasized Visible and near infrared photoluminescence of Pr$^{3+}$ doped oxy-chalcohalide glasses. Spectroscopic studies and down conversion luminescence in OH$^-$-free Pr$^{3+}$–Yb$^{3+}$ co-doped low-silica calcium alumino silicate glasses were studied by Borrero-González et al [27]. Manzani et al [28] studied orange emission in Pr$^{3+}$-doped fluoroindate glasses. Reddish-orange emission from Pr$^{3+}$ doped zinc alumino bismuth borate glasses were analyzed by Mahammuda et al [29].

In the present work, the studied glasses were prepared using the procedure given in chapter 2. The studied glass compositions are given below:

48Li$_2$B$_4$O$_7$+20BaF$_2$+10NaF+20MgO+2.0Pr$_6$O$_{11}$
48Li$_2$B$_4$O$_7$+20BaF$_2$+10NaF+20CaO+2.0Pr$_6$O$_{11}$
48Li$_2$B$_4$O$_7$+20BaF$_2$+10NaF+20CdO+2.0Pr$_6$O$_{11}$
48Li$_2$B$_4$O$_7$+20BaF$_2$+10NaF+20PbO+2.0Pr$_6$O$_{11}$,
48Li$_2$B$_4$O$_7$+20BaF$_2$+10NaF+10MgO+10CaO+2.0Pr$_6$O$_{11}$ and
48Li$_2$B$_4$O$_7$+20BaF$_2$+10NaF+10CdO+10PbO+2.0Pr$_6$O$_{11}$.

The main interest in the present study is to examine the variation of Judd-Ofelt intensity parameters, radiative lifetimes and emission cross sections with the variation of different modifier oxides in lithium-fluoro-borate glass matrix. From these studies, the information related to structural changes and certain transitions of Pr$^{3+}$ ion for laser excitation in different phosphate glass matrices are reported.

3.2 Results and discussion

3.2.1 Structural analysis

Fig. 3.1 shows the SEM images and EDS spectra of Pr$^{3+}$ doped Mg, Mg-Ca and
Figure 3.1. The SEM and EDS images of Pr$^{3+}$ doped a) Mg b) Mg-Ca and c) Cd-Pb based lithium-fluoro-borate glass.
Cd-Pb lithium-fluoro-borate glass matrix. The SEM image shows clear and smooth surface morphology with no clustering formation and confirms the amorphous nature of the present glass samples. The EDS spectra give identification of all elements (O, F, Mg, Ca, Cd, Pb, Ba and Pr) present in the investigated glass samples in terms of percentages.

The FT-IR spectra of Pr\(^{3+}\) doped lithium-fluoro-borate glass matrix with different modifier oxides are shown in Fig. 3.2. In general, the vibrational modes of borate network are mainly active in three infrared spectral regions. The observed IR band at 730 cm\(^{-1}\) is due to bonding vibrations of B-O-B linkages. The broad IR absorbance band at 960 cm\(^{-1}\) is due to non-bridging oxygen in the form of BO\(_4\) units. The IR absorbance band around at 1390 cm\(^{-1}\) is assigned to the asymmetric stretching vibrations of B-O bond of trigonal BO\(_3\) units. The IR peak around 2730 cm\(^{-1}\) is due to hydrogen bonding present in the lithium-fluoro-borate glass matrices. The strong absorbance band around 3400 cm\(^{-1}\) is owing to the hydroxyl or water groups present in the all glass matrices. The observations made in the present investigations are well agreed with the literature [30-36]. The band positions and their assignments for observed FTIR bands are reported in Table 3.1 for all the glass matrices.

### 3.2.2 Optical absorption spectra and Energy level analysis

Optical absorption spectra of Pr\(^{3+}\) doped different lithium fluoro-borate glasses in the ultraviolet (UV), visible (VIS) and near infrared (NIR) regions are recorded at room temperature and are shown in Fig. 3.3. The band assignments were made referring to Refs. [37, 38]. The spectra of all Pr\(^{3+}\) doped lithium fluoro-borate glasses are similar to each other and are comparable to other Pr\(^{3+}\)-doped glasses [39–41]. However, a slight variation in peak positions and intensities are noticed which is due to variation in the glass compositions. For all the Pr\(^{3+}\)-doped fluoro-borate glasses, 7 excited levels which includes \(^3\)P\(_2\), \(^3\)P\(_1\), \(^3\)P\(_0\), \(^1\)D\(_2\), \(^1\)G\(_4\), \(^3\)F\(_4\) and \(^3\)F\(_3\) levels have been observed. All the absorption bands originate from the ground state \(^3\)H\(_4\). The observed and calculated energy values of excited levels along with rms deviations are presented in the Table. 3.2. These energy values are evaluated by means of zero order energies and partial derivative values which are shown in the Table 3.3, Ref [46]. Further, the Racah (\(E^1\), \(E^2\) and \(E^3\)), spin-orbit
Figure 3.2. FT-IR spectra of Pr$^{3+}$ doped lithium-fluoro-borate glass with different modifier oxides.
Table 3.1.

