ABSTRACT

Glasses have attracted considerable attention because of their important applications. Glasses which have high chemical durability, good thermal, electrical and optical properties are being used in the fields such as microelectronics, optical fiber technology. The potential applications of glasses include in the development of solid state batteries, chemical sensors, fuel cells, solar energy concentrators, optoelectronic and integrated optical devices. They are useful in the investigation of diffusion in disorder systems. Glasses have many advantages over the crystalline materials. The glass composition can be varied over large ranges. Glass is isotropic with the absence of grain boundaries. Ionic transport in glasses is very important in the field of solid state ionics. EPR studies of transition metal ion doped glasses will yield valuable information on the effective ligand field symmetry and orbital geometry as well as the metal ligand bond nature. The study of optical absorption spectra of TM ions in glasses is another important aspect. There has been considerable interest in the EPR study of paramagnetic ions in glasses because of their application as photoconducting and laser materials.

In the present thesis entitled “Ionic Conductivity, Optical and EPR studies on some alkali haloborate glasses” research studies have been carried out on the preparation and characterization of some potassium and sodium based haloborate glasses with different compositions in pure
form and doped with the transition metal ions Cu$^{2+}$ and VO$^{2+}$. A second glass former P$_2$O$_5$ is also added to the glass composition. Different experimental techniques such as X-ray diffraction, Differential Scanning Calorimetry, DC ionic conductivity, Electron Paramagnetic Resonance and Optical absorption spectroscopy were used. The thesis contains four chapters. A brief description of each chapter is given below:

**Chapter-I – Introduction:** This chapter presents the formation and the structural aspects of the glass systems. The constitution of glass is presented. Ionic transport in the glasses is discussed. Different ionic transport and structural models are presented. Brief introduction about EPR and optical absorption are given. The aim and scope of the research work carried out is presented.

**Chapter-II – Experimental Techniques:** Different experimental techniques were employed in the present investigation for the preparation and characterization of the glass systems.

The basic glass systems prepared in pure form are given below:

1. $x$KCl-$(30-x)$K$_2$O-35B$_2$O$_3$-35P$_2$O$_5$ ($x = 1, 2, 3, 4, 5$ mole%)
2. $x$KBr-$(30-x)$K$_2$O-35B$_2$O$_3$-35P$_2$O$_5$ ($x = 1, 2, 3, 4, 5$ mole%)
3. $x$KI-$(30-x)$K$_2$O-35B$_2$O$_3$-35P$_2$O$_5$ ($x = 5, 10, 15, 20, 25$ mole%)
4. $x$NaCl-$(30-x)$Na$_2$O-35B$_2$O$_3$-35P$_2$O$_5$ ($x = 1, 2, 3, 4, 5$ mole%)
5. $x$NaBr-$(30-x)$Na$_2$O-35B$_2$O$_3$-35P$_2$O$_5$ ($x = 1, 2, 3, 4, 5$ mole%)
In these glass samples the alkali halide and alkali oxide contents were varied while the network formers $B_2O_3$ and $P_2O_5$ contents are kept constant. The above glass systems were doped with the transition metal ions $Cu^{2+}$ and $VO^{2+}$ for the EPR and optical absorption studies.

The experimental techniques employed in the present work are:

1. Melt quenching method
2. X-ray diffraction
3. Differential scanning calorimetry
4. DC electrical conductivity
5. Electron paramagnetic resonance spectroscopy and
6. Optical absorption spectroscopy.

The above mentioned glass compositions were prepared using the melt quenching technique.

The featureless and peak free X-ray diffractograms confirmed the amorphous nature of the glass samples prepared. The $T_g$ values were evaluated from the DSC thermograms. Brief description of the equipment used and the principles of the experimental techniques are presented in this chapter.

