CHAPTER  7

SUMMARY AND CONCLUSIONS

Heavy metal oxide (HMO) glasses find their importance as host matrices for good lasing candidates because of their low phonon energy, high mechanical and thermal stability, corrosion resistance and good solubility of rare earth ion. The incorporation of HMOs such as PbO or Bi$_2$O$_3$ into the borate glass matrix leads to an increase in its luminescence quantum efficiency. In the present work lead-bismuth-aluminum- borate glasses, doped with Nd$^{3+}$ and Pr$^{3+}$ ions have been prepared and the physical and optical properties were studied, especially the suitability of the samples prepared as the core material for optical fiber and active medium for solid lasers, with concentration variation of RE ions and host variation.

BLABIN glass samples have been fabricated and characterized for their physical and optical properties. The refractive index range from 1.740 to 1.749. The numerical aperture is 0.25 for all the glasses indicating them as potential candidates for core material of optical fiber.

The low rms deviation ranging from ± 40.13 to ± 57.47, obtained in the fitting analysis for experimental and calculated band positions, support the validity of the evaluated spectroscopic parameters. The Slater integrals $F^2/F^4$ and $F^2/F^6$ are in agreement with the other reported works. The bonding parameter is positive and <1 for all glass samples. Hence bonding observed in them is of covalent in nature. The spectroscopic quality factor $\chi$ <1 indicates these glasses as good lasing candidates. $\Omega_4$ and $\Omega_6$ values indicate that the rigidity of the present glasses under study increases with increasing concentration. BLABIN:1 glass has $\chi$ = 0.38 equivalent to that of Nd:YAG laser indicating it as a good lasing material. The values of branching ratios ($\beta_R$) and emission cross sections ($\sigma_e$) obtained for all the glasses are of high in magnitude for the lasing
transition $^4F_{3/2} \rightarrow ^4I_{11/2}$ indicating the glasses as good laser hosts and suitable for optical amplifier with window at 1.6 μm. The indirect and direct mobility gap values show a maximum for 0.5 mol% and minimum for 3.0 mol% concentration and decreasing trend from 1.5 to 3.0 mol% of Nd$_2$O$_3$. As the optical band gap values are low, indirect optical band gap ranges from 3.63 to 3.68 eV these glass matrices have good switching action and high lasing efficiency. The structural changes in the 3D glass network as well as in the local environments of the Nd$^{3+}$ ions take place due to the variation of the doping concentration of Nd$^{3+}$ ions, evident from FT-IR spectra. The coexistence of trigonal BO$_3$ and tetrahedral BO$_4$ units was evidenced by FT-IR spectroscopy.

BINLAB glass samples have been fabricated and characterized for their physical and optical properties. The physical and optical properties of these Nd$^{3+}$ doped glasses have been investigated. The refractive index range from 1.602 to 1.842 indicating the increase of RI with increase of PbO and decrease of B$_2$O$_3$. The numerical aperture values for these glasses range from 0.23 to 0.26 and so these glasses are potential candidates as core material for optical fiber.

The low rms deviation ranging from ± 73 to ± 85, obtained in the fitting analysis for experimental and calculated band positions, support the validity of the evaluated spectroscopic parameters. The free-ion ratios $F^2/F^4$ and $F^2/F^6$ of all studied glasses signify the radial integral part of the f–orbital of the Nd$^{3+}$ ions do not deviate much. The higher value of $\Omega_2$ parameter and the positive value of bonding parameter ($\delta$) for all investigated glasses signify stronger covalent bonds and lower symmetry around Nd$^{3+}$ ions. All these glasses have spectroscopic quality factor less than one, indicating that the lasing transition $^4F_{3/2} \rightarrow ^4I_{11/2}$ is relatively strong. The values of $\sigma(\lambda, p)$ for this transition are comparable to those of commercial
laser glasses LHG-8 and LG-750 reported in the literature. The higher values of experimental and predicted branching ratios \( \beta_R \) for the \( ^4\text{F}_{3/2} \rightarrow ^4\text{I}_{11/2} \) transition compared to other transitions indicate all the BINLAB:1-5 glasses are expected to be good laser hosts. Lead borate glasses are formed over a wide range of PbO concentrations. This large glass-forming region is advantageous for manufacture of structurally and optically different systems especially as potential solid-state laser materials emitting NIR light. The indirect optical band gap values exhibit decreasing tendency with the increase of PbO and decrease of B\(_2\)O\(_3\) indicating red shift. Low optical band gap values indicate low phonon energies and high lasing efficiency of the glasses which also reflect their good switching action. From FT-IR spectra functional groups were identified. The increase of PbO content to the glass matrix promotes the conversion of some BO\(_3\) units to BO\(_4\).

