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dc conductivity of molybdenum tellurite glasses

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The dc electrical conductivities of $(\mathrm{TeO_2})_{1-x}(\mathrm{MoO_3})_x$ ($x=0.4$, 0.5, 0.6 mol %) glasses are reported in the temperature range 100–400 K. Mott's model of thermally activated small polaron hopping between the nearest neighbors is found to be consistent with the data in the high-temperature range. Schnakenberg's model is found to be consistent with the temperature dependence of conductivity. The model parameters estimated from the best fits are reasonable and consistent with the composition of the glass.

I. INTRODUCTION

It is well known that several transition-metal oxides (TMO's) when heated with glass-forming substances like $\mathrm{TeO_2}$, $\mathrm{P_2O_5}$, $\mathrm{GeO_2}$, etc., form glasses on quenching the melt. The electrical conduction in these glasses occurs by thermally activated small polaron hopping from the low valence state to the high valence state of the transition-metal ion (like between $\mathrm{V^{+4}}$ and $\mathrm{V^{+5}}$ ions in vanadate glasses). The oxide glasses containing vanadium have been studied extensively.[1–6] dc electrical transport studies on glasses containing CuO are also reported.[7–11] There have been few studies on the electrical properties of the glasses containing molybdenum oxide.[12,13]

In the present study we report dc conductivity measurements on $(\mathrm{TeO_2})_{1-x}(\mathrm{MoO_3})_x$ ($x=0.4, 0.5, 0.6$ mol %) glasses in the temperature range 100–400 K. The objective of the present work is to study the effect of $\mathrm{MoO_3}$ content on the electrical properties of these glasses.

II. THEORETICAL BACKGROUND

The theoretical models used in the analysis of the experimental data are briefly described below. The electrical conduction in TM-ion-containing glasses is discussed by Mott[14] in terms of thermally assisted small polaron hopping between localized states. In the high-temperature range, i.e., $T>\theta_D/2$, the dc conductivity is due to small polaron hopping among the nearest neighbors and in the nonadiabatic regime it is given by

$$\sigma=\frac{\nu_0 N e^2 R^2}{kT}c(1-c)e^{-2\alpha R}e^{-W/kT}, \tag{1}$$

where σ is the conductivity at temperature T, ν_0 is the phonon frequency, c is the ratio of concentration of the TM ions in the low valence state to the total number of transition-metal ions N, R is the average hopping distance, α is the electron wave function decay constant of the $3d$ electron wave function, and W is the activation energy for conduction. Assuming a strong electron-lattice interaction, Austin and Mott[15] have shown that

$$\begin{aligned} W&=W_H+\tfrac{1}{2}W_D \quad \text{for } T>\theta_D/2\,, \\ W&=W_D \quad \text{for } T<\theta_D/4\,, \end{aligned} \tag{2}$$

where W_H is the polaron hopping energy and W_D is the disorder energy arising from energy difference of the neighboring sites. $\theta_D\approx h\nu_0/k$ is the Debye temperature and ν_0 the phonon frequency of the material. The tunneling term $\exp(-2\alpha R)$ in Eq. (1) reduces to unity if polaron hopping is in the adiabatic regime and the conduction is mainly controlled by the activation energy W. This model predicts an appreciable departure of linearity in $\log_{10}\sigma$ vs $1/T$ plot below a temperature $T=\theta_D/2$ indicating decrease in activation energy with the decrease in temperature.

A detailed theoretical model of the temperature dependence of conductivity is given by Schnakenberg.[16] According to this model, the conductivity at high temperature is due to optical multiphonon processes. With the decrease in temperature the multiphonon process is replaced by a single optical phonon process. At the lowest temperature the polaron hops with one or more acoustic phonons making up the energy difference between sites. The conductivity expression in this model is given by

$$\sigma\sim\frac{1}{T}\left[\sinh\left[\frac{h\nu_0}{2kT}\right]\right]^{1/2}\times\exp\left[-\left[\frac{4W_H}{h\nu_0}\right]\tanh\left[\frac{h\nu_0}{4kT}\right]\right]\exp\left[-\frac{W_D}{kT}\right], \tag{3}$$

where the symbols have their usual meaning as defined in Mott's model. The activation energy in this model decreases with the decrease in temperature.

