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Direct current electrical conduction in lead tungsten phosphate glasses

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Measurements have been made on d.c. electrical conductivity of semiconducting lead tungsten phosphate glasses (X mol% WO_3–(60-x) mol% PbO–40 mol% P_2O_5; $x = 10$, 20, 30, 40, 50 and 60) of six different compositions over a temperature range of 240 to 500 K. It is shown that the conduction can be described by a small polaron hopping model. When the WO_3 content is $\leqslant 30$ mol% the d.c. conductivity σ_{dc} decreases and the activation energy W increases with increasing WO_3 content and the glass samples exhibit predominant ionic conduction, however, when the WO_3 content is > 30 mol%, σ_{dc} increases and W decreases with the increase of tungsten ion concentration and the glass samples exhibit electronic conduction. The electronic conduction in these glasses having $x > 30$ mol% seems to be adiabatic. Greaves variable range hopping has been found to be valid. The value of the electron wavefunction decay constant α is of the order of 16 nm^{-1}. A minimum in the d.c. conductivity has been observed when the PbO concentration is 30 mol%.

1. Introduction

The electrical properties of semiconducting glasses have been of considerable interest in recent years. Transition metal oxide glasses having two different valence states of transition metal ions behave as electronic conductors. The loss of oxygen from the melt produces lower valence transition metal ions. Conduction in these glasses proceeds by electron hopping between high and low valence transition metal ions. There have been a few publications [1] on the electrical properties of the transition metal (TM) oxide glasses containing two different transition metal oxides or TM oxide with some ionic metal oxide [2]. These investigations are interesting since effects like the change in the activation energy due to the additional distortion of the lattice sites, reduction–oxidation interactions between the two transition metals in the melt and the effects of phase separation of glasses take place when a second metal oxide is introduced in the glass matrix containing one TM oxide. Also in alkali–TM oxide glasses transitions from ionic to electronic conduction have been reported with an increase in the concentration of TM ions.

Several research workers [3–7] have studied the different properties of tungsten phosphate glasses with different compositions. Most of the work has been reported on binary tungsten phosphate glasses. The present paper deals with d.c. conductivity measurements on lead–tungsten phosphate glass of six different compositions. The relative contribution of ionic and electronic conduction has been discussed. The variation of σ_{dc} with lead ion concentration has also been studied.

2. Experimental procedure

Six samples of PbO–WO_3–P_2O_5 glass system with composition 10, 20, 30, 40, 50 and 60 mol% WO_3 were prepared by melting the appropriate amount of WO_3, $Pb(NO_3)_2$ and P_2O_5 of analytical grade in a platinum crucible for 1 h at 1200 °C in air. The glass samples were then prepared by quenching the melt on a brass plate held at room temperature. The amorphous nature of the samples were determined by taking X-ray diffraction photographs. The absence of well defined Laue spots confirmed that the samples were amorphous.

Samples were ground with different grades of emery powders. The samples were then coated with silver paint in order to make the surfaces conducting. The samples were then annealed at 150 °C for 3 h to stabilize the contacts and to remove the mechanical stresses. Good ohmic contacts were verified from the linearity of I–V characteristics. Direct current conductivity has been measured using a Keithley 617 programmable electrometer. The density of the samples was determined by the displacement method.

3. Results and discussion

Values of the d.c. conductivity at 400 K for all the six samples have been inserted in Table I. Values of 60 mol% WO_3 glass at 350 K is 4.53 $\times 10^{-7}\,\Omega^{-1}\,cm^{-1}$ which is found to be comparable to that given by Mansingh *et al.* [3] for 67 mol% WO_3 glass which is $1.0 \times 10^{-6}\,\Omega^{-1}\,cm^{-1}$ at the same temperature. These values should be considered comparable taking into consideration the fact that the electrical properties of glasses are greatly affected by the condition of preparation and an order of magnitude agreement between the values reported by different authors may be considered to be in reasonably good agreement. A plot of $\log \sigma_{dc} T$ against $1000/T$ for

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TABLE I Measured values of σ_{dc} conductivity, activation energy W, number of molecules cm^{-3} of transition metal oxide N, distance between TMI ions R, density of the $PbO-WO_3-P_2O_5$ glasses

