PREFACE

Glasses doped with rare earth (RE) ions have attracted larger attention on account of their usefulness in various applications such as solid state lasers, LEDs, optical fibers, flat panel displays, planar waveguides and optical amplifiers. A good glass host is very essential for efficient luminescence of RE^{3+} ions. So, a variety of glass matrices such as oxides, fluorides, phosphates and oxyfluorides have been investigated to generate various optical properties. Among the oxide glasses, borotellurite glass network is a suitable host due to its excellent linear and nonlinear optical behaviour. Addition of heavy metal oxide to these borotellurite glass network decreases the phonon energy and reduces the non-radiative losses. In this regard, the heavy metal borotellurite glasses have been chosen as a host for RE doping and to enhance the luminescence efficiency.

The present thesis elaborates on the synthesis, structural and luminescence behaviour on Sm^{3+}, Eu^{3+} and Dy^{3+} doped heavy metal borotellurite glasses. The present work is to identify the appropriate chemical composition and optimum rare earth ion concentration for high luminescence yield. Structural and optical properties have been studied through XRD, FTIR, Raman, optical absorption, luminescence and decay measurements for the development of various optical devices. The thesis consists of eight chapters.

Chapter I gives a general introduction on the importance of lanthanide ions (Ln^{3+}), glasses and spectroscopy of Ln^{3+} doped glasses. This chapter provides a detailed account of various theoretical models such as Judd-Ofelt (JO) analysis to predict the radiative and non-radiative properties of the excited states of Ln ions. Inokuti-Hirayama (IH) model to analyse the energy transfer mechanism in the glasses has also been presented. In addition the calculation of colour coordinates in the CIE

(1931) chromaticity diagram, colour purity and correlated colour temperature are also given in this chapter.

An outline of the materials, methods and instrumentation employed are presented in chapter II. The RE^{3+} (Eu^{3+}, $Sm^{3+}$and Dy^{3+}) doped lead boro-telluro phosphate and oxyfluoro boro-tellurite glasses have been prepared via melt quenching technique. This chapter gives a detailed account on the experimental techniques employed in the characterization of these glasses.

The effect of lead oxide on the luminescence and structure of B_2O_3–TeO_2–P_2O_5–BaO–CdO–Sm_2O_3 glasses prepared by melt quenching technique is discussed in chapter third. Lower magnitude of the Ω_2 and bonding parameter values reveal the higher symmetry around the rare earth ion and the dominant ionic nature of the Sm–O bond. Luminescence spectra exhibits the four emission bands at 565 (yellow), 602 (orange), 646 (red) and 701 nm (deep red) respectively. Fluorescence intensity exhibits a maximum at 20 wt % PbO and beyond this luminescence quenching is observed. The luminescence decay measurements indicate the non-exponential behaviour. Addition of lead oxide is found to increase the quantum efficiency.

In chapter IV deals with the optical and other studies made on Eu^{3+} (0.05, 0.1, 0.25, 0.5, 1.0 and 2.0 wt %) incorporated lead boro–telluro–phosphate glasses. Lower symmetry and higher Eu–O covalence is observed from the negative values of bonding parameter (δ) and higher Ω_2 values. A deep red luminescence is observed from ${}^5D_0 \rightarrow {}^7F_2$ transition of Eu^{3+} ions in the title glasses. Increasing interaction among the Eu^{3+} ions, the quenching of stimulated emission cross-section (beyond 1 wt % of Eu_2O_3) is observed and is discussed in this chapter.

The preparation and characterization of Sm^{3+} ions doped lead boro-telluro-phosphate glasses is described in the fifth chapter. From the luminescence spectra, the strong transitions of Sm^{3+} ions $^4G_{5/2}\rightarrow^6H_{5/2}$ (565 nm), $^4G_{5/2}\rightarrow^6H_{7/2}$ (602 nm), $^4G_{5/2}\rightarrow^6H_{9/2}$ (648 nm) and a weak transition, $^4G_{5/2}\rightarrow^6H_{11/2}$ (709 nm) have been observed. The effect of luminescence quenching at higher concentrations of Sm^{3+} ion has been examined. Non exponential decay curves (≥ 0.5% of Sm_2O_3) could be fitted with IH (S=6) model, which confirms the dipole-dipole nature of the energy transfer between Sm^{3+} ions. For $^4G_{5/2}\rightarrow^6H_{7/2}$ transition, the higher magnitude of gain bandwidth, optical gain, stimulated emission cross-section and branching ratio have been observed for 0.5LBTPS glass.

Synthesis of white light emitting dysprosium doped lead boro–telluro–phosphate glasses and their spectroscopic behaviour are described in chapter VI. The ionic nature of the Dy^{3+} metal-ligand bond has been identified by the negative values of bonding parameter. The magnitude of the JO intensity parameters follow the trend as $\Omega_2>\Omega_4>\Omega_6$ for all the title glasses. At higher concentrations (≥ 0.5 % of Dy_2O_3**)** the decay becomes non-exponential and this matches well with S = 6 which confirms that the energy transfer between the Dy^{3+} ions is of dipole-dipole type.

Chapter VII deals with structural and luminescence behaviour of Eu^{3+} doped oxyfluoro boro-tellurite glasses synthesis by melt quenching technique. The influence of metal ions on the structure of borotellurite glasses were investigated through FTIR spectra. The addition of metal fluorides (AF_2=PbF_2, BaF_2, ZnF_2, CdF_2, SrF_2) to the oxyfluoro boro-tellurite based glass network, decreases the covalency between Eu and O^{2-}/F^- ions. The higher magnitude of Ω_2 of TBXFE glasses suggests the bonding of the Eu^{3+} ions with the ligand is of higher covalency. The metal cation (Pb^{2+}, Ba^{2+},

Zn^{2+}, Cd^{2+}, Sr^{2+}) with higher electronegativity decreases the lifetime of Eu^{3+} ions in the glass matrix when present as a modifier.

Chapter VIII gives a summary of the work, presented in chapter III to VII. The scope for further work on glasses to improve the quantum efficiency, gain bandwidth product and optical gain of the different rare earth glasses for visible laser and WLED applications is also presented in this chapter.