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High field electrical behaviour in lithium–phospho–vanadate glass system

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Abstract. **The high field electrical switching behaviour of lithium–phospho–vanadate glasses has been studied by determining the current–voltage characteristics. The investigated glasses exhibit temperature, thickness and composition dependent trends. At low current, the *I–V* characteristics obey Ohm's law followed by a negative resistance region where the bulk behaviour dominates and at higher values of current the sample goes to a low resistance state. The studied glasses exhibit memory type switching. It is suggested that electrical switching is due to the formation of conducting channels that are due to electronic origin while thermal effects dominate once the channels are formed resulting in crystallization.**

Keywords. **High field electrical behaviour; lithium–phospho–vanadate glass system.**

1. Introduction

High field electrical switching behaviour is one of the fascinating properties in oxide glasses, since it exhibits 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 the electrical switching behaviour as a function of temperature, material thickness and compositions (Mansingh and Dhawan 1983; Vaidyanathan *et al* 1995a; Panchal and Kanchan 1999). It has been well established that electrical switching may be either thermal, electro-thermal or purely electronic (Henish *et al* 1970; Boer 1971; Motani *et al* 1992). A number of amorphous semiconductors and FICs are known to exhibit negative resistance or 'switching' behaviour at high voltages (Chakravorthy and Mathews 1989; Vaidhyanathan *et al* 1995b). The phenomenon of negative resistance and switching in glasses 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 and power control devices (Asokan 2001). Lithium based systems fulfill voltage and energy density requirements and it has also been reported that electronic conductive glasses can be used as cathode materials (e.g. V_2O_5–P_2O_5 or V_2O_5–TeO_2) (Paguier *et al* 1983). In the present report, we have attempted to explain the switching phenomena on the basis of structural changes occurring due to the addition of modifier oxide (Li_2O).

2. Experimental

Glasses having a general formula, xLi_2O–$10P_2O_5$–$(90 - x)$ V_2O_5 (where x = 1·5, 2·5, 5, 10, 15 and 20 mol%), were prepared using analar grade lithium carbonate (Li_2CO_3), 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. Depending upon the composition, the mixtures were melted at 900–1000°C for about 30 min to ensure homogeneity and then quenched between copper blocks. The glasses were annealed for 1 h at 200°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 showed no sharp peaks indicating that the samples were amorphous in nature.

The high field behaviour of these glasses were studied using a custom built PC based system (Chatterjee *et al* 1994). Samples were mechanically polished using carborundum powder to a thickness of 0·15–0·3 mm. The sample, whose switching behaviour is to be studied, was 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

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Table 1. Composition, thickness and threshold voltages.

Li_2O (mol%)	P_2O_5 (mol%)	V_2O_5 (mol%)	Threshold voltage at $d = 0{\cdot}15$ mm (V)	Threshold voltage at $d = 0{\cdot}20$ mm (V)	Threshold voltage at $d = 0{\cdot}25$ mm (V)	Threshold voltage at $d = 0{\cdot}30$ mm (V)
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	348·5	381	407·5	444
20	10	70	409·5	441·5	460·5	489