Sample	$PbO-WO_3-P_2O_5$ (mol %)	Density ($g\,cm^{-3}$)	$N \times 10^{21}$ Molecules cm^{-3}	R_0 (nm)	σ_{dc} at 400 K ($\Omega^{-1}cm^{-1}$)	W at 400 K (eV)	W at 250 K (eV)
1	50–10–40	5.24	1.65	0.850	4.45×10^{-11}	0.88	–
2	40–20–40	5.08	3.18	0.680	1.58×10^{-11}	1.00	–
3	30–30–40	5.37	5.02	0.584	1.41×10^{-12}	1.03	–
4	20–40–40	4.52	5.61	0.563	1.77×10^{-10} 2.02×10^{-11} (at 350 K)	0.61 0.50	0.12
5	10–50–40	4.17	6.44	0.538	6.28×10^{-9} 1.14×10^{-9} (at 350 K)	0.47 0.46	0.22
6	0–60–40	4.86	8.93	0.480	1.99×10^{-6} 4.53×10^{-7} (at 350 K)	0.45 0.30	0.12 0.08 (at 108 K)

six samples of $PbO-WO_3-P_2O_5$ glasses having different compositions is shown in Fig. 1. All the glass samples show a smooth variation of conductivity with temperature. The conductivity is found to decrease with the increase in concentration of WO_3 from 10 to 30 mol %. Similar behaviour has been reported for other transition metal oxide glasses [2, 8–10]. Bogomolova *et al.* [8] have also reported that in the $BaO-V_2O_5-Fe_2O_3$ glass system the introduction of Fe_2O_3 initially causes a decrease in the conductivity by a factor of about 2 to 3. The conductivity then increases with the increase of Fe_2O_3 concentration. The plots shown in Fig. 1 for these three glasses having WO_3, 10, 20 and 30 mol % are linear and therefore the values of activation energy are independent of temperature. The activation energies are also high as compared to electronic conducting glasses. The glasses for these three compositions seem to exhibit predominant ionic conduction. Ionic conduction has also been observed in $PbO-V_2O_5-P_2O_5$ glass system [11] having higher concentration of PbO than V_2O_5. For the other three samples with concentrations of 40, 50 and 60 mol % of WO_3 the d.c. conductivity increases with the increase of WO_3 concentra-

