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Electrical Switching Behaviour in Lead Phosphovanadate Glasses

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Abstract

Electrical switching behaviour of lead phosphovanadate glasses were studied by determining the current-voltage characteristics. All the investigated glasses exhibit the dependence of threshold voltages on temperature, thickness and composition. Below holding current the I - V characteristics obey Ohms law followed by a negative resistance region where the bulk behaviour dominates and at higher values of current the samples goes to a low resistance state. The studied glasses exhibit memory type switching. It is suggested that the initial switching and channel formation are due to electronic, while thermal effects dominate in the formation of channels.

Key Words: Electrical switching, Phosphovanadate, Negative resistance.

1. Introduction

Electrical switching behaviour is a fascinating property of oxide glasses, as they exhibit reversible threshold and irreversible memory states. Several investigations have been initiated to study switching in glasses containing V_2O_5 , MoO_3 , Fe_2O_3 etc., with glass formers such as P_2O_5 , B_2O_3 , TeO_2 etc., to understand switching voltage as a function of temperature and material thickness [1–3]. It has been well established that electrical switching may be either thermal, electro-thermal or purely electronic. A number of amorphous semiconductors and FIC's are known to exhibit negative resistance or 'switching' behaviour at high voltage [4, 5]. The phenomenon of negative resistance and switching are of interest because they can be non-destructive, whereas the electric breakdown of insulators at high voltages is destructive. Switching phenomena in amorphous materials find applications in information storage or power control devices [6]. It has also been reported that electronic conductive glasses can be used as cathode materials (e.g. $V_2O_5 \cdot P_2O_5$ or $V_2O_5 \cdot TeO_2$) [7]. In the present communication, we attempt to explain the switching phenomena on the basis of structural changes occurring due to the addition of modifier oxide.

2. Experimental

Lead phosphovanadate glasses having a general formula $x PbO \cdot 10 P_2O_5 \cdot (90-x) V_2O_5$ (where $x = 1.5, 2.5, 5, 10, 15, 20, 25, 30, 35$ and 40 mol%) were prepared using analar grade lead monoxide (PbO),

vanadium pentoxide (V_2O_5) and ammonium dihydrogen orthophosphate ($NH_4H_2PO_4$) as starting materials. An appropriate quantity of weighed chemicals were mixed and thoroughly ground to homogenize the mixture. Mixtures were put into a porcelain crucible, kept inside a muffle furnace and then slowly heated to $500\text{ }^\circ\text{C}$ to avoid oozing out. Depending upon the composition, the mixtures were melted at $1000\text{ }^\circ\text{C}$ – $1100\text{ }^\circ\text{C}$ for about 30 minutes to ensure homogeneity and then quenched between brass blocks. The glasses were annealed for 2 hours at $150\text{ }^\circ\text{C}$ to remove thermal strains that could have developed during quenching. The prepared samples were crushed in a mortar to a fine powder and tested for amorphous nature of glass using a powder diffractometer (Rigaku DMAX - 1C). The X-ray diffractogram did not show sharp peaks, indicating that the samples were amorphous in nature (see Figure 1).

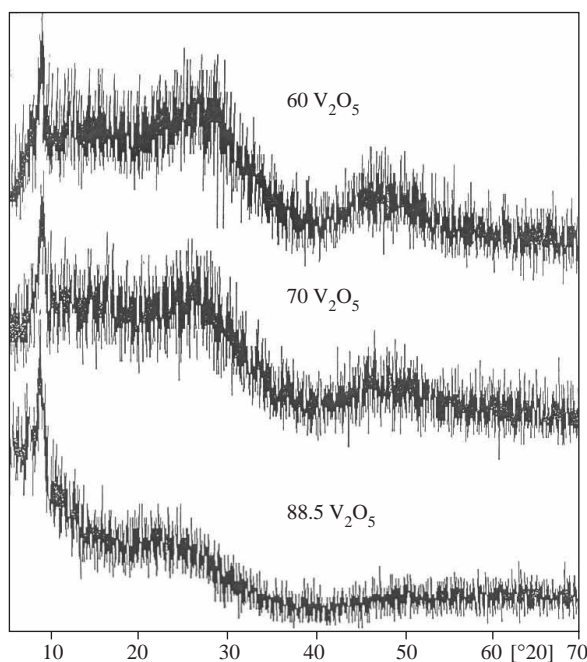


Figure 1. XRD spectra of $x\text{ PbO} \cdot 10\text{ P}_2\text{O}_5 \cdot (90-x)\text{ V}_2\text{O}_5$ glasses.

