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The preparation of cadmium phosphate and cadmium zinc phosphate glasses and their electrical and optical properties

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The preparation of a range of glasses based on $CdO-P_2O_5$ and $CdO-ZnO-P_2O_5$ is described and data are reported on density, electrical conductivity and optical absorption. The electrical conduction is electronic rather than ionic and is due to hopping between localized states. The optical absorption is due to forbidden indirect electronic transitions.

1. Introduction

During the last fifteen years the behaviour of electrons in glassy materials has been the subject of considerable research, much of it on the chalcogenide glasses [1] but a significant amount on oxide glasses [2] which show some similarity to the chalcogenides but also differences. There are some similarities between the energy band structures of crystalline and glassy non-metallic materials but whereas the crystalline materials show well-defined energy bands (with sharp conduction and valency band edges), the glassy materials show band-tailing into the normally forbidden energy gap [3]. Although in some respects the form of the electrical conductivity versus temperature relation for the glasses is of the form characteristic of an intrinsic semiconductor, the Fermi level may not be precisely in the middle of the band gap due to differences in the tailing or smearing of the valency and conduction bands [4].

One generally accepted model of conduction in amorphous materials [5] involves a narrow band of localized states near the centre of the band gap and another assumes two concentrations of trapping centres one in the upper part of the gap and the other in the lower part of the band gap, effectively pinning the Fermi level near the middle of the gap. The mode of preparation including the annealing treatment [6], structural defects and impurities, may all determine the precise form of the density-of-states function in the energy gap or the pseudo-gap. For example Stuke [7] has shown that annealing amorphous materials tends to reduce the density of dangling bonds, often regarded as a source of conduction electrons and thus the resistivity increases.

In the present paper we report basic measurements on cadmium phosphate and zinc cadmium phosphate glasses and make some suggestions about the energy band gaps in these materials.

2. Experimental work

2.1. Glass preparation

Analytical reagent grades of CdO, ZnO and P_2O_5 were used. All glasses were prepared as 45 g samples in alumina crucibles. The crucible was placed initially in a furnace at 500° C to minimize the tendency of P_2O_5 to evaporate, and then was transferred to a crucilite furnace at a high temperature of order 1050° C for 3 h. The melt was cast into discs 3 mm thick and 3 cm diameter on a stainless steel plate and the discs were then annealed at 500° C for 3 h to relieve mechanical stresses and some tendency for the freshly-formed discs to crack.

2.2. Density measurements

The densities of annealed specimens of x(CdO) mol% + $(1-x)P_2O_5$ mol% and of x(CdO) mol% + y(ZnO) mol% + $(1-\overline{x+y})P_2O_5$ mol% were measured by a displacement method using butane-2-one as the immersion fluid. The results are shown in Table I which summarizes most of the

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TABLE I Measured properties of $CdO-P_2O_5$ and $CdO-ZnO-P_2O_5$ glasses

Specimen	CdO (mol %)	P_2O_5 (mol %)	ZnO (mol %)	Relative density	Molar volume (cm^3)	Activation energy, $\Delta\epsilon$ (eV)	Optical gap, E_{opt} (eV)	Constant B (10^2 cm^{-1} eV^{-1})	ΔE (10^{-2} eV)	σ_0 (10^2 Ω^{-1} cm^{-1})	Colour
n	10	90	–	3.02_3	46.51	–	–	–	–	–	Opaque, colourless
m	15	85	–	3.11_7	45.10	–	–	–	–	–	Opaque, colourless
g	20	80	–	3.10_6	44.83	1.26	5.98	3.36	4.50	1.8	Transparent, whitish
f	25	75	–	3.21_1	43.10	1.22	5.88	3.67	4.50	2.1	Transparent, whitish
e	30	70	–	3.28_1	42.03	1.21	5.84	4.00	4.30	4.1	Transparent, whitish
d	35	65	–	3.32_4	41.28	1.19	5.64	4.00	4.30	5.0	Transparent, whitish
c	40	60	–	3.39_0	40.28	1.17	5.50	4.12	4.40	6.0	Transparent, whitish
b	45	55	–	3.53_3	38.45	1.10	5.28	4.27	4.40	1.2×10^1	
a	50	50	–	3.72_5	36.28	0.99	4.84	4.34	4.32	9.0×10^1	Slight pink colour
h	5	70	25	2.93_1	43.04	1.29	5.54	1.41	7.21	2.2	Slight pink colour
i	10	70	20	2.98_7	43.01	1.25_5	5.50	1.32	7.21	2.4	Slight pink colour
j	15	70	15	3.05_1	42.88	1.23_5	5.46	1.32	6.87	3.0	Slight pink colour
k	20	70	10	3.11_0	42.82	1.21	4.90	1.30	4.32	3.5	Slight pink colour
l	25	70	5	3.17_8	42.64	1.19	4.74	1.26	3.15	4.0	Slight pink colour