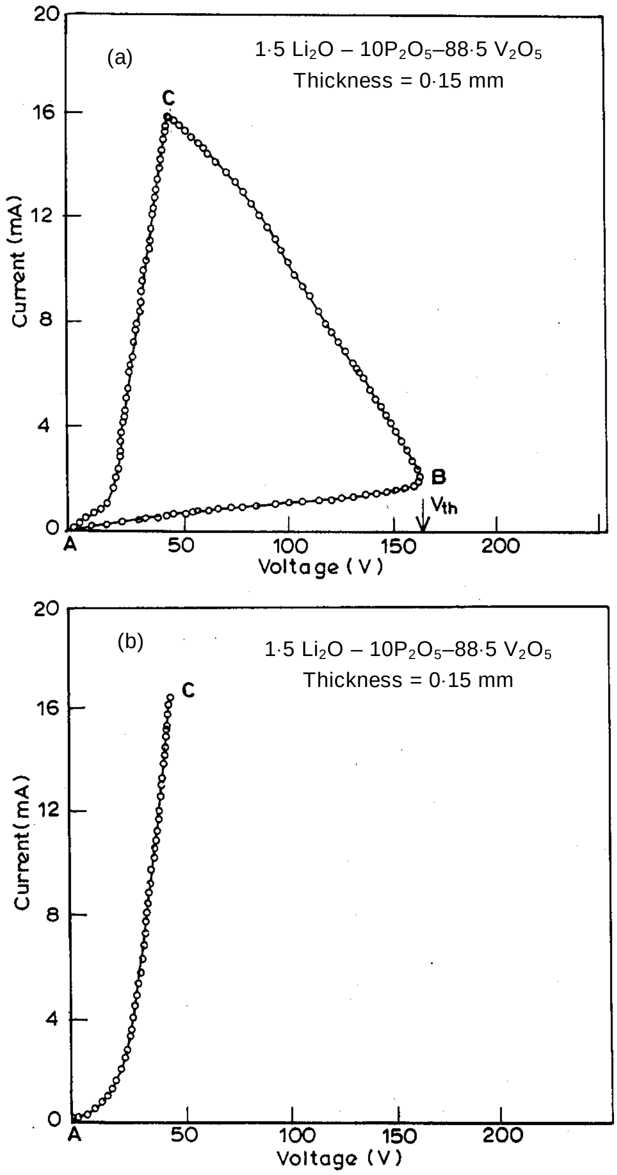

Figure 1. (**a**) *I–V* characteristics at room temperature and (**b**) *I–V* characteristics of the re-switched sample.

(0–50 mA) was passed through the sample and the voltage developed across was measured. The sample holder was kept in a temperature-controlled chamber to study the temperature effects on the sample.

3. Results and discussion

Electrical switching behaviour of Li_2O–P_2O_5–V_2O_5 glass system has been carried out over a wide range of composition, temperature and thickness. The threshold voltages are listed in table 1. Figure 1(a) shows typical *I–V* characteristics of a glass with 88·5 mol% of V_2O_5 (thickness of the sample kept at 0·2 mm). It is seen from figure 1(a) that the voltage increases with current initially, at threshold current, I_{th} (corresponding to a threshold voltage, V_{th}), the voltage starts decreasing with increasing current, passing through a negative resistance zone, to a low resistance state. In figure 1(a), 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 to as 'differential negative resistance zone' (Mansingh and Dhawan 1983) and CA indicates the switched region, which illustrates the conductive ON state of the sample. It is clear from the *I–V* cycles that, after reaching V_{th} an irreversible state having conductivity level more than 6 orders of magnitude higher is obtained. In samples exhibiting current controlled negative resistance (CCNR) behaviour with memory, once set, the low resistance state is retained (Chatterjee *et al* 1994). Any subsequent *I–V* cycles exhibit only the high conducting region, CA. When the experiment is repeated on the switched sample the shape of the graph is as shown in figure 1(b), indicating that the sample once switched, remains in the ON state (CA) which is a characteristic of memory switching.

The temperature dependence of threshold voltage (V_{th}) has been studied over a temperature range 300–333 K and the values of V_{th} are listed in table 2. The variation of threshold voltage with temperature is shown in figure 2. 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 (Mansingh and Dhawan 1983; Chatterjee *et al* 1994). The thickness dependence of *I–V* characteristics has been carried out and figure 3 shows the variation of V_{th} with sample thickness. As can be seen from figure 3, the V_{th} increases linearly with the sample thickness. Glasses of thickness > 0·4 mm did not show any switching behaviour. Over the entire composition range studied the glasses of varying thicknesses (0·15–0·3 mm) exhibit memory type of switching.

As explained in the literature the switching process is due to the formation of crystalline conducting channels between the electrodes at V_{th}, giving rise to low resistance state. The decrease in V_{th} with increase in temperature supports the idea that thermally generated conducting filaments are responsible for switching. As temperature increases, the molecular rearrangement becomes easier for the formation of localized conductive zones in the glass sample. The irreversible phenomenon has been attributed to the formation of a conducting filament in the switched region, which is understandably facilitated at higher temperature (Gohar *et al* 1997). Further, the thickness dependence of threshold voltage clearly reveals that switching in these glasses is a bulk effect.