The switching behaviour of these glasses were studied using a custom built PC based system [8]. Samples were mechanically polished using carborundum powder, to a thickness of 0.15–0.3 mm. Samples, whose switching behaviour was to be studied, were mounted in a spring-loaded cell between a point contact top electrode (cathode) and a flat plate bottom electrode made of brass. A programmable, constant direct current (0–50 mA) was passed through the sample and the voltage developed across was recorded by computer. The sample holder was kept in a temperature-controlled chamber to study the temperature effects on the sample.

3. Results and Discussions

Electrical switching behaviour of $\text{PbO} \cdot \text{P}_2\text{O}_5 \cdot \text{V}_2\text{O}_5$ glass system has been carried over a wide range of composition. The glass composition, thickness and switching voltages are listed in Table 1. Figure 2 shows a typical I-V characteristics of a glass with 1.5 mol% of PbO (the sample thickness kept at 0.2 mm). It is seen from Figure 2 that the voltage initially increases with current, but at threshold current I_{th} (with a corresponding threshold voltage V_{th}), the voltage starts decreasing with increasing current, passing through a negative resistance zone, to a low resistance state. In Figure 2, AB indicates Ohmic region, where the current is very small. This indicates that the *off* state is established. BC indicates the negative resistance region, which represents the transition from *off* state to *on* state. This transition is attributed to the formation of localized conductive zones across the sample and is referred as ‘differential negative resistance zone’ [2] and

CA indicates the switched region, which illustrates the conductive on state of the sample. It is clear from the I-V curves that, after reaching V_{th} (and an irreversible state), conductivity jumps more than 6 orders of magnitude [9]. Of samples exhibiting this Current Controlled Negative Resistance (CCNR) behaviour with memory, once the state is set, the low resistance state is retained [10]. Any subsequent I-V cycles exhibits only the high conducting region (AC), indicating that the sample once switched, remains in the switched on-state, which is a characteristic of memory switching.

Table 1. Composition, thickness and threshold voltages.

PbO mol%	P ₂ O ₅ mol%	V ₂ O ₅ mol%	Threshold voltage (V) d=0.15 mm	Threshold voltage (V) d=0.20 mm	Threshold voltage (V) d=0.25 mm	Threshold voltage (V) d=0.30 mm
1.5	10	88.5	161	193	230	270
5	10	85	227	257	273	221
10	10	80	293	333	356	391
15	10	75	310	348	374	419
20	10	70	348.5	381	407.5	444.4
25	10	65	360	411	432.6	468.4
30	10	60	409.5	441.5	460.5	507
35	10	55	426	469	489	Not switched
40	10	50	480	Not switched	Not switched	Not switched

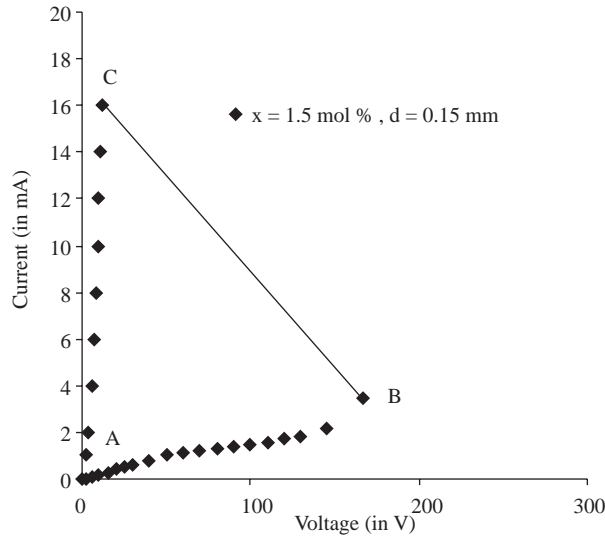


Figure 2. I-V characteristics of lead phosphovanadate (1.5 PbO · 10 P₂O₅ · 88.5 V₂O₅) glass.

