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A study of the electrical properties of molybdenum phosphate glasses

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A series of binary $MoO_3-P_2O_5$ and also ternary $MoO_3-P_2O_5-In_2O_3$ glasses were prepared and their electrical properties were investigated. The d.c. conductivity measurements show that the conduction in molybdenum phosphate glasses is by a hopping process in which the electrical charge transfers from Mo^{5+} to Mo^{6+} ion sites. The conductivity can be discussed in terms of the small polaron conduction mechanism. In contrast to vanadium phosphate glasses, the tunnelling term in the conductivity formula seems to make a significant contribution in molybdenum phosphate glasses and is associated with a hopping process in the non-adiabatic regime.

1. Introduction

Many transition-metal oxides form glasses when melted with P_2O_5 in proportions in which the transition metal ions are a major constituent. Electrical properties of such glasses containing transition metal ions were not studied until 1954 when Denton *et al.* [1] reported that $V_2O_5-P_2O_5$ glasses were n-type semiconductors. Since the discovery of such an effect in transition-metal oxide glasses, many studies have been reported on the system $V_2O_5-P_2O_5$ and a review of the compositions investigated up to 1964 has been given by Mackenzie [2], while reviews on the conduction processes are those of Mott [3], Austin and Mott [4], Owen [5] and Murawski *et al.* [6].

However the origin of semiconduction is recognized as an electron transfer of an unpaired d-electron of a transition metal ion in a low oxidation state $M(x+)$ to one in a higher oxidation state $M(y+)$ with the relative proportion of the reduced and oxidized states forming an important parameter in the explanation of the electrical properties of these glasses [7–10]. The vanadate system has been studied most thoroughly and information is also available on glasses containing FeO or Fe_2O_3, WO_3, MoO_3, CuO, TiO_2, and MnO [11]. In transition-metal oxide glasses electrical conduction does occur by the transport of electrons rather than ions and these glasses may be regarded as electronic semiconductors. Semiconductors were described by Seitz as materials having a temperature dependence of conductivity σ which is described by the relation $\sigma = \sigma_0 \exp - E_a/kT$ where σ_0 and E_a are practically constant for a given specimen.

2. Experimental methods

For d.c. conductivity measurements disc-shaped samples, 2 centimetres in diameter, were made and ground to a thickness of about 1 mm. After grinding, the samples were polished and then the evaporation of gold electrodes was carried out in vacuum. Because of the high resistance of molybdenum phosphate glasses it is preferred to use a guard-ring electrode configuration in order to eliminate the surface leakage and to measure the true bulk resistance of glasses. The samples were then heated at 200° C for two hours in order to harden the gold electrodes. Other kinds of electrodes such as silver and copper were used in order

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TABLE I Composition and density of glasses examined

Glass Number	P_2O_5 content (mol %)	MoO_3 content (mol %)	CaO content (mol %)	In_2O_3 content (mol %)	Relative density
8020	80	20	0	0	2.80
7030	70	30	0	0	2.82
6040	60	40	0	0	2.94
5050	50	50	0	0	3.00
4060	40	60	0	0	3.17
3565	35	65	0	0	3.27
3070	30	70	0	0	3.37
2575	25	75	0	0	3.50
2080	20	80	0	0	3.60
1585	15	85	0	0	3.72
402040	40	20	40	0	3.00
403030	40	30	30	0	3.11
404020	40	40	20	0	3.15
404515	40	45	15	0	3.15
405010	40	50	10	0	3.16
405505	40	55	0	5	3.39
405010	40	50	0	10	3.48

to study any effect of different electrodes. In order to confirm that the contacts were ohmic, this was checked by the observation of linear V–I characteristics up to nearly 1200 V, independent of the polarity of the applied bias. Table I shows the compositions of the glasses studied and their relative densities.