To study the effect of modifier oxide (Li_2O) on switching behaviour, the experiments were performed by varying the modifier oxide concentration from 1·5–20 mol%. The threshold voltages lie in the range of 161–489 V. All the glasses exhibit switching behaviour at room temperature, similar to those glasses containing transition metal oxides such as barium–vanadate (Gohar *et al* 1997), bismuth–vanadate (Ghosh 1988) and calcium–phospho–vanadate glasses containing iron etc (Hirashima 1987).

Figure 4 shows the variation of threshold voltage with V_2O_5 mol%. As can be seen from figure 4 the threshold voltage decreases linearly with increase in concentration of V_2O_5, for a given thickness (threshold voltage increases with increase of Li_2O). 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 can be attributed to the decrease in *V–V* distance as well as increase in redox-ratio $[V^{4+}/(V^{4+} + V^{5+})]$. 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 Li_2O is a network modifier. Phospho–vanadate glass is a continuous network of $[POO_{3/2}]^0$ and $[VOO_{3/2}]^0$ groups and the addition of Li_2O will modify these groups into $[POO_{2/2}O]^-$ and $[VOO_{2/2}O]^-$, respectively. The preferential modifica-

Table 2. Switching voltages at different temperatures.

Temperature (K)	Threshold voltage (V)
300	381
313	323
323	267
333	204

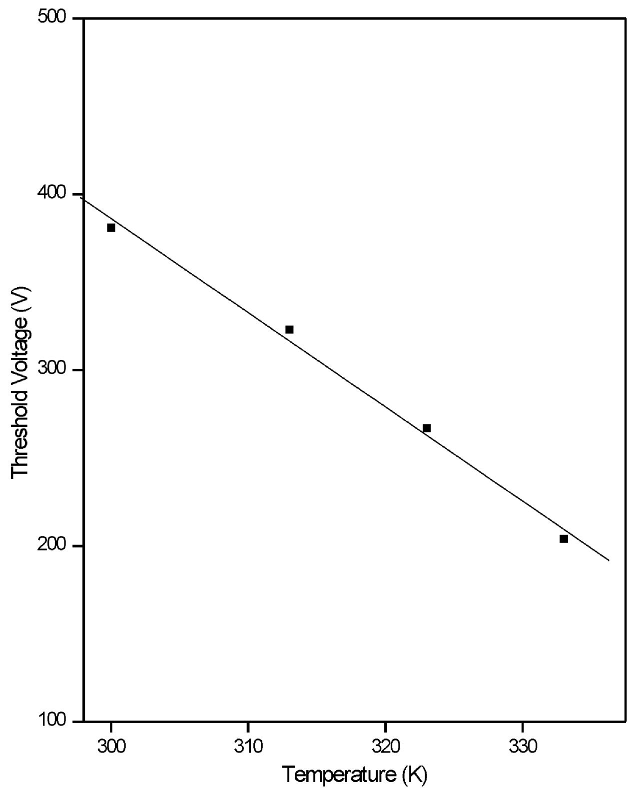

Figure 2. Variation of threshold voltage with temperature.

