Study of semiconducting glasses exhibiting non-linear V-I characteristics

3.1 Introduction

Glasses are isotropic solids, lacking three dimensional periodicity, not conforming to the rules of stoichiometry and passing gently into a liquid state, when heated through a thermal event known as glass transition. The important merits of glassy materials are structural homogeneity, ease of preparation; optical transparency makes them good candidates for specific technological applications compared to their crystalline counterparts [1-4]. Though the inherent complex nature of vitreous state makes it difficult to understand unambiguously the structure of amorphous materials, efforts one continuously being made to elucidate meaningful structure-property relations [5-10].

Glassy solid State devices are used to control the flow of current. The first applications of glassy semiconductors were switches. They are Ovonic threshold switch and Ovonic memory switch. Here device characteristics depend on the bulk properties of the semiconductor materials. The advantage of amorphous (Ovonic) materials is that they have impurity independent structure. They are of lower costs and stable operations. Ovonic switches are also highly resistant to the effects of radiation. Glassy memory devices have many advantages over conventional technology, including a higher packing density, lower programming current (5 mA), lower programming power (5 mW) and no fatigue problems. Also, they can be operated at high temperature (350°C) and long lifetime (over 10⁹ write/erase cycles) [11 - 13]. The switching behavior could be either threshold or memory type [14]. It may involve a stable current controlled negative resistance region (CCNR)
Recently, Pergament et al\[16\] reported that, electrical switching manifest itself in nonlinear current-voltage characteristics with s-type and n-type negative differential resistance, which is inherent in variety of materials, particularly transition metal oxides. A number of amorphous semiconductors and fast ion conductors are known to exhibit negative resistance or ‘switching’ behavior at high voltages\[14, 17\]. Switching is of technological importance because the phenomenon is non-destructive, whereas the electric breakdown of insulators at high voltages is destructive. In some amorphous materials it is observed that the ON-state is retained permanently and the current can be brought down to zero without affecting the ON-state of the material. Whereas, the OFF-state can be restored by passing a strong pulse of current and this behavior is known as memory switching. The sample once switched to ON-state is retained, then it can be used to ‘write’ or ‘register’ the information. The memory switches are of technological importance in making ROM panels. The structural transformation of the memory switched specimens in its ON-state is found to be crystalline and the crystallized regions are known to exhibit metallic conductivity analogous to small band gap semiconductor. Therefore, the memory state can read optically using laser scanning. Threshold switching is of importance for fabricating binary logic (ON - OFF) elements. Memory switching is associated with the formation of a conducting channel of crystallized portions. All switched samples have much higher conductivity than the unswitched glassy materials at the same temperature. Due to thermal activated mechanism, it is assumed that heat is generated in the switched portions and results in the permanent transformation of highly conducting material in those regions. Besides, the revival of the OFF-state in memory switched material can be
achieved by passing a steady pulse of current appears to be due to remelting of the crystalline region and transformed into a original amorphous state.

3.2 Non-linear V-I behavior and electrical switching

The device characteristics of Ovonic Threshold Switch (OTS) and Ovonic Memory Switch (OMS) show a reversible and quick transition between a highly resistive and conductive state affected by applied electric fields [11]. The main difference between the two devices is that, after being brought from the high resistance state to the conducting state, the OTS returns to its highly resistive state when the current falls below the holding current ($I_{th}$) value. On the other hand the OMS remains in the conducting state until a current pulse returns it to its highly resistive state. The OMS there by remembers the previous applied switching command, and it is from this property that the device receives its name. Intermediate resistance states are also possible for OMS devices, which can be used in applications requiring a ‘grey scale’. In all of these devices the transition between states are completely reversible. The composition of the active material determines whether the device functions as an OTS or OMS, and also affects the values of certain device parameters. The device geometry, such as thickness and cross sectional area of the active film also affects the numerical values of the device parameters. Voltage-current plot of the OTS is shown in the Fig. 3.1a. Conduction in the highly resistive state follows Ohm’s law at fields below $10^4$ V/cm. When the applied field is maintained at higher value, the dynamic resistance (1 - 10 MΩ at 1V and just prior to break down 0.1 - 0.5 MΩ) decreases monotonically with increase in voltage. If the applied voltage above a threshold value $V_{th}$, the OTS switches along the load line to the conducting state.
The transition time ‘τ,’ of this switching process has been shown to be less than $150 \times 10^{-12}$ s. The threshold voltage is a function of both film thickness and composition of active material and can be obtained in the range 2V - 300V.

Fig. 3.1 (a and b): Current - Voltage characteristics of the OTS and OMS
Current in the conducting state could be varied (increased or decreased) without significantly affecting the voltage drop across the device significantly. The dynamic resistance is of the order of 1 to 10 $\Omega$. Most of the voltage falls near the two contacts, due to barriers induced prior to switching; this accounts for about a 0.4 V drop. The field across the bulk is only about 1 kV/cm. If the current is decreased below a critical value $I_h$, the OTS switches back to the resistive state. $I_h$ depends on circuit parameters and also can be varied (typical values are 0.1 - 1 mA).

The ongoing description of the static characteristics of the OTS holds for a slowly varying applied voltage. Upon application of a fast rising pulse somewhat in excess of a threshold voltage, the OTS ordinarily does not immediately switch to the conducting state but remains in the high resistance state for a period of time $\tau_d$, called delay time. The magnitude of this delay time is strongly dependent on the extent to which the threshold voltage is exceeded. For an applied voltage pulse, slightly greater than $V_{th}$, $\tau_d$ can be several microseconds. However, it rapidly decreases with increasing voltage in excess of threshold, and essentially vanishes above a critical voltage i.e. proportional to sample thickness. Above this point the speed of switching is only circuit - limited, and total switching time less than $150 \times 10^{-12} \text{ s}$ have been observed.