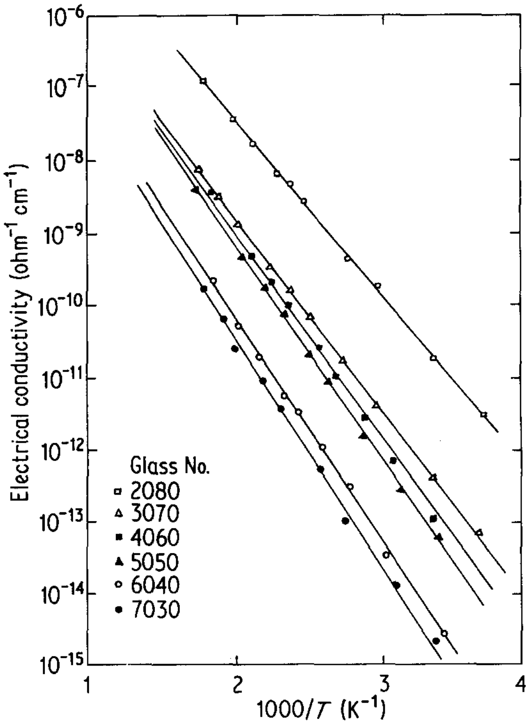

Figure 1 Conductivity of MoO_3–P_2O_5 glasses as a function of inverse temperature.

3. Experimental results

Figs. 1 and 2 show the variation of log σ as a function of reciprocal temperature over the range of measurement for molybdenum phosphate glasses. As can be seen a plot of log σ against $1/T$ gives a good straight line over a considerable range of temperature. Because of the difficulties in measuring currents less than 10^{-14} A with the equipment available, it was not possible to measure the

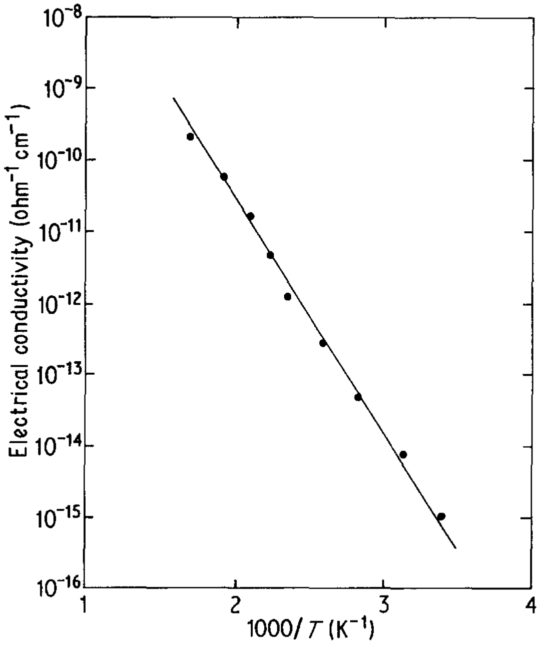

Figure 2 Conductivity of MoO_3–P_2O_5 glass (8020) as a function of inverse temperature.

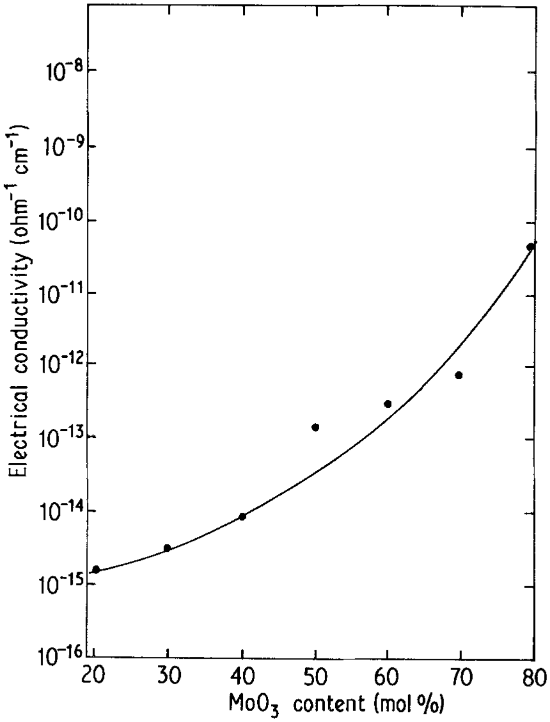

Figure 3 Conductivity of $MoO_3-P_2O_5$ glasses at room temperature as a function of MoO_3 content.