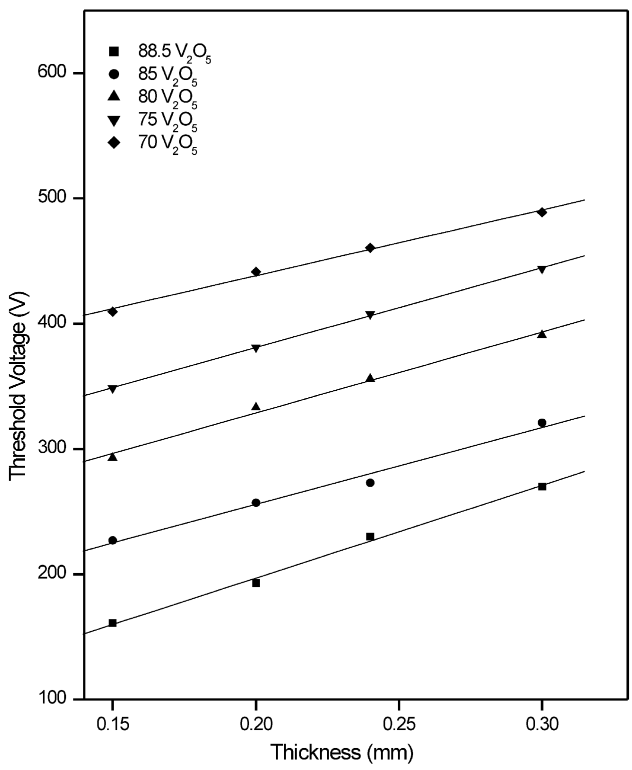

Figure 3. Variation of threshold voltage with thickness.

Table 3. Glass composition and network modification.

Glass composition (mol%)			
Li_2O	P_2O_5	V_2O_5	Network modification
1·5	10	88·5	3 $[POO_{2/2}O]^-$, 17 $[POO_{3/2}]^0$, 177 $[VOO_{3/2}]^0$
2·5	10	87·5	5 $[POO_{2/2}O]^-$, 15 $[POO_{3/2}]^0$, 175 $[VOO_{3/2}]^0$
5	10	85	10 $[POO_{2/2}O]^-$, 10 $[POO_{3/2}]^0$, 170 $[VOO_{3/2}]^0$
10	10	80	20 $[POO_{2/2}O]^-$, 160 $[VOO_{3/2}]^0$
20	10	70	20 $[POO_{2/2}O]^-$, 20 $[VOO_{2/2}O]^-$, 120 $[VOO_{3/2}]^0$

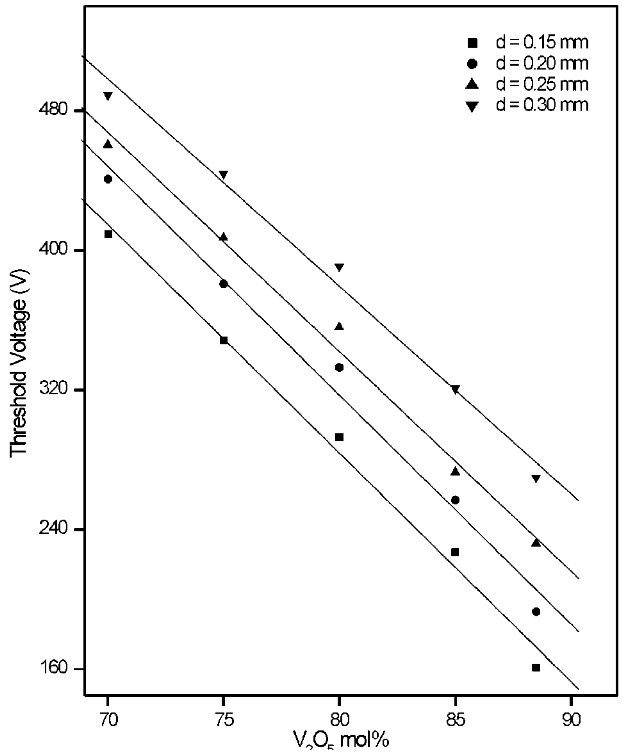

Figure 4. Variation of threshold voltage with V_2O_5 mol%.

tion is decided by electronegativity, the one with higher electronegativity $[POO_{3/2}]^0$ (χ = 3·01) modifies first, then $[VOO_{3/2}]^0$ (χ = 2·79) gets modified (Rao 2001). The electronegativities were calculated from Sanderson's principle. The glass composition and various groups due to network modification are listed in table 3. It is clearly seen in table 3 that with increase of Li_2O concentration there is a gradual decrease in $[VOO_{3/2}]^0$ groups due to the formation of $[POO_{2/2}O]^-$ and $[VOO_{2/2}O]^-$ groups. As a consequence, this will give rise to an open structure and may cause decrease 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

High field switching behaviour of lithium–phospho–vanadate glasses exhibit composition, thickness and temperature dependent trends. The observed switching phenomena indicate that the process is a bulk effect. All the investigated glasses with 1·5–20 mol% of Li_2O exhibit switching behaviour and it is of memory type. The switching voltages are seen to increase with the increase of Li_2O. 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.

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