6.1 SUMMARY

The present investigation is on "Studies on up-conversion luminescence of Er^{3+}/Yb^{3+} codoped lead bismuth borate glasses mixed with some IIIA group sesquioxides". The detailed results of present investigation are presented in this thesis. The results reported in the thesis presents a wide range review of both experimental and theoretical work on "Studies on up-conversion luminescence of Er^{3+}/Yb^{3+} codoped lead bismuth borate glasses mixed with some IIIA group sesquioxides". A systematic investigation is to prepare different compositions of glasses via melt quenching technique within the glass forming range and characterize through X-Ray diffraction, Optical absorption spectra, FTIR spectra and Photo luminescence spectra.

The compositions of the samples used in the present study are:

(i) $[100\text{-}(x+y)][0.5PbO\text{-}0.25Bi_2O_3\text{-}0.20B_2O_3\text{-}0.05Al_2O_3]\text{-}xEr_2O_3\text{-}yYb_2O_3$
$y = 0$ for $x = 0$, 0.2 and $y = 0.2$ for $x = 0$ to 1.0 (step 0.2)

(ii) $[100\text{-}(x+y)][0.5PbO\text{-}0.25Bi_2O_3\text{-}0.20B_2O_3\text{-}0.05Ga_2O_3]\text{-}xEr_2O_3\text{-}yYb_2O_3$
$y = 0$ for $x = 0$, 0.2 and $y = 0.2$ for $x = 0$ to 1.0 (step 0.2)

(iii) $[100\text{-}(x+y)][0.5PbO\text{-}0.25Bi_2O_3\text{-}0.20B_2O_3\text{-}0.05In_2O_3]\text{-}xEr_2O_3\text{-}yYb_2O_3$
$y = 0$ for $x = 0$, 0.2 and $y = 0.2$ for $x = 0$ to 1.0 (step 0.2)

6.2 CONCLUSIONS

The main conclusions drawn from the results of above studies are summarized below:

i. X-ray diffraction

The X-ray diffraction of all the compositions of Yb^{3+} and $Er3^{+}$ ions codoped $PbO–B_2O_3–Bi_2O_3$ glasses mixed with $Al_2O_3/Ga_2O_3/In_2O_3$ consist of broad diffuse haloes rather than sharp peaks. This confirms the amorphous state of all the prepared glasses.

ii. Optical absorption spectral studies of Yb^{3+} and Er^{3+} codoped $PbO–B_2O_3–Bi_2O_3$ glasses mixed with $Al_2O_3/Ga_2O_3/In_2O_3$

The optical absorption spectra of Yb^{3+} and Er^{3+} doped $PbO–B_2O_3–Bi_2O_3$ glasses mixed with $Al_2O_3/Ga_2O_3/In_2O_3$ recorded at room temperature have exhibited the following absorption bands:

Yb^{3+} : ${}^{2}F_{7/2} \rightarrow {}^{2}F_{5/2}$

Er^{3+} : ${}^{4}I_{15/2} \rightarrow {}^{4}F_{7/2}$, ${}^{2}H_{11/2}$, ${}^{4}S_{3/2}$, ${}^{4}F_{9/2}$, ${}^{4}I_{9/2}$, ${}^{4}I_{11/2}$ and ${}^{4}I_{13/2}$.

- ***Results of Optical absorption spectra of AEY glass system***

From optical absorption data, for AEY samples, optical band gap energy is found to decrease with increasing the concentration of Er^{3+} ions upto 0.8 mol% and increases for further increase of Er^{3+} ion concentration. The decrease in the optical band gap with the increase in the concentration of Er_2O_3 up to 0.8 mol% suggests increasing degree of depolymerization or concentration of bonding defects and non-bridging oxygens (NBO) in the glass network up to this concentration of Er_2O_3. Probably in this concentration range the aluminium ions may take network forming positions with AlO_4 structural units and alternate with BO_4 units. Such linkages may cause a decrease in the rigidity of the glass network and leads to the decrease in the optical band gap as observed.

