Preface

\[ \text{B}_2\text{O}_3 \text{ based glasses are attractive optical materials due to their unique structural and physicochemical properties. Borate glasses have attractive considerable scientific interest because of their potential applications like electro-optic switches, electro-optic modulators, solid state laser materials and non-linear optical parametric converters. In addition, they are often used as dielectric and insulating materials and it is known that borate glass constitutes a good shield against IR radiation. In recent years, glasses incorporated with transition metal ions have attracted a great deal of attention, because of their potential applications as lasers, photo-conducting devices, magnetic materials, especially for tunable solid state lasers, efficient phosphors etc.} \]

The properties of an alkali oxide glass which depend upon the mobility of alkali ions show a strong non-linear behavior when one kind of alkali ion is replaced by another is well known as Mixed Alkali Effect (MAE). It is not much studied in borate glasses. The objective of the present work is to provide a specific indication about mixed alkali effect by physical and spectral investigations on transition metal ions doped 20 ZnO + x Li2O + (30-x) Na2O + 50 B2O3 (5 ≤ x ≤ 25) ZLN glasses. In this system 0.1 mol % of transition metal oxides TiO2, Cr2O3, Fe2O3 and MoO3 are used as dopants. Physical properties of the prepared glass samples are evaluated and also the samples are characterized using spectroscopic techniques such as XRD, FT-IR, EPR and Optical absorption. In the present thesis the detailed physical and spectral investigations of transition metal ions doped mixed alkali zinc borate glasses are presented in eight chapters as follows.

Chapter 1 deals with the brief introduction of mixed alkali borate glasses and the basic necessary theories required for the analysis of physical and spectral investigations. The scope of work and basic features for the spectra of transition
metal ions was also discussed. Various textbooks, monographs and research publications were referred in developing the subject matter of this chapter.

Chapter 2 describes the preparation of the glasses and various experimental techniques employed to understand the mixed alkali effect in transition metal ions doped alkali zinc borate glasses. The instruments used for determining physical properties are presented along with their mode of operation. The basic theories and working principles of various techniques like XRD, Optical absorption; EPR and FT-IR are discussed briefly using schematic diagrams in this chapter.

Chapter 3 presents the results of physical and spectral investigations of mixed alkali zinc borate glasses. The physical parameters like refractive index, density, molar refractivity are evaluated with respect to the composition. Powder X-ray diffraction patterns of the glass samples confirm the amorphous nature. The FT-IR spectra reveal the interaction between alkali metal ions and borate glass network. From ultraviolet absorption edges the optical bandgap and Urbach energies are evaluated which confirm the structural variations with the composition of \( x \) mol \%. An abrupt change is observed at \( x = 20 \) mol \% showing mixed alkali effect.

Chapter 4 deals with the results of physical and spectral investigations on \( \text{Ti}^{3+} \) doped mixed alkali zinc borate glasses. The physical parameters of all the glasses are evaluated with respect to the composition. Powder X-ray diffraction pattern of the glass samples exhibit no peaks confirming the amorphous nature. The FT-IR spectra reveal the intensity of absorption bands of \( \text{B}_2\text{O}_3 \) structural units along with \( \text{TiO}_4 \) and \( \text{TiO}_6 \) units. The electron paramagnetic resonance spectra of all these glasses exhibit resonance signals that are characteristic of \( \text{Ti}^{3+} \). The optical absorption spectra also confirm the \( \text{Ti}^{3+} \) in tetragonally distorted crystal field. Urbach energies are evaluated which confirm the structural variations with
the composition of x mol %. Various crystal field, spin-Hamiltonian parameters are evaluated. The evaluated parameters of physical and spectral properties of all the glasses vary non-linearly and hence an abrupt change has been observed close to diffusivity crossover point i.e., at x = 15 mol %.


Chapter 5 elaborates the physical and spectral investigations on Cr³⁺ doped mixed alkali zinc borate glasses. No sharp peaks are observed in XRD spectra of the glass samples which confirm the absence of crystalline nature. The FT-IR spectra of these glasses reveal that the borate network consists of stretching vibrations of BO₃ and BO₄ units. The optical absorption spectra confirm the site symmetry of Cr³⁺ doped ZLNB glasses in distorted octahedral symmetry. The non-linear behavior in g values was observed by changing the concentrations of alkali contents. It is observed that the optical bandgap and Urbach energies exhibit MAE. All the samples are found to be strong and stable in structure with low values of Urbach energy which lie between 0.02 and 0.026 eV.

The results of Chapter 5 communicated as “Characterization of Cr³⁺ doped mixed Alkali Zinc Borate Glasses - Physical and Spectroscopic Investigations” to Optical Materials (UK) minor revision submitted online (2013).

Chapter 6 provides the evidence for mixed alkali effect with the help of spectral investigations on Fe³⁺ doped mixed alkali zinc borate glasses. Physical parameters are determined for all the glass samples with the change of
composition. Powder XRD patterns of prepared samples confirm the amorphous nature. The FT-IR spectra confirm the presence of BO\(_3\) and BO\(_4\) structural units. Optical absorption spectra confirm the distorted octahedral site symmetry for Fe\(^{3+}\) for ZLNB glasses. It is interesting to observe that the optical bandgap and Urbach energies exhibit MAE and confirms the structural variations with the concentrations of alkali ions.

The results of Chapter 6 are published as “Characterization of Fe\(^{3+}\) doped mixed alkali zinc borate glasses—Physical and spectroscopic investigations” in Journal of Non-Crystalline solids (Elsevier Publishing Ltd.) 365 (2013) 6-12 and also presented at Andhra Pradesh Science Congress (APSC-2012) at Acharya Nagarjuna University, Guntur during 14-16\(^{th}\) November, 2012.

Chapter 7 explains in detail the physical and spectral investigations on molybdenum ions doped ZLNB glasses. Powder XRD patterns of all the glass samples confirm the amorphous nature. FT-IR spectra of ZLNB glasses reveal the existence of Mo-O bands along with BO\(_3\) and BO\(_4\) structural units. Optical absorption spectra suggest that Mo\(^{5+}\) occupy distorted octahedral position. MAE is evident from the evaluated values of bandgap and Urbach energies. EPR spectra exhibited broad resonance signal which is the characteristic feature of Mo\(^{5+}\).

The results of Chapter 7 communicated as “Physical and Spectroscopic Investigations on Undoped and Molybdenum ions doped mixed alkali zinc borate glasses” to Journal of Molecular Structure (UK) submitted online (2014).

Chapter 8 discusses with the summary and conclusions drawn from the prepared ZLNB glasses. The Mixed Alkali Effect is observed in undoped and transition metal (Ti\(^{3+}\), Cr\(^{3+}\), Fe\(^{3+}\), Mo\(^{5+}\)) ions doped ZLNB glasses using physical and spectral investigations. Powder X-ray diffraction patterns confirmed the
existence of amorphous nature for all the ZLN B glass samples. From optical absorption studies, the non-linear shifting of absorption bands is observed close to the diffusivity crossover point i.e., $x = 15$ mol $\%$ for all the ZLN B glasses. An overview of mixed alkali effect is identified for undoped, divalent, trivalent (3d) transition metal ions and molybdenum ions doped ZLN B glass systems in order to have a clear understanding of MAE. At $x = 15$ mol $\%$ both refractive index and density values exhibit better non-linearity for all the ZLN B glasses. EPR and Optical absorption studies confirmed the distorted octahedral site symmetry for all the ZLN B glass systems. The evaluated bonding parameters for divalent ions exhibited ionic nature whereas for other ions these parameters show partial covalent nature.