In OMS, the properties of the highly resistive states are essentially the same as that of OTS. As indicated in the V-I characteristics of Fig. 3.1b, the OMS is switched to the conductive state when the threshold voltage is exceeded. It is switched back by current pulse. Memory switching is a reversible amorphous crystalline transition. Erasing is accomplished by providing a high current pulse that preferentially appears through the
conducting filament, thus exiting the crystalline phase. The surrounding amorphous material remains essentially unchanged during the entire process, and consequently acts as a heat sink which provides the rapid cooling necessary to reform the glass after the termination of current pulse.

Reversible (threshold type) or irreversible (memory type) electrical switching from a high resistance OFF-state to a low resistance ON-state has been in the literature in a variety of systems prepared by conventional melt quenching technique (muffle furnace). As pointed earlier the switching phenomenon in amorphous materials, exhibits useful applications in storage devices, power control devices oscillators etc. [4]. In this chapter we report memory type electrical switching phenomenon exhibited in microwave synthesized $xV_2O_5.20Li_2CO_3.(80-x) \ [0.4ZnO+0.6 \ B_2O_3]$ where $x=10,20,30,40 \ and \ 50$ and $xMoO_3:10Li_2O: \ (90-x)P_2O_5 \ where \ x=40,50,60,70 \ and \ 80$ glass systems and possible origin for this phenomenon.

### 3.3 Memory switching

As pointed out in the previous sections, the memory switching in glass is basically of thermal or electronic origin. The memory switching can be considered as a steady-state thermal breakdown in a homogeneous dielectric material of thickness ‘d’ and having a large area. It can be assumed that the electrodes are so thin so as to constitute no thermal impediment to the ambient medium [18]. Here, two quantities of interest are the thermal conductivity of the material and external thermal conductivity ($\lambda$), which reveals the heat lost by the dielectric through the electrode surface. A dimensionless quantity ‘c’ is defined as $c = \lambda d/(2k)$. If $c >> 1$, the dielectric functions as a thermally thick slab and $c << 1$, it is said
to be thermally thin. In the first case, the temperature drop within the material is greater than at the boundary and secondly there is a non-uniform temperature. In the latter case, the drop in temperature at the boundary is higher because heat loss at the electrodes is larger. In this stage a uniform temperature distribution prevails within the sample. The threshold voltage is proportional to the square root of thickness of the slab [19]. Although glasses exhibit very interesting thermal, mechanical, optical and chemical properties, in this thesis special emphasis has been given to the fascinating electrical properties they exhibit.

3.4 A brief review

Although vast majority of the work on switching behavior was concentrated on chalcogenide glasses, in recent years, there are reports which have shown that even oxide glasses also exhibit non-linear V – I characteristics and exhibit switching behavior. These glasses are mainly semiconducting or fast ion conducting. In the following section, a brief account of switching behavior mainly in oxide glasses are given followed by the present investigations:

<table>
<thead>
<tr>
<th>Glass system</th>
<th>Remarks</th>
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<tbody>
<tr>
<td>1) V₂O₅ - TeO₂; 20 - 80 mol% V₂O₅ [20]</td>
<td>E. Gattef et.al has put forth the idea of switching behavior in vanadium glasses. They have analyzed the data of switching characteristics, divided into three regions ie, Volt-Ampere characteristics exhibit nonlinearity for low voltages less than one volts, followed by linear</td>
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</table>
region then again enters into non linear region for high voltage followed by a breakdown, also exhibiting negative resistance region. The sample exhibits reversible switching for low current less than critical value and memory state at higher value of current showing that there exists conducting filaments. The power density which is the product of threshold voltage and current shows small changes for various temperatures and different composition of the samples. Authors have suggested that the switching at initial stage and formation of channel is due to electronic or microscopic in homogeneity. The Thermal effect becomes predominant once the channel is formed.

| 2) $10\text{TeO}_2-10\text{SiO}_2-80\text{V}_2\text{O}_5$ and $30\text{TeO}_2-10\text{CdO}-60\text{V}_2\text{O}_5$ [21] | Authors have suggested a method to explain monopolar and bipolar switching. They have emphasized that the existence of VO$_2$ in vanado-phosphate glasses results in conductive channel which is the origin of switching action. The literature reveals that when high electric field is applied, there is a transition from monopole to bipolar operation demonstrates memory ability and the memory effect is reversible. |
| 3) $\text{BaF}_2-\text{V}_2\text{O}_5,60-75\text{V}_2\text{O}_5$ mol%.[22] | The samples show a threshold behavior with high resistance and memory behavior with a low resistance. The characteristics of the low resistance state depend on field emission at initial current with an electrothermal reversing impulse. The high resistance state is interpreted in terms of a space charge limited initial current with field emission and electrothermal effects on switching. The low resistance |
behavior was seen to be affected by the internal heating of the sample.