Assignment of measured FT-IR band positions of Pr\(^{3+}\) doped lithium-fluoro-borate glass matrix with different modifier oxides.

<table>
<thead>
<tr>
<th>S.No</th>
<th>Mg</th>
<th>Ca</th>
<th>Cd</th>
<th>Pb</th>
<th>Mg-Ca</th>
<th>Cd-Pb</th>
<th>Assignment</th>
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<tbody>
<tr>
<td>1</td>
<td>707</td>
<td>693</td>
<td>699</td>
<td>704</td>
<td>706</td>
<td>705</td>
<td>Bending of B-O-B linkage vibrations</td>
</tr>
<tr>
<td>2</td>
<td>903</td>
<td>900</td>
<td>915</td>
<td>917</td>
<td>924</td>
<td>918</td>
<td>BO(_4) stretching in pyroborate groups</td>
</tr>
<tr>
<td>3</td>
<td>1337</td>
<td>1348</td>
<td>1335</td>
<td>1312</td>
<td>1357</td>
<td>1324</td>
<td>Stretching vibrations of BO(_3) groups</td>
</tr>
<tr>
<td>4</td>
<td>2921</td>
<td>2922</td>
<td>2920</td>
<td>2925</td>
<td>2918</td>
<td>2922</td>
<td>Due to hydrogen bonding</td>
</tr>
<tr>
<td>5</td>
<td>3401</td>
<td>3402</td>
<td>3416</td>
<td>3394</td>
<td>3392</td>
<td>3404</td>
<td>Fundamental stretching of OH groups</td>
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</table>

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Pr\(^{3+}\) ion doped lithium-fluoro-borate glasses
Figure 3.3. Optical absorption spectra of Pr$^{3+}$ doped lithium-fluoro-borate glass with different modifier oxides.
Table 3.2.
Experimental (E_{exp}) and calculated (E_{cal}) energies and various spectroscopic parameters with hydrogenic ratios (E^1/E^3, E^2/E^3) of Pr^{3+} doped lithium fluoro-borate glass with different modifier oxides.

<table>
<thead>
<tr>
<th>S.No</th>
<th>Energy level</th>
<th>Mg</th>
<th>Ca</th>
<th>Cd</th>
<th>Pb</th>
<th>Mg-Ca</th>
<th>Cd-Pb</th>
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<tr>
<td></td>
<td></td>
<td>E_{exp}</td>
<td>E_{Cal}</td>
<td>E_{exp}</td>
<td>E_{Cal}</td>
<td>E_{exp}</td>
<td>E_{Cal}</td>
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<td>3^F_3</td>
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<td>6369</td>
<td>6587</td>
<td>6364</td>
<td>6588</td>
<td>6354</td>
</tr>
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<td>2</td>
<td>3^F_4</td>
<td>6960</td>
<td>6897</td>
<td>6960</td>
<td>6863</td>
<td>6951</td>
<td>6854</td>
</tr>
<tr>
<td>3</td>
<td>1^G_4</td>
<td>9960</td>
<td>10089</td>
<td>9960</td>
<td>10034</td>
<td>9939</td>
<td>10013</td>
</tr>
<tr>
<td>4</td>
<td>1^D_2</td>
<td>16915</td>
<td>16943</td>
<td>16915</td>
<td>16903</td>
<td>16949</td>
<td>16936</td>
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<tr>
<td>5</td>
<td>3^P_0</td>
<td>20752</td>
<td>20663</td>
<td>20752</td>
<td>20647</td>
<td>20760</td>
<td>20652</td>
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<tr>
<td>6</td>
<td>3^P_1</td>
<td>21292</td>
<td>21350</td>
<td>21292</td>
<td>21333</td>
<td>21297</td>
<td>21333</td>
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<tr>
<td>7</td>
<td>3^P_2</td>
<td>22558</td>
<td>22700</td>
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Rms deviation

