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The electrical properties of cadmium phosphate glasses at high electric fields

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The cadmium phosphate glasses previously described by the authors are further examined in relation to their electrical conduction properties at high applied fields and also when the fields are sufficiently high for memory switching to occur. The conduction at high electric fields ($> 2 \times 10^4$ V cm^{-1}) is believed to be due to thermally activated hopping of electrons and to field-lowering at the electrodes as predicted by Schottky. The relative significance of the Schottky and Poole–Frenkel processes is discussed. The memory switching observed in thin samples at high applied fields is shown by electron diffraction studies to be associated with field-induced crystallization of a localized region of the glass film.

1. Introduction

A recent paper described the optical and electrical properties of cadmium phosphate glasses [1] and here the properties of such glasses beyond the ohmic region are reported for fields greater than 4.5×10^4 V cm^{-1} at room temperature and for very thin samples memory switching phenomena are observed.

In general, high-field phenomena in glassy materials are ascribed to either Schottky (electrode-limited) or Poole–Frenkel (bulk-limited) effects [2] and Jonscher has suggested [3] that these effects will arise typically at fields of order 10^4 V cm^{-1}. Barton studied a range of glasses containing iron [4] and was able to fit his experimental data to the Poole–Frenkel expression

$$I \propto \exp(\beta_{PF} E^{\frac{1}{2}}/kT),$$

where I is current, E is electric field, k is the Boltzmann constant, T is absolute temperature and β_{PF} is given by the expression

$$\beta_{PF} = (e^3/\pi\epsilon_R\epsilon_0)^{\frac{1}{2}}$$

where ϵ_R is the relative permittivity, ϵ_0 is the permittivity of free space and e is the electronic charge. Austin and Garbett [5] suggested that hopping in transition metal oxide glasses is due to an effective field which may be enhanced by barriers arising from fluctuations in the local disorder.

2. High-field voltage–current characteristics

A range of compositions of glasses was studied and typical results are presented in Fig. 1 for a glass sample of composition 50 mol% CdO, 50 mol% P_2O_5.

The departure from linearity of a log V–log I plot is observed at fields of 4.5×10^4 V cm^{-1} and greater but the linear region extends to higher field values at the higher temperatures. The analysis of the data presents some difficulties. Any analysis based on field-assisted barrier height reduction (Schottky or Poole–Frenkel models) involves initially plotting log I versus $V^{\frac{1}{2}}$ (Fig. 2) and the slope of the high-field region of the curve suitably adjusted for specimen thickness yields an experimental value of β. Traditionally, a comparison is then made between the theoretical value of β_{PF} defined earlier or β_S (Schottky) which is equal to $\frac{1}{2}\beta_{PF}$. In order to determine a value for the high-frequency permittivity for substitution in the equations for β_{PF} or β_S, we constructed prisms from our glasses and made measurements of refractive index, typically of order 1.6, and in no case did the square of the refractive index exceed a value of 3. A similar

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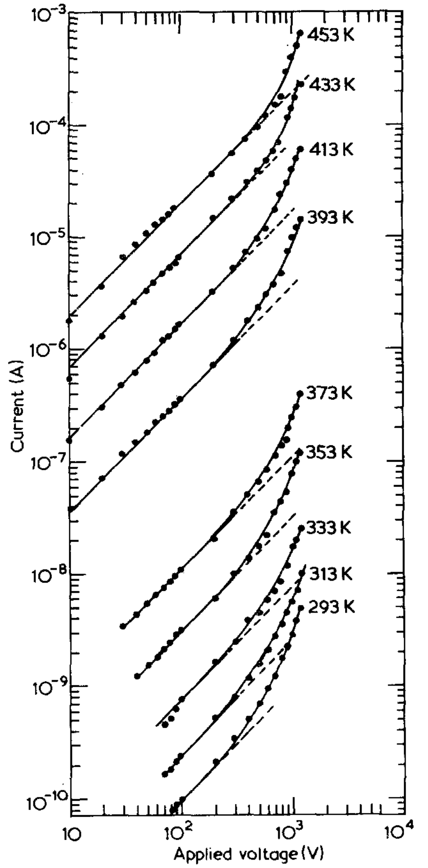

Figure 1 Voltage–current characteristics for a 50 mol% CdO–50 mol% P_2O_5 glass specimen at various temperatures.

observation was made by Barton [4] for a number of glasses containing iron and transition metals. Thus we took a lower limit of relative permittivity of 2.5 which gives an upper limit to the appropriate theoretical values of β_{PF} or β_S. These values are then $\beta_{PF} \simeq 7.4 \times 10^{-4}$ eV cm$^{\frac{1}{2}}$ V$^{-\frac{1}{2}}$ and $\beta_S = 3.7 \times 10^{-4}$ eV cm$^{\frac{1}{2}}$ V$^{-\frac{1}{2}}$. Our experimental values measured on many samples at room temperature lay in the range 2.5 to 5.4×10^{-4} eV cm$^{\frac{1}{2}}$ V$^{-\frac{1}{2}}$. The mean value of these results lies close to the theoretical value of β_S and it thus appears that the Schottky model is more appropriate to our glasses than the Poole–Frenkel, although it is accepted that local barriers arising from the disorder examined on a microscopic scale may contribute to the high-field phenomena [5].