III. EXPERIMENT

The glasses of composition $(\mathrm{TeO_2})_{1-x}(\mathrm{MoO_3})_x$ ($x=0.4, 0.5, 0.6$ mol %) were synthesized using (99.99%) pure powders of tellurium oxide and molybdenum oxide in the appropriate ratio. The mixture was calcined at 200 °C for 6 h and then melted in a platinum crucible at 1000 °C in an electric furnace. The melt was held at this temperature for about 15 min and then rapidly quenched between two copper blocks. The amorphous nature of the glasses was ascertained from x-ray diffraction and infrared spectroscopic studies. The density of the glass samples was measured by Archimedes principle. The EPR spectra indicate the formation of $\mathrm{MoO_5}$ groups in these glasses.[17] The reduced transition-metal ion concentration ($\mathrm{Mo^{+5}}$) was estimated by double integration of the EPR spectra of the glasses recorded at room temperature on an X-band JEOL spectrometer using

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TABLE I. Various physical parameters of molybdenum tellurite glasses.

Composition (mol % MoO_3)	Density ($g\,cm^{-3}$)	N (10^{22} cm^{-3})	Mo^{+5} (10^{20} cm^{-3})	$c = Mo^{+5}/N$	R (Å)	r_p (Å)
40	4.84	0.81	0.41	0.0051	4.98	2.00
50	4.68	0.98	0.59	0.0060	4.67	1.88
60	4.67	1.17	0.85	0.0073	4.40	1.77

$CuSO_4 \cdot 5H_2O$ as standard. The total number of transition-metal ions was determined from the composition of the glasses. The dc electrical conductivity measurements on the disc-shaped samples of about 0.5 mm thickness were carried out by a Keithley 617 Programmable electrometer in a cryostat fitted with a temperature controller. The linear *I-V* characteristic between electrodes was verified. To relieve the samples of any mechanical stress and to stabilize the silver electrodes, the glasses were annealed at a temperature around 150 °C for 2 h.

IV. RESULTS AND DISCUSSION

The physical parameters of the present glass system are shown in Table I. The density of the glass shows slight decrease with increase in MoO_3 content. The c value is small and shows slight increase with increase in MoO_3 content.

The conductivity measurements as a function of temperature were carried out on several samples with $(TeO_2)_{1-x}(MoO_3)_x$ ($x = 0.4, 0.5, 0.6$ mol %) composition. The conductivity of the samples of the same composition taken from different batches prepared under identical conditions showed agreement within 5% in their room-temperature conductivity. The dc conductivity on the same sample in different runs agreed within 2%. The lower limit of the temperature range utilized was decided by the experimental difficulty of measuring currents less than 10^{-14} A with the equipment available.

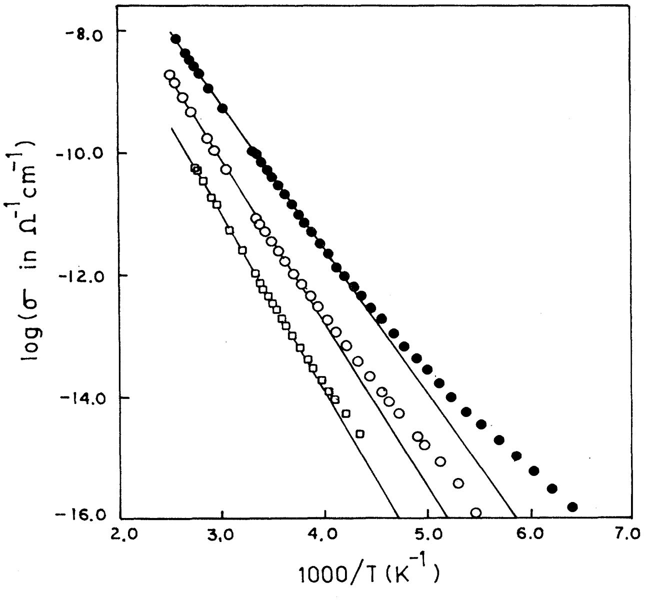

FIG. 1. Plot of logarithm (base 10) of conductivity vs temperature inverse for $(TeO_2)_{1-x}(MoO_3)_x$ glasses. $x = 0.4$ (□), $x = 0.5$ (○), $x = 0.6$ (●). The solid lines are the best linear fits as per Mott's model [Eq. (1)].