<table>
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<tr>
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<th>E^1/E^3</th>
<th>E^2/E^3</th>
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<tr>
<td></td>
<td>±120</td>
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</tr>
<tr>
<td>E^1</td>
<td>4652.1</td>
<td>4637.2</td>
</tr>
<tr>
<td>E^2</td>
<td>21.3</td>
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<td>E^3</td>
<td>453.9</td>
<td>453.7</td>
</tr>
<tr>
<td>\xi_{4f}</td>
<td>809.9</td>
<td>800.2</td>
</tr>
<tr>
<td>E^1/E^3</td>
<td>218.9</td>
<td>217.2</td>
</tr>
<tr>
<td>E^2/E^3</td>
<td>10.2</td>
<td>10.2</td>
</tr>
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</table>
Table 3.3.
Zero order energies and partial derivatives of Pr$^{3+}$ ion. [Ref. 46]

<table>
<thead>
<tr>
<th>Energy level</th>
<th>$E_{0J}$</th>
<th>$dE_{J}/dE^1$</th>
<th>$dE_{J}/dE^2$</th>
<th>$dE_{J}/dE^3$</th>
<th>$dE_{J}/d\xi_{4f}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$^3H_4$</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>$^3H_5$</td>
<td>2083</td>
<td>-0.0565</td>
<td>7.5934</td>
<td>0.1499</td>
<td>3.0361</td>
</tr>
<tr>
<td>$^3H_6$</td>
<td>4255</td>
<td>-0.0504</td>
<td>7.8087</td>
<td>-0.1006</td>
<td>5.8923</td>
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<tr>
<td>$^3F_2$</td>
<td>4894</td>
<td>-0.0108</td>
<td>13.9914</td>
<td>8.6043</td>
<td>0.8408</td>
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<tr>
<td>$^3F_3$</td>
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<td>-0.0566</td>
<td>7.5932</td>
<td>8.8501</td>
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<tr>
<td>$^3F_4$</td>
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<td>0.6911</td>
<td>-94.8890</td>
<td>7.2036</td>
<td>2.8596</td>
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<td>$^1G_4$</td>
<td>9522</td>
<td>1.1391</td>
<td>-142.331</td>
<td>6.3466</td>
<td>6.2486</td>
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<td>$^1D_2$</td>
<td>16740</td>
<td>1.7600</td>
<td>266.628</td>
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<td>3.1588</td>
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<td>$^3P_0$</td>
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<td>0.0267</td>
<td>7.5933</td>
<td>41.5436</td>
<td>1.8808</td>
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<td>$^3P_1$</td>
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<td>-0.0565</td>
<td>7.5934</td>
<td>41.8566</td>
<td>3.0361</td>
</tr>
<tr>
<td>$^1I_6$</td>
<td>20603</td>
<td>1.9372</td>
<td>77.378</td>
<td>15.8007</td>
<td>3.6798</td>
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<td>$^3P_2$</td>
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<td>28.1607</td>
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<td>$^1S_0$</td>
<td>47836</td>
<td>8.8600</td>
<td>7.5929</td>
<td>9.1566</td>
<td>4.1913</td>
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interaction parameters ($\xi_{4f}$) and hydrogenic ratios ($E^1/E^3$ and $E^2/E^3$) are calculated and are also reported in a Table 3.2. The variation of these parameters from one glass to another explains about structural changes by perturbation. The $E^1$ value decreased when Mg is combined with Ca whereas increased when Cd is combined with Pb in borate glasses. The $E^2$ parameter alters to higher value when Mg is combined with Ca whereas lower value when Cd is combined with Pb in present borate glass. It is also observed that the spin-orbit interaction ($\xi_{4f}$) values decreased in both the mixed modifier oxides (Mg-Ca and Cd-Pb). The hydrogenic ratios, $E^1/E^3$ and $E^2/E^3$ remain almost same over for all Pr$^{3+}$ doped lithium fluoro-borate glass matrix with different modifier oxides. This implies that Pr$^{3+}$ ions are subjected to the similar force field irrespective of different modifier oxides.

The spectral intensities of the observed bands in the optical absorption spectra are often expressed in terms of oscillator strengths of forced electronic dipole transitions. The experimental oscillator strengths ($f_{\text{exp}}$) have been measured by numerical integration [42]. The experimental oscillator strengths obtained from the absorption spectra and calculated values using the resultant Judd–Ofelt parameters for all the Pr$^{3+}$ doped lithium fluoro-borate glasses with different modifier oxide glasses are given in Table 3.4 along with their respective rms deviations. The higher magnitude of oscillator strength ($f_{\text{exp}}$) for $^3H_4 \rightarrow ^3P_2$ transition indicates that the intensity of the absorption band depends strongly on the neighboring ligands [43]. Among all the single modifier oxide glasses magnesium and calcium borate glasses possess higher spectral intensities. However decreasing of spectral intensity was observed when magnesium combines with calcium oxide and cadmium combined with lead in borate glass.

