Memory Switching Behavior of bulk Fast Ion Conducting AgI-Ag$_2$O-MoO$_3$ Glasses

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Abstract

The switching behavior of fast ion conducting AgI-Ag$_2$O-MoO$_3$ glasses has been investigated thoroughly, over a wide range of compositions within the glass forming region, proportioning a balance between glass matrix former (MoO$_3$) and glass matrix expander (AgI), in order to understand the switching mechanism of bulk samples with inert electrode. The ion transport, the agility to reach the threshold voltage ($V_{th}$), $V_{th}$ – composition ($x$) profile and thickness dependence of $V_{th}$ have been explained in the light of Mott-Gurney model for electric field driven thermally activated ion hopping. A feature of alteration in memory behavior from reversible to irreversible, due to a change in electrode type from active to passive has been observed and discussed. Being a decoupled system, the $V_{th}$ – $x$ profile exhibits a seemingly scattered nature while the glass transition temperature ($T_g$) – $x$ profile increases monotonically, indicating a growing network connectivity. These two profiles together narrow down the composition region where the most thermally stable, fast switching performing samples, with a minimum power loss lie. During switching, a metallic filament forms between the two electrodes. Raman and Energy-dispersive X-ray spectroscopy studies find no traces of molybdenum, oxygen and electrode material in the filament. Scanning electron microscopic images show a bubble formation in the vicinity of anode – electrolyte interface which is analogous to oxidation reaction; however, no evidence of an anionic transport has been found. This in turns helps us to understand the corrosion mechanism in the glass matrix due to the electrochemical process. Overall, the present work aims to understand some crucial issues regarding the memory behavior of AgI-Ag$_2$O-MoO$_3$ glasses to enable us to exploit the material for non-volatile memory applications.

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1. Introduction

Fast ion conducting (FIC), AgI-Ag₂O-MoO₃ glasses have been investigated for nearly three decades, for their relatively high ionic conductivity in the solid phase at room temperature (10⁻⁵-10⁻² Ω⁻¹ cm⁻¹) [1]. Most of these studies [1-6] have been mainly focused on the ionic conductivity, glass formation, ionic transport, structure, transport models, etc. Particularly, various techniques such as, Infrared Spectroscopy (IR) [4-5], Raman Spectroscopy [7], Impedance Spectroscopy [8], high pressure transport behavior [9-10], Mechanical relaxation [11-12], Fourier Transform Raman Spectroscopy [13], Nuclear Magnetic Resonance (NMR) [13-14], X-ray absorption near edge structure (XANES) [15], Extended X-ray absorption fine structure (EXAFS) [15-19], Neutron diffraction [20], AC conductivity [21] etc. have been used to probe the structure and understand the transport phenomena. With the help of these experimental investigations and theoretical studies using Reverse Monte Carlo method [22-24] the understanding of the structure and ionic conductivity of FIC glasses has been developed significantly. Further, several models have been proposed which include weak electrolyte model [25], diffusion path model [3], chemical model [26], cluster model (for Borate and Phosphate glasses) [27-28], Model against AgI clustering (for Molybdate and Tungstate glasses) [20], mixed iodine - oxygen coordination model [22-24], fractal Nano-channel model [29] etc. to understand the transport behavior of FIC glasses. In addition, efforts have also been made to exploit these materials for different applications such as solid-state electrolytes in batteries, ambient temperature oxygen sensor, chemical sensor, electron beam recording materials [30] etc.