Figure 1 shows the variation of a logarithm of electrical conductivity σ as a function of inverse of temperature for various glass compositions. It is observed that these plots are nonlinear implying a temperature dependence of activation energy. This kind of variation in $\log_{10}\sigma$ vs $10^3/T$ is characteristic of small polaron hopping conduction mechanisms in TMO-containing glasses.[14–16] The polaron radius r_p can be estimated from the equations given by Bogomolov *et al.*[18] for a nondispersive system as

$$r_p = \frac{1}{2}\left[\frac{\pi}{6N}\right]^{1/3} . \tag{4}$$

Using the N values from Table I, r_p is calculated and listed in Table II. The r_p value is small and comparable to the reported values for other glass systems.[1–4,12] This shows the presence of strong electron-phonon interaction and formation of small polarons in the present glasses. The conductivity of these glasses is about 4–5 orders of magnitude lower than that of tellurium vanadate glasses containing a similar amount of TeO_2 and about 1 order of magnitude higher than molybdenum phosphate containing a similar amount of MoO_3. Figure 1 shows that $\log_{10}\sigma$ varies almost linearly in the temperature range 240–400 K indicating an almost constant activation energy. The deviation from linearity starts at around 240 K and increases with the decrease in temperature. These results are in accordance with Mott's small polaron hopping model. The temperature 240 K at which the departure from linearity in $\log_{10}\sigma$ vs $1/T$ plots occurs can give an estimate of θ_D (Debye temperature). The estimated $\theta_D/2 = 240$ K give $\nu_0 = 1.0 \times 10^{13}$ Hz for the present glasses. The solid lines in Fig. 1 are the linear least-squares fits used to obtain the activation energy, W, for various glasses and listed in Table II. The activation energy decreases and the conductivity increases with the increase in MoO_3 content. The activation energy is smallest for the glass having highest conductivity. This is consistent with Eq. (1), but the variation in the preexponential term might be present and can lead to deviations of the experimental data from the equation. This can be ascertained from a $\log_{10}\sigma$ vs W plot at a fixed high temper-

TABLE II. Various electrical parameters of molybdenum tellurite glasses.

Composition (mol % MoO_3)	σ at 364 K ($\Omega^{-1}cm^{-1}$)	W (eV)	ν_0 (adia) (10^{11})	α (Å^{-1})
40	5.62×10^{-11}	0.72	2.81	0.59
50	3.98×10^{-10}	0.66	2.30	0.61
60	2.11×10^{-9}	0.59	1.42	0.67

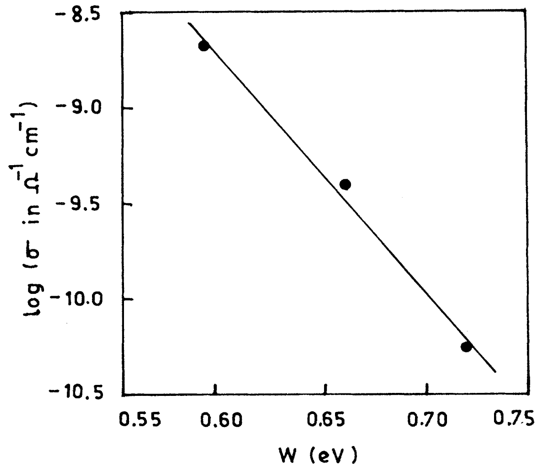

FIG. 2. Plot of logarithmic (base 10) of conductivity vs activation energy for different compositions of $(TeO_2)_{1-x}(MoO_3)_x$ glasses.

ature, say 364 K. Figure 2 shows such a plot to be a straight line. This shows that the preexponential term of Eq. (1) inclusive of $e^{-2\alpha R}$ is virtually constant and W appears to dominate the factors which determine the conductivity.

The ν_0 (adiabatic) for various glasses estimated from Eq. (1) (taking $e^{-2\alpha R}=1$) using physical parameters are also listed in Table II. The IR spectra[17] of different compositions of these glasses are very similar and show an absorption band around 500 cm^{-1} which gives a phonon frequency of $\approx 1.50\times 10^{13}$ Hz. The ν_0 (adiabatic) is almost independent of composition and is about 2 orders of magnitude smaller than the phonon frequency estimated from $\log_{10}\sigma$ vs $1/T$ plots and IR studies. This discrepancy could be explained by taking into account the effect of interaction between polarons, i.e., correlation effects.[1] This would imply that the factor $c(1-c)$ in Eq. (1) should be replaced by $c(1-c)^{n+1}$. However, it is difficult to final any reasonable value of n because of the very small value of c in these glasses. The value of $\nu_{0(\text{adiabatic})}$ can be made close to the optical phonon frequency ($\approx 10^{13}$ Hz) by considering N to have values lower than the actual measured values and assuming that only a fraction of sites participates in conduction.[19] However, the value of N needed would be of the order of 10^{19} and if such a small fraction of sites were to participate in conduction then the variation of conductivity with composition cannot be easily explained.