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<tbody>
<tr>
<td>4) <strong>V$_2$O$_5$-GeO$_2$-PbO</strong>, [23]</td>
<td>It was found that memory switching when PbO is present and threshold switching in its absence. Switching voltage seems to depend on melting atmosphere, I-V characteristics under dc and ac and pulse conditions, crystallization effect and temperature. The authors suggest memory switching is accompanied with the development of a channel between the electrodes whereas threshold switching is due to a conductivity anomaly of previously precipitated crystalline phase of VO$_2$.</td>
</tr>
<tr>
<td>5) <strong>0.4TeO$_2$-0.6V$_2$O$_5</strong>**, [24]</td>
<td>The electrical behavior of glass samples was studied by determining the I-V characteristic. The results show deviations from Ohm’s law with increasing current density, leading to maximum voltage at large current densities. This electrical behavior, is termed as a switching phenomenon and is interpreted assuming that the Joule heating effect resulting from the current passing through the sample induces large increase in the conductivities.</td>
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<tr>
<td>6) <strong>V$_2$O$_5$-TeO$_2$: 40-55 V$_2$O$_5$ mol%</strong>, [25]</td>
<td>A Ghosh et.al has discussed about switching mechanism of V$_2$O$_5$-TeO$<em>2$ glasses and has shown that these glasses exhibit memory switching. Change in conductance was attributed due to change in temperature. The threshold voltage, V$</em>{th}$ decrease with temperature indicating that electro-thermal mechanism is responsible for the switching mechanism.</td>
</tr>
<tr>
<td>7) <strong>V$_2$O$_5$-Bi$_2$O$_3$: 70-95</strong></td>
<td>The authors have suggested that in these glasses, at lower applied</td>
</tr>
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<td>8) AgI-Ag2O- MoO3/\nWO3 (50 : 25 : 25), [14]</td>
<td>The authors have investigated the electrical switching characteristics in these glasses. Glasses were prepared by microwave technique. According to them the AgI based FIC glasses exhibit a current controlled memory switching behavior. A model has been proposed to explain the switching behavior of these glasses.</td>
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<tr>
<td>9) xFe2O3-(35-x)BaO-65V2O5, x = 0 - 12.5 mol%, [27]</td>
<td>Authors have told that switching in these glasses follows the electro-thermal model. Structural modification in the glassy matrix seems to play crucial role in switching. Activation energy for switching was found and it was lower than those values estimated from the d.c conductivity measurements. The results show a discontinuity for the $V_{th}$ with Fe2O3 content. This is due to cauterization of Fe$^{3+}$ ions and their interaction with VO$<em>4$- units. The equation, $\sigma</em>{th} = \sigma_0 \exp (-W/kT)$ and $\sigma_{th} = \sigma_0^{0.613} + 0.015$ is used to describe the threshold conductivity and its relation with dc conductivity.</td>
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<td>10) TeO2-V2O5-P2O5 60-90 mol% V2O5</td>
<td>M. H. Cohen et.al have found the effects due to application of high electrical field in these glasses by two types of electrode arrangement</td>
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and $P_2O_5 = 10\, \text{mol}\%$, [28]

(i) gap type electrode arrangement and (ii) sandwich type electrode arrangement. For first type of devices, current controlled negative resistance and formation of crystalline regions were seen when high field was applied. Memory type switching was seen in the second type of devices were usually made of blown glass films. The authors have observed switching phenomenon due to applied voltage is of Poole-Frenkel type.

11) $20K_2O:(75-y)V_2O_5 : yB_2O_3 : 5Fe_2O_3$.  
$y = 0 - 35\, \text{mol}\%$ [29]

Switching voltages in these glasses decreases exponentially with increasing temperature, indicating that the cause of switching is due to Joule heating. It is observed that increase of $V_2O_5$ content enhances the conductivity, which requires less input power. The radiation loss from the sample expected to be a function of input power.

12) $xAg_2O - (50-x)P_2O_5 - 50V_2O_5$,  
$x=10,15,20,30,40$. [30]

Eraiah et.al have analyzed the V-I characteristics of these glasses which exhibit memory switching. Switching voltages decreases with increase in temperature. Threshold voltages depend on the thickness of the sample indicating that the phenomenon of switching is bulk effect. Authors emphasized the formation of crystalline conducting channels in the sample.

13) $P_2O_5 - CuO - ZnO$, [31]

In these glasses, V-I characteristics showed that glasses exhibits memory switching. The increased threshold voltages with decrease in temperature of the sample and the concentration of CuO content. The results were analyzed in view of the formation of crystalline
<table>
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<th>System</th>
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<tr>
<td>V$_2$O$_5$-SrO-FeO, [32]</td>
<td>The authors have studied the glass samples of V$_2$O$_5$-SrO-FeO and showed that they exhibit a threshold switching phenomenon. The holding current and the threshold voltages were showed a strong dependence on the temperatures. The activation energy required for switching was calculated. Electro thermal mechanism could be applicable for these glasses.</td>
</tr>
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<td>V$_2$O$_5$-Fe$_2$O$_3$-TeO$_2$, [33]</td>
<td>In these glasses, the network structure of glass built of VO$_5$ polyhedra and exhibit polaronic conductivity. The conductivity in V$_2$O$_5$-Fe$_2$O$_3$-TeO$_2$ glasses are mainly due to hopping of electrons along the bonds (V$^{4+}$ → O → V$^{5+}$).</td>
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<tr>
<td>V$_2$O$_5$-ZnO-SrO-FeO, [34]</td>
<td>Glasses in the system V$<em>2$O$<em>5$-SrO-ZnO-FeO have exhibited a threshold switching. The threshold fields E$</em>{th}$ were found to increase with ZnO content. The threshold voltage (V$</em>{th}$) decrease with the increasing temperature. Also, the observed threshold voltages are found to increase with thickness of the sample. The activation energy W$_0$ for switching in these glasses was found to increase when ZnO content was increased. The electro-thermal process was found to be well suited for these glasses.</td>
</tr>
<tr>
<td>Fe$_2$O$_3$-BaO V$_2$O$_5$, [35]</td>
<td>Authors have discussed the switching characteristics of Fe$_2$O$_3$-BaO-V$_2$O$_5$ glasses on the basis of the electro-thermal model. It was found to</td>
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be memory type of switching. Conductivity in these glasses was enhanced by two orders of magnitude. This was due to the formation of filaments between the electrodes. The threshold voltages were controlled by the composition and the structure of glasses. Also due to crystallization there was decrease in threshold voltage.