B. Vaidhyanathan et al. have earlier reported on the memory behavior of bulk silver iodide based FIC glasses with different glass formers, and of varying thicknesses; however, the thickness dependence of Vth of these glasses has not been fully understood in their work [31-32]. Also, their interpretation of switching mechanism differs considerably from the conventional perspective; for the metal-insulator-metal (MIM) structured cation based ionic memories, active metal anode gets oxidized and gets dissolved into the solid electrolyte and reduced to the cathode, forming metallic filament [33-34]. Vaidhyanathan et al. have suggested a probable mechanism that consists of both cathodic reduction of Ag⁺ ion and anodic oxidation of [MoO₄]²⁻ ion, along with both cationic and anionic transport. The present work primarily focuses on the understanding of the memory behavior of the bulk AgI-Ag₂O-MoO₃ glasses of different compositions; especially, on the role of passive electrode in the memory behavior of the bulk electrolyte. The results obtained in the electrical switching experiments and scanning electron microscopy (SEM), are understood on the basis of the conventional viewpoint and Vaidhyanathan’s proposition. The Mott-Gurney model for electric field driven, thermally activated ion hopping has been used to understand ion transport, thickness dependence and Vth – x profile to classify the samples according to their switching behavior.
The electrical switching phenomenon is generally exemplified by a rapid transition from a high resistance OFF state (HRS) to a low resistance ON state (LRS). The HRS of the present samples is ~10 MΩ, and the LRS is ~1-2 Ω for a 0.2 mm thick sample. The results obtained indicate that AgI-Ag₂O-MoO₃ glasses exhibit a near ideal, fast, memory type (irreversible) switching behavior with very low power dissipation. Unlike the MIM structured cation based ionic memories; a voltage sweep from positive to negative bias cannot alter the memory from LRS to HRS in these samples. The reason behind the irreversibility has been discussed in terms of the switching mechanism and electrode type.

The present study suggests the possibility of using this FIC glass for resistive memory applications; it also reveals the role played by the electrode on the memory behavior, the criteria for better switching performance. In addition, the present study brings out an important understanding of the electrochemical processes that govern the switching mechanism of the bulk system with passive electrodes.

2. Experimental

A. Glass Preparation

Bulk, AgI-Ag₂O-MoO₃ glasses have been prepared by microwave melting – metal plate quenching method. The fundamental idea behind AgI based solid electrolytes with high ionic conductivity at room temperature, is to hinder the α → β phase transition at lower temperatures, by introducing stabilizer ions into the lattice [35], i.e. preserving the α-AgI at much lower temperature; in other words, a lower phase transition temperature [36]. This can be efficiently achieved by microwave irradiation technique; the β — α phase transition occurs at around 100°C in this case [36, 37]. The microwave energy interacts with the crystal via phonon coupling and the low-lying transverse optic (TO) modes dominate; Ag⁺ mostly moves in these low energy modes that leads to Frankel defects in the structure, allowing ionic conduction [37].

Table 1 summarizes the mole percentage of the constituent materials. All the constituent materials have an individual significance. MoO₃ is a conditional glass former; unlike other nonmetal oxides (e.g. SiO₂, GeO₂, P₂O₅ etc.), pure liquid of MoO₃ essentially requires a network modifier (e.g. Na₂O, Li₂O, Ag₂O etc.) to form glass [38]. The other importance of MoO₃ is revealed later in this paper.

The introduction of a dopant salt, e.g. AgI in the glassy matrix causes expansion of the matrix by forming free volume/pathways and thus enhances the ionic conductivity [39]. The compositions are planned in a way to understand the balance between matrix former and matrix expander; higher AgI concentration causes stable, non-conductive β-phase formation, AgI crystallization; while lower AgI concentration in the matrix causes less ionic conductivity, thermal instability and brittleness. Thus for a higher ionic conductivity, a balance in composition is essential. Our present compositions surround the
central composition \((\text{AgI})_{50}(\text{Ag}_2\text{O})_{25}(\text{MoO}_3)_{25}\) \([1,4]\); while keeping \(\text{Ag}_2\text{O}\) molar concentration fixed and changing the \(\text{AgI}/\text{MoO}_3\) molar ratio proportionately.

| Sample Level | Mole percentage |
|--------------|-----------------|
|              | AgI  | Ag\(_2\)O | MoO\(_3\) |
| Sample 1     | 60   | 25         | 15         |
| Sample 2     | 57.5 | 25         | 17.5       |
| Sample 3     | 55   | 25         | 20         |
| Sample 4     | 52.5 | 25         | 22.5       |
| Sample 5     | 50   | 25         | 25         |
| Sample 6     | 47.5 | 25         | 27.5       |
| Sample 7     | 45   | 25         | 30         |
| Sample 8     | 42.5 | 25         | 32.5       |
| Sample 9     | 40   | 25         | 35         |

**Table 1**: Mole percentage of AgI, Ag\(_2\)O and MoO\(_3\)

The required quantities of AgI (99.9%), Ag\(_2\)O (99.9%) and MoO\(_3\) (99.9%) are thoroughly mixed in an Agate stone mortar and placed in a silica crucible, inside a microwave oven, operating at 2450 MHz with a continuous power level of 900 watts maximum. After 10-12 minutes, the yellow homogenous melt is quenched down to room temperature in between two stainless steel plates. As AgI is highly photosensitive, the prepared samples have been well preserved in steel container to avoid photo induced modifications. X-ray diffraction studies (XRD) have been conducted using a Bruker Powder diffractometer with CuK\(_\alpha\) radiation in the 2\(\theta\) range from 10\(^o\) to 90\(^o\) at a rate of 10\(^o\)/min. The X-ray diffraction study confirms the amorphous nature of the samples.