3.2.3 J-O intensity parameters

The Judd–Ofelt parameters ($\Omega_\lambda$, where $\lambda$=2, 4 and 6) are obtained from least-square analysis of observed oscillator strengths and squared reduced matrix elements $|U^3|$ for all the electric dipole transitions (presented in Table 3.5) using conventional expression explained in Chapter 2 and are compared with the values obtained for different modifier oxides in Table 3.6. In the present work, the trend of the J-O intensity parameters is in the order of $\Omega_6 > \Omega_4 > \Omega_2$ for all the Pr$^{3+}$ doped lithium fluoro-borate
Table 3.4.

Experimental and calculated spectral intensities of \((fx10^{-6})\) of certain excited states of \(Pr^{3+}\) doped lithium fluoro-borate glass with different modifier oxides.

<table>
<thead>
<tr>
<th>S.No.</th>
<th>Energy level</th>
<th>Mg (f_{exp})</th>
<th>Mg (f_{cal})</th>
<th>Ca (f_{exp})</th>
<th>Ca (f_{cal})</th>
<th>Cd (f_{exp})</th>
<th>Cd (f_{cal})</th>
<th>Pb (f_{exp})</th>
<th>Pb (f_{cal})</th>
<th>Mg-Ca (f_{exp})</th>
<th>Mg-Ca (f_{cal})</th>
<th>Cd-Pb (f_{exp})</th>
<th>Cd-Pb (f_{cal})</th>
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<td>2</td>
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<td>3.29</td>
<td>8.91</td>
<td>3.23</td>
<td>8.25</td>
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<td>6.34</td>
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<td>3.15</td>
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</tr>
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<td>(^3P_0)</td>
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<td>4.99</td>
<td>3.27</td>
<td>4.44</td>
<td>2.59</td>
<td>3.70</td>
<td>2.84</td>
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<td>2.58</td>
<td>3.76</td>
<td>3.20</td>
<td>4.12</td>
</tr>
<tr>
<td>4</td>
<td>(^1D_2)</td>
<td>4.83</td>
<td>4.32</td>
<td>5.17</td>
<td>4.34</td>
<td>4.46</td>
<td>3.47</td>
<td>4.31</td>
<td>3.86</td>
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<td>4.74</td>
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<tr>
<td>5</td>
<td>(^1G_4)</td>
<td>0.95</td>
<td>1.25</td>
<td>0.58</td>
<td>1.25</td>
<td>0.41</td>
<td>0.99</td>
<td>0.44</td>
<td>1.11</td>
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<td>1.08</td>
<td>0.42</td>
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<td>2.74</td>
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<td>(^3F_3)</td>
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<td>20.41</td>
<td>19.76</td>
<td>19.95</td>
<td>19.76</td>
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Rms deviation: ± 3.48 ± 3.12 ± 2.65 ± 2.13 ± 2.82 ± 2.63
Table 3.5.

Squared reduced matrix elements of Pr$^{3+}$ ion. [Ref. 47]

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<th>$| U^4 |^2$</th>
<th>$| U^6 |^2$</th>
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<td>0.2012</td>
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<td>0</td>
<td>0.0333</td>
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</tr>
<tr>
<td>$^3F_2$</td>
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<td>0.4030</td>
<td>0.1173</td>
</tr>
<tr>
<td>$^3F_3$</td>
<td>0.0653</td>
<td>0.3465</td>
<td>0.6982</td>
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<tr>
<td>$^3F_4$</td>
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<td>0.0503</td>
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<td>$^1G_4$</td>
<td>0.0011</td>
<td>0.0073</td>
<td>0.0266</td>
</tr>
<tr>
<td>$^1D_2$</td>
<td>0.0027</td>
<td>0.0174</td>
<td>0.0534</td>
</tr>
<tr>
<td>$^3P_0$</td>
<td>0</td>
<td>0.1729</td>
<td>0</td>
</tr>
<tr>
<td>$^3P_1$</td>
<td>0</td>
<td>0.1702</td>
<td>0</td>
</tr>
<tr>
<td>$^3P_2$</td>
<td>0</td>
<td>0.0360</td>
<td>0.1360</td>
</tr>
</tbody>
</table>
Table 3.6.