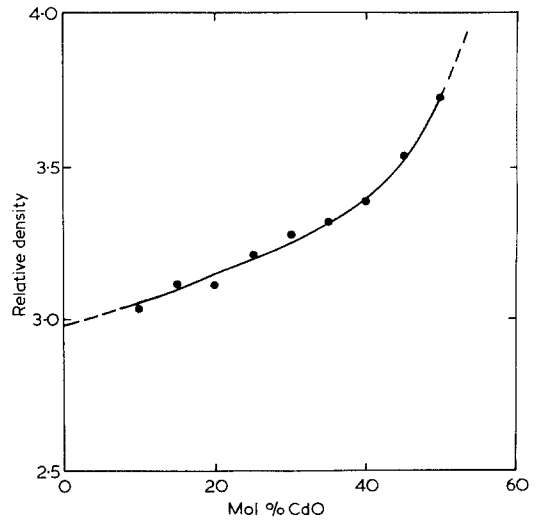

Figure 1 Density of some $CdO-P_2O_5$ glasses as a function of composition.

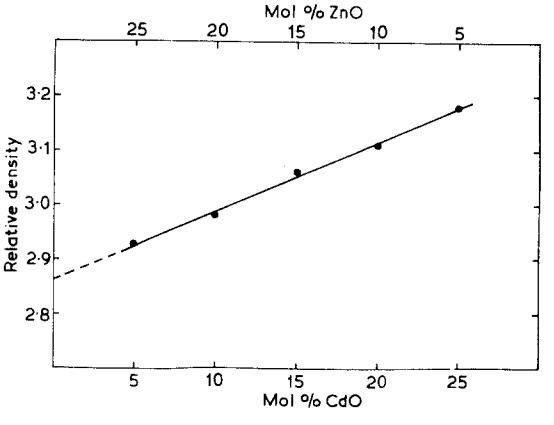

Figure 2 Density of some $CdO-ZnO-P_2O_5$ glasses as a function of composition. (P_2O_5 content constant at 70 mol %.)

measurements reported in this paper. Fig. 1 shows the glass density as a function of composition for $CdO-P_2O_5$ glasses and Fig. 2 similar data for $CdO-ZnO-P_2O_5$ glasses.

2.3. X-ray diffraction

The X-ray diffraction patterns determined with the Debye–Scherrer camera using Ni-filtered Cu$K\alpha$ radiation showed no discrete lines but only diffuse haloes, characteristic of glassy structures.

2.4. Electrical measurements

The specimens were ground and polished to discs about 2 mm thick and gold electrodes were deposited by vacuum evaporation. A guard-ring was evaporated on one side of each of the specimens. A stabilized d.c. voltage source and a Keithley 610C Electrometer were used for the measurements of voltage and current and all measurements were made with the specimens in a vacuum of $\sim 10^{-5}$ Torr and over a temperature range 20 to 360° C. For some glasses, a constant d.c. potential of 500 V was applied for a period of 8 h and the current flowing was monitored continuously.

2.5. Optical measurements

The absorption edges of all the glasses listed in Table I were measured for well-polished bulk glass specimens, 2 mm thick, annealed at 500° C for 3 h, and on thin films. A Perkin–Elmer spectrophotometer was used for measurements, all of which were carried out at room temperature.