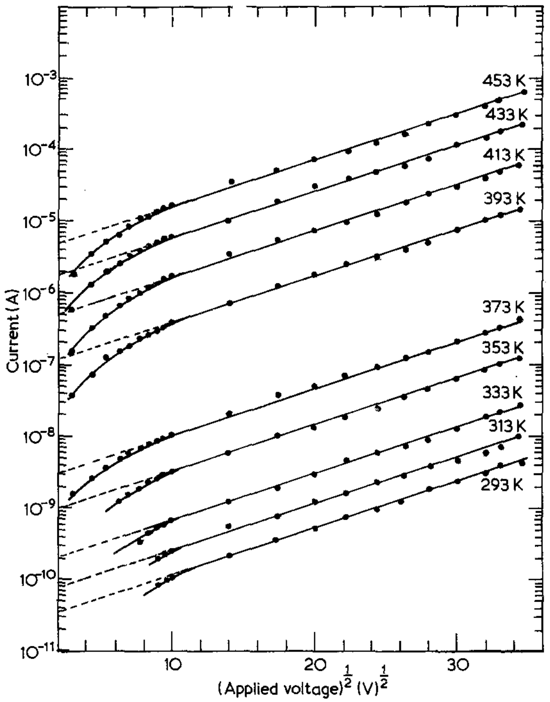

Figure 2 Voltage–current characteristics from Fig. 1 replotted to test origin of high-field characteristic.

From the experimental value of β and assuming the dominant conduction mechanism to be the Schottky model, we may estimate the permittivity of the glass samples and these are listed in Table I. The temperature variation of permittivity derived in this manner is also shown in Table II. The values of permittivity listed in Table I are similar in magnitude to those obtained for a number of

TABLE I Characteristic non-ohmic data for $CdO–P_2O_5$ glasses

Specimen	Composition (mol%)		Thickness (μm)	Relative density	Cd–Cd spacing R (Å)	Estimated relative dielectric constant ϵ_R
	CdO	P_2O_5				
a	50	50	40	3.72_5	4.93	2.37
b	45	55	20	3.53_3	5.23	3.08
c	40	60	104	3.39_0	5.51	3.60
d	35	65	18	3.32_4	5.81	4.40
e	30	70	12	3.28_1	6.14	5.60
f	25	75	20	3.21_1	6.39	6.4
g	20	80	20	3.10_6	7.19	–

TABLE II Estimated relative dielectric constant for a 50–50 $CdO-P_2O_5$ glass at different temperatures

Temperature (K)	293	313	333	353	373	393	413	433	453
Dielectric constant	2.37	2.14	1.94	1.74	1.55	1.40	1.27	1.15	1.06

glasses by other workers and are rather lower than the high values (assuming experimental β_{PF}) obtained by Barton [4] on a range of glasses containing iron, and by Lacharme and Isard [6] for a range of silicate glasses containing Group I, Group II elements, and also aluminium. This provides further evidence for the correctness of an assumption concerning the appropriateness of choosing β_S or β_{PF} for comparison with the experimental value of β.

The usual concentration formula [7], $R = (1/N)^{\frac{1}{3}}$ was used to estimate the average cadmium ion spacing R, N being the ion concentration, and these are also shown in Table I. However, when analysing the results in more detail, the image force contribution has to be included in the expression for the distance of the potential maximum from the centres of the region of local disorder.

If $V(r)$ is the potential at a distance r from such a centre, r_0 is the distance from the centre to the point of rapid rise of potential, then

$$V(r) = -\frac{e^2}{4\pi\epsilon_R\epsilon_0 r_0} - eEr_0$$

is the normal expression for $V(r)$ but in order to correct for the image force the final expression will be $\frac{1}{4}$ of the above. E is the electric field.

