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MEMORY SWITCHING IN CADMIUM ZINC PHOSPHATE GLASSES

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A range of samples of glasses is shown to exhibit memory switching at an applied voltage of order of 10—20 V. Electron diffraction examination of glass films prior to switching and subsequently, and also after having switched off by a high-current pulse, show that switching on is associated with a local amorphous to crystalline transition.

1. *Introduction*

During the past few years a variety of switching and memory effects have been observed in different glassy materials[1-3]. The switching, by two terminal contacts to the glassy semiconductros and related materials, has aroused considerable interest in promising cheap memory. A current controlled negative resistance in copper-calcium-phosphate glasses was observed by Drake et al.[4]. But main difficulty in these materials is that reproducible results cannot be obtained. Much of the basic ideas regarding the explanation of switching phenomenon is described by Mott and Davis[5] and Mott[6] suggested that switching takes place due to the rearrangement of local atomic structure in glassy materials. Hogarth and Ghauri[7] reported that memory switching, in thin samples of cadmium phosphate glasses at high electric fields studied by electron diffraction, is accociated with field induced crystallization of a localized region of the glass film.

In this present investigations, a report on memory effects and structural changes during switching in cadmium zinc phosphate glasses is described.

2. *Experimental work*

The samples used in the present investigations were prepared as 60 g specimens from the admixture of analytical reagent grade of CdO, ZnO and P_2O_5. The P_2O_5 percentage was kept constant at 60 mol % in these samples while the percentage of CdO and ZnO was changed between 0 and 40 mol%. The alumina crucible, containing admixture, was placed initially in an electric muffled furnace at 500°C for 30 min to fuse the P_2O_5 into admixture and to minimize the tendency of P_2O_5 to evaporate at high temperatures. Later on, the crucible was transferred to another muffled furnace at a temperature of $1150 \pm 10°$ C. The time required to prepare the melt, 2 h, was kept constant and the melt was stirred from time to time for homogeneity. Thin samples were prepared by blowing with an alumina tube in air and specimens in the thickness range of 3 μm—40 μm were obtained, as measured using a sigma comparator. Air drying colloidal silver paint was used as an electrode material. All the thin film samples were annealed at 200° C for about 2 h before electroding. The X-ray diffraction pattern showed no discrete lines.

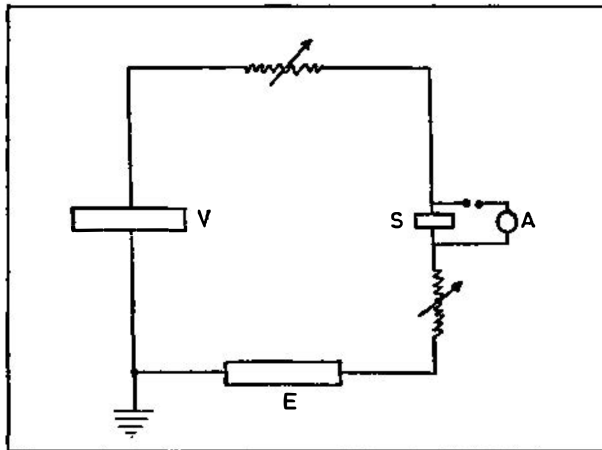

Fig. 1. Electrical circuit used for voltage-current characteristics. V-Voltage supply; S-Sandwich sample; E-Electrometer; A-Avometer.

A simple voltage-current measuring device was employed, similar to that described by Moridi and Hogarth[8]. Fig. 1 illustrate the circuit used for observation of the voltage-current characteristics. The 1 MΩ resistors served to limit the current flowing through the circuit and this current were generally negligible in the off-state. Just after switching a small amount of potential difference appears acrross the switched device which is measured by avometer. A typical voltage-current characteristic is shown in Fig. 2, and similar curves were obtained for specimen of all the compositions. To avoid from oxidation, all the measurements were made in vacuum of $\sim 1.33 \times 10^{-3}$ Pa.

The structural changes in the switched regions of the thin glass samples were studied using a *JEM*—7 electron diffraction pattern following the technique described by Hogarth and Ghauri[7]. The accelerating voltage used was 80 kV.