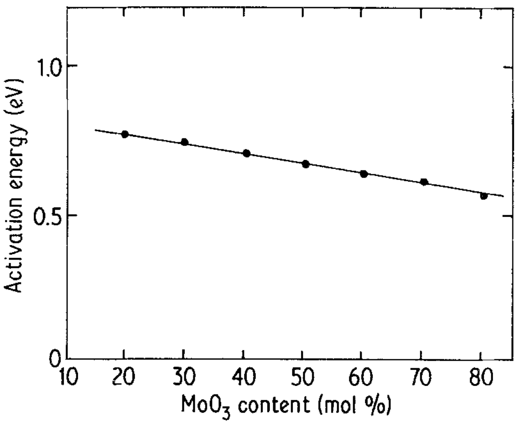

Figure 5 Activation energy of $MoO_3-P_2O_5$ glasses as a function of MoO_3 content.

conductivity of glasses at temperatures lower than room temperature except for glasses Nos. 3070 and 2080 which were measured down to 0° C. It may be noted from Fig. 3 that at a fixed temperature the d.c. conductivity increases non-uniformly with increasing MoO_3 content and this confirms that the conductivity is dependent on the MoO_3 content of the glass. Similar results have been obtained for vanadate glasses [12]. Fig. 4 illustrates the time dependence of the resistance of molybdenum phosphate glasses, and it can be seen that the resistivity is constant, so conduction is electronic rather than ionic. Molybdenum phosphate glasses have rather high values of activation energy and the conductivity shows a large variation with temperature and any error in temperature measurements can produce a large discrepancy in the appropriate conductivity. Fig. 5 shows the variation of activation energy with MoO_3 content and indicates that with increase of MoO_3 in the glasses the activation energy decreases linearly. Fig. 6 presents the variation of activation energy as a function of R, the average Mo–Mo ion spacing and shows that with the increase of ion-spacing the activation energy increases.

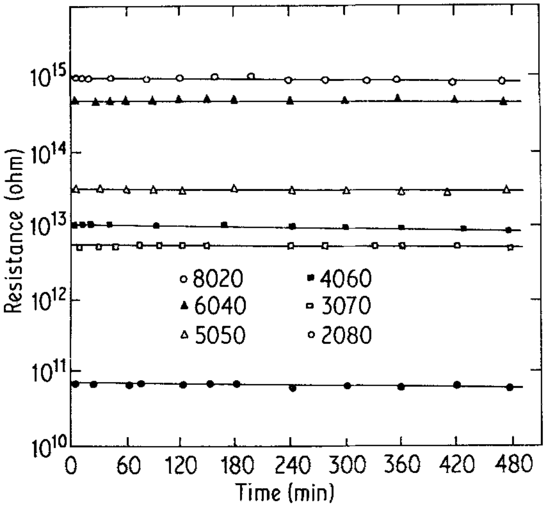

Figure 4 Time dependence of the resistance of $MoO_3-P_2O_5$ glasses.

In order to study the effect of different electrode materials, copper and silver were used and results were the same as obtained using gold electrodes. This can be taken as a proof that the measured values represented the bulk conductivtiy of glasses and are substantially independent of any surface phenomena.

In order to study the effect of In_2O_3 on molybdenum phosphate glasses two different compositions in the ternary system of $MoO_3-P_2O_5-In_2O_3$ were studied. Table II and Fig. 7 show the variation of d.c. conductivity against $1/T$ for a glass containing 10% In_2O_3. The conductivity decreases slightly with substitution of In_2O_3 for MoO_3. The time independence of the resistance for $MoO_3-P_2O_5-In_2O_3$ glasses confirms that conduction in this system is electronic.

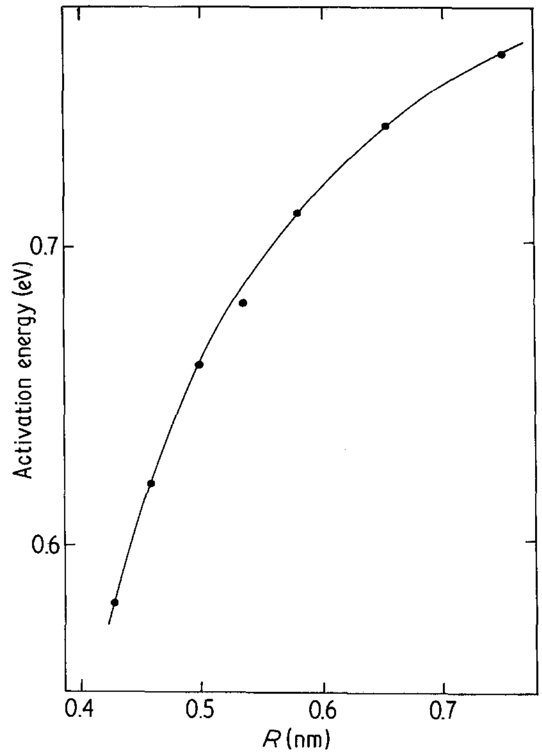

Figure 6 Activation energy as a function of mean site ion spacing for the MoO_3–P_2O_5 glasses.