<table>
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<th>3.5 Summary</th>
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<tr>
<td>Electrical switching in semiconducting glasses exhibited application towards memory types of devices. There are several reports which deal with switching in chalcogenide glasses. Some of the oxide glasses showed a rapid transformation from resistive OFF-state to a negative resistance ON-state at a certain value of the applied voltage. This phenomenon is known as ‘Switching’ and depends on the composition, thickness and temperature of the sample. It may be noted that the high field switching mechanism could be thermal or electronic. Glasses exhibiting switching phenomenon have attracted interest due to their potential applications in electrochemical batteries, electronic and photonic devices [36, 37] and their practical use in resistors [38]. Besides, glasses that exhibit switching behavior have applications in the information storage [39, 40]. In the thermal mechanism, it is assumed that the heat is generated in switched regions between the electrodes. This results in the permanent transformation to high conductivity material in those regions. Glasses exhibiting semiconducting and FIC behavior was also investigated to find the possibility of using these glasses in memory type devices. A brief literature survey has been carried out to show that the glasses containing V$_2$O$_5$ with several</td>
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</table>
other glass forming oxides such as $P_2O_5$, $TeO_2$ etc. exhibit switching behavior. The switching parameters such as threshold voltage seem to depend on thickness as well as temperature. On the basis of these observations the switching characteristics have been explained based on the formation of conducting channels, phase transformation, crystallization etc. and the switching phenomenon is associated with bulk property of the material. Near ideal switching has been observed even in fast ion conducting glasses based AgI. In these glasses, switching is associated with electronic process with chemical origin of glass formers.

### 3.6 Experimental details

Four series of glasses have been prepared for electrical switching studies:

i) $xNa_2SO_4:y [0.8NaPO_3 + 0.2MoO_3]$ where $x=5,10,15,20$ and $25$; $y= (100-x) : MNP$ - series

ii) $xNa_2SO_4:y [0.8NaPO_3 + 0.2V_2O_5]$ where $x=5,10,15,20$ and $25$; $y= (100-x) : NPV$ - series.

iii) $x V_2O_5 . 20 Li_2O. (80-x) [ y B_2O_3 : z ZnO ]$ where $10 \leq x \leq 50$ and $(y/z)=1.2$ : VZB - series

iv) $xMoO_3:10Li_2O: (90-x) P_2O_5$ where $40\leq x\leq 80$; MLP - series.

These glass systems have been synthesized by microwave heating method for electrical switching studies. The details of synthesis and characterization are described in Chapter-2. The high field electrical effect was studied by using a pc-based system [19]. The block diagram of a typical experimental setup used for studying high field electrical switching in glasses is shown in Fig. 3.2. The experimental set up consists of an excitation
source, a high-speed data acquisition system with a sample holder, a temperature controller
and an IBM PC. The investigated glass samples are polished by using silicon carbide
powder (No. 400 and 600, Carborundum, Manchester-17, United Kingdom) to a thickness
of about 0.015 - 0.04 cm. The polished sample, whose electrical switching measurements
are to be carried out, is mounted in the sample holder, which is kept in a oven whose
temperature is controlled with the help of a sensor. Output of the high field excitation
source (voltage-current) is fed to the sample through a reference resistor and the voltage
across the reference resistor and the voltage across the sample are noted using a Dual
Channel Digital Storage Oscilloscope. Voltage measured across the reference resistor gives
information about current through the sample and the potential developed across the
sample.

Fig. 3.2 Experimental set up used for threshold voltage measurements.
3.7 Results and discussion

All the investigated glasses prepared using different systems have been characterized by XRD study and DSC analysis. Both the characterizations clearly confirm the amorphous nature of the glasses. In the present work four series of glasses synthesized by microwave heating route for electrical switching studies. The detail of the synthesis using microwave heating method is described in Chapter-2.

3.7.1 Electrical switching Phenomenon

The electrical Switching behavior of MNP, NPV, VZB and MLP glass systems have been carried out in a wide range of composition. MNP and NPV glasses have not been switched even when the thickness of the glass sample varied from 0.15 mm to 0.3mm. Surprisingly in VZB glasses only VZB4 and VZB5 glasses exhibited switching while VZB1, VZB2 and VZB3 glasses did not show any switching. In the case of VZB4 glasses switching is seen for d=0.15mm and 0.20mm while in VZB5 glasses switching is observed for d = 0.15 – 0.3mm. Further, the temperature dependence of electrical switching is studied over a temperature range 300K to 333K. The threshold voltages, sample thickness and composition are listed in Table. 3.1 to 3.4. Results in the tables reveal the following:

i) Switching strongly depends on the composition.

ii) Switching depends on the thickness of the sample and

iii) Switching depends on the thermal conditions of the sample.

