Preface

Glasses are a particular class of non-crystalline solids which are distinguished by the presence of unique thermal characteristic known as glass transition. All glasses share two common characteristics. First is that, no glass has a long range, periodic atomic arrangement. The second and even more important is that every glass exhibits time-dependent glass transformation behavior. This behavior occurs over a temperature range known as the glass transformation region. A glass can thus be defined as "an amorphous solid completely lacking in long range, periodic atomic structure and exhibiting a region of glass transformation behavior." Any material, inorganic, organic or metallic formed by any technique, which exhibits glass transformation behavior is glass. For making glasses, the rate of cooling is very important during the solidification. A slower cooling rate brings the liquid into crystalline and faster converts it into amorphous or non-crystalline state. A non-crystalline state of a solid is also known as poly crystalline or glassy state. Various types of glasses like inorganic oxide glasses, chalcogenide glasses, halide glasses, metallic glasses, spin glasses etc can be formed.

Among inorganic oxide glasses, vanadate glasses are of great importance. Vanadium pent oxide when heated above its melting point partly dissociates and loses some oxygen. This result in a non-stoichiometric oxide where part of the V^{+5} ions are reduced to a lower oxidation state, mostly V^{+4} ions which have a $3d^1$ configuration. Vanadium ions in different oxidation states yield semiconducting properties due to a hopping process of the unpaired 3d electron (or a small polaron) from V^{+4} to V^{+5} ions.

Materials, in which charge transport mainly occurs through the motion of ions (i.e. fast ion conducting glasses) are used as solid electrolyte in batteries, electroactive sensors etc but there are mixed conducting materials as well which have both ions and electrons as conducting species and they are used as electrode materials. As it is known that in silver, sodium, lithium based binary or ternary glasses ionic conductivity occurs due to the transport of Li^+, Na^+ or Ag^+ ions but the addition of transition metal oxides makes them electronic or mixed electronic-ionic conductors depending upon the composition. We have prepared glasses using BaO, Ag_2O, TeO_2 and V_2O_5, in which BaO and Ag_2O are glass modifiers while V_2O_5 and TeO_2 are glass formers. In these glasses electronic conductivity occurs due to the "electronically active" oxide (V_2O_5) and ionic conductivity is due to the "ionically active" network modifier (Ag_2O).

The present thesis is concerned with the preparation, characterization and conductivity studies on the silver based barium Vanado-tellurite glasses. The following three series of glass systems have been prepared and discussed in the present thesis.

1) x (BaO : 1.5 Ag_2O) - (95-x) V_2O_5 – 5 TeO_2;

   where x=25, 30,35,40,45.

2) 10 BaO-y Ag_2O-(85-y) V_2O_5-5 TeO_2;

   where y= 20, 25,30,35,40,45,50,55.

3) 5 BaO-z Ag_2O-35 V_2O_5- (60-z) TeO_2;

   where z= 25, 30,35,40,45,50,55,60.

The thesis has been divided into the following chapters.

Chapter one gives general introduction of glasses. Different types of glasses like halide glasses, metallic glasses, chalcogenide glasses, spin glasses are also discussed in short with their examples. Different structural theories like Goldschmidt's radius ratio criteria and Zachariasen's random network theory along with the kinetic theory of glass is also included.

Chapter two presents the theoretical background of various studies done on samples. It begins with the introduction of transition metal oxide glasses, small polaron conduction and mixed conducting system. Different models of dc conductivity like Mott's model, Schnakenberg's model, molecular crystal model etc are discussed. To interpret the dispersion behavior of glasses different models for ac conductivity like Jonscher's universal model, jump relaxation model etc are also discussed. Finally, at the end the theoretical background of various characterization studies like X-ray diffraction, IR spectroscopy, DSC technique and transport number measurement by EMF method are also included in this chapter.

Chapter three deal with the experimental details of all studies undertaken to pursue the present work. Sample preparation technique is discussed along with the other experimental techniques like XRD, FTIR and DSC to investigate the structural and thermal properties of glasses. Transport number measurement by EMF method is also given. X-ray diffraction was performed using Schimadzu X-ray diffractometer to confirm the amorphous nature of the samples. DSC thermograms have been taken using DSC 2910 TA Instruments to obtain glass transition temperature of the prepared samples. FTIR spectrometer (Bruker model vertex 70) is used to study different structural units present in the glass system. Densities of the glass samples were measured by 'Archimedes Principle'.

For conductivity measurement Solartron 1260 Impedance analyzer is used in the frequency range from 1 Hz to 32 MHz at different temperatures. DC Conductivity has been calculated from the extrapolation of frequency dependent ac conductivity. Keithley electrometer 6514 is also used for measuring dc conductivity in first series.

Chapter four discusses the results of various characterization studies done on samples. Peak free pattern of the XRD spectrum confirms the amorphous nature of the samples. DSC thermograms provide the valuable information about the glass transition temperature and crystallization temperature of these glasses. IR Spectroscopy is a fingerprint for the identification of different functional groups and types of bond formation. Silver ion transport number measurement by EMF method is also calculated which shows mixed conducting nature (electronic and ionic) of the samples. Variation of density and molar volume with modifier is also given in this chapter.

Chapter five contains the results of dc conductivity of the prepared glasses. Arrhenius behavior of conductivity and the calculated values of activation energies are also given. Effect of modifier on conductivity in three different series is discussed in detail. Non-Adiabatic hopping in polaronic conducting system, Different polaronic conducting parameters like V-V spacing (R_{V-V}), polaron radius (r_p) etc. have been discussed. For ionic dc conductivity silver ion concentration N_{Ag} and jump distance R_{Ag-Ag} is also calculated from density data.

Chapter six explains the results of frequency dependent ac conductivity and the relaxation studies of different glass system in different frequency and temperature range. Scaling of the conductivity spectra at different temperatures and compositions have also been performed using scaling process. Dielectric and Modulus formalism are also used to analyze the obtained results.

Chapter seven gives the conclusion from the above characterization results, ac and dc conductivity, dielectric and modulus studies and their dependence on the temperature and composition of the present system have been summarized here.