Judd-Ofelt intensity parameters ($\Omega_x \times 10^{-20}$) (cm$^2$) of Pr$^{3+}$ doped lithium-fluoro-borate glass with different modifier oxides.

<table>
<thead>
<tr>
<th>S. No</th>
<th>Glass</th>
<th>$\Omega_2$</th>
<th>$\Omega_4$</th>
<th>$\Omega_6$</th>
<th>$\Omega_4/\Omega_6$</th>
<th>Trend</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Mg (Present work)</td>
<td>4.03</td>
<td>7.61</td>
<td>23.62</td>
<td>0.32</td>
<td>$\Omega_6 &gt; \Omega_4 &gt; \Omega_2$</td>
</tr>
<tr>
<td>2</td>
<td>Ca (Present work)</td>
<td>4.60</td>
<td>6.85</td>
<td>24.06</td>
<td>0.28</td>
<td>$\Omega_6 &gt; \Omega_4 &gt; \Omega_2$</td>
</tr>
<tr>
<td>3</td>
<td>Cd (Present work)</td>
<td>4.38</td>
<td>5.74</td>
<td>19.01</td>
<td>0.30</td>
<td>$\Omega_6 &gt; \Omega_4 &gt; \Omega_2$</td>
</tr>
<tr>
<td>4</td>
<td>Pb (Present work)</td>
<td>5.11</td>
<td>4.87</td>
<td>21.72</td>
<td>0.22</td>
<td>$\Omega_6 &gt; \Omega_4 &gt; \Omega_2$</td>
</tr>
<tr>
<td>5</td>
<td>Mg-Ca(Present work)</td>
<td>1.31</td>
<td>5.79</td>
<td>20.92</td>
<td>0.28</td>
<td>$\Omega_6 &gt; \Omega_4 &gt; \Omega_2$</td>
</tr>
<tr>
<td>6</td>
<td>Cd-Pb(Present work)</td>
<td>1.96</td>
<td>6.33</td>
<td>20.61</td>
<td>0.31</td>
<td>$\Omega_6 &gt; \Omega_4 &gt; \Omega_2$</td>
</tr>
<tr>
<td>7</td>
<td>Fluoro borate [23]</td>
<td>16.78</td>
<td>23.72</td>
<td>3.36</td>
<td>7.06</td>
<td>$\Omega_4 &gt; \Omega_2 &gt; \Omega_6$</td>
</tr>
<tr>
<td>8</td>
<td>Boro phosphate [43]</td>
<td>3.12</td>
<td>7.21</td>
<td>5.81</td>
<td>1.23</td>
<td>$\Omega_4 &gt; \Omega_6 &gt; \Omega_2$</td>
</tr>
<tr>
<td>9</td>
<td>Tellurite [44]</td>
<td>3.81</td>
<td>5.81</td>
<td>4.10</td>
<td>1.42</td>
<td>$\Omega_4 &gt; \Omega_6 &gt; \Omega_2$</td>
</tr>
</tbody>
</table>
glasses except for Pb glass. It is of interest to study the variation in the Judd–Ofelt parameters across all Pr$^{3+}$ doped lithium fluoro-borate glasses with different modifier oxides. Thus, the $\Omega_3$ parameters are compared with other Pr$^{3+}$ doped glasses. Among the three J-O parameters, $\Omega_2$ explains about covalency between Pr-O group which leads to play a key role to explain the variation of non-centro symmetric potential around ligand field, while $\Omega_4$ and $\Omega_6$ parameters indicate the bulk properties of the glass such as viscosity and basicity of the matrix. Among all the single modifier oxides based lithium-fluoro-borate glasses, lead borate glass shows higher $\Omega_2$ and magnesium borate glass shows lower $\Omega_2$. It explains the asymmetry variation with the higher and lower covalancy between Pr-O bond respectively. The $\Omega_2$ parameter changes to lower in two mixed modifier oxides (Mg-Ca and Cd-Pb) which explains lower asymmetry around the ligand field and covalancy between Pr-O bond. These evaluated $\Omega_2$ parameters are compared to the other fluoro borate [33], borophosphate [43] and tellurite [44] glasses.