From the facts observed in the switching measurements we made a hypothesis that increasing the content of the transition metal oxide (V$_2$O$_5$ and MoO$_3$) has a considerable
impact on switching behaviour. Therefore, we prepared MLP glass with high transition metal oxide (TMO) concentration (from 40 to 80 mol%). All the synthesized glasses were showed switching behaviour at ambient temperature and also exhibited temperature dependence. The composition, thickness and threshold switching voltages are presented in Tables 3.3 and 3.4. Figure 3.3 show a typical voltage – current characteristic curves of MLP1 glass with 80 MO$_3$ mol% and 0.2mm thick. It is evident from Fig. 3.3, that the current increases with the voltage and reaches a threshold value. The current corresponding to the threshold voltage ($V_{th}$) is called the holding current ($I_{th}$). The sample reaches a ON-state through a negative resistance zone. In Fig. 3.3, AB represents the Ohmic region where the current is below the holding current and the region indicates the OFF state of the sample. BD represents the negative resistance region. Hence, BD represents the transition
from the OFF-state to ON state and it is essentially due to the formation of localized conductive zones across the specimen. This region is referred to as “differential negative resistance zone” [8]. CA in Fig. 3.3 represents the switched ON-state of the sample, which clearly illustrates the conductive state of the sample. From Fig. 3.3, it can be inferred that just above $V_{th}$, the voltage across the sample is decreased quickly. Suddenly, the current through the sample increases and reaches the low resistance state, which is the ON-state.

A random decrease in the voltage across the specimen can be attributed to the formation of localized conductive channels. These conductive channels arise as a consequence of narrow hot conductive paths formed, whose area of cross section is very much smaller than the area of the sample [41, 42]. Besides, the hot conductive channels are assumed to be formed due to Joule-heating [41]. The flow of large current through the sample results in
Table 3.1 Sample code, composition, specimen thickness and threshold voltage

<table>
<thead>
<tr>
<th>Code</th>
<th>Na$_2$SO$_4$ mol%</th>
<th>NaPO$_3$ mol%</th>
<th>MoO$_3$ mol%</th>
<th>$V_{th}$ (in V) $d=0.15$ mm</th>
<th>$V_{th}$ (in V) $d=0.20$ mm</th>
<th>$V_{th}$ (in V) $d=0.25$ mm</th>
<th>$V_{th}$ (in V) $d=0.30$ mm</th>
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<tbody>
<tr>
<td>MNP1</td>
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<td>76</td>
<td>19</td>
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<td>Not switched</td>
<td>Not switched</td>
<td>Not switched</td>
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<tr>
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<td>18</td>
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<td>Not switched</td>
<td>Not switched</td>
<td>Not switched</td>
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<tr>
<td>MNP3</td>
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<td>68</td>
<td>17</td>
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<td>Not switched</td>
<td>Not switched</td>
<td>Not switched</td>
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<tr>
<td>MNP4</td>
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<tr>
<td>MNP5</td>
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<td>60</td>
<td>15</td>
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Table 3.2 Sample code, composition, specimen thickness and threshold voltage

<table>
<thead>
<tr>
<th>Code</th>
<th>Na$_2$SO$_4$ mol%</th>
<th>NaPO$_3$ mol%</th>
<th>V$_2$O$_5$ mol%</th>
<th>$V_{th}$ (in V) $d=0.15$ mm</th>
<th>$V_{th}$ (in V) $d=0.20$ mm</th>
<th>$V_{th}$ (in V) $d=0.25$ mm</th>
<th>$V_{th}$ (in V) $d=0.30$ mm</th>
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<tbody>
<tr>
<td>NPV1</td>
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<td>19</td>
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<td>Not switched</td>
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<td>Not switched</td>
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<td>Not switched</td>
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<tr>
<td>NPV5</td>
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<td>15</td>
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<td>Not switched</td>
<td>Not switched</td>
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Table 3.3 Sample code, composition, specimen thickness and threshold voltage

<table>
<thead>
<tr>
<th>Code</th>
<th>$V_2O_5$ mol%</th>
<th>$Li_2O$ mol%</th>
<th>$ZnO$ mol%</th>
<th>$B_2O_3$ mol%</th>
<th>$V_{th}$ (in V) $d=0.15$ mm</th>
<th>$V_{th}$ (in V) $d=0.2$ mm</th>
<th>$V_{th}$ (in V) $d=0.25$ mm</th>
<th>$V_{th}$ (in V) $d=0.3$ mm</th>
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<td>20</td>
<td>28</td>
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<td>Not switched</td>
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<td>Not switched</td>
</tr>
<tr>
<td>VZB 2</td>
<td>20</td>
<td>20</td>
<td>24</td>
<td>36</td>
<td>Not switched</td>
<td>Not switched</td>
<td>Not switched</td>
<td>Not switched</td>
</tr>
<tr>
<td>VZB 3</td>
<td>30</td>
<td>20</td>
<td>20</td>
<td>30</td>
<td>Not switched</td>
<td>Not switched</td>
<td>Not switched</td>
<td>Not switched</td>
</tr>
<tr>
<td>VZB 4</td>
<td>40</td>
<td>20</td>
<td>16</td>
<td>24</td>
<td>521</td>
<td>530</td>
<td>Not switched</td>
<td>Not switched</td>
</tr>
<tr>
<td>VZB 5</td>
<td>50</td>
<td>20</td>
<td>12</td>
<td>18</td>
<td>504</td>
<td>510</td>
<td>522</td>
<td>538</td>
</tr>
</tbody>
</table>

