PREFACE

This thesis describes the investigations on sodium-zinc-borate glasses and zinc-borate glasses with Fe$_2$O$_3$, V$_2$O$_5$ and (Fe$_2$O$_3$+V$_2$O$_5$) glasses.

Chapter 1 gives a general introduction to glasses, glass formation, models of glass formation, preparation of glasses, glass transition etc. and to various types of oxide glasses with their structural features.

Chapter 2 describes the preparation and characterization of the glasses investigated. Glasses were prepared by melt quenching technique. Samples prepared were checked for their amorphous nature by x-ray diffraction which did not show any sharp peaks, a characteristic of amorphous nature. Classes were also checked for their glass transition temperatures. Density of the glasses prepared was measured as a function of glass composition.

Chapter 3 is divided into two parts-Part I is a review on d.c electrical conductivity studies (ionic) in oxide glasses like on silicate, borate, phosphate, germanate glasses etc. It describes the variation of conductivity/resistivity and activation energy with temperature and alkali/non-alkali concentration. Part I also reviews the conductivity studies on glasses exhibiting mixed alkali and mixed cation effect.
Part II of Chapter 3 is divided into two sections. Section A deals with the temperature dependence of resistivity in the $x \text{Na}_2\text{O} - y \text{ZnO} - (100-x-y) \text{B}_2\text{O}_3$ and $(30-x) \text{Na}_2\text{O} - x \text{ZnO} - 70 \text{B}_2\text{O}_3$ glasses. In both the series of glasses the temperature dependence of resistivity has been studied over the temperature range, 400 to 700K. In the first series we have observed that for ZnO concentrations of 5, 10 and 15 mol% and for $\text{Na}_2\text{O}$ concentrations of 10 to 25 mol%, the values of resistivity and activation energy decrease with increase of $\text{Na}_2\text{O}$. This behaviour has been observed in most of the alkali based oxide glasses and the variation of the activation energy is discussed in the terms of Anderson and Stuart model. The addition of ZnO in binary glass system has also increased the resistivity and this effect is more pronounced initially and subsequent addition has only marginal effect. In the second series of glasses, we have observed that the resistivity and activation energy increase with the gradual substitution ZnO in place of $\text{Na}_2\text{O}$. This behaviour is similar to that observed in silicate and phosphate glasses in which an alkali was substituted by divalent alkaline earth oxide. This effect is known as the mixed cation effect and is explained in terms of the Independent path model.

Section B deals with the pressure dependence of resistivity in the $10 \text{Na}_2\text{O} - x \text{ZnO} - (90-x) \text{B}_2\text{O}_3$ and $x \text{Na}_2\text{O} - 10 \text{ZnO} - (90-x) \text{B}_2\text{O}_3$ glass system. The normalized resistivity has been measured up to 80 kbar. In the first series we have
observed that for 5-15 mol% of ZnO, the resistivity increases with increase of pressure and reaches a maximum at a certain pressure and then with further increase in the pressure the resistivity decreases resulting in a well defined peak and the resistivity begins to level off at still higher pressures. The pressure corresponding to the peak is found to be a function of ZnO concentration; it increases with increase of ZnO content. In the second series, for 10 and 15 mol% Na₂O the resistivity versus pressure graph shows a similar behaviour whereas for higher concentrations the resistivity increases with increase of pressure. These results are discussed in terms of borate glass structure.

Chapter 4 is also two divided into parts, Part I is a review on d.c. conductivity (electronic) studies in semiconducting oxide glasses. The variation of resistivity and activation energy as a function of concentration of Fe₂O₃, V₂O₅ and (Fe₂O₃+V₂O₅) respectively is discussed in these glasses.

Part II of Chapter 4 describes the resistivity measurements in zinc borate glasses containing Fe₂O₃, V₂O₅ and (Fe₂O₃+V₂O₅). The measurements were carried out in the temperature range of 350-700K. In glasses containing Fe₂O₃, we have observed that the resistivity and activation energy decrease with increase of Fe₂O₃ concentration (4 to 14 mol%) and with further increase of Fe₂O₃ (from 14 to 16 mol%) the
resistivity and activation energy suddenly drop to very low values. This sudden change was attributed to partial crystallization of the glass as indicated by our X-ray and Mossbauer effect studies. In glasses containing V$_2$O$_5$ also we have observed continuous decrease of resistivity and activation energy with increase of V$_2$O$_5$ concentration (6 to 44 mol%). The decrease of resistivity and activation energy with increase of transition metal oxide is observed in most of the semiconducting glasses and is explained in terms of the small polaron theory. In glasses containing (Fe$_2$O$_3$+V$_2$O$_5$), we have observed that the values of resistivity and activation are smaller than those in glasses containing single transition metal oxide as observed in calcium borate glasses containing different transition metal oxides. This is attributed to electron hopping between ions of different transition metal oxides. We have also reported studies on zinc vanadate glasses.

Chapter 5 deals with Mossbauer effect and EPR studies on zinc borate glasses containing Fe$_2$O$_3$, V$_2$O$_5$ and (Fe$_2$O$_3$+V$_2$O$_5$). Mossbauer effect studies show that in 45 ZnO-(55-x) B$_2$O$_3$-x Fe$_2$O$_3$ glass, when the Fe$_2$O$_3$ concentration increases (4 to 14 mol%) the values of isomer shift and quadrupole splitting decrease smoothly. These values indicate that iron in this glass system is in the Fe$^{3+}$ state with tetrahedral coordination. The decrease in both isomer shift
and quadrupole splitting is due to increase in the s-electron density and site symmetry. Glasses with 16% Fe$_2$O$_3$ show small values of line width and quadrupole splitting typical of microcrystalline particles. In x ZnO-(95-x) B$_2$O$_3$-5 Fe$_2$O$_3$ Mossbauer effect studies show that the isomer shift decreases with increase of ZnO concentration (45 to 65 mol%) whereas the quadrupole splitting is almost unaffected. Studies have also been carried out on sodium-zinc-borate glasses with Fe$_2$O$_3$.

EPR studies on zinc borate glasses with Fe$_2$O$_3$ show signals at $g=4.20$ for lower concentrations of Fe$_2$O$_3$ ($<2$ mol%) With increase of Fe$_2$O$_3$ concentration the signal at $g=4.20$ shows a decrease in the intensity and a broad signal develops at $g=2.0$. The broad signal is due to magnetic interaction of Fe-Fe ions and the signal at $g=4.20$ is due to Fe$^{3+}$ in tetrahedral coordination. In glasses containing V$_2$O$_5$ the EPR spectra showed well defined hyperfine structure and this is due to V$^{4+}$ ion present in vanadyl complex [VO]$_2^{2+}$. The observed spectra were interpreted in terms of axial Spin Hamiltonian. In glasses containing both (Fe$_2$O$_3$+V$_2$O$_5$), the hyperfine splitting of vanadium was completely deformed and a broad signal at $g=2.0$ was observed.