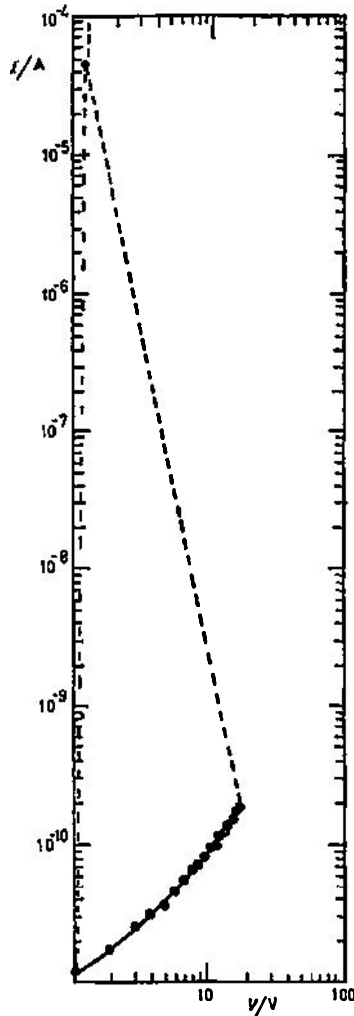

Fig. 2. Voltage-current characteristics of 35 mol % CdO — 5 mol % ZnO — 60 mol % P_2O_5 glass samples, annealed at 200° C, of thickness of 5 μm showing memory switching.

The cross-sectional area of the pressure contacts was 0.26 cm^2 and such constacts were used instead of silver paint.

3. *Results and discussion*

A typical voltage-current characteristic of 35 mol % CdO — 5 mol % ZnO — 60 mol % P_2O_5 is shown in Fig. 2. An increase in applied voltage results in a current which increases so rapidly that it becomes a super-linear function of

voltage, and further, beyond this threshold voltage results in a decrease in resistance. Some observations were made which follows as:

a. Switching is more readily observed with films which have been annealed at 200° C than with unannealed films.

b. The thicker films show a tendency to switch at higher temperatures. Devices in the range of 10 μm—18 μm thickness usually switched in the temperature range 273 K to 453 K but thicker samples, 25 μm, did not switched even for an applied voltage of 1200 V. However, on heating to 473 K, it switched to an *on* state at applied voltage of 500 V and subsequently the device showed memory switching even at room temperature.

c. It is more difficult to switch off the device at high temperatures than at low temperatures. In such cases, the temperature of the samples was reduced and the off-state recovered by resetting current of a. d. c. pulse of 0.2—0.5 mA and of opposite polarity.

d. For new devices a high applied voltage is needed for initial switching and in the following a successive switching cycles a lower voltage was needed but threshold values were not reproducible.

e. When the polarity of the device was reversed, the same behaviour was observed, indicating that device characteristic was symmetrical.

Similar observations were made for the all compositions as described in Table 1.

TABLE 1

Specimen	Composition (60 mol % P_2O_5) CdO	ZnO	Thickness	Threshold voltage	R_{off}	R_{on}
a	35	5	5 μm	18 V	$9.5 \times 10^{10} \Omega$	$2.5 \times 10^4 \Omega$
b	30	10	6 μm	16 V	$7.0 \times 10^9 \Omega$	$5.6 \times 10^4 \Omega$
c	25	15	8 μm	16 V	$4.0 \times 10^{10} \Omega$	$3.8 \times 10^4 \Omega$
d	20	20	6 μm	15.6 V	$6.0 \times 10^{10} \Omega$	$4.2 \times 10^4 \Omega$
e	15	25	4 μm	13.7 V	$7.4 \times 10^{10} \Omega$	$1.2 \times 10^5 \Omega$
f	10	30	5 μm	12.0 V	$3.2 \times 10^{11} \Omega$	$2.8 \times 10^5 \Omega$
g	5	35	3 μm	10.4 V	$5.7 \times 10^{11} \Omega$	$4.3 \times 10^5 \Omega$

Typical switching data for CdO — ZnO — P_2O_5 glasses.