### 3.2.4 Hypersensitive transition

For Pr$^{3+}$-doped glasses, $^3H_4 \rightarrow ^3P_2$ transition is found to be highly sensitive to the environment and the intensity vary significantly with environment due to strong 4f–5d mixing. It is called hypersensitive transition (HST). In addition, the higher values of $||U^j||^2$ of this level is considered as an important factor for the hypersensitive nature of this level [45]. The shifting of band position of HST has been observed in all the present glasses. It shows structural changes in different modifier oxide glasses. The band positions of HST of Pr$^{3+}$ in different lithium-fluoro-borate glasses are presented in Table 3.6. The degree of covalency of Pr–O bond decreases/increases with the shift of peak wavelength of HST towards lower/higher wavelengths due to nephelauxetic effect. It is observed from the table that the HST band position shifted towards shorter wavelength with increasing atomic weight of modifier cation Mg (24.30), Ca (40.07), Cd (112.41) and Pb (207.2). For magnesium to magnesium-calcium and cadmium to cadmium-lead glass there is a shift of HST towards longer wavelength but the $\Omega_2$ parameter decreased indicating some structural changes. It might be due to interaction of M-O bonding relating to the corresponding modifier oxides. The host materials with larger values of spectroscopic quality factors are more potential for stimulated emission. From Table 3.6,
it is observed that there is not much variation in the magnitudes of $X(=\Omega_4/\Omega_6)$ values for different modifier oxides of borate glasses. But $X$ value is lower for lead and higher for magnesium glass and these values are compared with the $\text{Pr}^{3+}$ doped other glass matrices such as fluoro-borate [33], boro-phosphate [43] and Tellurite [44] glasses in Table 3.6

### 3.2.5 Radiative properties of electric-dipole transitions in $\text{Pr}^{3+}$ ion

Using J-O parameters, the characteristic radiative properties of various excited levels in $\text{Pr}^{3+}$ ion have been estimated by means of conventional formulae taken from Chapter 2. The radiative transition probabilities ($A_T$), lifetimes ($\tau$), branching ratios ($\beta$) and integrated absorption cross-sections ($\Sigma$) are calculated and are presented in Table 3.7. It is observed from the table that both $^3P_0$ and $^3P_1$ excited levels exhibit similar lifetime values. And it has been observed that the higher lifetime value for $^1D_2$ and $^3F_3$ excited levels. Table 3.7 also shows the branching ratios ($\beta$) and absorption cross-section ($\Sigma$) values of prominent transitions of different excited levels for all the $\text{Pr}^{3+}$ ion doped lithium-fluoro-borate glass with different modifier oxides. It is observed from the table that the higher $\beta$ and $\Sigma$ values are observed for $^3P_1\rightarrow^3H_5$, $^3P_0\rightarrow^3H_4$ and $^3F_3\rightarrow^3H_4$ transitions. Among all the single modifier oxide glasses magnesium glass exhibits higher $\beta$ and $\Sigma$ values. It is also observed from the table that the $\beta$ and $\Sigma$ values are increased in the case of mixed modifier oxides (Mg-Ca, Cd-Pb).

### 3.2.6 Emission spectra-stimulated emission cross-section

To record the luminescence spectra of $\text{Pr}^{3+}$ doped lithium-fluoro-borate glass, the excitation spectra were recorded by monitoring the emission peak at 604 nm as shown in Fig. 3.4. The visible emission spectra of the Pr-doped lithium-fluoro-borate glass with different modifier oxides are illustrated in Fig. 3.5. under an excitation source of 445 nm. Four broad emission bands $^3P_0\rightarrow^3H_4$, $^3P_1\rightarrow^3H_5$, $^1D_2\rightarrow^3H_4$ and $^3P_0\rightarrow^3F_2$ centered approximately at 488, 530, 604 and 638 nm with FWHM values of ~16, ~15, ~26 and ~17 nm, respectively are observed. Among all these emittive transitions, blue emitted $^3P_0\rightarrow^3H_4$ transition exhibits higher intensity than other transitions. The large stimulated emission cross-section ($\sigma_p$) of a luminescence transition is one of the important parameter used to predict a laser active medium. Table 3.8 gives the peak wavelengths ($\lambda_p$),
Table 3.7.

Total radiative transition probabilities ($A_T$) (s$^{-1}$) and radiative lifetimes ($\tau_R$) (μs) of certain excited states and branching ratios ($\beta$) (%) and integrated absorption cross-sections ($\Sigma \times 10^{18}$) (cm$^{-1}$) of energy transitions of Pr$^{3+}$ doped lithium fluoro-borate glass with different modifier oxides.