- ***Results of Optical absorption spectra of GEY glass system***

From optical absorption data, for GEY samples, optical band gap energy is found to increase with increasing the concentration of Er^{3+} ions upto 0.6 mol% and decreases for further increase of Er^{3+} ion concentration. The increase in the optical band gap with the increase in the concentration of Er_2O_3 up to 0.6 mol% suggests decreasing degree of depolymerization or concentration of bonding defects and non-bridging oxygens (NBO) in the glass network up to this concentration of Er_2O_3. This is due to the fact that Ga^{3+} ions go into substitutional positions with GaO_4 structural units and alter the glass network upto 0.6 mol%. Beyond this concentration Ga^{3+} ions, isolate the rare-earth ions from RE-O-RE bonds and form Ga-O-RE bonds. Such linkages may cause an increase in the rigidity of the glass network and leads to the increase in the optical band gap as observed.

- ***Results of Optical absorption spectra of IEY glass system***

From optical absorption data, for IEY samples, optical band gap energy is found to increase with increasing the concentration of Er^{3+} ions upto 0.6 mol% and decreases further for further increase of Er^{3+} ion concentration. The increase in the optical band gap with the increase in the concentration of Er_2O_3 up to 0.6 mol% suggests decreasing degree of depolymerization or concentration of bonding defects and non-bridging oxygens (NBO) in the glass network up to this concentration of Er_2O_3. This is due to the fact that In^{3+} ions go into substitutional positions with InO_4 structural units and alter the glass network upto 0.6 mol%. Beyond this concentration In^{3+} ions, isolate the rare-earth ions from RE-O-RE bonds and form In-O-RE bonds. Such linkages may cause an increase in the rigidity of the glass network and leads to the increase in the optical band gap as observed.

- The comparision of Optical band gap and cut-off wavelength values of AEY, GEY and IEY glass systems are presented in Table 6.1.

Table 6.1. Optical band gap values of the studied glass systems

Glass system	Range of Cut-off wavelength (nm)	Range of optical band gap values (eV ±0.01)	Value of cut-off wavelength for 1.0 mol% Er^{3+} ions	Value of optical band gap for 1.0 mol% Er^{3+} ions
AEY	382-417	3.02 - 3.24	408	3.02
GEY	400-428	2.88 - 3.08	410	3.01
IEY	410-432	2.86 - 3.04	432	2.86

- From optical absorption data for 1.0 mol% of Er^{3+} ions, the cut-off wavelength found highest (432 nm) for IEY glass samples. For AEY and GEY glass samples 408, 410 nm, respectively.

- The optical band gap energy for 1.0 mol% of Er^{3+} ions was found lowest (2.86 eV) for indium doped sample, whereas AEY and GEY glasses are having 3.02, 3.01 eV, respectively.

➢ The highest value of cut-off wavelength of IEY glass suggests high efficiency of the glass.

❖ **J-O analysis**

➢ *J-O analysis of AEY glass system*

By performing least square fitting analysis the J-O parameters for AEY glass system are computed and are found to show the following order for Er^{3+}, the order is $\Omega_2 > \Omega_4 > \Omega_6$. The higher value of Ω_2 indicates the highest covalent character of this glass. Referring to the data on emission transitions in the present glass system, the transition $^4F_{9/2} \rightarrow {}^4I_{15/2}$ has the highest value (52%) of β_r among various transitions. This transition may therefore be considered as a possible laser transition.

➢ *J-O analysis of GEY glass system*

By performing least square fitting analysis the J-O parameters for GEY glass system are computed and are found to show the following order for Er^{3+}, the order is $\Omega_2 > \Omega_4 > \Omega_6$. The higher value of Ω_2 indicates the highest covalent character of this glass. Referring to the data on emission transitions in the present glass system, the transition $^4F_{9/2} \rightarrow {}^4I_{15/2}$ has the highest value (55%) of β_r among various transitions. This transition may therefore be considered as a possible laser transition.