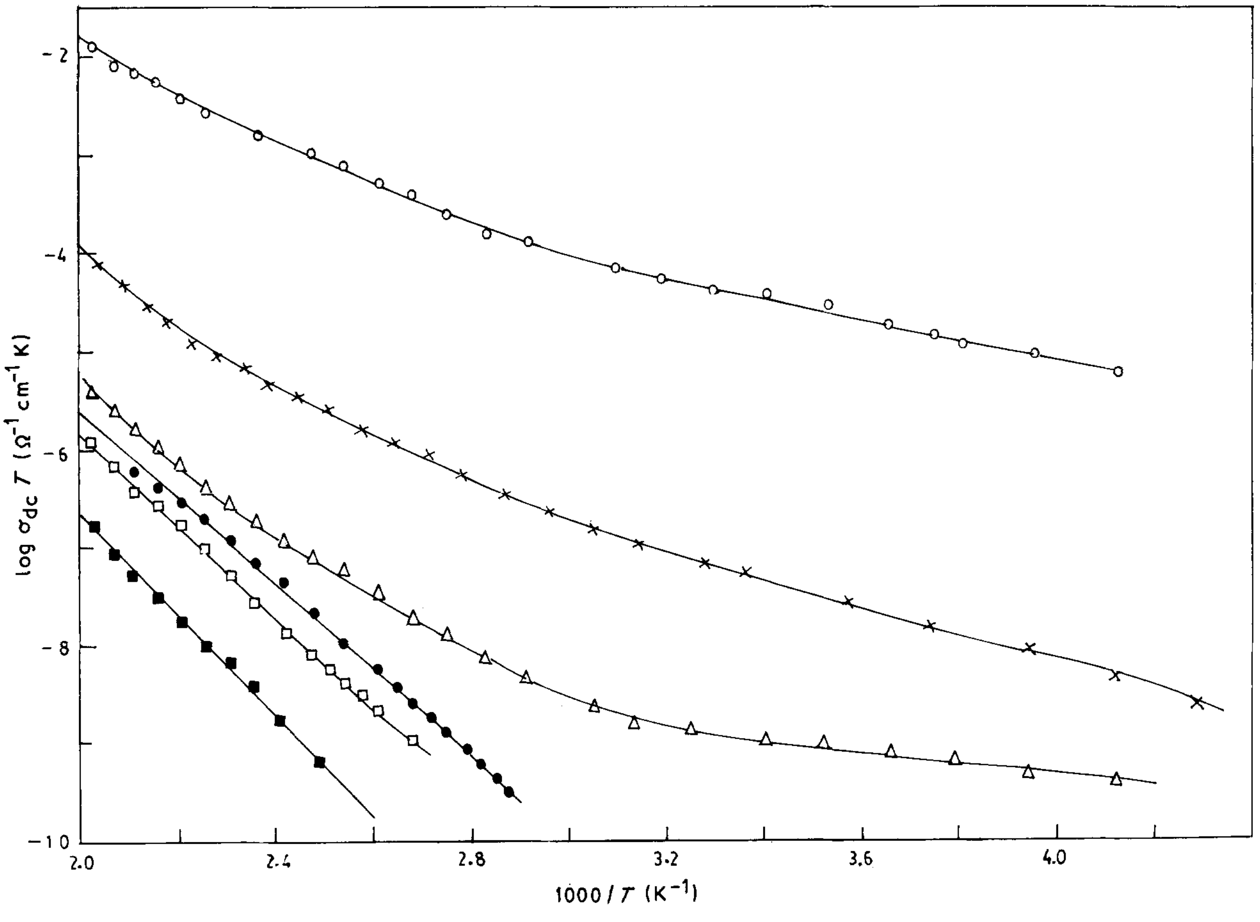

Figure 1 Plot of σ_{dc} against $1000/T$ of the $PbO-WO_3-P_2O_5$ glasses. (Mol % WO_3: ● 10, □ 20, ■ 30, △ 40, × 50, ○ 60)

tion. For these concentrations the plot of $\log\sigma_{dc}T$ against $1000/T$ is non-linear and therefore the activation energy is temperature dependent. The slopes of all the six samples above 350 K are almost independent of temperature. The high temperature activation energy has been calculated at this temperature and the values of the activation energy are reported in Table I. For the last three samples in which the activation energy is temperature dependent the values of activation energy has also been calculated at 250 K (and also at 108 K for the sixth sample only) and the values have been inserted in Table I. The high temperature activation energy for 60 mol % WO_3 glass at 350 K is found to be 0.30 eV which is comparable to that reported by Mansingh *et al.* [3] for 67 mol % WO_3 glass (0.35 eV) system within experimental error. Values of activation energy for the samples having WO_3 concentration > 30 mol % are seen to decrease with the increase of WO_3 concentration. These findings, namely (i) non-linear plots of $\log\sigma_{dc}T$ against $1000/T$ and also (ii) the high temperature activation energy decreases with the increase of WO_3 concentration for the last three samples, indicates electronic conduction in these glasses. The electronic conduction is due to the hopping of a polaron from the lower valence state (W^{5+}) to the higher valence state (W^{6+}).

The variation of σ_{dc} with W is shown in Fig. 2 at 350 K. The plot shows that the values of the d.c. conductivity tends to be smaller in those glasses having a higher value of activation energy. This is in agreement with the results published by Sayer and Mansingh [12] and by Chung and Mackenzie [13] for vanadium phosphate glasses.

Austin and Mott [14] have suggested that d.c. conduction in transition metal oxide glasses takes place by small polaron hopping and is expressed by the relation

$$\sigma_{dc} = \nu_0 \frac{Ne^2R^2}{kT} C(1 - C)\exp(-2\alpha R) \times \exp(-W/kT) \qquad (1)$$

where the various parameters have their usual meaning.