<table>
<thead>
<tr>
<th>Energy level</th>
<th>Mg</th>
<th>Ca</th>
<th>Cd</th>
<th>Pb</th>
<th>Mg-Ca</th>
<th>Cd-Pb</th>
</tr>
</thead>
<tbody>
<tr>
<td>$^3P_1$</td>
<td>80256</td>
<td>78129</td>
<td>65677</td>
<td>63545</td>
<td>59312</td>
<td>63329</td>
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<tr>
<td>$^3P_0$</td>
<td>79351</td>
<td>76859</td>
<td>65170</td>
<td>61389</td>
<td>57150</td>
<td>61752</td>
</tr>
<tr>
<td>$^1D_2$</td>
<td>8213</td>
<td>8304</td>
<td>7052</td>
<td>7512</td>
<td>5987</td>
<td>6345</td>
</tr>
<tr>
<td>$^3F_3$</td>
<td>2674</td>
<td>2682</td>
<td>2164</td>
<td>2307</td>
<td>2233</td>
<td>2248</td>
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</tbody>
</table>

<table>
<thead>
<tr>
<th>Transition</th>
<th>$\beta$</th>
<th>$\Sigma$</th>
<th>$\beta$</th>
<th>$\Sigma$</th>
<th>$\beta$</th>
<th>$\Sigma$</th>
<th>$\beta$</th>
<th>$\Sigma$</th>
<th>$\beta$</th>
<th>$\Sigma$</th>
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<tbody>
<tr>
<td>$^3P_1 \rightarrow ^3H_5$</td>
<td>38</td>
<td>39.61</td>
<td>37</td>
<td>37.87</td>
<td>37</td>
<td>30.81</td>
<td>35</td>
<td>29.15</td>
<td>42</td>
<td>32.51</td>
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<tr>
<td>$^3P_0 \rightarrow ^3H_4$</td>
<td>44</td>
<td>39.47</td>
<td>41</td>
<td>35.42</td>
<td>40</td>
<td>29.73</td>
<td>32</td>
<td>22.06</td>
<td>47</td>
<td>29.98</td>
</tr>
<tr>
<td>$^1D_2 \rightarrow ^3F_4$</td>
<td>21</td>
<td>8.35</td>
<td>23</td>
<td>9.33</td>
<td>25</td>
<td>8.7</td>
<td>28</td>
<td>10.10</td>
<td>12</td>
<td>3.48</td>
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<tr>
<td>$^1D_2 \rightarrow ^3H_4$</td>
<td>50</td>
<td>6.87</td>
<td>49</td>
<td>6.91</td>
<td>46</td>
<td>5.51</td>
<td>48</td>
<td>6.10</td>
<td>59</td>
<td>5.97</td>
</tr>
<tr>
<td>$^3F_3 \rightarrow ^3H_4$</td>
<td>88</td>
<td>26.34</td>
<td>88</td>
<td>26.43</td>
<td>87</td>
<td>21.11</td>
<td>88</td>
<td>22.95</td>
<td>91</td>
<td>22.66</td>
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Figure 3.4. Excitation spectrum of Pr$^{3+}$ doped magnesium lithium-fluoro-borate glass.
Figure 3.5. Emission spectra of Pr$^{3+}$ doped lithium-fluoro-borate glass with different modifier oxides.
Table 3.8.

Emission band positions ($\lambda_p$, nm), effective bandwidths ($\Delta \nu_{\text{eff}}$, cm$^{-1}$), radiative transition probabilities ($A$, s$^{-1}$), peak stimulated emission cross-sections ($\sigma_p \times 10^{20}$ cm$^2$) and branching ratios ($\beta_R$, %) of Pr$^{3+}$ doped lithium fluoro-borate glass matrix with different modifiers oxides.