➢ *J-O analysis of GEY glass system*

By performing least square fitting analysis the J-O parameters for IEY glass system are computed and are found to show the following order for Er^{3+}, the order is $\Omega_2 > \Omega_4 > \Omega_6$. The higher value of Ω_2 indicates the highest covalent character of this glass. Referring to the data on emission transitions in the present glass system, the transition $^4F_{9/2} \rightarrow {}^4I_{15/2}$ has the highest value (58%) of β_r among various transitions. This transition may therefore be considered as a possible laser transition.

- The comparison of J-O parameters (Ω_2, Ω_4 and Ω_6) for AEY, GEY and IEY glass systems is presented in Table 6.3.

Table 6.2 J-O parameters of AEY, GEY and IEY glass systems

Glass system	Ω_2 (10^{-20} cm^2)	Ω_4 (10^{-20} cm^2)
AEY	1.13	0.88
GEY	4.89	1.41
IEY	5.34	1.75

➢ Among the three glass systems IEY glass system is having highest Ω_2 value. This indicates the highest covalent character of this glass.

➢ Among all the three glass systems IEY glass system is having highest branching ratio (58%) for $^4F_{9/2} \rightarrow {}^4I_{15/2}$ transition, which is to be considered as possible laser transition.

iii. FTIR spectral studies of Yb^{3+} and Er^{3+} codoped $PbO–B_2O_3–Bi_2O_3$ glasses mixed with $Al_2O_3/Ga_2O_3/In_2O_3$

➢ ***Results of FTIR spectra of AEY glass system***

The FTIR spectra of AEY glass system shows characteristic bands corresponding to the different vibration modes of the various functional groups present in the glass system. The bands for AE0Y0 glass sample were cited at ~488, ~730, ~ 935 and ~1280 cm^{-1}. A band cited in the region ~488 - 495 cm^{-1} is identified due to bending vibrations of Bi_2O_3 pyramidal units and also due to Pb-O-B bending vibrations. This region may also consist of bands due to network modifying AlO_6 octahedral groups. A band cited in the region ~706 - 730 cm^{-1} is identified due to vibrations of B-O-B linkages and also due to network forming AlO_4 tetrahedral groups.

From the spectra it was observed that the intensity of band corresponding to AlO_4 tetrahedral groups decreases from 0 mol% of Er^{3+} ions (AE0Y0) to 0.8 mol% of Er^{3+} ions (AE8Y2), whereas the intensity of band observed due to AlO_6 octahedral groups increases. Beyond this concentration the trend is reversed. The band in the region ~935 – 989 $cm^{-1}$is attributed due to stretching vibrations of B-O bands in BO_4 units. With increasing the concentration of Er^{3+} ions upto 0.8 mol% this band is found to shift from lower wavenumber to higher wavenumber (~935-989 cm^{-1}) beyond this concentration shift of this band is towards higher wavenumber (~965 cm^{-1}).

The band cited in the region ~1266-1280 cm^{-1} is identified due to stretching modes of borate triangles BO_3 and BO_2O^- units. With increasing the concentration of Er^{3+} ions upto 0.8 mol% this band found to shift from higher wavenumber to lower wavenumber (~1280-1271 cm^{-1}) beyond this concentration shift of this band is towards higher wavenumber (~1279 cm^{-1}).

- ***Results of FTIR spectra of GEY glass system***

The FTIR spectra of GEY glass system shows characteristic bands corresponding to the different vibration modes of the various functional groups present in the glass system. The bands for GE0Y0 glass sample were cited at ~482, ~613, ~707, ~ 955 and ~1234 cm^{-1}. A band cited in the region ~482 - 497 cm^{-1} is identified due to bending vibrations of Bi_2O_3 pyramidal units and also due to Pb-O-B bending vibrations. A band cited in the region ~613 - 620 cm^{-1} is identified due to network forming GaO_4 tetrahedral groups.

From the spectra it was observed that intensity of band corresponding to GaO_4 tetrahedral groups increases from 0 mol% of Er^{3+} ions (GE0Y0) to 0.6 mol% of Er^{3+} ions (GE6Y2), beyond this concentration the trend is reverse. This is due to the fact that Ga^{3+} ions go into substitutional positions with GaO_4 structural units and alter the glass network upto 0.6 mol%. Beyond this concentration Ga^{3+} ions, isolate the rare-earth ions from RE-O-RE bonds and form Ga-O-RE bonds. Such declustering effect leads to the larger spacing between RE ions and may contributes for the enhancement of fluorescence emission.

