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Electrical switching and spectroscopic studies of silver-vanado-phosphate glasses

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Abstract High field electrical switching studies on *x* Ag_2O – (50–*x*) P_2O_5 –50V_2O_5 glasses have been carried out as a function of sample thickness, composition and temperature. The I–V characteristic show that switching in these glasses is memory type. The switch voltages are found to decrease with increase of temperature, on the other hand, the voltages increase with the thickness of the sample. The experimental findings clearly reveal that switching in these glasses is a thermally assisted bulk effect. The results obtained are explained on the basis of formation of crystalline conducting channels. Another notable observation is that the glass with 15 mol% Ag_2O concentration only exhibits the switching property at room temperature. This aspect is examined in view of various structural groups present in these glasses with the help of spectroscopic studies; IR and MAS–NMR measurements have been carried out. IR studies of these glasses show characteristic absorption peaks corresponding phosphate and vanadium vibrations in the network. ^{31}P MAS–NMR chemical shift show presence of $[POO_{3/2}]^0$ and $[POO_{2/2}O]^-$ groups.

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Introduction

Electrical switching is an interesting property exhibited by many solids. It refers the transition from an insulating OFF state to a conducting ON state, at electric fields around 10^5 V/cm. The phenomenon of switching can be current controlled or voltage controlled and it can be reversible (threshold type) or irreversible (memory type). In some cases memory switched samples can be brought back to the initial OFF state by the application of a current pulse.

There are only few reports available in the literature on the electrical switching studies of oxide glasses containing Ag_2O and V_2O_5 [1–4]. Silver ion conducting glassy materials is important because of their ability to show relatively high ionic conductivities at room temperature. The applications of these materials are mostly directed towards their use as solid electrolytes in micro-batteries, oxygen sensors etc [5–7].

In this communication, we present high field electrical behavior on phospho-vanadate glasses containing Ag_2O. Interestingly, all glasses studied show memory type electrical switching. Further, the switching voltage is found to thickness and temperature dependent, clearly indicating the switching in glasses is a bulk and thermal process in these glasses. The structural aspect of these glasses has been discussed in view of IR and MAS–NMR spectroscopy.

Experimental procedure

Glasses were prepared by the conventional melt quenching method. The starting materials, silver oxide (Ag_2O), ammonium dihydrogen orthophosphate

($NH_4H_2PO_4$) and vanadium pentoxide (V_2O_5) (all AR grade) were weighed in appropriate quantities. The well-grounded mixtures were heated in porcelain crucibles at about 800–900 °C in a muffle furnace for about 30 min. The melt were stirred to ensure homogeneity and quenched between two brass blocks kept at room temperature. The glasses so obtained in the above manner were confirmed to be amorphous nature by X-ray diffraction, which did not show any sharp peaks.

The I–V characteristic behavior of xAg$_2$O–(50–x) P_2O_5–50V_2O_5 glasses were studied using a custom built PC based system. The detailed experimental set up has been described elsewhere [8]. Samples are mechanically polished to different thickness 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 voltage developed across the sample was measured. The glass compositions studied along with threshold switching voltages at different temperature and sample thickness are listed in Tables 1 and 2 respectively.

The Infrared spectra were recorded at room temperature by using a double beam IR spectrometer (Perkins Elmer 580) in the region of 400–2000 cm^{-1}. ^{31}P MAS–NMR spectra were recorded with a Bruker MSL-300 solid-state high-resolution spectrometer operating at 121.495 MHz (magnetic field 7.05T). A delay time of 30 μs was allowed between pulses to ensure relaxation of the phosphorus nucleus, chemical shift values were calculated with respect to ^{31}P resonance in 85% H_3PO_4.

Results and discussion

High field electrical switching

High field electrical switching studies have been carried over a wide range of composition and temperature. A typical I–V characteristic of a glass with 15Ag$_2$O mol% is shown in Fig. 1. In Fig. 1 the region AB is ohmic where the current is small and this indicates the OFF state. The region BC is the negative resistance region, which represents transition from OFF state to ON state. Finally, the region CA indicates the switched region, which illustrate the conducting ON state of the sample.