<table>
<thead>
<tr>
<th>S.No</th>
<th>Transition</th>
<th>Parameters</th>
<th>Mg</th>
<th>Ca</th>
<th>Cd</th>
<th>Pb</th>
<th>Mg-Ca</th>
<th>Cd-Pb</th>
</tr>
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<tbody>
<tr>
<td>1</td>
<td>$^3P_0 \rightarrow ^3H_4$</td>
<td>$\lambda_p$</td>
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<td>488</td>
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<td>489</td>
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<td>488</td>
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<td></td>
<td></td>
<td>$\Delta \nu_{\text{eff}}$</td>
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<td>684</td>
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<td>676</td>
<td>461</td>
<td>588</td>
</tr>
<tr>
<td></td>
<td></td>
<td>$A$</td>
<td>35091</td>
<td>31372</td>
<td>26348</td>
<td>19466</td>
<td>26571</td>
<td>28942</td>
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<tr>
<td></td>
<td></td>
<td>$\sigma_p$</td>
<td>5.78</td>
<td>5.31</td>
<td>4.75</td>
<td>3.34</td>
<td>6.66</td>
<td>5.70</td>
</tr>
<tr>
<td></td>
<td></td>
<td>$\beta_R(\text{exp})$</td>
<td>34</td>
<td>34</td>
<td>32</td>
<td>25</td>
<td>24</td>
<td>29</td>
</tr>
<tr>
<td></td>
<td></td>
<td>$\beta_R(\text{cal})$</td>
<td>44</td>
<td>41</td>
<td>40</td>
<td>32</td>
<td>47</td>
<td>46</td>
</tr>
<tr>
<td></td>
<td>$^3P_0 \rightarrow ^3H_4$</td>
<td>$\lambda_p$</td>
<td>604</td>
<td>604</td>
<td>603</td>
<td>604</td>
<td>603</td>
<td>604</td>
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<tr>
<td></td>
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<td>772</td>
<td>766</td>
<td>1022</td>
<td>734</td>
<td>772</td>
<td>723</td>
</tr>
<tr>
<td></td>
<td></td>
<td>$A$</td>
<td>4070</td>
<td>4065</td>
<td>3254</td>
<td>3593</td>
<td>3519</td>
<td>3498</td>
</tr>
<tr>
<td></td>
<td></td>
<td>$\sigma_p$</td>
<td>0.93</td>
<td>0.94</td>
<td>0.56</td>
<td>0.87</td>
<td>0.80</td>
<td>0.85</td>
</tr>
<tr>
<td></td>
<td></td>
<td>$\beta_R(\text{exp})$</td>
<td>60</td>
<td>60</td>
<td>62</td>
<td>70</td>
<td>68</td>
<td>66</td>
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<td>$\beta_R(\text{cal})$</td>
<td>50</td>
<td>49</td>
<td>46</td>
<td>48</td>
<td>59</td>
<td>55</td>
</tr>
</tbody>
</table>
effective band widths (Δν_{eff}), radiative transition probabilities (A_T) and stimulated emission cross-sections (σ_P) along with branching ratios values (β_{exp} and β_{cal}) of the observed transitions. The stimulated emission cross-sections (σ_P) are maximum for the \(^3P_0 \rightarrow \(^3H_4\) transition and minimum for \(^1D_2 \rightarrow \(^3H_4\) transition. The experimental branching ratios (β_{exp}) were calculated from the luminescence spectra and the same is compared with the predicted branching ratio values from J–O theory. The measured branching ratio for \(^1D_2 \rightarrow \(^3H_4\) transition is higher and it performs greater value in Pb glass, explains good laser excitation among all the glasses.

### 3.3 Conclusions

The amorphous nature of different Pr\(^{3+}\) doped lithium-fluoro-borate glass matrices were confirmed by SEM images. Spectroscopic properties of Pr\(^{3+}\) doped lithium-fluoro-borate glass have been investigated using optical absorption and emission spectra. Using optical absorption spectra, Judd–Ofelt parameters, Ω_λ (where λ=2, 4 and 6) are obtained for all glass matrices. Ω_2 parameter is higher in lead glass matrix and lower in magnesium glass matrix among four glass matrices (Mg, Ca, Cd and Pb) indicated higher and lower covalencies in these two glass matrices respectively and hence asymmetry around the Pr\(^{3+}\) ion is higher and lower in these two glass matrices respectively. The variation of Ω_2 parameter with the spectral intensity of hypersensitive transition was discussed. Based on intensity parameters, covalency of Pr–O bond and rigidity of different fluoroborate glass matrices are discussed. Using these Judd–Ofelt intensity parameters, radiative transitions rates (A_T), branching ratios (β_R), radiative lifetimes (τ_R) and stimulated emission cross-sections (σ_P) of certain transitions are reported. From the radiative parameters of all the glass matrices it is found that the emission transition, \(^3P_0 \rightarrow \(^3H_4\) showed higher stimulated emission cross-section in magnesium (5.78x10\(^{-20}\) cm\(^2\)) and calcium (5.31x10\(^{-20}\) cm\(^2\)) lithium fluoro-borate glass matrices. The stimulated emission cross-section is increased when magnesium is combined with calcium (Mg-Ca, 6.66x10\(^{-20}\) cm\(^2\)), hence it is suggested that these glass matrices are useful for laser excitation.
Chapter 3

Pr$^{3+}$ ion doped lithium-fluoro-borate glasses

References

Pr$^{3+}$ ion doped lithium-fluoro-borate glasses