No significant change is found in the band cited at ~707 cm^{-1} and is attributed to the vibrations of B-O-B linkage. A band cited in the region ~924-955 cm^{-1} is assigned to asymmetric stretching vibrations of B-O bands in BO_4 units. With increasing the concentration of Er^{3+} ions upto 0.6 mol% this band is found to shift from higher wavenumber to lower wavenumber (~955-924 cm^{-1}) beyond this concentration shift of this band is from lower to higher wavenumber (~925-938 cm^{-1}). The band cited in the region ~1234-1284 cm^{-1} is identified due to asymmetric stretching modes of borate triangles BO_3 and BO_2O^-. With increasing the concentration of Er^{3+} ions upto 0.6 mol% this band found to shift from lower wavenumber to higher wavenumber (~1234-1278 cm^{-1}) beyond this concentration shift of this band is from higher to lower wavenumber (~1280-1284 cm^{-1}).

- ***Results of FTIR spectra of IEY glass system***

The FTIR spectra of IEY glass system shows characteristic bands corresponding to the different vibration modes of the various functional groups present in the glass system. The bands for IE0Y0 glass sample were cited at ~493, ~708, ~ 919 and ~1272 cm^{-1}. A band cited in the region ~490 - 500 cm^{-1} is identified due to bending vibrations of Bi_2O_3 pyramidal units and also due to Pb-O-B bending vibrations. No significant change is found in the position of the band cited at ~708 cm^{-1} and is attributed due to the vibrations of B-O-B linkage.

A band cited in the region ~895-918 cm^{-1} is assigned to asymmetric stretching vibrations of B-O bands in BO_4 units. With increasing the concentration of Er^{3+} ions upto 0.6 mol% this band is found to shift from higher wavenumber to lower wavenumber (~918-905 cm^{-1}) beyond this concentration shift of this band towards higher wavenumber (918 cm^{-1}). The band cited in the region ~1213-1274 cm^{-1} is identified due to asymmetric stretching modes of borate triangles BO_3 and BO_2O^- units. With increasing the concentration of Er^{3+} ions upto 0.6 mol% this band found to shift from lower wavenumber to higher wavenumber (~1213-1274 cm^{-1}) beyond this concentration shift of this band is towards lower wavenumber (~1246 cm^{-1}).

iv. Photoluminescence spectra of Yb^{3+} and Er^{3+} codoped $PbO–B_2O_3–Bi_2O_3$ glasses mixed with $Al_2O_3/Ga_2O_3/In_2O_3$

The luminescence spectra of all the three glasses doped with Yb^{3+} and Er^{3+} ions recorded at room temperature in the visible region exhibited the following prominent emission bands:

$^2H_{11/2} \rightarrow {}^4I_{15/2}$ (Green), $^4S_{3/2} \rightarrow {}^4I_{15/2}$ (Green) and $^4F_{9/2} \rightarrow {}^4I_{15/2}$ (Red)

- From upconversion studies it was observed that under 980 nm excitation AEY, GEY and IEY glass systems exhibited green and red emissions.
- In all the three glass systems the green emission is weak and red emission is very prominent.
- The wavelengths of green and red emissions of three glass systems are given in Table 6.3.

Table 6.3 Wavelengths of green and red emissions of three glass systems

Glass system	Wavelengths (nm)	
	Green	Red
AEY	525, 545	654
GEY	529, 542	656
IEY	529, 542	656

- From the Table 6.3 it was found that there is no significant shift in the wavelengths of green and red emissions with varying the IIIA group elements (Al, Ga & In).