The temperature dependence of threshold voltage V_{th} has been studied over temperature range 300 K–333 K and the threshold voltages are listed in Table 2. The variation of threshold voltage with temperature is shown in Figure 3. The threshold voltage is found to decrease with increase of temperature. The observed variation of threshold voltage is similar to those reported in the literature [2, 11].

Table 2. Switching voltages at different temperatures.

Temperature in K	Threshold Voltage (V)	
	$d = 0.2 \text{ mm}$ $x = 5 \text{ mol\%}$	$d = 0.2 \text{ mm}$ $x = 40 \text{ mol\%}$
300	381	480
313	323	444
323	267	403
333	204	356

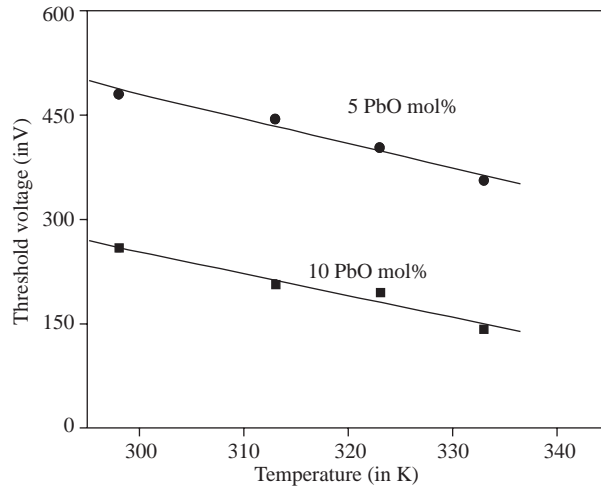


Figure 3. Variation of threshold voltage with temperature.

The thickness dependence of I-V characteristics has been examined. Figure 4 shows the variation of V_{th} with sample thickness. As can be seen from Figure 4, V_{th} increases linearly with the thickness. Glasses of thickness greater than 0.4 mm did not show any switching behaviour. Over the entire composition range studied the glasses of varying thickness (0.15–0.3 mm) exhibited memory switching, none of the samples exhibited threshold-switching behaviour.

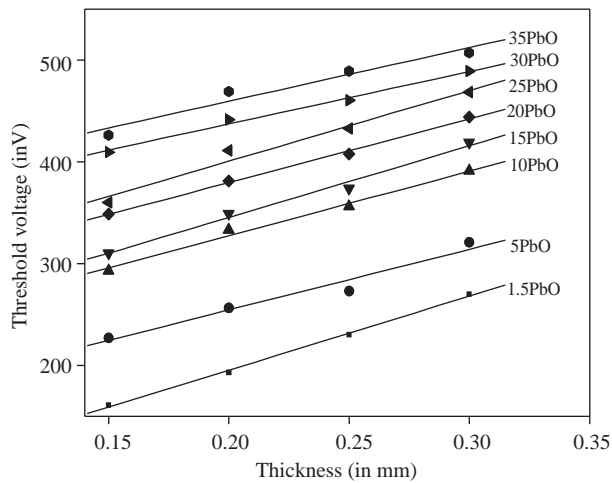


Figure 4. Variation of threshold voltage with thickness.

As explained in the literature the switching process is due to the crystalline conducting channels formed between the electrodes at V_{th} , giving rise to the low resistance state. The decrease in V_{th} with increase in

temperature supports the idea that thermally generated conducting channels are responsible for switching. As temperature increases the molecular rearrangement becomes easier for the formation of localized conducting zones in glass sample. The irreversible phenomenon has been attributed to the formation of conducting channels in the switched region, which is understandably facilitated at higher temperature [12]. Further, the thickness dependence of threshold clearly reveals that switching in these glasses is a bulk effect.