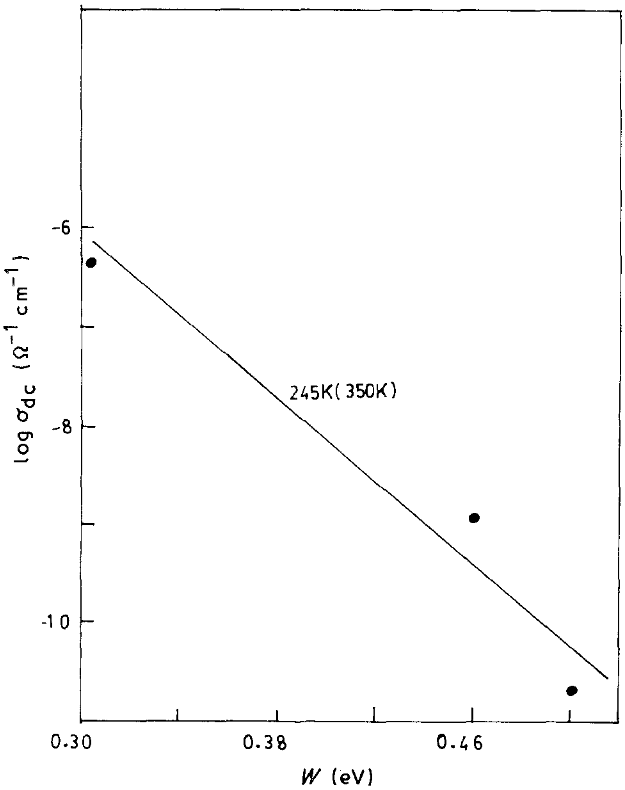

Figure 2 Plot of σ_{dc} against W for PbO–WO_3–P_2O_5 glasses. The open value corresponds to that evaluated from the slope.

The activation energy W is the sum of polaron hopping energy W_H and disorder energy W_D which might exist between the initial and final sites due to the variation in the local arrangements of ions. Austin and Mott [13] have shown that

$$W = W_H + \tfrac{1}{2}W_D \quad \text{for } T > \theta_D/2 \qquad (2)$$

$$W \approx W_D \quad \text{for } T < \theta_D/4 \qquad (3)$$

where θ_D is the Debye temperature defined by $\hbar\omega_0 = k\theta_D$, which is characteristic of the average optical phonon frequency. A detailed theory of this temperature dependence applicable to phosphate glass has been given by Schnakenberg [15]. According to Equation 3 low temperature activation energy may be taken as a disorder energy, W. Low temperature activation energy when taken as the limiting value of disorder energy and equated to the phonon energy $\hbar\omega_0$, yields a value of $\nu_0 \approx 3.08 \times 10^{12}$ Hz sec^{-1}. These values are similar to the values reported for V_2O_2–P_2O_5 glasses [12].

The coupling constant has been evaluated using the relation $\gamma = W_P/\hbar\omega_0$, where $W_P = 2W_H$. The value of γ has been evaluated to be equal to 10.5. This value of γ can be used to calculate the effective mass of the polaron given by

$$m_P = m^* \exp(\gamma) \qquad (4)$$

where m^* is given by

$$m^* = (\hbar/2\omega_0R^2) \qquad (5)$$

m^* is the effective mass of the electron in the undisturbed lattice. The estimated value of m_P turns out to be $\approx 10^4 m^*$. These values of γ and m_P confirm the presence of a strong electron phonon interaction in these glasses leading to a strong localization of electron on the sites and formation of small polaron in the present system of glass. The values are inserted in Table II.