Typical switching data for these glasses, as listed in Table 1, indicate the measured values of resistance in the *off* and *on* states. Before switching, the electron diffraction pattern was characteristic of a glass for all compositions and indeed after switching off a similar pattern was observed, as shown in Fig. 3, for a 35 mol % CdO — 5 mol % ZnO — 60 mol % P_2O_5 glass sample. For similar samples the electron diffraction patterns are typical of the kind shown in Fig. 4 when memory

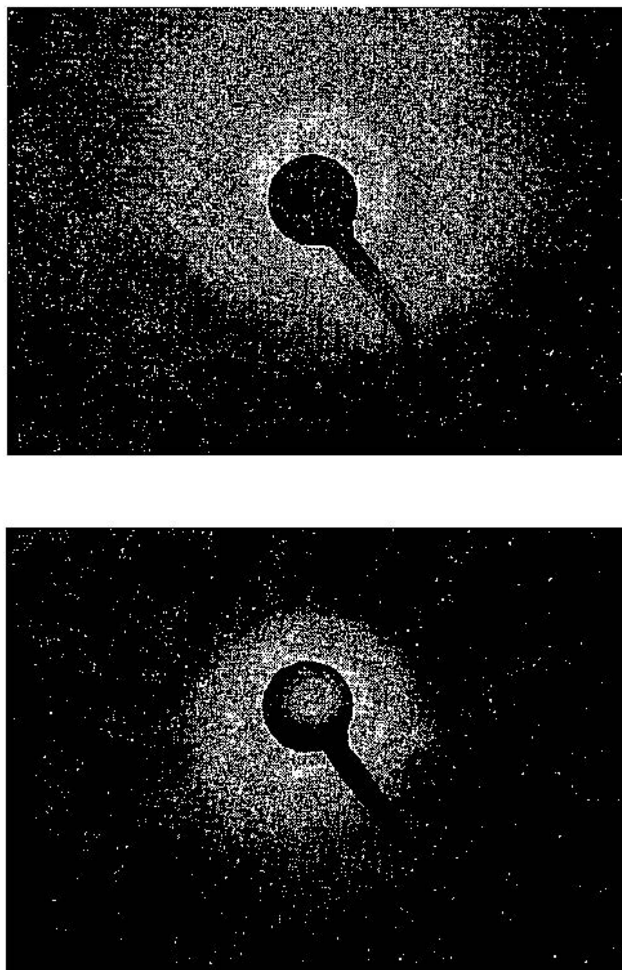

Fig. 3. Electron diffraction pattern of thin glass layer of 35 mol % CdO — 5 mol % ZnO — 60 mol % P_2O_5 glass. a) Before switching region; b) Off-state region.

switching has occured and the devices are in the *on* state. The filament formed in the *on* state is of crystalline material[10]. It is reasonable to expect that transformation from the glassy state to crystalline state took place during the first operation of switching device.

All of the above results are compatible with a theory for the behaviour which is based on the crystallization or partial crystallization of the glass along a filamentary path between the electrodes. Such filamentary paths may aggregate to form a relatively high conductance path and thereby to account for the memory switching[8,11–13]. The energy dissipated between the electrodes will be responsible for the crystallization and subsequently improved conductivity and, to some extent, temperature and applied fields may be regarded as complementary.

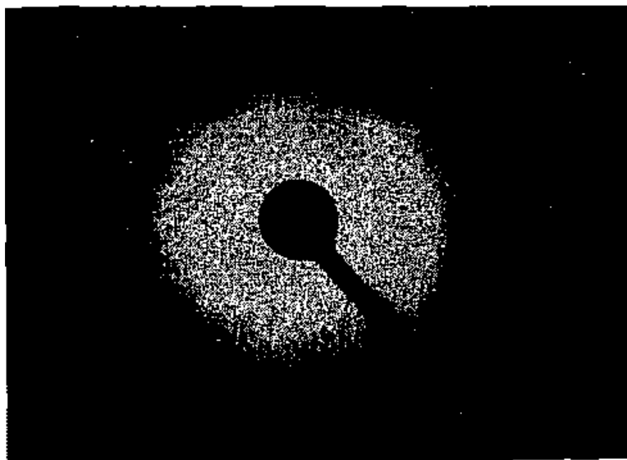

Fig. 4. Electron diffraction pattern of thin glass layer of 35 mol % CdO — 5 mol % ZnO — 60 mol % P_2O_5 after switching on.

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MEMORIJSKI EFEKT PREKAPČANJA U KADMIJ-CINK FOSFATNIM STAKLIMA

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Originalni znanstveni rad

Rad pokazuje da se u nizu uzoraka fosfatnog stakla javlja memorijski efekt prekapčanja kod napona između 10 i 20 V. Ispitivanjem elektronske difrakcije na staklenim filmovima prije prekapčanja, poslije njega te nakon što je film strujnim impulsom vraćen u početno stanje utvrđeno je da je za efekt odgovoran prijelaz materijala iz amorfnog u kristalinično stanje.