The effect of modifier oxide (PbO) concentration on the switching behaviour has also been studied by varying the modifier oxide concentration from 1.5–40 mol%. The threshold voltages lie in the range of 161–507 V. All the glasses exhibit switching behaviour at room temperature, similar to those glasses containing transition metal oxides such as barium vanadate [12], bismuth vanadate [13] and calcium phosphovanadate glasses containing iron, etc. [14].

Figure 5 shows the variation of threshold voltage with PbO mol%. As can be seen from Figure 5, the threshold voltage increases linearly with increase in concentration of PbO, for a given thickness. The composition dependence of electrical switching could be probably due to the structural origin. In glasses containing V_2O_5 , the conductivity has been known to increase with increase of V_2O_5 concentration and this is attributed to the decrease in V-V distance as well as increase in redox-ratio $[V^{4+}/(V^{4+} + V^{5+})]$ [15]. We therefore tried to correlate this aspect by considering the various structural groups likely to form in these glasses. Here, P_2O_5 and V_2O_5 behave as glass formers, while PbO can behave both as network modifier and as a network former. During modification it is important to decide which $[POO_{3/2}]^0$ and $[VOO_{3/2}]^0$ of the structural groups modified preferentially. This preference in modification is decided by electronegativity: those with higher electronegativity $[POO_{3/2}]^0$ ($\chi=3.01$) modify first, after which $[VOO_{3/2}]^0$ ($\chi=2.79$) is modified. The electronegativities have been calculated from Sanderson's principle [16]. The modifying role of PbO can be represented via the disassociation

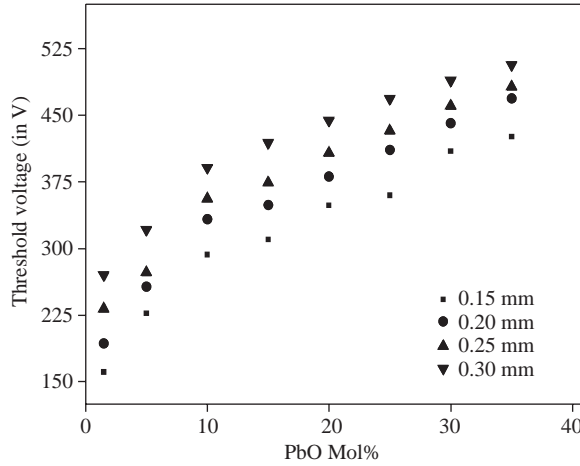
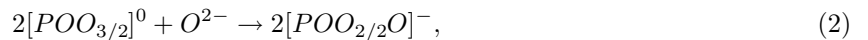


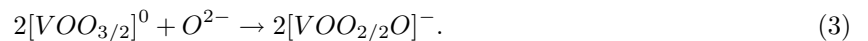
Figure 5. Variation of threshold voltage with PbO mol%.



The modification of $P_2O_5 \equiv [POO_{3/2}]^0$ can be written as



and similarly



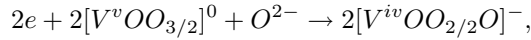
The glass composition, and various groups due to network modification, are listed in Table 3. Even more importantly for the problem of electronic conductivity, we consider the following reaction, which occurs at the high temperature of the glass forming melts before quenching:

Table 3. Glass composition and network modification.