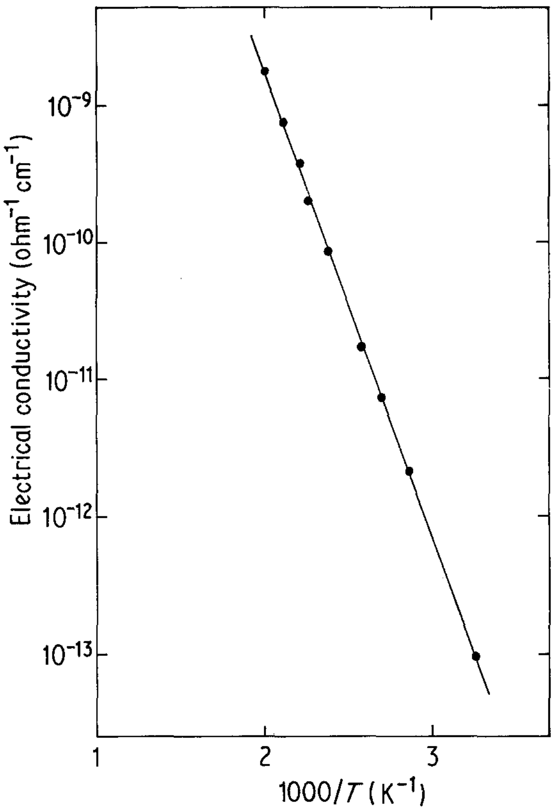

Figure 7 Conductivity of MoO_3–P_2O_5–In_2O_3 glass (4050, 10 mol% In) as a function of inverse temperature.

4. Discussion

We believe that the mechanism of conduction in molybdenum phosphate glasses is similar to that of vanadium phosphate glasses [11]. ESR studies showed the existence of only one significant reduced state (Mo^{5+}) [7]. Lynch *et al.* [9] have reported that the conductivity increases with increasing Mo^{5+}/Mo^{6+} ratio, therefore, in view of these results the conduction in molybdenum phosphate glasses may be assumed to be due to hopping of electrons from the low valence state (Mo^{5+}) to the higher state (Mo^{6+}) which is in accordance with proposed mechanism of conduction in other transition-metal oxide glasses.

The interaction between the electrons and lattice is sufficiently strong to produce a small polaron. The value of the polaron radius can be

TABLE II Parameters of the glasses examined

Glass number	Concentration of sites, N (cm^{-3} × 10^{-21})	Site spacing R (nm)	Fraction of reduced sites, C	Activation energy, E_a (eV)	Relative dielectric constant, ϵ'	Annealing temperature (° C)
8020	2.37	0.750	–	0.76	16.5	350
7030	3.57	0.654	–	0.74	16.1	350
6040	4.96	0.586	–	0.71	20.5	350
5050	632	0.540	–	0.67	20.0	350
4060	8.01	0.499	0.87	0.65	21.6	350
3070	9.90	0.465	0.24	0.62	21.2	350
2080	12.06	0.436	0.13	0.57	29.3	350
405505	7.50	0.510	–	0.77	26.0	350
405010	6.70	0.530	–	0.75	30.1	350
4060	7.83	0.503	–	0.80	14.9	250
4060	8.36	0.492	–	0.64	27.4	500

TABLE III Derived parameters of the glasses

Glass number	r_P experimental (nm)	r_P theory (nm)	ν_{ph} (Hz)	α (nm^{-1})	Annealing temperature (° C)	σ_0 (ohm^{-1} cm^{-1})
8020	0.112	0.302	–	–	350	8×10^{-5}
7030	0.115	0.263	–	–	350	1×10^{-4}
6040	0.133	0.236	–	–	350	1.5×10^{-4}
5050	0.134	0.217	–	–	350	1×10^{-3}
4060	0.140	0.201	0.06×10^{10}	8.1	350	6×10^{-4}
3070	0.139	0.187	0.05×10^{9}	9.7	350	4×10^{-3}
2080	0.151	0.175	0.03×10^{9}	11.8	350	3×10^{-2}
405505	0.132	0.205	–	–	350	–
405010	0.129	0.213	–	–	350	–
4060	0.130	0.202	–	–	250	–
4060	0.150	0.198	–	–	500	–

obtained by using the following relation

$$W_P = \frac{e^2}{2\epsilon_P r_P}$$

where W_P is the polaron binding energy, r_P is the polaron radius and ϵ_P is the effective dielectric constant given by $1/\epsilon_P = 1/\epsilon - 1/\epsilon'$.