Table 2 Thickness and threshold voltage of 15Ag$_2$O–35P_2O_5–50V_2O_5 glass

Thickness of the samples	Threshold Voltage at 300 K
0.12 mm	688 V
0.20 mm	780 V
0.22 mm	792 V
0.25 mm	800 V

Further, the glass continues to be in the low resistance (ON) state even after electric field reduced to zero, which is a typical characteristic of memory type switching [1]. Table 1 gives the switching voltages and corresponding glass compositions. It may note from the Table 1 that glass samples with 15 mol% of Ag$_2$O show switching at room temperature while other compositions exhibit switching behavior only at higher temperatures.

Figures 2 and 3 show the variation of threshold voltage as a function of temperatures and the sample thickness. The threshold voltages decrease with increase of temperature (Fig. 2) whereas it varies inversely with the sample thickness (Fig. 3). The ohmic region (AB in Fig. 1) indicates a bulk resistance, which controls a current in this region. The negative resistance region (BC in Fig. 1) is normally attributed to space charge limited current and low resistance conducting state (CA in Fig. 1) is due to formation of crystalline conducting channel, which are found between electrodes [2, 9]. The temperature dependence of threshold voltage (which decreases with increase of temperature) indicates that the thermally generated conducting filaments are responsible for switching property. As temperature increases the molecular arrangements and

Table 1 Composition, thickness and threshold voltage of the glass samples

Serial No.	Glass composition			Threshold voltage at 300 K	Threshold voltage at 313 K	Threshold voltage at 323 K	Threshold voltage at 333 K
	Ag$_2$O	P_2O_5	V_2O_5				
1	10	40	50	Unswitched	640 V	632 V	600 V
2	15	35	50	Unswitched	624 V	560 V	496 V
3	20	30	50	Unswitched	632 V	568 V	528 V
4	30	20	50	Unswitched	Unswitched	Unswitched	624 V
5	40	10	50	Unswitched	Unswitched	592 V	168 V
6	30	10	60	Unswitched	600 V	576 V	536 V
7	15	15	70	432 V	296 V	256 V	192 V

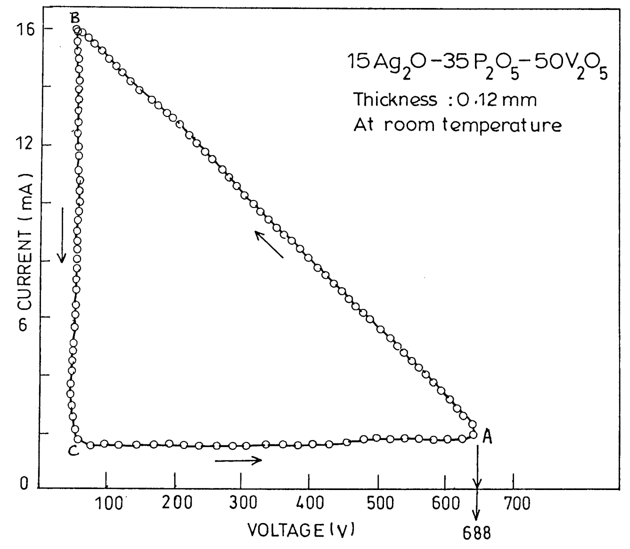

Fig. 1 I–V characteristics of $15Ag_2O–35P_2O_5–50V_2O_5$ glass at room temperature