Incorporating this requirement and evaluating the curve for minimum potential, i.e. putting $V(r) = 0$, we have

$$\frac{1}{4}\frac{e^2}{4\pi\epsilon_R\epsilon_0 r_0} = eEr_0.$$

Thus

$$r_0^2 = \tfrac{1}{4}\beta_S^2/Ee^2$$

$$r_0 = \tfrac{1}{2}\beta_S/E^{\frac{1}{2}}e.$$

TABLE III Distance of potential maximum from regions of local disorder

	Glass					
	a	b	c	d	e	f
Distance (Å) (Shottky)	58	48	46	39	28	19
Separation of potential barriers (Å) [5]	47	57	61	61	67	75

Using this theory the distances of the potential maximum r_m were calculated for the various glass samples and are listed in Table III and are of the order of a few ionic spacings as would be expected. A calculation was also made using the theory of Austin and Garbett [5] and estimates of the distances between potential barriers arising from local disorder are also shown in Table III from the formula

$$R = kT/eE.$$

Agreement is fairly close between the two series of values for the glasses approximating to a 50 mol%–50 mol% composition but they diverge considerably as the CdO/P_2O_5 ratio decreases.

It may thus be concluded that the Schottky analysis of the high-field phenomena provides the best approximation to an explanation of the experimental results but there are still further refinements necessary. Some success is achieved by combining the idea of Austin and Garbett that local disorder regions within the glass samples play some role in the overall observed effects. By making some assumptions about localized image force barrier lowering, the derived values of distances between such regions are of the predicted order of magnitude, i.e. several ionic spacings.

3. Memory switching

3.1. Introduction

In many chalcogenide and oxide glasses the application of a threshold voltage across a metal–glass–metal assembly when the glass layer is very thin leads to a change in the resistance of the sample from a very high value and the low-resistance state remains even though the electric field is removed. The high-resistance state may be recovered by the application of a re-setting pulse of current higher than that previously flowing through the device. Drake *et al.* [8] gave the first details of switching using a $CuO-CaO-P_2O_5$ glass and more details of the switching properties of such a glass were given by Moridi and Hogarth [9] who showed the crystallization of the switched region of the glass and its restoration to a non-crystalline condition when re-set to the high-

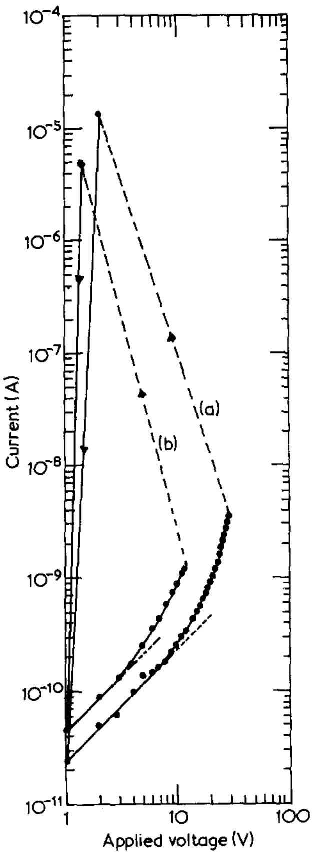

Figure 3 Voltage–current characteristics of two CdO–P_2O_5 glass samples showing memory switching. (a) 6 μm thick, (b) 4 μm thick.

resistance state. Saji and Kao [10] have recently suggested that the filament formed by the application of a threshold voltage and leading to a threshold switching characteristic may consist of a mixture of amorphous and crystalline domains but the filament responsible for memory switching may consist of crystalline domains only as demonstrated by Moridi and Hogarth [9]. There is no doubt that in memory switches the formation of a conducting filament is involved. Cohen *et al.* [11] suggest that the memory action occurs by switching initially to a filamentary threshold on-state and the current maintained then enables slow crystallization to take place and a memory state to form. Holzinger and Holzinger [12] reported memory switching in Cu_2O–P_2O_5–CdO glasses but no observations of such phenomena in simple CdO–P_2O_5 glasses have been made.

3.2. Experimental work

Thin samples of a range of CdO–P_2O_5 glasses were prepared by blowing, using an alumina tube, and specimens in the thickness range 2 to 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 testing. A simple measuring circuit was used, similar to that described by Moridi and Hogarth [9]. For some experiments, small-area pressure contacts were used. The high resistors (1 MΩ each) served as current limiters after the devices switched to the on-state.

A typical voltage–current characteristic is shown in Fig. 3 and similar curves were obtained for specimens of all the compositions used, by increasing the applied voltage in steps and recording the current. All the glasses were studied in vacuum but only those containing more than 35 mol% CdO could be studied in air. Glasses containing less than this tended to devitrify as a result of attack by atmospheric water vapour.

Structural changes in the switched regions of the glass samples were studied using a JEM 7 electron diffraction set following the technique described by Moridi and Hogarth [9] for CuO–CaO–P_2O_5 glasses. The accelerating voltage used was 80 kV. The cross-sectional area of the pressure contacts was 0.26 cm^2 and such contacts were used instead of the silver paint.