Using experimental values of the static dielectric constant ϵ' and taking the high frequency dielectric constant $\epsilon_\infty = 4$ [12] and $W_p = 2E_a$ where E_a is the activation energy for conduction, the polaron radius can be calculated. The polaron radius can also be estimated from the simplified formula $r_p = 1/2\ (\pi/6N)^{1/3}$. Table III illustrates the variation of polaron radius for our glasses.

Mott has discussed the conduction process in terms of hopping between localized states and has proposed an expression for the conductivity of the form,

$$\sigma = \nu_{ph} \frac{Ne^2R^2}{kT}\ C(1-C)\exp\left(-2\alpha R_e - E_a/kT\right) \tag{1}$$

where R is the mean site spacing, N is the number of sites for the transition metal ions per unit volume, C is the fraction of sites occupied by an electron and therefore in the low valency state, ν_{ph} is a jump frequency, α is a tunnelling probability, T is the absolute temperature and E_a is the activation energy for conduction.

Assuming that a strong electron–lattice interaction exists, the activation energy E_a is the result of polaron formation with binding energy W_H and energy difference W_D which might exist between the initial and final sites due to variations in the local arrangements of ions. Austin and Mott [4] showed that

$$E_a = W_H + \tfrac{1}{2} W_D \qquad T > \theta_D/2$$

and

$$E_a = W_D \qquad T < \theta_D/4$$

where θ_D, defined by $k\theta_D = \hbar\omega_0$ is a temperature characteristic of the average optical–phonon frequency. In this formula ω_0 is the longitudinal optical phonon frequency and $\hbar$ is the reduced Planck constant.

The polaron model predicts a departure from a linear log σ against $1/T$ plot at a temperature T of $(1/2)\ \theta_D$. Taking the vibration band at 300 cm^{-1} to be the same as the optical phonon frequency ν, the value obtained for $(1/2)\ \theta_D$ is about 216 K, and as can be seen from experimental results there is no departure from the linearity in molybdenum phosphate glasses over the measured temperature range (RT ~ 300 K) which does not cover the temperature of $T = (1/2)\theta_D$. The values of ν_{ph} obtained from Equation 1 neglecting the tunnelling term $\exp(-2\alpha R)$ are shown in Table III. It is seen that there is a variation in estimated value with composition. Mansingh *et al.* [14] explained this on the basis of correlation effects and replacing $(1-C)$ in Equation 1 by $(1-C)^{n+1}$ with $n = 5$, but in molybdenum phosphate glasses it cannot be explained by taking any reasonable value of n in correlation effects. The value of ν_{ph} can be made close to the optical phonon frequency (~ 10^{13} Hz) by considering N to have values lower than the actual measured values and assuming that only some of the sites participate in conduction. However the value of N needed would be as low as

10^{18} cm^{-3} and if such a small fraction of sites were to participate in conduction then the variation of conductivity with composition cannot be easily explained.

Murawski *et al.* [6] studied d.c. conductivity in a series of iron oxide glasses and showed that the influence of the tunnelling term must be taken into consideration. If we retain this term, Equation 1 can be used to calculate the value of α assuming $\nu_{ph} \simeq 10^{13}$ Hz for all glasses. The calculated values of α are also shown in Table III. It is difficult to explain the variation of α with composition but its numerical values for all the compositions are fairly close to the range predicted by Mansingh *et al.* [14]. Hence it may be reasonable to assume that the tunnelling term in Equation 1 cannot be neglected. In molybdenum phosphate glasses, variable range hopping was rejected by Mansingh *et al.* [14] because analysis of the conductivity against temperature data gave a value of α about 1.62×10^{11} A^{-1} which seems unacceptable.

The decrease in the conductivity with substitution of In_2O_3 for MoO_3 with a constant percentage (40 mol %) of P_2O_5 may be explained by saying that the increase of In_2O_3 causes a decrease in the MoO_3 content and hence leads to an increase of both Mo–Mo ion spacing and activation energy. (Table II). This as a consequence leads to a decrease in conductivity which is in accordance with Equation 1.

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