Composition mol%			Network modification	Network forming
PbO	P ₂ O ₅	V ₂ O ₅		
1.5	10	88.5	3 [POO _{2/2} O] ⁻ , 17 [POO _{3/2}] ⁰ , 177 [VOO _{3/2}] ⁰	03[PO _{4/2}] ²⁺
2.5	10	87.5	5 [POO _{2/2} O] ⁻ , 15[POO _{3/2}] ⁰ , 175 [VOO _{3/2}] ⁰	05[PO _{4/2}] ²⁺
5	10	85	10[POO _{2/2} O] ⁻ , 10[POO _{3/2}] ⁰ , 170 [VOO _{3/2}] ⁰	10[PO _{4/2}] ²⁺
10	10	80	20 [POO _{2/2} O] ⁻ , 160 [VOO _{3/2}] ⁰	20[PO _{4/2}] ²⁺
20	10	70	20 [POO _{2/2} O] ⁻ , 20 [VOO _{2/2} O] ⁻ , 120 [VOO _{3/2}] ⁰	20[PO _{4/2}] ²⁺ + 20[VO _{4/2}] ²⁺
25	10	65	20 [POO _{2/2} O] ⁻ , 30 [VOO _{2/2} O] ⁻ , 80 [VOO _{3/2}] ⁰	20[PO _{4/2}] ²⁺ + 30[VO _{4/2}] ²⁺
30	10	60	20 [POO _{2/2} O] ⁻ , 40 [VOO _{2/2} O] ⁻ , 60 [VOO _{3/2}] ⁰	20[PO _{4/2}] ²⁺ + 40[VO _{4/2}] ²⁺
35	10	55	20 [POO _{2/2} O] ⁻ , 50 [VOO _{2/2} O] ⁻ , 40 [VOO _{3/2}] ⁰	20[PO _{4/2}] ²⁺ + 50[VO _{4/2}] ²⁺
40	10	50	20 [POO _{2/2} O] ⁻ , 60 [VOO _{2/2} O] ⁻ , 20 [VOO _{3/2}] ⁰	20[PO _{4/2}] ²⁺ + 60[VO _{4/2}] ²⁺

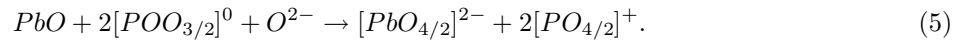


This represents the loss of oxygen step:



which in turn represents the reduction step $V^v \rightarrow V^{iv}$. During the later reduction step, the electron in V^{iv} occupy one of its d-orbitals.

The PbO may also get incorporated into the network. The following scheme of the reaction represents the incorporation of $PbO \equiv [PbO_{2/2}]$:



The reaction suggests that, by incorporation of PbO into the network, the structure $\begin{array}{c} | \\ -P \\ | \end{array} = 0$ is converted into $\begin{array}{c} | \\ -P^+ - O- \\ | \end{array}$. Here PbO is treated as a network former and is represented as $[Pb_{4/2}]^+$ units

and Pb presumably is in tetrahedral position. Similar reaction can occur in $V_2O_5 \equiv 2[VOO_{3/2}]^0$ units. The incorporation of ZnO and PbO into the network of glasses have been reported earlier [15, 17, 18]. The incorporation of PbO, therefore, requires either $[POO_{3/2}]^0$ or $[VOO_{3/2}]^0$ be converted into $[PO_{4/2}]^+$ or $[VO_{4/2}]^+$. The network forming and network modifying is given in Table 3. However, formation of $[VO_{4/2}]^+$ by the reaction such as (5) would suppress the formation of conducting electrons because envisaged reactions put a greater demand on available oxygen and no oxygen loss can occur. Also, even if an electron is placed on a $[VO_{4/2}]^+$ unit, it would act as deep trap for the electron and conductivity can only decrease. Consequently, the threshold voltage would increase with the increase of PbO mol%.

The modifying role of PbO resulted in the formation of $[POO_{2/2}O]^{-}$. As a result of this, there will an open structure and may cause increase in V-V distance and there will be reduction in the formation of localized conducting channels per unit area of the glass sample.

4. Conclusions

Electrical switching behaviour of lead phosphovanadate glasses exhibits composition, thickness and temperature dependent trends. The observed switching phenomenon indicates that the process is a bulk effect. All the investigated glasses with 1.5–40 mol% PbO exhibit switching behaviour and it is of memory type. The switching voltages are seen to increase with the increase of PbO. Memory switching in these glasses is attributable to the formation of conducting channels. The temperature and thickness dependence indicate that switching is a bulk effect. The compositional dependence of the threshold voltage is explained on the basis of structural modifications occurring in these glasses.

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