**B. Material Characterizations**

Differential Scanning Calorimetric (DSC) studies have been performed using a Mettler Toledo 822e ADSC instrument with STAR\(^e\) software. Thermal scans are done in the temperature range 40\(^o\)C to 250\(^o\)C at a rate of 3\(^o\)/min for samples \(~ 15\) mg of approximately equal thickness; Argon is used as the purge gas, at a flow rate of 75 ml/min. Raman spectroscopic studies of the solid samples have been performed in a Horiba Jobin Yvon (LabRAM HR) spectrometer. The present sample is photosensitive to 514.5 nm Argon laser; the exposure leaves a permanent visibly dark spot on the sample which is basically crystallization due to laser heating \([13]\). In order to avoid that, a near IR (NIR) source of 784.8 nm diode laser is used. Scanning Electron Microscope (SEM) and Energy-dispersive X-ray spectroscopy (EDS)
study across the vertical cross section of the metallic filament in the switched portion of a sample has been performed in a high resolution ULTRA 55-GEMINI SEM.

C. Electrical Switching Experiment

The electrical switching experiments have been carried out using a Keithley source meter (model 2410) controlled by Lab VIEW 6i (National Instruments). The source meter is capable of sourcing a current in the range of 0-21 mA at a maximum compliance voltage of 1100 V. Samples carefully polished to 0.20 mm thickness using 400 and 4000 grade emery sheet, are placed in between a spring loaded point contact top electrode and a flat plate bottom electrode made of brass.

3. Results and Discussions

A. Thermal Characterization; Glass Transition Temperature (T_g) and Composition

For any potential solid state device (SSD) material, scaling is an important factor to improve density, performance, power consumption and cost effectiveness. Apparently, higher scaling factor results in larger data size that reaches overheating point quicker, causing device malfunctioning, lack of data persistency and data loss. Thus, to attain chip level reliability, thermal characterization is an important concern not only in chip level but also in the bulk material. Differential Scanning Calorimetry (DSC) is a sensitive, non-perturbing thermo-analytic technique, primarily used to determine characteristic temperatures e.g. crystallization (T_c), melting (T_m), glass transition temperature (T_g) etc. and energetics of phase transition, thermal stability, conformational changes and to investigate thermodynamic properties [40].

Figure 1 shows the DSC thermograms of samples (from up to down) having a gradual decrement in AgI and increment in MoO_3 concentration. S1, S2 and S3, samples with a high AgI concentration exhibit two exothermic and two endothermic peaks, with T_g of 42.5°C, 48°C and 52°C respectively. The first exotherm at 83°C for S1 is due to AgI crystallization [14] that shifts towards the second exothermic peak while lowering the AgI concentration. The first endotherm at ~ 152°C is assigned to β → α transition of AgI [14]. In the early studies on devitrification, metastability and phase diagram of the pseudo-binary system (AgI)_{1-x}(Ag_2MoO_4)_x (0.1 ≤ x ≤ 0.9), the second exotherm at ~ 110°C has been assigned to the crystallization of the metastable compound 2AgI-Ag_2MoO_4 (2:1), and the second endotherm at ~ 180°C is due to the decomposition of the eutectic between AgI and the 2:1 compound [41]. S3, S4 and S5 show a very small endothermic hump resulting an incongruent melting, caused by this eutectic impurity. From S4 to S9, the compositions with relatively lower AgI concentration do not display the exotherm for AgI crystallization and the endotherm for β → α transition. S7, S8 and S9 with higher MoO_3 concentration
show only one exotherm at ~ 157°C. These exotherms are sharper for S8 and S9. The sharpness is caused by fast phase transformation.

