Preface

For decades, issues with scalability, stability and reliability in non-volatile storage devices, enticed researchers to explore the horizon of advanced materials and technologies. Ionic memory devices which are based on ion transport and electrochemical metallization process are very recent discovery to this exploration. Though practically challenging, this filament based resistive switching phenomena can be scaled down to atomic level which would certainly attain the scalability limit. With this promise, this RRAM technology is a potential candidate for the next generation non-volatile memory technology.

In this thesis, one of these RRAM materials, α-AgI based silver molybdate glasses are investigated to explore the switching mechanism and thermal and electrochemical behavior. This thesis comprises of 8 chapters; brief summaries of each chapter are discussed below.

Chapter 1 deals with fundamentals of the present thesis. It starts with separating the topic of the thesis into two aspects: technical and material. First, technical aspect has been focused by introducing an overview of the trends in memory technology, followed by emerging memory technologies. It selects one type of technology among others: Resistance Random Access Memory or RRAM. Basic principle of RRAM is discussed and further the focus is made on one of its sub-class namely ionic memory, its basic switching mechanism, and classifications such as Cationic RRAM in which the conduction process is based on cations. The discussion subsequently shifts towards material aspect such as what is the nature of material used in Cationic RRAM. The technical aspect is concluded with mentioning of some problems that can be solved by manipulating the material which is basically the objective of the thesis. In addition, the discussion dives deep into the Cation RRAM material, solid state electrolyte (SSE), its conduction process based on sub-lattice disorder, defect structure and classifications of point defects. It also focuses on one of the important SSE materials, α-AgI, its structure, phase transition, etc.

In the first chapter, before discussing AgI based ion conducting glasses, few important topics on glass has been discussed, namely glass transition phenomena, heat capacity, entropy, Kauzmann's paradox, structural and chemical elements of glass formation and bond ionicity. After discussing fast ion conducting glasses in general and AgI based and some models of ion transport, the objective of the present thesis has been indicated.

Chapter 2 focuses on the material synthesis, characterization, analysis, computation and other experimental details. This includes electrical switching, thermal (Differential Scanning Calorimetry (DSC) and Alternating Differential Scanning Calorimetry (ADSC)), structural (Raman, X-ray diffraction (XRD), X-ray photoelectron spectroscopy (XPS), Scanning electron microscopy (SEM), Energy Dispersive X-ray spectroscopy (EDX)) and electrochemical (Cyclic voltammetry (CV), Electrochemical Impedance spectroscopy (EIS)) characterizations.

Chapter 3 focuses on the earlier works. A group of fast-ion conducting, α-AgI based oxide glasses has been discussed from perspective of electrical switching, thermal and structural behavior. This chapter also puts some light on the switching behavior of some of the new samples.

Chapter 4 deals with the electrical switching behavior of bulk $(AgI)_{50}$-$(Ag_2O)_{25}$-$(MoO_3)_{25}$ glasses with ON state current and thickness. The performance of the electrical switching behavior has been characterized by two parameters, namely threshold voltage and power dissipation. This chapter focuses on the dependence of these two parameters on thickness and ON state current.

Chapter 5 deals with the fundamental understanding of switching mechanism, ion transport in bulk and role of inert electrode in the electrical switching behavior of $(AgI)_{50+x}$-$(Ag_2O)_{25}$-$(MoO_3)_{25-x}$, for $(-10 \leq x \leq 10)$ glasses. Metallization in bulk, behavior of threshold voltage profile over composition and corrosion reactions are few of the challenges. In this work, the switching behavior of bulk, fast ion conducting $(AgI)_{50+x}$-$(Ag_2O)_{25}$-$(MoO_3)_{25-x}$, for $(-10 \leq x \leq 10)$ glasses has been investigated, in order to understand the switching mechanism of bulk samples with the inert electrodes. By using inert electrodes, the switching becomes irreversible, memory type. The switching mechanism is an electrochemical metallization process. The inert electrodes restrain ionic mass transfer but exhibit a low barrier to electron transfer allowing the cathodic metallization reaction to reach Nernst equilibrium faster. The cations involved in this process transport thorough the free volume within the glass structure and the transport follows Mott-Gurney model for electric field driven thermally activated ion hopping conductivity. This model along with the thermal stability profile provide a narrow region within composition with better switching performance based on swiftness to reach threshold voltage and less power loss. Traces of anionic contribution to metallization are absent. Moreover, anodic oxidation involves reactions that cause bubble formation and corrosion.

Chapter 6 is focused on the rigidity percolation phenomena in a fast ion conducting, conditional glass forming system $(AgI)_{50+x}$-$(Ag_2O)_{25}$-$(MoO_3)_{25-x}$. To find out where, why and how the rigidity percolation phenomenon occurs within the range of $(-12.5 \leq x \leq 5)$, calorimetry and photoelectron spectroscopy experiments have been performed. The temperature dependence of heat capacity

(normalized) at glass transition temperature (T_g), exhibits fluctuations for samples with higher AgI concentration. This specific quality is an attribute of a fragile glass. The wide composition range of glass formation in this system accommodates both the fragile and strong glasses, and therefore a fragility threshold. The heat capacity (absolute) values, at T_g when plotted over the whole range of compositions, exhibits an abrupt sign shift, from negative to positive, revealing the fragility threshold. The appearance of negative heat capacity has been corroborated with the thermodynamic behavior of nanoclusters. This technique has been identified as a novel method to recognize the existence of nanoclusters in this type of glasses. The photoelectron spectroscopy study shows the formation of essential covalent structural units, [– Mo – O – Ag – O–] and complex molybdenum oxides in the positive heat capacity region. Finally, the non-reversing enthalpy profile has been studied over the whole composition range. The global, square well minima sandwiched between floppy and stress rigid region has been identified to be the intermediate phase, within the range $32.25 \leq MoO_3$ concentration ≤ 35.

Chapter 7 deals with the Electrochemical Impedance Spectroscopy and Raman studies that are performed on fast ion conducting, $(AgI)_{50+x}$-$(Ag_2O)_{25}$-$(MoO_3)_{25-x}$ for ($-10.5 \leq x \leq 3.75$) glasses to understand the features of structure, ion migration and their correlation. These features essentially involve diffusion and relaxation. The coefficients associated with diffusion process, especially, the diffusion coefficient, diffusion length and relaxation time have been determined by applying Nguyen-Breitkopf method. Besides, by tuning the concentration of the constituents, it is possible to obtain samples which exhibit two important structural characteristics: Fragility and Polymeric phase formation. The present study essentially addresses these issues and endeavors to figure out the corroboration among them. The relaxation behavior, when scrutinized in the light of Diffusion Controlled Relaxation model, ascertains the fragility threshold which is also identified as the margin between the two types of polymeric phases. Simultaneously, it fathoms into the equivalent circuitry, its elements and their behavioral changes with above mentioned features. The power law behavior of A.C. conductivity exhibits three different non-Jonscher type dispersive regimes along with a high frequency plateau. The sub-linearity and super-linearity remain significantly below and above the Jonscher's carrier transport limit, $0.5 \leq n \leq 0.9$. Finally, by observing the behavior of the crossover between these sub-linear and super-linear (SLPL) regimes, an intuitive suggestion has been proposed for the appearance of SLPL, namely oxygen vacancy formation at higher frequency.

Chapter 8 summarizes all the significant results and explains the future scope of this thesis work.