BLABIP glass samples have been fabricated and characterized for their physical and optical properties. The refractive index is about 1.74 for all the glass samples. The numerical aperture value does not vary much with concentration and \( \text{NA}=0.25 \) indicates the suitability of the material as core material for optical fiber. The low rms deviation ranging from \( \pm 12 \) to \( \pm 48 \), obtained in the fitting analysis for experimental and calculated band positions, support the validity of the evaluated spectroscopic parameters. The sum of Slater parameter, \( \Sigma F^K \), indicates the net electrostatic interaction experienced by Pr\(^{3+}\) ions in the host matrix. The positive value of bonding parameter \( \delta \) indicates that the bonds between Pr\(^{3+}\) ion and ligands are covalent in nature. The quality of the least square fit given by rms deviation between the experimental and calculated oscillator strengths better when the hypersensitive transition \( ^3\text{H}_4 \rightarrow ^3\text{P}_2 \) is omitted, ranges from \( \pm 0.7.6 \) to \( \pm 1.038 \).
J-O intensity parameters of all the glass samples follow the order $\Omega_4 < \Omega_2 < \Omega_6$. For all the glass samples high value of $\Omega_2$ indicates the covalent nature of the ion-ligand bond as expected from bonding parameter and the $\Omega_2$ value increases with increase of concentration indicating increase in the covalence and asymmetry of ion-ligand bond. Spectroscopic quality factor $\Omega_4/\Omega_6$ is less than one and range from 0.25 to 0.77. The parameters $\Omega_4$ and $\Omega_6$ have high values indicting high rigidity for all the glass samples, which increase with increase of concentration. Thus the obtained J-O parameters indicate that the present glasses are more potential lasing candidates.

The changes in the line profiles of electric dipole line strengths ($S'_{ed}$) and radiative transition probabilities ($A_R$) of certain lasing transitions of Pr$^{3+}$ indicate small change in the concentration of Pr$^{3+}$ changes the network structure of the glass and the local environment of the optically active ion.

The emission bands corresponding to $^3P_0 \rightarrow ^3H_4$ and $^1D_2 \rightarrow ^3H_4$ transitions are more intense compared to $^3P_1 \rightarrow ^3H_5$ and $^3P_0 \rightarrow ^3F_2$ transitions. The emission band of the transition $^3P_1 \rightarrow ^3H_5$ has been almost merged with that of $^3P_0 \rightarrow ^3H_4$ transition. In the case of $^1D_2$ level the quenching of the emission intensity has been observed and at 0.10 mol% the intensity is maximum. Hence BLABIP:3 glass is selected for laser amplification with the transition $^1D_2 \rightarrow ^3H_4$. The high values of emission cross-sections indicate that these glass matrices are good laser active media. With increase of concentration, ($\sigma_e$) value increases from 0.03 mol% to 0.50 mol% except at 0.30 mol%, indicating the increase in the gain parameter. Application of J-O theory to Pr$^{3+}$ ion in analyzing the radiative parameters yield poor agreement.

From FT-IR spectra functional groups were identified.
BIPLAB glass samples have been fabricated and characterized for their physical and optical properties. The refractive index range from 1.616 to 1.856 indicating the increase of RI with increase of PbO and decrease of B₂O₃. The numerical aperture (NA) value range from 0.23 to 0.26 indicating the suitability of the material as core material for optical fibers. The higher magnitude refractive indices of all the five glasses make them to fit as the lasing candidates and core materials of the optical fiber.

The rms deviation of the observed and calculated energies range from ± 14.62 to ± 18.838, in good agreement with the literature. The sum of Slater parameter, ΣFrK, indicates the net electrostatic interaction experienced by Pr³⁺ ions in the host matrix. The positive value of bonding parameter δ indicates that the bonds between Pr³⁺ ion and ligands are covalent in nature. The quality of the least square fit given by rms deviation between the experimental and calculated oscillator strengths is better when the hypersensitive transition ⁴H₄ → ⁴P₂ is omitted, ranges from ± 0.843 to ± 1.223.