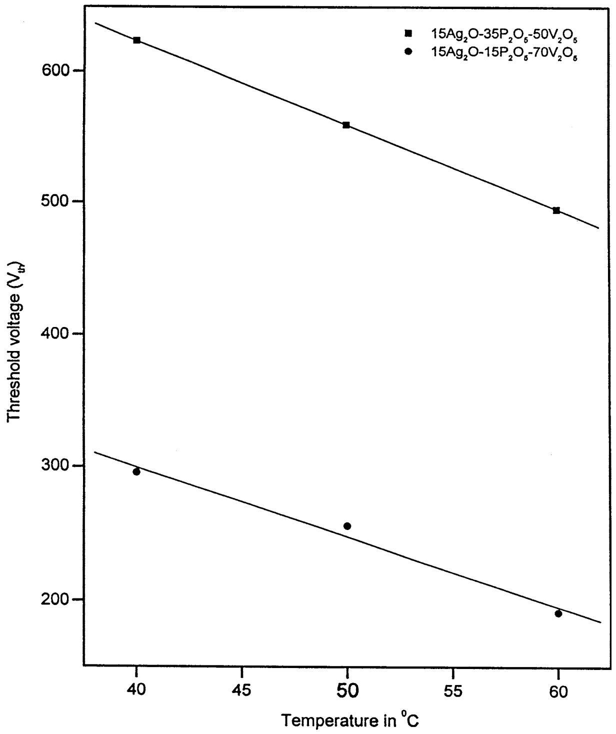

Fig. 2 Variation of threshold voltage at different temperatures

transition becomes easier in glasses, which causes further formation of conducting filaments. In addition to this the irreversible phenomena is attributed to the formation of conducting filaments in the switched region which is likely to facilitated at higher temperatures. The thickness dependence of threshold voltage suggests that the memory type switching is a bulk effect.

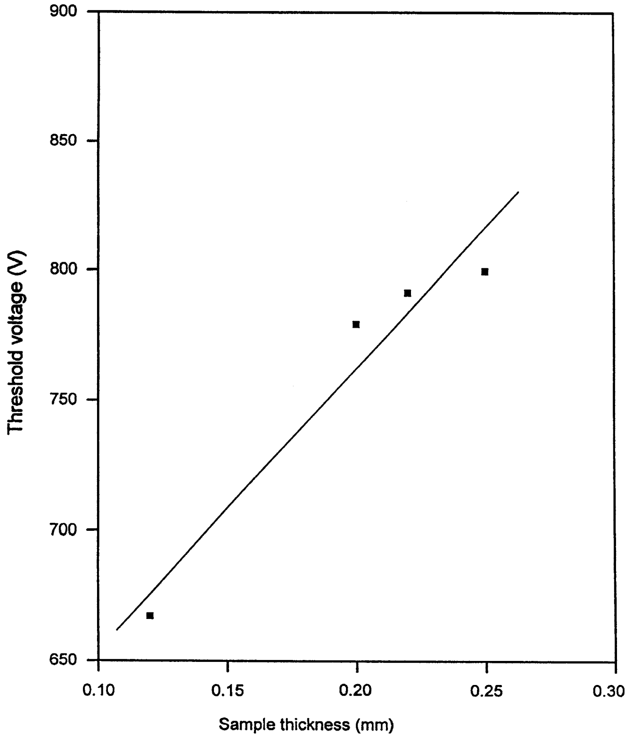

Fig. 3 Variation of threshold voltage versus sample thickness for $15Ag_2O–35P_2O_5–50V_2O_5$ glass

Another interesting feature, which can be observed from Table 1, is that the glass with only 15 mol% Ag_2O concentration exhibits switching property. This fact could be probably due to presence of critical composition of the particular phosphate group. To examine this a glass with $15Ag_2O–15P_2O_5–70V_2O_5$ was also prepared for the comparative study. In the present glass system P_2O_5 being the network former and is represented as $[POO_{3/2}]^0$. Addition of modifier oxide Ag_2O leads to creation of two connected $[POO_{2/2}O]^-$ groups. The concentration of $[POO_{2/2}O]^-$ groups is same in both glasses containing 15 Ag_2O. The presence of critical composition of $[POO_{2/2}O]^-$ groups is probably responsible for the switching at room temperature. The group concentration of various species were calculated on the basis of Sanderson electronegativity principle [10]. For $15Ag_2O–35P_2O_5–50V_2O_5$ and $15Ag_2O–15P_2O_5–70V_2O_5$, the concentration is $30[POO_{2/2}O]^-40[POO_{3/2}]^0$ $100[VOO_{3/2}]^0$ and $30[POO_{2/2}O]^-$ $70[VOO_{3/2}]^0$ respectively. In both glasses the concentration of $[POO_{2/2}O]^-$ group is same which seem to be responsible for switching at RT. The presence of various structural groups IR and ^{31}P MAS–NMR studies have been carried and the results are discussed below.