3. Experimental results

3.1. Electrical measurements

Copper and silver electrodes were used in addition to gold, and led to the same values of electrical conductivity as measured with the gold electrodes. The measured conductivity was not dependent on the sample thickness. The variation of current with time for a fixed applied voltage is shown in Figs. 3 and 4 for a variety of glass compositions and there is a difference of behaviour between glasses of the two systems. For $CdO-P_2O_5$ glasses, apart from a short term initial variation in current with time, the current is essentially constant over an extended period and points to the absence of polarization phenomena and to conduction by electrons rather than by ions. For $ZnO-CdO-P_2O_5$ glasses there is some evidence

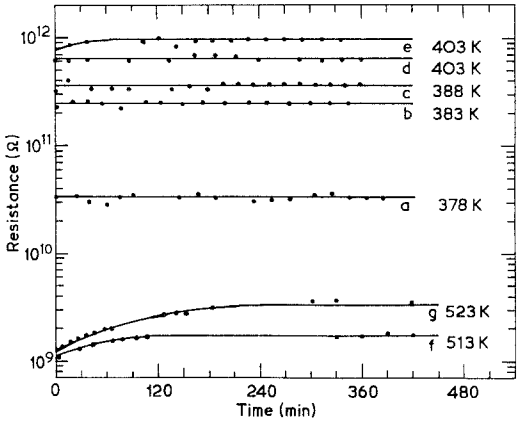

Figure 3 The resistance of some $CdO-P_2O_5$ glass samples as a function of time and application of a fixed voltage.

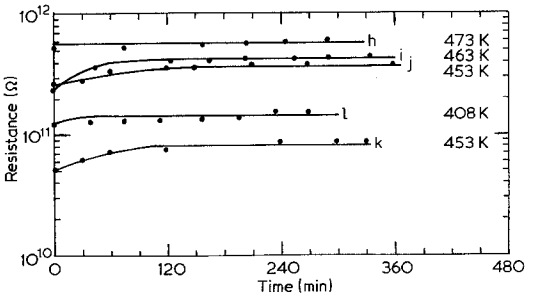

Figure 4 The resistance of some $CdO-P_2O_5$ glass samples as a function of time and application of a fixed voltage.

of ionic conduction and for both systems some ionic conduction is inferred from the measurements made at ~473 K.

The variation of electrical conductivity, σ, with temperature, T, is shown in Fig. 5 for $CdO-P_2O_5$ glasses and Fig. 6 for $ZnO-CdO-P_2O_5$ glasses. The graphs of $\log \sigma$ versus $1/T$ are linear over some five decades of current and the extrapolated values of σ_0 for $1/T = 0$ lie in the range 10^2 to $10^4\ \Omega^{-1}\ cm^{-1}$ as expected for amorphous materials [8].

3.2. Optical measurements

The absorption coefficients, α, were determined near the edge for the whole range of glass compositions and the results may be displayed in a number of ways as functions of photon energy $\hbar\omega$. The most satisfactory results were obtained by plotting the quantity $(\alpha\hbar\omega)^{1/2}$ as functions of $\hbar\omega$ as suggested by Davis and Mott [5] for forbidden indirect transistions. A selection of typical results is shown in Figs. 7 and 8.

4. Discussion

The summarized results in Table I are typical of a wide range of samples examined. The density values of $CdO-P_2O_5$ glasses agree generally with the published data of Elyard *et al.* [9] and of Kordes and Bonn [10] but there are no data in the literature on the densities and molar volumes of $x(CdO) + y(ZnO) + [1-(x+y)](P_2O_5)$ where x and y are fractions. However, an extrapolation of the results shown in Fig. 1 leads to a value of 2.98 for the relative density of P_2O_5 glass and an extrapolation of the curve in Fig. 2 leads to a value of relative density of 2.84 for a glass containing 30 mol % ZnO and 70 mol % P_2O_5, in good agreement with the results of Anvary [11] when no CdO is present in the glass. The linear variation in density with increased concentration of the

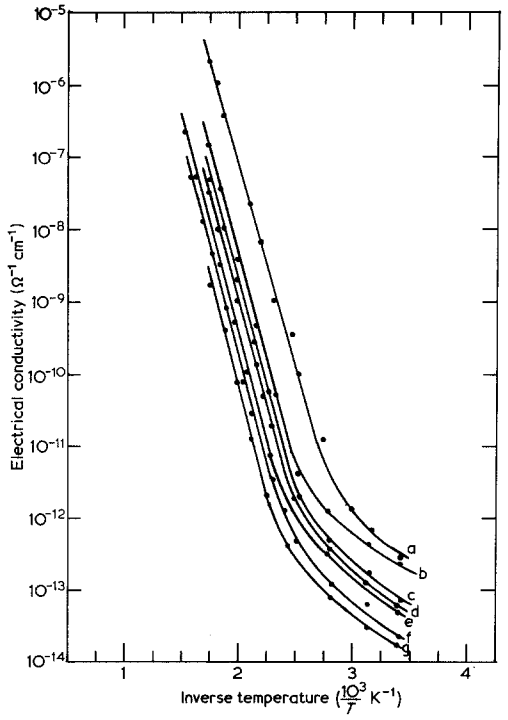

Figure 5 Conductivity as a function of inverse temperature for some $CdO-P_2O_5$ glasses.