It is observed that Ω₆ > Ω₄ > Ω₂ for BIPLAB:1,2 and 4 glasses and Ω₄ > Ω₆ > Ω₂ for BIPLAB:3 and 5 glasses. The parameter Ω₂ is associated with asymmetry of the ligand field near the rare earth ion. Ω₂ value are in the order BIPLAB:1 > BIPLAB:5 > BIPLAB:3 > BIPLAB:2 > BIPLAB:4. The higher values of Ω₂ obtained for BIPLAB:1, 3 and 5 glasses in the present study indicate that the asymmetry and covalence of the ligand field at the rare earth site are higher as expected from bonding parameter. The spectroscopic quality factor Ω₄ / Ω₆ observed range from 0.954 to 1.047 indicating that these glasses are fairly rigid as compared to other glasses reported in literature [146]. Thus the obtained J-O parameters indicate that the present glasses are more potential lasing candidates.
The emission bands corresponding to $^3P_0 \rightarrow ^3H_4$ and $^1D_2 \rightarrow ^3H_4$ transitions are more intense compared to $^3P_1 \rightarrow ^3H_5$ and $^3P_0 \rightarrow ^3F_2$ transitions. The emission band of the transition $^3P_1 \rightarrow ^3H_5$ has been almost merged with that of $^3P_0 \rightarrow ^3H_4$ transition. Computed radiative life times for the transitions are in the order $^3F_4 > ^1G_4 > ^1I_6 > ^3P_1 > ^3P_0 > ^3P_2$. Higher life times comparative to others' indicate better lasing transitions. It is observed that the branching ratios of the transitions $^3P_1 \rightarrow ^3F_3$, $^3P_0 \rightarrow ^3F_2$, $^1D_2 \rightarrow ^3F_4$, $^1G_4 \rightarrow ^3H_5$, $^3H_6$ exhibit higher values. An important lasing transition for optical fiber is $^1G_4 \rightarrow ^3H_5$. In the present glasses this transition exhibits high values of branching ratios. This property is observed for ZBLN, (Ge$_5$S$_2$)$_{80}$ (Ge$_9$S$_3$)$_{20}$ and Ga-La-S fluoride and sulfide glasses for optical fibers. Emission peak wavelengths($\lambda_p$) show the red shift that may be attributed to the site distribution of Pr$^{3+}$ ions in the vicinity of ligand fields. The values of $\sigma_e$ for $^3P_0 \rightarrow ^3H_4$ transition are in the order BIPLAB:3 > BIPLAB:5 > BIPLAB:1 > BIPLAB:4 > BIPLAB:2 and for $^1D_2 \rightarrow ^3H_4$ transition are in the order BIPLAB:4 > BIPLAB:5 > BIPLAB:3 > BIPLAB:1 > BIPLAB:2. The high values of emission cross-sections indicate that these glass matrices are good laser active media indicating the increase in the gain parameter. Application of J-O theory to Pr$^{3+}$ ion in analyzing the radiative parameters yield poor agreement between calculated and experimental values due to the strong f-d mixing which is not accounted by the theory.

Both indirect and direct mobility gap values show a non-uniform variation with increase of PbO content and decrease of B$_2$O$_3$ content indicating the variation of switching action, which might be due to the change in the number of non-bridging oxygen atoms. The variation in the values of optical band gap energy can thus be attributed to the similar variation in the phonon-assistant indirect transitions.
From FT-IR spectra functional groups were identified. The increase of PbO content to the glass matrix promotes the conversion of some BO$_3$ units to BO$_4$.

In the case of Nd$^{3+}$ doped glasses the emission windows are: 1.33 μm for $^4F_{3/2} \rightarrow ^4I_{13/2}$, 1.061 μm for $^4F_{3/2} \rightarrow ^4I_{11/2}$ and 0.91 μm for $^4F_{3/2} \rightarrow ^4I_{9/2}$. In the case of Pr$^{3+}$ doped glasses the emission windows are: 0.492 μm for $^3P_0 \rightarrow ^3H_4$ and 0.60 μm for $^1D_2 \rightarrow ^3H_4$. In Nd$^{3+}$ doped glasses the transition $^4F_{3/2} \rightarrow ^4I_{11/2}$ is more intense and so attractive for laser operation at around 1.06 μm and $^4F_{3/2} \rightarrow ^4I_{13/2}$ transition with window at 1.33 μm is suitable for optical amplifier for the second generation telecommunications. With increase of lead content the intensity of all the lasing transitions in both Nd$^{3+}$ and Pr$^{3+}$ doped glasses increases and so also with the increase of concentration, except for $^1D_2 \rightarrow ^3H_4$ in the case of Pr$^{3+}$ doped glasses where self quenching takes place. BLABIP:3 is the better one among BLABIP: 1-5 glasses to have more intense lasing action for $^1D_2 \rightarrow ^3H_4$ transition. Thus Nd$^{3+}$ and Pr$^{3+}$ doped glasses with higher concentration and with higher lead content are better lasing candidates. Hence when these glass materials are drawn in the form of fibers, they are quite suitable for signal amplifier for communication in the second telecom window. Such optical amplifiers easily compensate for the losses in the processing and distribution of optical signals while maintaining the high band width and low cross talk.

**FUTURE PLAN OF WORK**

Proposed to study the temperature and pressure dependence of spectral properties of Nd$^{3+}$ and Pr$^{3+}$ ions doped in all of these glass matrices and their physical properties at higher concentrations. Also planned to study the suitability of the glass systems as laser hosts, optical amplifiers and core materials for optical fibers with temperature variation.