- ***Results of Photoluminescence spectra of AEY glass system***

In AEY glasses the intensity of red emission increases with increasing the concentration of Er^{3+} upto 0.8 mol% and decreases further increasing the concentration of Er^{3+}. At this concentration the value of optical band gap is minimum. This is attributed to the increase in the concentration of AlO_6 structural units at the expense of AlO_4 structural. Beyond 0.8 mol% concentration AlO_4 structural units seemed to be dominating over AlO_6 structural units.

- ***Results of Photoluminescence spectra of GEY glass system***

In GEY glasses, the intensity of red emission decreases with increasing the concentration of Er^{3+} upto 0.6 mol% and increases for further increasing the concentration of Er^{3+}. This is due to the fact that Ga^{3+} ions go into substitutional positions with GaO_4 structural units alter the glass network upto 0.6 mol%. Beyond this concentration Ga^{3+} ions, isolate the rare-earth ions from RE-O-RE bonds and form Ga-O-RE bonds. Such declustering effect leads to the larger spacing between RE ions and contributes for the enhancement of fluorescence emission.

- ***Results of Photoluminescence spectra of IEY glass system***

In IEY glasses intensity of red emission decreases with increasing the concentration of Er^{3+} upto 0.6 mol% and increases further increasing the concentration of Er^{3+}. This is due to that In^{3+} ions go into substitutional positions with InO_4 structural units alter the glass network upto 0.6 mol%. Beyond this concentration In^{3+} ions, isolate the rare-earth ions from RE-O-RE bonds and form In-O-RE bonds. Such declustering effect leads to the larger spacing between RE ions and contributes for the enhancement of fluorescence emission.

- Fig. 6.1 shows the graph drawn between ionic radii of IIIA group elements (Al, Ga & In) and intensities of red emission for 1 mol% of Er^{3+} ions.

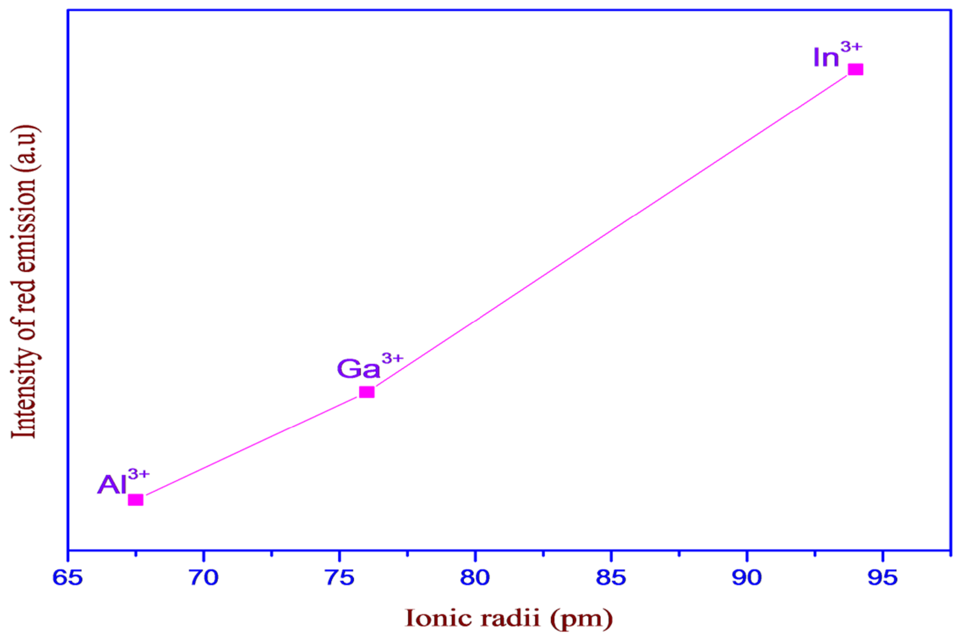

Fig. 6.1 Ionic radii of IIIA group elements (Al, Ga & In) verses intensities of red emission for 1 mol% of Er^{3+} ions

➢ From Fig. 6.1 it was found that intensity of red emission increases with increasing the value of ionic radii of IIIA group elements. As indium is having highest ionic radius than aluminum and gallium, the intensity of red emission in IEY glasses is higher than AEY and GEY glasses and increases for the higher concentration of Er^{3+} ions.