Figure 1: DSC thermogram of the samples; Heat flow (arbitrary units) vs. Temperature (°C)

Figure 2 shows the $T_g$ and stability ($T_x - T_g$) profile with respect to composition. $T_g$ rises almost linearly with the MoO$_3$ concentration because of an increase in covalent Mo–O bond in the matrix which causes increased network connectivity. However, this does not ensure better thermal stability. The glass stability factor, $T_x - T_g$, indicates the devitrification tendency of a glass when heated above $T_g$. In the present results, the decreasing stability profile for S9 and S8 is interesting to note. As the network connectivity increases within the system, while the network essentially constitutes of covalent type bonds, a transition in conformational entropy takes place that results in stability downturn. This can be a matter of further research.
The plateau region from S7 to S5 corresponds to the maximum glass stability for these samples, indicating a higher glass forming ability. With increasing AgI concentration, stability factor decreases towards S1 because of AgI crystallization. Hence the DSC study, on one hand, classifies the composed samples based on their thermodynamic attributes and on the other, provides a preliminary insight into the structural counterpart of thermal behavior and composition.

### B. Memory type Electrical Switching Behavior

The input direct current, which is a triangular pulse which increases from 0 to $I_{\text{max}}$ (for this particular study, $I_{\text{max}} = 1 \text{ mA}$) and then decreases to 0 in steps of 0.01667 mA (approx.) with a time period of 0.125 seconds for each step, is passed through the sample (Figure 3a) and the voltage developed across the sample is measured simultaneously (Figure 3b). AgI-Ag$_2$O-MoO$_3$ glass normally has a very high resistance ($\sim 10 \text{ M}\Omega$) and can be considered to be in ON state. As the current increases gradually to the value of threshold current, $I_{\text{th}}$, the voltage across the electrodes increases to the maximum value (from A to B, Figure 3b) called threshold voltage, $V_{\text{th}}$. Beyond $I_{\text{th}}$, the voltage drops abruptly (from B to C, Figure 3b) and any further change in applied current cannot reshape the voltage profile significantly (from C to E, Figure 3b). In other words, the effective volume of the electrolyte that is in contact with the electrodes latches permanently at a very low resistance state. Unlike the RESET current impulse for chalcogenide
glasses [42] or a bipolar voltage sweep for MIM structured polycrystalline (AgI)_{0.2}(Ag_{2}MoO_{4})_{0.8} solid electrolyte [34], no RESET/erase mechanism works for the present case. Therefore, because of only write-read sweep, the switching behavior has been recognized as an irreversible memory type which is particularly important for non-erasable read-only memory technology. Figure 3c and 3d show the I-V characteristics of representative AgI-Ag_{2}O-MoO_{3} glasses of 0.2 mm thickness.

![Figure 3](image_url)

Figure 3: (a) Applied triangular current pulse (mA) with step size ~ 0.01667 mA/0.125 s (b) Measured voltage vs. Number of points (arb. units) (c) I-V characteristics of Sample 3 - (AgI)_{55}(Ag_{2}O)_{25}(MoO_{3})_{20} (d) I-V characteristics of Sample 7 - (AgI)_{45}(Ag_{2}O)_{25}(MoO_{3})_{30}

C. The Switching Mechanism

The switching phenomenon has been understood in the framework of cation based resistive switching mechanism [33, 43-45] that involves an electrochemical metallization process. Principally, the active anode oxidizes and produces cations (M → M^{z+} + ze^-) that migrate across the solid electrolyte as a result of applied electric field. This migration follows the Mott-Gurney model for electric field driven, thermally activated ion hopping [45]. The dependence of ionic current density (i) on electric field (E) is given by:
\[ i = 2ze\alpha\theta \left[ \exp \left( -\frac{W^0}{kT} \right) \right] \left[ \sinh \left( \frac{uzeE}{2kT} \right) \right] \ldots \ldots \ (1) \]

Where \( c \) is the mobile cation (\( M^{z+} \)) concentration, \( \alpha \) is jump distance of ions, \( \nu \) is a frequency factor, \( k \) is Boltzmann’s constant, \( T \) is temperature, \( W^0 \) is a symmetric energy barrier for thermally activated ion hopping; electric field, \( E = \Delta\phi_{SE}/d \); where \( \Delta\phi_{SE} \) is the potential drop across the electrolyte and \( d \) is the thickness.

As these cations reach to the inert cathode, cathodic deposition takes place (\( M^{z+} + ze^- \rightarrow M \)) and a successive coagulation of cations causes the metallic filament formation between two electrodes, inverting the state into low resistance state (LRS). The RESET occurs when the electrode polarity is altered and as a result, active electrode oxidation ceases to happen.