**Chapter-III – DC Ionic Conductivity Studies:** In this chapter the DC ionic conductivity studies on pure samples are carried out at different temperatures. A brief review of the earlier research work done on the
conductivity of halide and other glass systems are presented. The glass systems studied are:

1. $x\text{KR}-(30-x)\text{K}_2\text{O}-35\text{B}_2\text{O}_3-35\text{P}_2\text{O}_5$ ($x = 1, 2, 3, 4, 5$ mole% and $R = \text{Cl}, \text{Br}$)
2. $x\text{KI}-(30-x)\text{K}_2\text{O}-35\text{B}_2\text{O}_3-35\text{P}_2\text{O}_5$ ($x = 5, 10, 15, 20, 25$ mole%)
3. $x\text{NaR}-(30-x)\text{Na}_2\text{O}-35\text{B}_2\text{O}_3-35\text{P}_2\text{O}_5$ ($x = 1, 2, 3, 4, 5$ mole% and $R = \text{Cl}, \text{Br}$)

In all the glass systems the network former ($\text{B}_2\text{O}_3$ and $\text{P}_2\text{O}_5$) contents were kept constant while the network modifier ($\text{K}_2\text{O}$ and $\text{Na}_2\text{O}$) and the doping slat ($\text{KCl}, \text{KBr}, \text{KI}, \text{NaCl}, \text{NaBr}$) contents were varied.

The DC ionic conductivity which was measured at different temperatures was found to increase with increasing temperature and obeyed Arrhenius relation. Activation energies were evaluated from the slopes of the conductivity plots. The isothermal conductivity plots at different temperatures were also drawn. In potassium glass systems $x\text{KR}-(30-x)\text{K}_2\text{O}-35\text{B}_2\text{O}_3-35\text{P}_2\text{O}_5$ the conductivity was found to vary in a non-linear manner with KR ($R = \text{Cl}, \text{Br}, \text{I}$) content. The isothermal conductivity plots exhibited inflections due to halide ion effect. The dc ionic conductivity studies were carried on $x\text{NaR}-(30-x)\text{Na}_2\text{O}-35\text{B}_2\text{O}_3-35\text{P}_2\text{O}_5$ ($x = 1, 2, 3, 4, 5$ mole% and $R = \text{Cl}, \text{Br}$) glass system. The activation energies were evaluated from the conductivity plots. Variation of isothermal conductivity with halide ($\text{NaCl}, \text{NaBr}$) content was studied.

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It was observed that the variation was non-linear. It was found that the variation of activation energy with the halide content was non-linear.

As observed from the present work the conductivity and the activation energy of the glass systems depend on the halide and oxide ion contents. In all the glass systems studied the alkali halide content was increased while the alkali oxides content was decreased. A significant variation in conductivity was observed. It was observed from the similar studies of alkali glasses, that the glass network was not strongly modified by the addition of halide salt. The results obtained in the present work were explained on the basis of diffusion path model (DPM). The results may be explained in terms of the large potential energy difference resulting from the existence of two types of anions, halide and oxygen. The conductivity will mainly be controlled by the nature and the presence of the diffusion path in the glass system containing two different anions, i.e., halide and oxygen. The DPM claims two types of alkali ions, which are referred to as mobile and immobile. The presence of potential wells will make the difference obscure between mobile and immobile cations. Computer simulation experiments and EXAFS results supported the existence of two types alkali ions surrounded by halide and oxide ions. Hence, the non-linear variation was explained in terms of the large potential difference of the anions, halide and oxygen.

**Chapter-IV – EPR and Optical Absorption Studies:** In this chapter EPR studies were carried out on the glass systems containing
Cu$^{2+}$ and VO$^{2+}$ transition metal ions as the spin probes. The glass systems studied with the spin probe Cu$^{2+}$ were xKR-(30-x)K$_2$O-35B$_2$O$_3$-34P$_2$O$_5$-1CuO [$x = 1, 2, 3, 4, 5$ and mole %, $R = \text{Cl, Br}$]; xKI-(30-x)K$_2$O-35B$_2$O$_5$-34P$_2$O$_5$-1CuO [$x = 5, 10, 15$ and 25 mole %] and xNaBr-(30-x)Na$_2$O-35B$_2$O$_5$-34P$_2$O$_5$-1CuO [$x = 1, 2, 3, 4, 5$ mole %].