Since the Mott [16] variable range hopping is valid in general, only below 150 K and the d.c. conductivity for the tungsten glasses could not be measured in the low temperature range because of the low conductivity of the samples, therefore Mott's variable range hopping could not be applied. Greaves [17] has suggested variable range hopping at intermediate temperatures which is given by the expression

$$\sigma_{dc}T^{1/2} = A\exp(-B/T^{1/4}) \qquad (6)$$

where A and B are constants and B is given by

$$B = 2.1[\alpha^3/kN(E_F)]^{1/4} \qquad (7)$$

Plots of log $(\sigma T^{1/2})$ against $T^{-1/4}$ are shown in Fig. 3. These plots are linear which indicates that

TABLE II Parameters of PbO–WO_3–P_2O_5 glasses from low temperature activation energy and Greaves variable range hopping

Glass composition (mol % WO_3)	W at 250 K (eV)	ν_0 Hz sec^{-1}	γ	m_p/m^*	Greaves hopping	
					Slope	$\alpha(nm^{-1})$
40	0.12	2.90×10^{13}	10.17	$2.61 \times 10^3_{m^*}$	135	16.0
50	0.22	5.3×10^{13}	4.27	$0.72 \times 10^2_{m^*}$	110	12.2
60	0.12	2.90×10^{13}	7.00	$1.10 \times 10^3_{m^*}$	75	07.3

Greaves variable range hopping may be valid. The slope of these plots has been used to calculate the electron wavefunction decay constant using Equation 7. Assuming a reasonable value of $N(E_F) \approx 10^{20}\,eV^{-1}\,cm^{-3}$ for localized states [18] Equation 7 gives $\alpha = 16\,nm^{-1}$ which is within the range suggested by Austin and Garbett [19] and also by Mansingh *et al.* ($20\,nm^{-1}$) for tungsten phosphate glasses [3]. Values of α have been inserted in Table II. This value is also comparable to the value estimated ($11\,nm^{-1}$) from a.c. conductivity measurements [20].

The plot of log σ_{dc} against activation energy W at a temperature of 350 K is shown in Fig. 2 (for the glasses having concentration greater than 30 mol %) which shows a linear behaviour. (Hirashima *et al.* [11] have also shown linear plot for higher concentration of V_2O_5 only.) The thermal activation energy, therefore, dominates over the pre-exponential factor inclusive of $\exp(-2\alpha R)$ of Mott's expression (Equation 1) for the conductivity, therefore, polaron hopping at higher temperatures is thermally activated. Murawski *et al.* [21] and Sayer and Mansingh [12] have suggested that a check whether the hopping is adiabatic or non-adiabatic can be made by estimating the temperature from the slope of the plot of logσ_{dc} against W for different concentration. If the estimated temperature T_e is close to the temperature at which d.c. conductivity data have been plotted, the hopping will be adiabatic, otherwise hopping will be non-adiabatic. In the present case the estimated temperature T_e has been evaluated to be 245 K which, though not so close is yet roughly comparable to 350 K at which the data have been plotted, therefore, the hopping of polaron can be described as adiabatic. Murawski *et al.* [22] have also reported that WO_3–P_2O_5 glass systems follow the adiabatic approximations.

The plot of logσ_{dc} against mol % PbO at the temperature of 400 K has been shown in Fig. 4. Direct current conductivity first decreases with an increase of PbO up to about 30 mol % whereas it increases with further increase of PbO. Ghosh and Chaudhuri [23] have also reported that the d.c. conductivity decreases with increasing content of Sb_2O_3 in V_2O_5–Sb_2O_3–P_2O_5 glass up to about 25 mol % and it increases with further increase of Sb_2O_3 concentration. Bogomolova *et al.* [8] have also reported the decrease of σ_{dc} up to 7 wt % Fe_2O_3 in barium–vanadium phosphate glasses doped with Fe_2O_3 concentration. These research workers have explained this behaviour in terms of the pre-exponential factor which increases slowly up to 7 wt % Fe_2O_3 and increases rapidly when Fe_2O_3 content