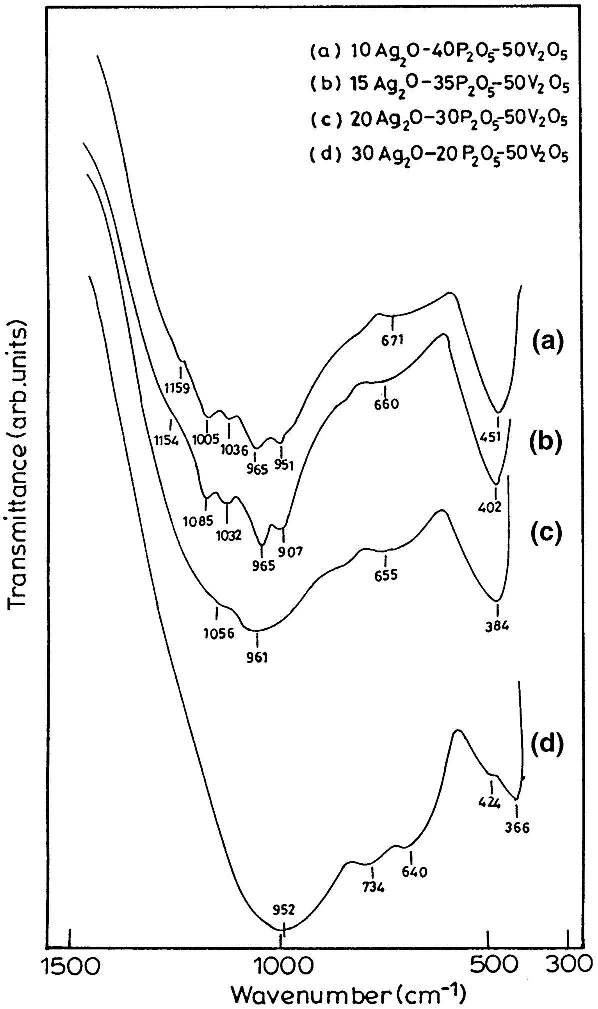

Fig. 4 IR spectra of Ag_2O–P_2O_5–V_2O_5 glasses

Infrared studies

The infrared absorption spectra of xAg$_2$O– (50–x) P$_2$O$_5$ – 50V$_2$O$_5$ glasses of various compositions have been recorded in the region from 400 to 2000 cm^{-1}and are shown in Fig. 4. The glass with 10 mol% Ag$_2$O and 15 Ag$_2$O show weak absorption around 1100 cm^{-1} which are attributed to P=O oxygen stretching of [POO$_{3/2}$]^0 groups [11–13]. Although the reported values of P=O vibrations are 1250 cm^{-1} since progressive addition of Ag$_2$O leads to modification of [POO$_{3/2}$]^0 and [POO$_{2/2}$O]$^-$ groups. This causes weakening of phosphate network and hence P=O peak vibrations are being red shifted. For higher concentrations of Ag$_2$O this peak completely vanishes indicating the presence of [POO$_{2/2}$O]$^-$ groups. In the initial concentration of Ag$_2$O the peaks around 1000–1050 cm^{-1} are attributable to stretching modes of P–O$^-$ non-bridging oxygens [14, 15]. This feature is also suppressed at higher concentration of Ag$_2$O. The weak peaks around 725 cm^{-1} are due to bending modes of P–O–P. The peak around 950 cm^{-1} is due to stretching modes of V=O [16–18] which is consistently present in all the glass samples and becomes broader when Ag$_2$O concentration is greater than 20 mol%. This is likely to be due to modification of [VOO$_{3/2}$]^0 groups at higher modifier concentrations. The peaks around 650 cm^{-1} are attributable to bending modes of O–V–O [19]. The low frequency peaks around 400 cm^{-1} are likely to arise due to cage vibration frequencies of Ag$^+$ ions. The splitting of peaks in the region stretching of P–O–P and V–O–V vibrations is due to mixed linkage such as P–O–V [20].