Table 3.4 Sample code, composition, specimen thickness and threshold voltage

<table>
<thead>
<tr>
<th>Code</th>
<th>$MoO_3$ mol%</th>
<th>$P_2O_5$ mol%</th>
<th>$Li_2O$ mol%</th>
<th>$V_{th}$ (in V) $d=0.15$ mm</th>
<th>$V_{th}$ (in V) $d=0.20$ mm</th>
<th>$V_{th}$ (in V) $d=0.25$ mm</th>
<th>$V_{th}$ (in V) $d=0.30$ mm</th>
</tr>
</thead>
<tbody>
<tr>
<td>MLP1</td>
<td>80</td>
<td>10</td>
<td>10</td>
<td>162</td>
<td>193</td>
<td>230</td>
<td>270</td>
</tr>
<tr>
<td>MLP2</td>
<td>70</td>
<td>20</td>
<td>10</td>
<td>228</td>
<td>259</td>
<td>278</td>
<td>301</td>
</tr>
<tr>
<td>MLP3</td>
<td>60</td>
<td>30</td>
<td>10</td>
<td>294</td>
<td>336</td>
<td>366</td>
<td>398</td>
</tr>
<tr>
<td>MLP4</td>
<td>50</td>
<td>40</td>
<td>10</td>
<td>349</td>
<td>381</td>
<td>407</td>
<td>444</td>
</tr>
<tr>
<td>MLP5</td>
<td>40</td>
<td>50</td>
<td>10</td>
<td>409</td>
<td>443</td>
<td>470</td>
<td>495</td>
</tr>
</tbody>
</table>
an excess of thermal energy generated in the sample itself. There are instances that, when
the applied voltage decreased gradually, the current through the sample was found to revert
back to the high resistance state (OFF-state), such a switching phenomenon is considered
to be threshold type.

Such a threshold switching mechanism was not been seen in any of the investigated
glass systems. The electronic model is not applicable to the present glass systems while
electrothermal model is one of the suitable mechanisms which can be used to explain the
switching behavior in glassy materials [37]. Usually, in the materials obeying
electrothermal mechanism, $V_{th}$ shift towards lower voltage side which the current through
the samples shift towards higher values when the temperature of the sample is increased
step-wise [44].

The above said experimental procedure is repeated on the switched sample. The
shape of the $V$-$I$ characteristics curve is quite different Fig. 3.4 clearly indicate that the
sample once switched, it remains in the ON-state (AC), which is the essential requirement
for memory switching. Both VBZ and MLP glass systems exhibited only memory type
switching. There are three mechanisms used to describe the switching phenomenon in
oxide glasses:

i) Pure electronic mechanism [45, 46]. The phenomenon involves two processes
   namely double-injection and a carrier tunnelling.

ii) Thermal origin of switching, which suggests that the low resistance ON- state
    arises from Joule-heating, such heating bring about a reversible phase
    transformation in the sample [43, 47].
iii) The electrothermal mechanism in which the very nature of switching behaviour is of electronic in nature. Such a process is initiated primarily due to thermal effects [48, 49].

There are instances where both memory and threshold switching was exhibited in simple ternary glass systems. Regan et. al [50] reports that P₂O₅-V₂O₅-CuO glasses showed both memory and threshold switching phenomenon. Bansal et al [51] have reported threshold switching in Fe₂O₃-K₂O- V₂O₅ glasses system. Whereas, memory switching was reported by Mansingh et. al [52] in V₂O₅-TeO₂ glasses, Ahmed et al [53] and Gohr et al [54] in iron-barium-vanadate glasses.

Recently, researchers have reported that switching behavior in transition metal doped glasses prepared by melt quenching method and some of them also pointed out ionic character have to be lowered, which in turn lowers the ionic conductivity by adding divalent oxides [55]. Besides, the covalent character in the glasses can be increased by adding TMO’s [56], which contributes to electronic conductivity. Hence we made an attempt to analyze the conductivity mechanism operating in switched/unswitched glasses. The details are given in Chapters 4-6.

### 3.7.2 Thickness and composition dependence of threshold voltage

It is evident from Tables: 3.1to 3.4, MNP and NPV glass systems did not exhibit switching behavior while VZB glasses exhibited switching behavior for higher V₂O₅ concentrations (40mol% and 50mol %) and thickness less than 0.25mm (Fig. 3.5). However, in the case of MLP glass system switching was seen in all glass compositions
and thicknesses varied from 0.15mm to 0.30mm. The effect of thickness on the V-I characteristics of the investigated glasses has also been carried out on all the compositions. Figure 3.6 shows the variation of threshold voltage with the sample thickness for different compositions. It is evident from Fig. 3.6 that the threshold voltages increase with the thickness of the sample. Also, glasses with \( d > 0.4 \text{mm} \) did not exhibit switching behavior. In both VZB and MLP glass series, over the range of studied compositions and thickness ranging from \( d = 0.15 \text{mm} \) to \( d = 0.30 \text{mm} \) exhibited memory type of switching.

### 3.7.3 Temperature dependence of threshold voltage

The temperature dependence of switching behavior has also been carried out for MLP2 and MLP5 glasses over a range of temperatures. The threshold voltages are listed in Table 3.5, the threshold voltage, \( V_{\text{th}} \) lie in the range of 395V to 441V for MLP5 glass and
$V_{th}$ lie between 225V and 256V for MLP2 glass. Figure 3.7 shows the variation of $V_{th}$ with temperature. The variations seen in Fig. 3.6 are similar to various other glass systems reported in the literature [7-9]. Three important inferences obtained from Figs. 3.6 & 3.7 are:

i) Threshold voltages decrease with increasing MoO$_3$ content. $(V_{th})_{MLP5} > (V_{th})_{MLP2}$.

ii) As temperature increases threshold voltages also decreases, which is ascribed to Joule-heating.

iii) As thickness of the specimen increases $V_{th}$ decreases.