In this present study, point contact bronze electrodes are used; thus the anode oxidation and dissolution does not take place because of higher contact potential between electrode and electrolyte. Energy-Dispersive X-Ray spectroscopic (EDS) study on the switched spot of a sample does not show any traces of constituents of bronze in the metallic filament. Thus, only ions within the solid-electrolyte take part in conduction and filament formation. The present electrolyte consists of \( Ag^+ \), \( I^- \) and \([MoO_4]^{2-} \) ions \([4, 5]\) and due to size constraints, only \( Ag^+ \) ions get involved in conduction process.

As discussed in the glass preparation section, the glassy matrix constitutes of the glass former \( MoO_3 \) and network modifier \( Ag_2O \) while the dopant ions (\( Ag^+ \) and \( I^- \)) do not contribute directly to the network formation but remain decoupled from the network, expand the network by creating free volume when introduced into the system \([29, 39]\). The \( Ag^+ \) ions transport due to applied electric field occurs through these free volumes. Once the cations get in contact with the inert cathode, metallization initiates as \( Ag^+ + e^- \rightarrow Ag \). This metallic Ag keeps expanding through the free volume until the electrodes get shorted; in other words, the measured voltage profile continues from point A to B in figure 3b, up to \( V_{th} \) where the short happens. The I/V profile within A and B (figure 3b), where the ions hop from site to site while driven by electric field, follows the Mott-Gurney model (Equation 1). The significance of fitting this specific segment of the curve with Mott-Gurney model lies in the understanding of the \( V_{th} \)– \( x \) profile that will be discussed in the next section.

Once the filament is formed, it works like a unipolar fuse that remains unchanged with electrode polarity alteration. Furthermore, an effort to melt the filament thermally with RESET current impulse can deform the neighboring glass matrix. So, clearly, the electrode and contact types are so important that just
by changing them from low work function active electrode [34] to a high contact potential inert electrode alters the memory type from reversible to irreversible.

D. \( V_{th} \) and Composition

\[ \text{Figure 4:} \text{ The variation of } V_{th} (V), \text{ with } \text{MoO}_3 \text{ concentration (mole percentage) of AgI-Ag}_2\text{O-MoO}_3 \text{ glasses} \]

\( V_{th} \) shows the \( V_{th} \) variation with \( \text{MoO}_3 (x) \) and AgI concentration. \( V_{th} \) is a switching parameter used to establish a performance based classification of the materials. Faster the switching happens, smaller the value of \( V_{th} \) becomes. Furthermore, the area under the I/V profile is directly proportional to the power loss during switching and \( V_{th} \) is one of the measuring parameter of that area. The seemingly scattered nature of the plot confirms a loose correlation but there are two important aspects to describe the nature of this plot. The agility to reach \( V_{th} \) would depend on the nature of Mott-Gurney model fitted segment of I/V profile in Figure 3 and hence, on the parameters that constitutes the ion transport mechanism. In Equation 1, the only composition related parameter is \( c \), the mobile cation (\( M^{2+} \)) concentration. Interestingly, not all Ag\(^{+} \) ions are mobile [5] and the mobile ion concentration depends on the environment surrounding the Ag\(^{+} \) ions; whereas, long range migration pathway requires a mixed iodine-oxygen coordination instead of an entire iodine environment because the pathways in this case gets
restricted to very local region of few Å [23-24]. Thus, for a particular sample, where there is balanced mixed iodine-oxygen coordination around Ag⁺ ions, mobile ion concentration \( c \) increases. Now \( c \) plays a role of a multiplicative constant in the Mott-Gurney model of the form,

\[
i = cA\sinh(BV) \quad \ldots \quad (2)
\]

Where \( A = 2ze\alpha\theta[\exp(-W_a^0/kT)] \), \( B = az/2kdT \) and \( V = \Delta\varphi_{SE} \). An increase in \( c \) would cause steepness rise in the \( I/V \) profile and hence a lower \( V_{th} \). This happens to Sample 5, \((\text{AgI})_{50}(\text{Ag}_2\text{O})_{25}(\text{MoO}_3)_{25}\), the central composition, exhibits the lowest value of \( V_{th} \).