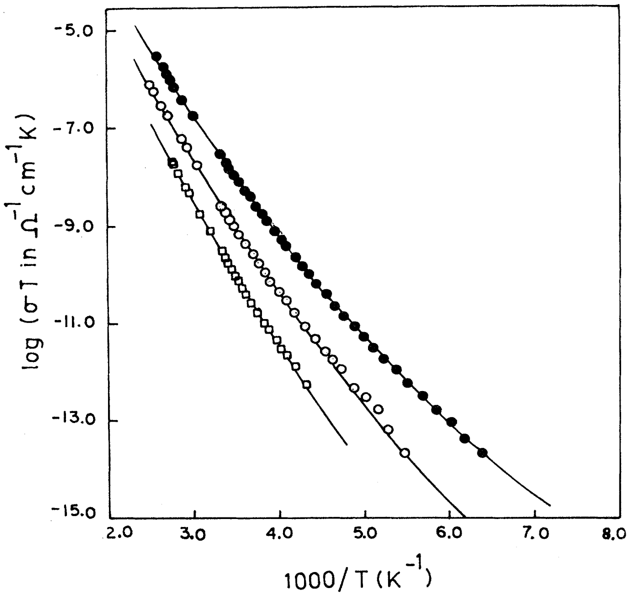

FIG. 3. Plot of $\log_{10}(\sigma T)$ vs $10^3/T$ of the experimental data of Fig. 1. The solid curves are the best fits to Schnakenberg's model [Eq. (3)].

TABLE III. Parameters obtained by fitting Schnakenberg's model to the experimental data.

Composition (mol % MoO_3)	ν_0 (10^{13} Hz)	W_H (eV)	W_D (eV)	$\gamma = W_H/h\nu_0$
40	1.1	0.66	0.07	15.5
50	1.2	0.61	0.08	13.1
60	1.3	0.56	0.09	11.1

The studies on iron phosphate glasses[20] and molybdenum phosphate glasses[12] have shown that the tunneling term cannot be neglected. By retaining this term in Eq. (1) the value of α can be estimated assuming $\nu_0 \approx 10^{13}$ Hz for all the glasses. The estimated values of α are given in Table II. These values are within the limits predicted by Austin and Garbett.[21] The tunneling term in Eq. (1) therefore cannot be neglected and the conduction in the present glass system takes place in the nonadiabatic regime. From Tables I and II it can be seen that the requirements of applying small polaron theory viz. $\alpha^{-1} < r_p < R$ are fulfilled in all the compositions of this glass system.

The temperature-dependent activation energy as observed from the experimental data in Fig. 1 is consistent with the prediction of the Schnakenberg model.[16] Figure 3 shows the experimental data and the theoretical curves (solid lines) obtained from Eq. (3). The values of the parameters ν_0, W_H, and W_D obtained from the best fits of the theoretical curves to the experimental data are given in Table III. The hopping energy W_H decreases with the increase in MoO_3 content. The ν_0 value is close to the value obtained from Mott's model and IR studies. The disorder energy W_D value is close to the prediction of the Miller-Abrahams theory.[22] Using the ν_0 and W_H values one can calculate the value of the small polaron coupling constant $\gamma = W_H/h\nu_0$. The calculated values of γ which are between 11.1 and 15.5, are listed in Table III The value of $\gamma > 4$ usually indicates strong electron-phonon interaction in solids.[15]

V. CONCLUSIONS

The electrical conductivity of $(TeO_2)_{1-x}(MoO_3)_x$ ($x=0.4,0.5,0.6$ mol %) glasses as a function of temperature is presented. The high-temperature conductivity data are explained in view of Mott's polaron model. The temperature dependence of the activation energy is consistent with the predictions of Schnakenberg's polaron hopping model. The best fit of this model to the experimental data gives the value of the physical parameters which are found to be reasonable.

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