**Fig. 3.6** Variation of $V_{th}$ versus thickness for different compositions of the sample
Table 3.5 Threshold voltages at various temperatures

<table>
<thead>
<tr>
<th>Temperature (K)</th>
<th>Threshold voltage (V) 40MoO$_3$</th>
<th>Threshold voltage (V) 70MoO$_3$</th>
</tr>
</thead>
<tbody>
<tr>
<td>303</td>
<td>441</td>
<td>256</td>
</tr>
<tr>
<td>313</td>
<td>422</td>
<td>245</td>
</tr>
<tr>
<td>323</td>
<td>409</td>
<td>236</td>
</tr>
<tr>
<td>333</td>
<td>395</td>
<td>225</td>
</tr>
</tbody>
</table>

3.7.4 Activation energy for switching voltage

The activation energy, $W_o$ for switching [44] is calculated using the relation

$$V_{th} = V_0 e^{W_0/k_BT},$$

where $k_B$ is the Boltzmann constant, $V_0$ is the temperature independent parameter and $T$ is the absolute temperature. A graph of log ($V_{th}$) versus $(\frac{1000}{T})$ is shown in Fig. 3.8. The slopes obtained from regression analysis are used to calculate the activation energy ($W_0$) for threshold switching. The values $W_0$ are mentioned in Fig. 3.8. The values of activation energy are low but dependent on composition. The variation of $V_{th}$ on temperature is exponential; this is clearly indicating that the mechanism of conduction in the investigated glasses is of electrothermal type. The variation of log ($R_{th}$) with $(\frac{1000}{T})$ for two compositions is shown in Fig. 3.9. It is evident from the Fig. 3.9 that both the compositions obey the Arrhenius relation.
\[ \frac{V_{th}}{I_{th}} = R_{th} = R_0 e^{\frac{E_r}{K_B T}} \]  

(3.1)

where \( K_B \) is the Boltzmann constant. The activation barriers for conduction in the present glasses are found to depend on composition. This composition dependence of activation energy may be attributed to the redox ratio \( C = \frac{M_{05^+}^{4+}}{M_{05^+}^{4+} + M_{04^+}^{4+}} \) in the case of MLP glasses while in VZB glasses \( C = \frac{V_{s5^+}}{V_{Total}} \). These values are comparable with those reported by Aziz et.al [37].

![Graph](image.png)

**Fig. 3.7** Variation of \( V_{th} \) versus temperature

The resistance \( R_0 \) in the above equation is the temperature independent parameter and \( E_r \) is the activation energy for the conduction process. The monotonic increase of \( \log (R_{th}) \) against \((1000/T)\) can be considered as an evidence for the applicability of the
electrothermal mechanism, that is applicable to discuss the experimental data obtained. The activation energy for conduction is given in figure. 3.9. The observed change in activation energy may be related to the structural modification occurring due to the variations in MoO₃ content. As MoO₃ content increases the Mo-Mo distance decreases while the redox ratio \( \left( \frac{\text{Mo}^{4+}}{\text{Mo}^{4+} + \text{Mo}^{5+}} \right) \) increases. As a consequence of this charge carriers easily pass via aliovalent sites. It is very important to note that the crystalline conducting channels formed between the two electrodes are mainly responsible for the switching phenomenon to occur. The applied voltage at which the sample switched is the threshold voltage \( V_{th} \). At this voltage, the sample attains a low resistance state. The phenomenon of switching in oxide glasses readily exhibit temperature as well as thickness dependence. As the temperature of the sample is increased, \( V_{th} \) of the investigated glass decreases. The dependence of \( V_{th} \) on temperature supports the idea of the

![Graph](image-url)

**Fig. 3.8** Variation of \( V_{th} \) versus \( (1000/T) \)
formation of thermally generated local conductive-channels which are responsible for switching. When the temperature of the specimen increases the molecular rearrangement supports the formation of localized conductive channels or zones in the bulk material of the sample. However the irreversible

![Graph](image)

**Fig. 3.9** Variation of log(\(R_{th}\)) versus (1000/T)

phenomenon can be ascribed to the formation of crystalline conductive channel in the switched region. This phenomenon is usually facilitated at higher temperatures [16], further, it can be noted the dependence of threshold voltage on thickness reveals the bulk effect.

The dependence of \(V_{th}\) on composition is shown in Fig. 3.6. As can be seen from Fig. 3.6, \(V_{th}\) is decreasing with MoO₃ concentration. The observed composition dependence of threshold voltage can be explained on the basis of the structure of molybdo-
phosphate glass. To study the effect of structure on threshold voltage, a simple structural model is proposed.