The second aspect to understand the \( V_{th} - x \) profile comes from the context of its roughly increasing nature. AgI-Ag₂O-MoO₃ is a decoupled system i.e. in this solid electrolytic glassy system, all the physical processes that are associated with the network structure and ion transport are decoupled [46]. Hence the increment of \( V_{th} \), because of lessening of mobile ion concentration in the glasses with higher MoO₃ concentration, is not as well defined as \( T_g - x \) profile in Figure 2. And the importance of this decoupled system lies in the fact that electrochemical applications in the decoupled system are possible below \( T_g \) with significant cation mobility, that distinguishes it from coupled system [47]. A requirement for higher temperature to initiate electrochemical processes and hence, the electrical switching in a system would be costly and vulnerable to heat induced damages. Moreover, the thickness dependence of \( V_{th} \) is also evident from Equation 2.

### E. SEM and Raman; Evidence of Cathodic Oxidation

Microstructures of the surface of un-switched sample (Figure 5a) and the vertical cross-section of the metallic filament of the switched samples (Figure 5b) are examined by scanning electron microscopy (SEM). The chemical nature of the filament and base surface, examined by EDS, shows around 73.66% increase in silver and 37.84% increase in iodine weight percentage (Wt. %) in the filament than the base glass. No traces of electrode material have been found in the filament. Comparative normalized Raman spectrum of un-switched and switched sample is shown in Figure 5c. Raman peaks for an un-switched sample are: Ag⁺ restrahlen mode near 75 cm⁻¹ [46], Ag–I mode at 95 cm⁻¹; \( \nu_2(E) \), \( \nu_4(F_2) \), \( \nu_3(F_2) \) and \( \nu_1(A_1) \) modes for MoO₄ tetrahedra appears at 305 cm⁻¹, 332 cm⁻¹, 826 cm⁻¹ and 878 cm⁻¹ respectively; a new Mo–O bond stretching peak appears at 900 cm⁻¹, for a composition region where \( \text{Ag}_2\text{O/MoO}_3 < 1 \) [13]. After switching, a coagulation of silver occurs due to filament formation which exhibits an intensity enhancement of Ag–I mode and a complete absence of Mo–O modes of molybdate. Figure 5e shows a schematic of the filament formation and the switching mechanism.
Figure 5: (a) SEM image of the surface of un-switched sample. (b) SEM image of the same surface after switching; metallic filament formation between electrodes. (c) Normalized Raman spectrum of Un-switched and switched \((\text{AgI})_{32.5}(\text{Ag}_2\text{O})_{25}(\text{MoO}_3)_{32.5}\) sample. (d) Bubble formation, near Anode. (e) Schematic of the filament formation between two electrodes.

The globule and bubble formation is one of the most interesting results that we find in our SEM/EDS study. The globule in Figure 5(a, inset) is caused by substantial oxygen containment than the base glass, 41.06% (Wt. %). After switching, bubbles form near anode, shown in Figure 5(d). A similar type of bubble formation due to surrounding partial pressure of oxygen and vacuum conditions has been observed in Au/SrTiO\(_3\)/Pt system where the switching mechanism is based on Oxygen transport and dislocations [48]. This evokes to reconsider the oxidation reaction in anode speculated earlier [31]. The oxidation reactions have been suggested as follows:

(a) \([\text{MoO}_4]^2- \rightarrow [\text{MoO}_4]^0 + 2e^-\)

(b) \([\text{MoO}_4]^0 \rightarrow \text{MoO}_3 + \frac{1}{2} \text{O}_2\)
According to the suggestions, the charge transport involves a reduction of $2\text{Mo}^{6+} \rightarrow 2\text{Mo}^{5+}$ and formation of extensive chains of $[\text{Mo}^{5+}\text{O}_{6/2}]^{1-}$ units; this clearly involves last two reactions (c and d). In the present study, the bubble formation occurs only in the vicinity of anode–electrolyte interface and not in the whole effective volume because there are no traces of excessive molybdenum or oxygen in the filament. Thus the extensive chain formation of $[\text{Mo}^{5+}\text{O}_{6/2}]^{1-}$ units, that causes the $2\text{Mo}^{6+} \rightarrow 2\text{Mo}^{5+}$ reduction is not happening. And hence, only first two reactions (a and b) are taking place where the molybdate ion $[\text{MoO}_4]^{2-}$ is being reduced to molybdenum tri-oxide and oxygen that results in bubble formation.