MAS–NMR studies

Figure 5 shows the MAS–NMR spectra of select glasses containing 15, 20 and 40 mol% of Ag$_2$O. All the three spectra clearly show a strong signal centered around –17 ppm, which is attributable to ^{31}P in [POO$_{3/2}$]^0 groups. In case of spectra (a) and (b) the weak signal centered around 33 ppm is attributable to ^{31}P in [POO$_{2/2}$O]$^-$ groups. This peak is not being seen in glasses containing higher concentration of Ag$_2$O.

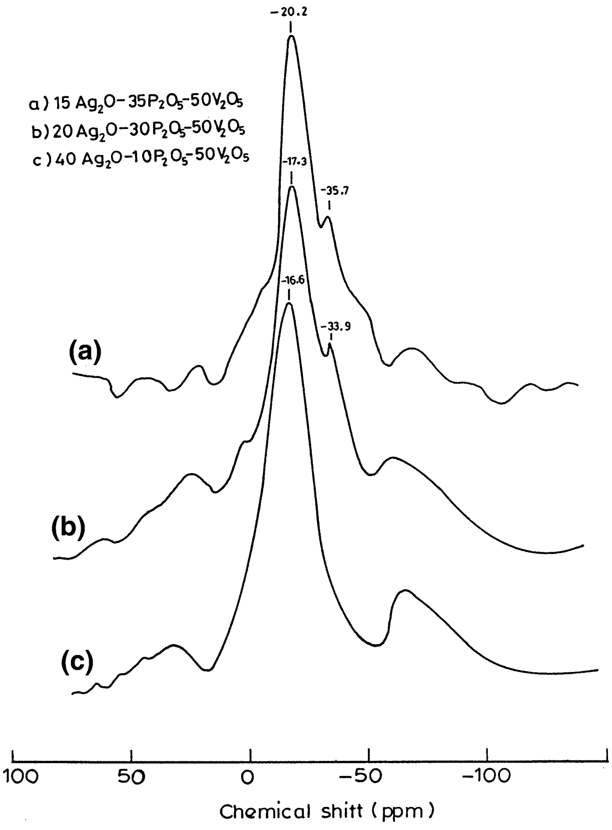

Fig. 5 ^{31}P MAS–NMR OF Ag_2O–P_2O_5–V_2O_5 glasses

The IR and MAS–NMR studies clearly show that phosphate groups are modified $[POO_{3/2}]^0$ and $[POO_{2/2}O]^-$groups. The concentration $[POO_{2/2}O]^-$ seem to be crucial for switching behavior.

Conclusions

In this paper we have described the high field electrical switching properties of Ag_2O-P_2O_5-V_2O_5 glasses. Temperature, thickness and composition dependence of switching voltage indicates that the process is a bulk effect an memory type. The glasses 15 mol% of Ag_2O show switching property at room temperature, while other compositions show switching property only at higher temperatures. Switching in these glasses are attributed to the formation of crystalline conducting channel between the electrodes at switching voltage. IR studies of these glasses show characteristic absorption peaks corresponding to phosphate and vanadium vibrations. ^{31}P MAS–NMR studies show the presence of $[POO_{3/2}]^0$ and $[POO_{2/2}\ O]^-$ groups. These studies clearly show that $[POO_{2/2}O]^-$ groups seem to be crucial for switching behavior.

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