### 3.7.5 Structural correlation

The basic structure of Molybdo-Phosphate consists of octahedral $[\text{MoO}_6]^{\circ}$ units and tetrahedral $[\text{POO}_3]^{\circ}$ units. These units form structure made up of chemically ordered network consists of P-O-P, Mo-O-Mo and Mo-O-P or P-O-Mo connectivity’s. The modification of such a network can be systematically represented by the equation $\text{Li}_2\text{O} \rightarrow \text{O}_2^\circ + 2 \text{Li}^\circ$. The oxide ion ($\text{O}_2^\circ$) carries a negative charge of magnitude two units, which drifts towards a linkage (bond), where the electrostatic interaction energetically favorable. This interaction results in bond breaking. As a result of this non-bridging oxygen’s (NBOs) are formed. However a hierarchical order of bond breaking is dictated by the affinity for oxide ion ($\text{O}_2^\circ$). The average electronic gravity of the network forming oxides controls the chemical affinity. The average electro negativity of the structural units is listed in Table 3.6. The values of electro negativities are calculated using Sanderson’s method [34]. It is clear from the above table that $[\text{MoO}_{10}]^{\circ}$ units have the highest electro negativity; hence these units get modified all along the range of compositions investigated. The resultant structural motifs are presented in the Table 3.7. Since the concentration of lithium oxide is limited to 10mol%, only $20 [\text{MoO}_{10}]^{\circ}$ get modified. The other important consequence of the investigated glass system is that the coordination of molybdenum changes from octahedral coordination to tetrahedral coordination while the phosphorous retains its tetrahedral coordination. As the concentration of MoO$_3$ is increased from 40-80mol% the values of threshold voltages decrease from 495V to 162V when the thickness
Table 3.6: Structure motifs, species and group electronegativity.

<table>
<thead>
<tr>
<th>Structural units</th>
<th>Species</th>
<th>Electronegativity</th>
</tr>
</thead>
<tbody>
<tr>
<td>([\text{MoO}_2]^+)</td>
<td>[M₁]</td>
<td>3.06</td>
</tr>
<tr>
<td>([\text{MoO}_2\text{O}_4]^2-)</td>
<td>[M₂]</td>
<td>2.49</td>
</tr>
<tr>
<td>([\text{MoO}_4\text{O}_2]^2-)</td>
<td>[M₁']</td>
<td>2.03</td>
</tr>
<tr>
<td>([\text{POO}_2]^+)</td>
<td>[Q₃]</td>
<td>3.02</td>
</tr>
<tr>
<td>([\text{POO}_2\text{O}_4]^2-)</td>
<td>[Q₂]</td>
<td>2.42</td>
</tr>
<tr>
<td>([\text{POO}_2\text{O}_4]^2-)</td>
<td>[Q₁]</td>
<td>2.02</td>
</tr>
</tbody>
</table>

is varied from 0.3mm to 0.15mm. It is important to note that all the investigated glasses whose thickness lie between 0.15mm to 0.3mm showed negative resistance or switching behavior at room temperature. A similar behavior was reported by Pergament etal [16] in barium vanadate glass, Vaidhyanathan et al [14] in bismuth vanadate glass, Gattef et al [20] in calcium–phospho-vanadate glasses containing iron. Figure 3.6 represents the variation of \(V_{\text{th}}\) with \text{MoO}_3 \text{ mol%}. It is evident from Fig. 3.6 that the \(V_{\text{th}}\) values monotonically decreases with increasing \text{MoO}_3 content for a given thickness of the sample. This composition dependence of threshold voltage could be due to structural origin. It has been reported in the literature that the conductivity in glasses containing transition metal oxide increases with TMO concentration. A similar trend was seen in the investigated glasses ie. as the concentration of \text{MoO}_3 increases conductivity increases and can be attributed to Mo-Mo distance and the redox ratio \((=\frac{\text{Mo}^{4+}}{\text{Mo}^{4+} + \text{Mo}^{5+}})\). In view of this, an attempt is made to correlate the variations seen in the threshold voltages with the network
structure of the glass. The structural units formed in these glasses play an important role. Hence the composition dependence of $V_{th}$ is correlated to the structure of the investigated glasses and the structural groups formed due to network modification. It is evident from Table 3.7 that step-wise increase of MoO$_3$ there is a gradual decrease in [POO$_{3/2}$]$^0$ units. As a consequence of this structure becomes more compact and may cause decrease in Mo – Mo distance and there will be enhancement in the formation of localized conducting channels per unit area of the glass sample. Hence the structural modifications brought about by the oxide ion in molybdo-phosphate glass affect the threshold voltages. The scheme of

**Table 3.7 Network modification of Li$_2$O-MoO$_3$-P$_2$O$_5$ glass system along with composition**

<table>
<thead>
<tr>
<th>Composition (mol%)</th>
<th>Network modification</th>
</tr>
</thead>
<tbody>
<tr>
<td>MoO$_3$</td>
<td>Li$_2$O</td>
</tr>
<tr>
<td>40</td>
<td>10</td>
</tr>
<tr>
<td>50</td>
<td>10</td>
</tr>
<tr>
<td>60</td>
<td>10</td>
</tr>
<tr>
<td>70</td>
<td>10</td>
</tr>
<tr>
<td>80</td>
<td>10</td>
</tr>
</tbody>
</table>

modification considered here is well supported by IR and Raman and neutron scattering studies reported recently [57].
3.8 Conclusion

Electrical switching behavior of MNP, VZB, NPV and MLP glasses showed composition, temperature and thickness dependence. The phenomenon of switching is memory type for all the four series of glasses investigated here. Three important inferences obtained from the experiment:

i) Threshold voltages decrease with increasing MoO$_3$ content. ($V_{th}\text{}_{\text{MLP5}} > V_{th}\text{}_{\text{MLP2}}$).

ii) As temperature increases threshold voltages also decreases, which is ascribed to Joule-heating.

iii) As thickness of the specimen increases $V_{th}$ decreases.

The phenomenon of switching in the investigated glasses may be attributed to the formation of conducting channels between the electrodes and also due to the thermal mechanism. Variations observed in switching voltages are correlated to the structural origin, which reveals that the modification of basic structural units leads to the formation of the defects (NBO’s) and the co-ordination changes occur in the glass matrix.
References