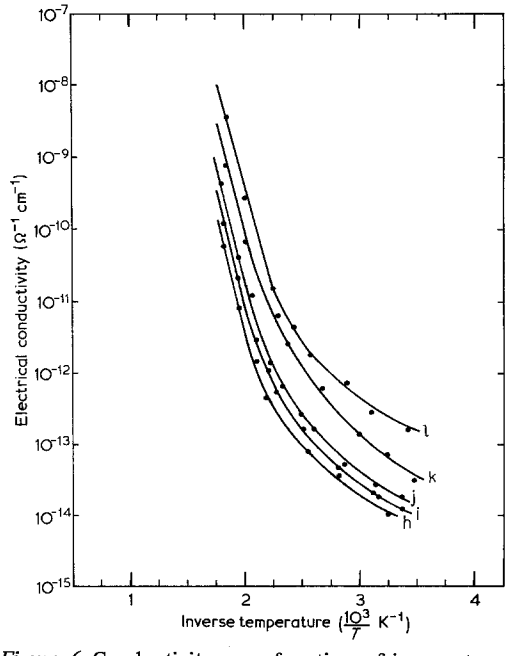

Figure 6 Conductivity as a function of inverse temperature for some $CdO-ZnO-P_2O_5$ glasses.

modifying oxide signifies an increased rigidity in the glass structure, i.e. the P–O–P bond is breaking with the addition of modifying oxide, giving singly bonded oxygen and providing an excellent example of the Zachariasen network theory [2].

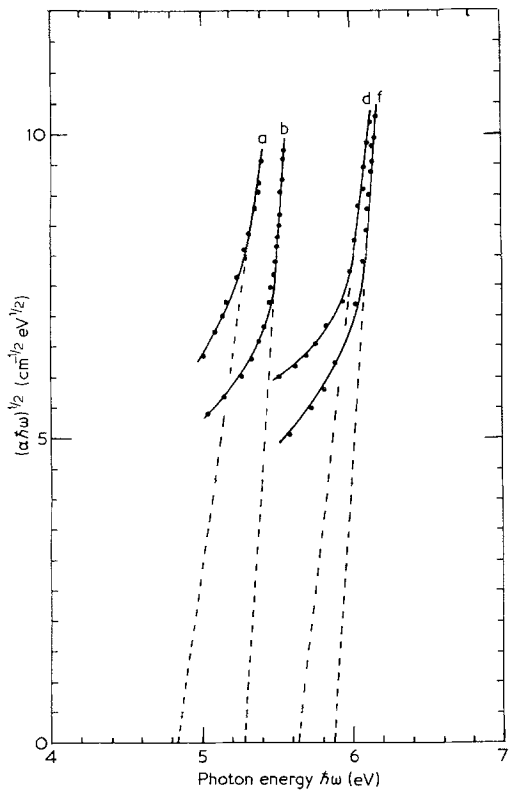

Figure 7 Optical absorption edges of $CdO-P_2O_5$ glass samples.