The EPR spectra were recorded at X-band frequencies at room temperature with 100 KHz field modulation using EPR spectrometer model JEOL-FE-1x. The optical absorption spectra were recorded with Shimadzu UV-VIS-NR-3100 spectrophotometer in the wave length range 200-1200 nm. In all the above glass systems studied the EPR spectra consisted of three weak hyperfine components in the low magnetic field side, while the fourth hyperfine component was overlapped with the perpendicular component. The perpendicular components were not resolved and a single intense line was observed. The isotopic splittings corresponding to $^{63}$Cu and $^{65}$Cu were not resolved owing to the nearly identical nuclear moments, and large line widths resulting from the random orientation of magnetic complexes in the glasses. It was observed that the high field side of EPR spectra were more intense than the low field side. An axial spin-Hamiltonian was used in the analysis of EPR spectra. The spin-Hamiltonian parameters were evaluated. It was observed that $g_\parallel > g > g_e$ ($g_e = 2.0023$) and $A_\parallel > A$. From the values of the spin-Hamiltonian parameters and shape of the EPR spectra it can be concluded that the ground state of the Cu$^{2+}$ is $d_{x^2-y^2}$ orbital ($^2B_{1g}$ state),
the Cu$^{2+}$ ions being located in octahedral sites, with tetragonal distortion. The variation of the $g_\| \text{ and } A_\|$ with alkali halide content was found to be non-linear, which may be attributed to the change of ligand field strength at the site of Cu$^{2+}$. This may be attributed to the structural changes in the glasses. Replacement of alkali oxide by the alkali halide causes a change in the property composition. The changes in the spin-Hamiltonian parameters with varying halide concentration may be attributed to the change in electron cloud density at the Cu$^{2+}$ ion as halide ions replace some of the oxygen ions of copper. The field produced by the array of halide ions will be lower than the field due to oxygens. Therefore, the non-linear variation of $g_\|$ and $A_\|$ with alkali halide content may be due to the replacement of oxygen ligands by halide, as the replacement influences the field at the site of Cu$^{2+}$ ions.

The optical absorption spectra of all the glasses exhibited a broad absorption band near IR region, which was assigned to $^2B_{1g} \rightarrow ^2B_{2g}$ transitions ($\Delta E_{xy}$). Variation of $\lambda_{\text{max}}$ of optical absorption with alkali halide content was non-linear. The in-plane $\sigma$-bonding ($\alpha^2$), in-plane $\pi$-bonding ($\beta_1^2$) and out-of-plane $\pi$-bonding ($\beta^2$) were evaluated using the EPR and optical data. The normalized covalency parameters $\tau_\pi$ and $\tau_\sigma$ were also evaluated.

The glass systems mentioned above were also studied with VO$^{2+}$ as the spin probe. The EPR spectra of all the glass samples containing
vanadyl ions were characteristic of hyperfine interaction of a single unpaired electron with the $^{51}$V nucleus, whose nuclear spin is $I = 7/2$. The spectra consisted of two sets of eight hyperfine lines corresponding to the parallel and perpendicular components. The spin-Hamiltonian parameters were evaluated using the standard procedures. It was found that $g_{||} < g_{\perp}$ and $A_{||} > A_{\perp}$. Therefore, it may be concluded that V$^{4+}$ ions exist as VO$^{2+}$ ions in octahedral coordination with tetragonal compression. The symmetry of vanadyl ions is $C_{4v}$ and the ground state is $d_{xy}$ orbital. The values of $\Delta g_{||}/\Delta g_{\perp}$ which measure the tetragonality of the vanadium site were calculated. The variation of $\Delta g_{||}/\Delta g_{\perp}$ with alkali halide content was found to be non-linear. The $\frac{\Delta g_{||}}{\Delta g_{\perp}}$ was maximum for 3KCl-27K$_2$O-35B$_2$O$_3$-33P$_2$O$_5$-2V$_2$O$_5$ indicating more tetragonal distortion. In 1NaBr-29Na$_2$O-35B$_2$O$_3$-33P$_2$O$_5$-2V$_2$O$_5$, the $\frac{\Delta g_{||}}{\Delta g_{\perp}}$ value was minimum indicating improvement of octahedral symmetry around the vanadyl ion. The covalency rates $(1-\alpha^2)$ and $(1-\nu^2)$ were estimated. The contribution of the 3$d_{xy}$ electron to the hyperfine structure was also calculated.