ABSTRACT

Development of new rare earth (RE) doped host materials for their applications in photonic devices is possible only by synthesizing and characterizing mechanically, thermally and optically. Optimization of optical properties of glasses is a very important task prior to their application for optical devices. Optical spectroscopy is the mandatory technique to explicate the absorption and emission properties of RE^{3+} doped glasses. Emission properties of RE^{3+} ions change drastically from host to host as well as by the variation of their concentration in the host. This behaviour of the RE^{3+} ions has made the researchers to search for new materials with different compositions to investigate and elucidate their behaviour in different hosts with different concentrations. In order to identify the new glass hosts for optical devices, the present thesis explores the results of the investigations carried out by the author on **Absorption and Emission Characteristics of Dy^{3+}, Sm^{3+}, Eu^{3+}, Tb^{3+} and Er^{3+} ions Doped Zinc Alumino Bismuth Borate Glasses",** dealing with the spectroscopic investigations (absorption, excitation, emission and decay spectral studies) of Dy^{3+}, Sm^{3+}, Eu^{3+}, Tb^{3+} and Er^{3+} ions in Zinc Alumino Bismuth Borate Glasses.

We have selected a glass system containing a good glass former B_2O_3 added with heavy metal oxides (Bi_2O_3) and network modifiers such as ZnO and Al_2O_3. We have optimized the fabrication conditions to prepare a good optical glass system namely Zinc Alumino Bismuth Borate (ZnAlBiB) to host rare earth ions such as Dy^{3+}, Sm^{3+}, Eu^{3+}, Tb^{3+} and Er^{3+} at relatively larger concentrations.

The main objectives of the thesis are

1. To optimize the conditions of fabrication of a good optical glass doped with certain rare earth ions such as Dy^{3+}, Sm^{3+}, Eu^{3+}, Tb^{3+} and Er^{3+} for wide range of optoelectronic applications.
2. Extensive physical and structural characterization of glasses by measuring the properties such as refractive index, density etc.
3. To study the absorption, excitation and emission spectral features of the prepared doped glasses and to understand the glass host dependence.

4. Evaluation of emission cross sections and quantum efficiencies of the prepared doped glasses by understanding the emission and absorption spectral data along with emission decay measurements.
5. Optimization of the concentration of the rare earth ion in the prepared novel glassy systems for lasing potentialities, fiber amplifiers and light emitting diodes.

The thesis organized in *eight* chapters as summarized below.

Chapter 1: Introduction

This chapter elaborately introduces updated history and state-of-the art glass technology, spectroscopic properties of rare earth ions, crystal field levels, glassy properties and several other advantages of glassy materials. Relevant theoretical calculations used to analyze the absorption, emission and decay spectral measurements have been outlined. Experimental and theoretical estimations of absorption oscillator strengths, application of Judd-Ofelt theory (JO) for the measurement of radiative properties (such as emission cross-sections, quantum efficiency) of different excited states and color coordinates have been elaborately presented.

Chapter -2

This chapter mainly focuses on the fabrication strategies utilized in preparing glassy materials, especially from conventional melt quenching technique. Determination of various physical properties for the prepared glasses is presented. Wide varieties of equipments used during the experiments of optical absorption, excitation, static and dynamic emission measurements and confocal emission images are clearly elucidated.

Chapter- 3

This chapter describes Dy^{3+} doped ZnAlBiB glasses prepared by using melt quenching technique with the following chemical composition 20 ZnO + $8Al_2O_3$ + $(12\text{-}x)Bi_2O_3$ + $60B_2O_3$ + xDy_2O_3 (where x = 0.5, 1.0, 1.5, 2.0 and 2.5 mol%) and characterized by optical absorption and luminescence studies. The glassy structure of the prepared host material has been confirmed through XRD measurements. From the measured oscillator strengths of the absorption spectra, the JO parameters have been determined and employed in analyzing the radiative properties of the prepared glasses. The