3.3. Discussion of switching results

Fig. 3 makes it clear that for low applied voltages the samples are ohmic and that the superlinear curves obtained at higher applied fields may be explained in terms of the previous discussions of high-field effects.

For new devices a high applied voltage is needed for the initial switching, typically 200 to 600 V. Lower values are needed in successive switching cycles and the threshold voltage values are not reproducible. On removal of the applied voltage following switching on, the device can be re-set by applying a d.c. pulse of 0.2 to 0.5 mA and of opposite polarity. When the device is in the on-state, the voltage–current characteristic is linear since the device resistance is very low and the current is largely determined by the series resistors. Switching is more readily observed with films which have been annealed at 200° C than with non-annealed films and the thicker films show a tendency to switch only at elevated temperatures. For a given film the threshold voltage decreases steadily as the temperature increases

TABLE IV Typical switching data for $CdO-P_2O_5$ glasses

Specimen no.	Composition mol %		Thickness (μm)	R_{off} (Ω)	R_{on} (Ω)	Mean forming voltage	Remark
Specimen no.	CdO	P_2O_5				(V)	Remark
a	50	50	6	9.7×10^9	1.4×10^5	279	At room temperature
b	45	55	10	3.0×10^9	7.0×10^4	313	At room temperature
c	40	60	8	1.0×10^{10}	2.0×10^6	379	At room temperature
d	35	65	6	9.0×10^{10}	3.1×10^4	548	At room temperature
e	30	70	9	8.0×10^8	5.3×10^4	–	At 353 K
f	25	75	10	4.2×10^6	1.1×10^4	–	At 353 K
g	20	80	20	8.0×10^7	4.1×10^3	–	At 413 K

but it is more difficult to switch off devices at higher temperatures (up to 200° C typically.) In such cases the temperature of the samples must be reduced in order to recover the off-state, even with the re-setting current pulse. The switching behaviour of the samples is not significantly dependent on the polarity of the applied voltage.

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. The energy dissipated between the electrodes will be responsible for the crystallization and subsequent improved conductivity and, to some extent, temperature and applied field are complementary.

Before switching, the electron diffraction pattern was characteristic of a glass and indeed after switching off, a similar pattern was observed as shown in Fig. 4a for a 50–50 glass sample. For similar samples the electron diffraction patterns are typically of the kind shown in Fig. 4b and c. Fig. 4b is for a thicker sample (5 μm) and shows evidence of aggregated crystallites. Fig. 4c is for a somewhat thinner (2 μm) sample and shows evidence of almost complete crystallization.

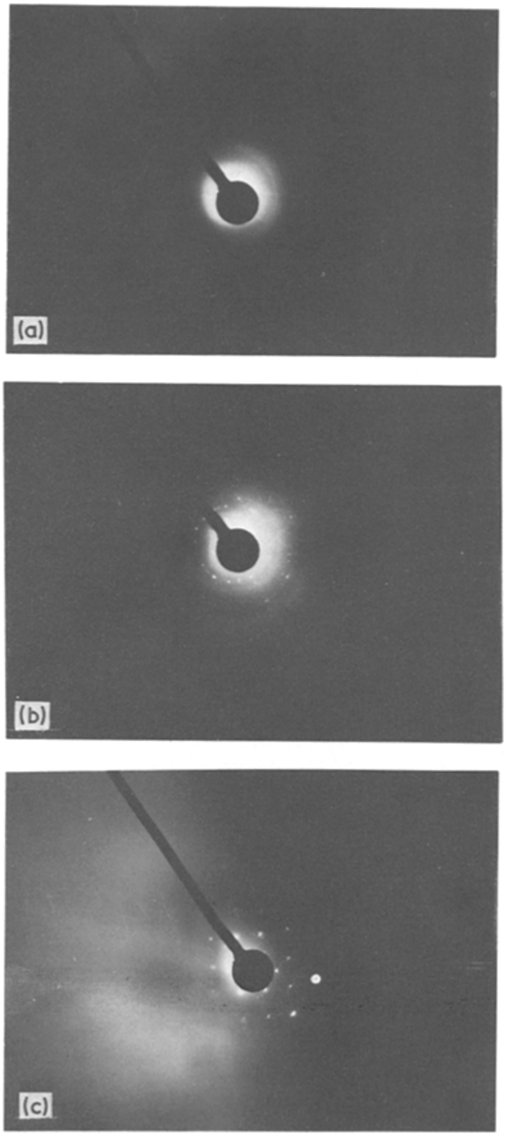

Figure 4 Electron diffraction patterns from thin layers of $CdO-P_2O_5$ glasses (a) before switching, (b) after switching on, (c) after switching on. (Thin sample almost perfectly crystallized.)

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