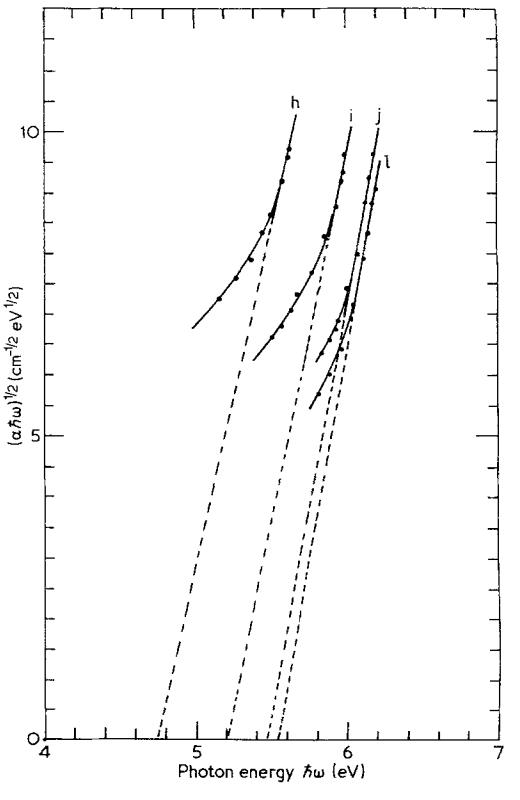

Figure 8 Optical absorption edges of $CdO-ZnO-P_2O_5$ glass samples.

In considering the results of optical and electrical measurements, some account must be taken of the supposed energy band diagrams including density-of-states curves for the glasses. The largest energy measured is normally the optical energy gap, E_{opt}, and this may be identified with the pseudo-gap as postulated by Mott [3] and by Cohen *et al.* [13]. The values obtained by extrapolation of the $(\alpha\hbar\omega)^{1/2}$ versus $\hbar\omega$ curves to $(\alpha\hbar\omega)^{1/2} = 0$ are listed in Table I and shown to be dependent in a systematic manner on glass compositions. The addition of ZnO to the glasses leads to an effective reduction in E_{opt}. The connection between the optical and electrical properties is made when the general expression for optical absorption coefficient in terms of the matrix elements for optical transistions, refractive index, n_0, angular frequency of the radiation, ω, and the density-of-states function, is simplified, assuming that the matrix element $D(E)$ has the same value whether or not the initial and final states are localized, that the densities of states at the band edges are linear functions of the energy and that transitions for which both initial and final states are localized are improbable [5].

Then

$$\alpha(\omega) = B(\hbar\omega - E_{opt})^2/\hbar\omega$$

and

$$B = \frac{4\pi}{c}\,\frac{\sigma_0}{n_0 \Delta E};$$

σ_0 is the extrapolated value of electrical conductivity obtained by taking the value of σ at $1/T = 0$ and ΔE the width of the tail of localized states in the band gap. As stated previously, the values of σ_0 for our samples lie in the range 10^2 to $10^4\ \Omega^{-1}\ cm^{-1}$ and together with the values of B are given in Table I.

From the graphs of $\log\sigma$ versus $1/T$ the activation energy values were calculated and are also listed in Table I. If the conduction process were generally an activation across a mobility gap, then a value of this gap energy would be obtained by doubling the appropriate activation energy value. However, this process leads to a value of less than half the value of E_{opt} for similar samples and materials. It is, therefore, possible to discount excitation across the mobility gap and the value of activation energy $\Delta\epsilon$ is more probably an indication of excitation of electrons from a band of

traps into the conduction band or from the valence band into a trapping level. The deviation from linearity in the $\log \sigma$ versus $1/T$ curves at low temperatures is probably associated with localized defects such as dangling bonds in the material. The values of σ_0 are consistent with the picture of carriers in localized states near the band edges and taking part in a hopping process. These localized states may well arise from an excess of Cd^{2+} ions leading to a narrow band [14] (4*d*-like) when mixed with P_2O_5 or from the formation of dangling bonds as suggested for As_2Se_3 [15]. The increase in conductivity and decrease in activation energy observed when an admixture of ZnO as little as 5 mol% is added to the glass may also give evidence of the presence of dangling bonds [16].

Although the curves of $(\alpha\hbar\omega)^{1/2}$ versus $\hbar\omega$ in Figs. 7 and 8 lead to acceptable values of E_{opt} by extrapolation, the curves at lower values display deviations from linearity. The tails to the curves are more nearly exponential in energy. Redfield and Afromowitz [17] suggest that this region of the absorption edge is related to imperfections in the material while Vasilyev *et al.* [18] suggest that the spectral dependence can be related to a distribution of the density of meta-stable states within the gap. Clearly this region of the absorption edge is not fully understood and further work is needed.

The values of the band tailing ΔE are also listed in Table I. The value is virtually constant for the range of $CdO-P_2O_5$ compositions but the addition of ZnO to the glasses makes a significant difference.

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