intensity of Dy^{3+}emission spectra increases up to 1 mol % of Dy^{3+} ion concentration and beyond the concentration quenching is observed. The optimum concentration of Dy^{3+} ions for ZnAlBiB glassy materials to act as good lasing material has been discussed by measuring the branching ratios and emission cross sections for the two prominent emission transitions such as $^4F_{9/2} \rightarrow ^6H_{15/2}$ and $^4F_{9/2} \rightarrow ^6H_{13/2}$ observed in visible region. Based on the visible emission spectra, large stimulated emission cross sections and high branching ratios observed for $^4F_{9/2} \rightarrow {}^6H_{13/2}$ transition, for all these glasses suggest the utility of these materials as lasing materials. Among all the ZnAlBiB glasses studied, a glass with 0.5 mol % of Dy^{3+} ions was found to be a best luminescent material for the development of lasers and photonic devices operating in visible region. The CIE chromaticity coordinates evaluated from the emission spectra under the excitation of different n-UV wavelengths confirm the possibility of generating white light emission in principle from these ZnAlBiB glasses. Among all the excitation wavelengths, it was found that ZnAlBiB glasses are quite useful under 357 nm excitation for n-UV based white light emitting diodes. The results discussed in this chapter have already appeared in an international journal **"Journal of Luminescence 139 (2013) 119-124".**

Chapter- 4

This chapter present the results of the optical studies of Sm^{3+} ions doped ZnAlBiB glasses with composition 20 ZnO + 10 Al_2O_3 + (10-x) Bi_2O_3 + 60 B_2O_3 + x Sm_2O_3 (x = 0.1, 0.5, 1.0, 1.5, 2.0 and 2.5 mol%) prepared by using melt quenching technique and characterized for their lasing potentialities in visible region by using the techniques such as optical absorption, emission and decay spectral measurements. The JO parameters evaluated from the measured oscillator strengths of the absorption spectra of these glasses are used to calculate radiative properties for various fluorescent levels of Sm^{3+} ions. The excitation spectra recorded for these glasses exhibit several excitation bands in visible region indicates the suitability of commercial UV blue laser diodes and bluish green LEDs as suitable pumping sources for these titled glasses. The emission spectra recorded for all these glasses by using the 410 nm Continuous wave (CW) laser gives four emission bands in visible region. Among them, $^4G_{5/2} \rightarrow {}^6H_{7/2}$ transition is more intense and $^4G_{5/2} \rightarrow {}^6H_{7/2}$ is moderate for all these glasses and is responsible for distinct orange and red emission. This very distinct and intense orange-red emission from all these glasses are further confirmed by confocal

photoluminescence images obtained at 410 nm CW laser excitation. Based on the emission spectral features, stimulated emission cross section, branching ratios and quantum efficiencies observed for $^4G_{5/2} \rightarrow {}^6H_{7/2}$ transitions for all these glasses suggested the feasibility of using these materials as visible lasers in orange-red (598 nm) visible region. The CIE Chromaticity coordinates evaluated from the emission spectra of all these glasses also confirms the same thing. From the measured emission cross-sections, branching ratios, quantum efficiencies, confocal photoluminescence images and the CIE chromaticity coordinates evaluated, it was concluded the 1 mol % Sm^{3+} ions concentration is optimum in ZnAlBiB Glasses for the development of visible orange-red lasers (598 nm) in principle. All these results discussed in this chapter are published in an international journal **"Spectrochimica Acta Part A: Molecular and Biomolecular Spectroscopy 125 (2014) 53–60)"**

Chapter 5

This chapter describes the luminescence characterization of Eu^{3+} doped ZnAlBiB glasses having composition $20ZnO + 8Al_2O_3 + (12\text{-}x)\ Bi_2O_3 + 60B_2O_3 + xEu_2O_3$ (x= 0.1, 0.5, 1.0, 2.0 and 2.5 mol %) using melt quenching technique.. These glasses prepared by using melt quenching technique and characterized for their luminescence behavior using the spectroscopic techniques such as absorption, excitation, emission, decay profiles and confocal images. Limited number of absorption bands are observed for these Eu^{3+} doped ZnAlBiB glasses constrained us to evaluate the JO parameters needed to evaluated the radiative properties of the these glasses. The emission spectra of Eu^{3+} ions in these glasses when excited at 410 nm using CW laser show the characteristics of Eu^{3+} ions with more intense visible red emission corresponding to $^5D_0 \rightarrow {}^7F_2$ transition. This intense visible red emission further confirmed by confocal photoluminescence images recorded for all these glasses under 410 nm CW laser excitation. The JO parameters estimated from the emission spectral information are used to estimate the important radiative properties such as transition probability, branching ratio and emission cross- sections for the prominent emission levels. Various radiative properties measured for Eu^{3+} doped ZnAlBiB glasses speaks that these glasses at higher concentration of Eu^{3+} ions were most suitable for intense red emission. From the evaluated emission cross-sections, branching ratios, confocal photoluminescence images and CIE chromaticity coordinates, it was concluded that 2.5 mol % of Eu^{3+} ions in ZnAlBiB glasses is quite suitable for visible red emission applications. The content