➢ The comparison of branching ratios β_r for $^4F_{9/2} \rightarrow {}^4I_{15/2}$ (Er^{3+}) emission for all the three series of the glasses showed the largest values for glass mixed with In_2O_3 (IEY glass system).

➢ The higher value of branching ratio for In_2O_3 mixed glasses among the three glasses studied are connected not only with the higher radiative relaxation probability but also with a reduction of the non-radiative transition probability. This is possibly due to the low electron–phonon coupling of the Ln^{3+} ion with the high-energy phonons in case of In_2O_3 mixed glasses and relatively higher degree of this coupling with low-energy phonons for Al_2O_3 and Ga_2O_3 mixed glasses.

6.3 SCOPE FOR FUTURE WORK

Glass science has reached a very interesting stage in its development, with scope for a wider ranging investigation of technologically oriented glasses. From a scientific point of view they are of great interest since they allow for studying long term resistance against devitrification and water corrosion. Glasses find applications in various fields such as ultrafast optical switching, passive optical device applications and hard disk drives. In recent years, the upconversion fluorescence of infrared light to visible light by rare earth ions doped glasses and crystals has been investigated extensively, due to the possibility of infrared-pumped visible lasers and the potential applications in areas such as color display, optical data storage, and medical diagnostics, broadband fiber amplifier, efficient lasing, and photonic devices.

The investigations of optical and photoluminescence properties of glasses presented in this thesis has yielded precious information which will be helpful in the preparation of upconversion lasers. This thesis represents a comprehensive study of the photoluminescence properties of Yb^{3+}, Er^{3+} ions in lead bismuth borate glasses mixed with $Al_2O_3/Ga_2O_3/In_2O_3$. Summing up the entire work presented in this thesis, it is felt that the study of various spectroscopic studies of Yb^{3+} and Er^{3+} doped $PbO–B_2O_3–Bi_2O_3$ glasses mixed with $Al_2O_3/Ga_2O_3/In_2O_3$ glasses have yielded some valuable information which will be useful for the above mentioned practical applications of these materials.

Photoluminescence studies of these glass systems are of immense interest to prepare efficient luminescent glassy materials for upconversion lasers. Lead bismuth borate glasses are proved to be good hosts for lasing ions. Hence it is of interest to carry out photoluminescence properties of these glasses by doping with various rare earth ions. This helps in identifying high efficiency glassy host materials for laser devices. Further work must be carried out to get insight into the other rare earth ions in these materials. In continuation to the work carried out in the present investigation, it would be useful to prepare glass systems for different desired application with various glass hosts. This will help to choose a better host for a given rare earth dopant.

<u>Papers published</u>

1. "Upconversion Kuminescence in Er^{3+}/Yb^{3+} Codoped Lead Bismuth Indium Borate Glasses"

Y Raja Rao, K Krishnamurthy Goud, E Ramesh Kumar, M Chandra Shekhar Reddy and B Appa Rao

International Journal of Recent Development in Engineering and Technology, **Volume 3, Issue 1** (2014) 122-130.

2. "Spectroscopic properties of Er^{3+} and upconversion luminescence in Er^{3+}/Yb^{3+} codoped lead bismuth alumina borate glasses"

Raja Rao Y, Krishnamurthy Goud K, Srinivas M and Appa Rao B.

International Journal of Luminescence and Applications, **32 (Spl issue III)** (2013) 170-173.

3. "Luminescence studies of $PbO-Bi_2O_3-Ga_2O_3-B_2O_3$ glasses doped with Er^{3+} / Yb^{3+}"

Raja Rao Y, Krishnamurthy Goud K and Appa Rao B

AIP conference proceedings, **1536** (2013) 661-662.

Conferences / Seminars attended :

1. *"International Conference on Materials Science and Technology"*
   June 10-14 2013, Department of Physics, St. Thomas College, Pala, Kottayam, Kerala.

2. *"National Conference on Luminescence and its Applications"*
   January 8-10, 2013, PESIT, Bengaluru.