In case of MIM structured Ag (active)/Electrolyte/Pt (inert) system [33-34], oxidation reaction does not take place. However, as the electrode type is changed, oxidation takes place near anode along with the irreversible memory type switching. There are other important significances of the observed oxidation reaction; (I) it is an effective visual measure of corrosion in the glassy matrix. The $[\text{MoO}_4]^{2-} \rightarrow \text{MoO}_3$ reduction directly affects the glass matrix, (II) this confirms the earlier claim of oxidation reaction [31], though partially. The conduction process is primarily dominated by thermally activated cation hopping and no evidence of oxygen transport has been found. And hence the metallic path essentially constitutes silver, not molybdenum.

4. Conclusion

Switching of bulk, fast ion conducting AgI-Ag$_2$O-MoO$_3$ glasses has been revisited to understand the electrochemical mechanism responsible for the switching and to solve some important questions from earlier works. During the pursuit, we have explored some important aspects regarding the material and mechanism. Novel microwave technique has been used to prepare the AgI-Ag$_2$O-MoO$_3$ glasses over a wide range of compositions. In order to determine the characteristic temperatures and understanding the thermodynamic states of solid state device materials, we have performed rigorous DSC studies. It has been found that the $T_g$ increases monotonically because higher MoO$_3$ concentration introduces more network connectivity in the form of covalent Mo–O bonds of the glass former. However, neither higher network connectivity nor a higher dopant salt concentration confirms better thermal stability. The thermally stable samples remain in a narrow region, surrounding the central composition (AgI)$_{50}$(Ag$_2$O)$_{25}$(MoO$_3$)$_{25}$. 
Electrical switching studies for samples with 0.2 mm thickness have been performed. These ion conducting bulk glasses exhibit fast, near ideal, irreversible memory type switching, with very less power loss. The switching mechanism is slightly different from earlier reported mechanism for MIM structured device. The inert electrode does not dissolve into the glass matrix; only ions within the electrolyte transports, following the Mott-Gurney model for electric field driven thermally activated ion hopping. The cations, transport through the pathway volume and gets metallized when in contact with cathode, forming a metallic filament inside the pathway volume that cannot be altered or resettled with RESET impulse.

The seemingly scattered profile of $V_{\text{th}}$ with composition has been understood with the help of Mott-Gurney model. The compositional contribution to the equation appears as a multiplicative constant, $c$, the mobile ion concentration that steepens the I/V profile while reducing the $V_{\text{th}}$. The mobile ion concentration within the system depends on a balanced mixed iodine-oxygen coordinated environment around the cations. The thermally stable, central composition and some of the surrounding compositions exhibit lower values of $V_{\text{th}}$ indicating the presence of balanced mixed iodine-oxygen coordination in these glasses. These two features, thermal stability and lower value of $V_{\text{th}}$, qualify these compositions for potential solid state device (SSD) applications. The scattered nature has another aspect: the present glass in study, is a decoupled system where physical processes that are associated with network structure and ion transport are decoupled. This feature is evident from the monotonically increasing profile of $T_g$ and scattered nature of $V_{\text{th}}$. In this context, there is another importance of the present glass; electrochemical processes in a decoupled system can take place below $T_g$ which qualify this glass as a very cost effective solution for filament based memory technology.

A comparative Raman study, along with SEM and EDS study, between un-switched and switched sample confirms an agglomeration of silver and iodine during switching, without any traces of molybdenum, oxygen and electrode material. SEM image near the anode exhibits bubble formation that is analogous to oxidation reaction near anode which is related to corrosion due to the electrochemical process. This also confirms the earlier claim of oxidation reaction in the sample but opposes any evidence of anionic migration and any contribution of molybdenum and oxygen in the formed filament. Thus, taken together, firstly, the central composition, $(\text{AgI})_{50}(\text{Ag}_2\text{O})_{25}(\text{MoO}_3)_{25}$, is a thermally stable, decoupled system with better electrochemical and switching performance below $T_g$, exhibits most efficient switching behavior with a smaller value of $V_{\text{th}}$ and less power loss because of the presence of balanced mixed iodine-oxygen coordination. Secondly, the memory behavior can be exploited further by changing the electrode type from active to passive that initiate oxidation reaction in the vicinity of anode – electrolyte interface. This conclusion agrees with the earlier claim but contradicts that molybdenum and oxygen has any
significant contribution in forming filament. Thirdly, Mott-Gurney model has been successfully applied to understand the switching mechanism, $V_{th}$-x profile and thickness dependence.

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