in this chapter is published in an international journal "**Journal of Luminescence 156 (2014) 80-86**.

Chapter-6

This chapter describes the results obtained for Tb^{3+} ions doped ZnAlBiB glasses having composition $20ZnO + 10Al_2O_3 + (10\text{-}x)\ Bi_2O_3 + 60\ B_2O_3 + xTb_2O_3$ (where x=0.1, 0.5, 1.0, 1.5, 2.0, 2.5 and 3 mol %) to study their suitability for green emitting luminescent devices. The glasses used in this study were prepared by the conventional melt quenching technique and studied their optical absorption, photoluminescence and decay spectral properties. The JO parameters evaluated from the experimental oscillator strengths were used to measure the radiative properties for the prominent luminescence transition of Tb^{3+} ions in these glasses. The photoluminescence spectra recorded for all these ZnAlBiB glasses show blue and green emission from $^5D_3$ and $^5D_4$ states respectively. The intensities of the both blue and green emissions increases continuously up to 2.5 mol % Tb^{3+} ions concentration and beyond decreases. The continuous increase in green emission intensity up to 2.5 mol % of Tb^{3+} ions has been attributed to the non-radiative cross relaxation process. On the other hand, the lifetimes measured for these glasses are found to be decreasing with increase in Tb^{3+} ion concentration. Such kind of decrease in measured lifetimes with increasing in Tb^{3+} ions concentration is attributed to resonance energy transfer through the cross relaxation mechanism. Based on the emission spectra, stimulated emission cross-sections, branching ratios and quantum efficiency value obtained from the green emission for all these glasses suggest the feasibility of using these glasses for green luminescence. The CIE chromaticity coordinates evaluated from the emission spectra also confirms the same thing. Within the concentration range studied, it was found that, 2.5 mol % of Tb^{3+} ions in ZnAlBiB glasses is found to be the potential candidate for green luminescence applications at 542 nm in principle. The results narrated in this chapter are published in an international **"Journal of Luminescence 156 (2014) 180-187.**

Chapter- 7

This chapter elucidates the optical absorption, emission and up-conversion spectral studies of Er^{3+} doped ZnAlBiB glasses having composition $20\ ZnO{+}10\ Al_2O_3{+}(10\text{-}x)\ Bi_2O_3{+}60\ B_2O_3 + x\ Er_2O_3$ where (x=0.1, 0.5, 1.0 and 2.0 mol %) prepared by using

melt quenching technique and characterized for their lasing potentialities. The JO parameters measured from energies of the absorption bands are used to evaluate radiative properties of the prepared glasses. Visible and near infrared emission spectra have been recorded by exciting these glasses at 980 nm using diode laser. Infrared to visible up-conversion spectral features have also been recorded to understand the up-conversion process possessed by ZnAlBiB glasses doped with Er^{3+}ions. All these results obtained in this investigation indicate that Er^{3+} doped ZnAlBiB glasses are found to be potential candidates for mid-infrared lasers and visible up-conversion process. All such interesting results obtained related to this work are communicated to an international journal "**Journal of Luminescence" (2015) 163, 55-63.**

Chapter-8

Finally chapter-8 presents the comprehensive understating of results obtained in the present study, precise conclusions and future scope of the work. Overall the present work gives the detailed spectral properties of rare earth ions in ZnAlBiB glasses, with an aim to understand and optimize the glass composition for better luminescence efficiency. The future scope of the work to improve the luminescent efficiency of these ZnAlBiB glasses by the optimization of co dopant ions concentration has been proposed.