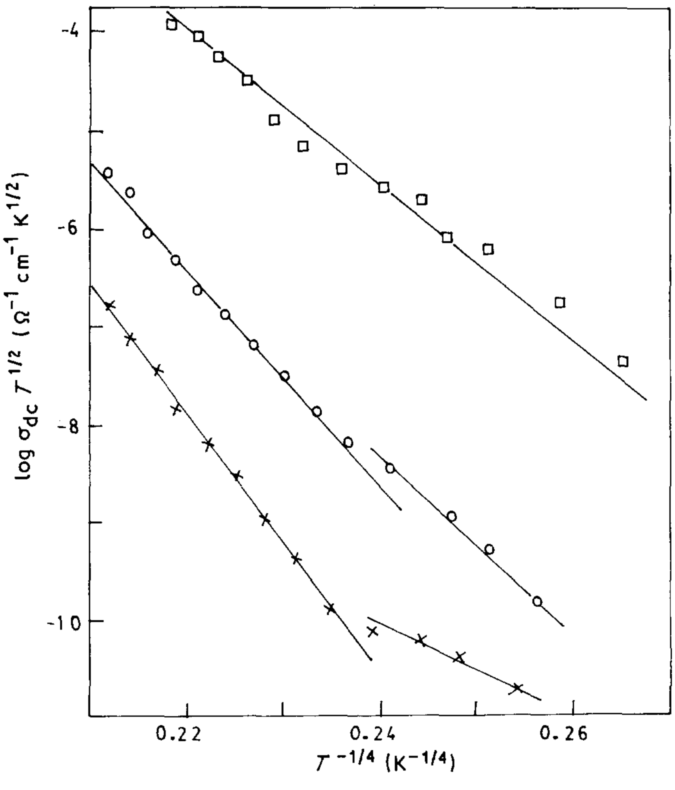

Figure 3 Plot of $\log(\sigma T^{1/2})$ against $T^{-1/4}$ for three compositions of PBO–WO_3–P_2O_5 glasses having $x > 30$ mol %. (× 40 mol % WO_3, ○ 50 mol % WO_3, □ 60 mol % WO_3)

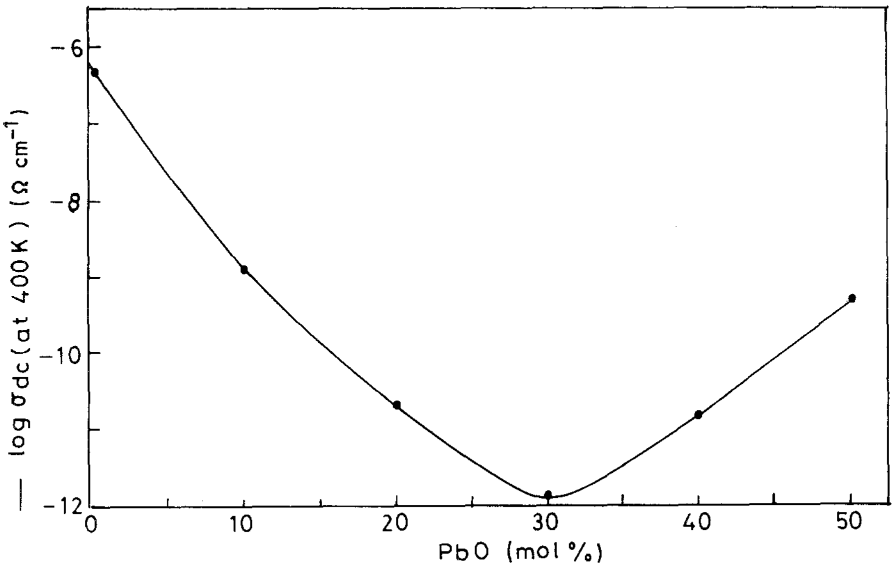

Figure 4 Plot of σ_{dc} against mol % of PbO.

exceeds 7 wt %. In the present case the pre-exponential factor has been found to decrease rapidly up to 30 mol % of PbO whereas this factor increases slowly with further increase of PbO concentration.

4. Conclusions

Direct current electrical conductivity of lead–tungsten phosphate glasses for six different compositions has been studied over a temperature range 240 to 500 K. When the concentration of WO_3 is $\leqslant 30$ mol % the value of σ_{dc} decreases and the value of W increases with increasing WO_3 content and the glass samples exhibit predominant ionic conduction. However, when the WO_3 concentration is > 30 mol %, σ_{dc} increases and W decreases with the increase of tungsten concentration and the glass samples exhibit predominant electronic conduction which seems to be in the adiabatic regime. Greaves variable range hopping has been found to be valid and the value of α has been evaluated to be 16 nm^{-1}. Direct current conductivity shows a minimum when PbO concentration is ~30 mol %.

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