dc conductivity of V_2O_5-containing zinc tellurite glasses

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The dc electrical conductivities of $(TeO_2)_{0.8-x}$-$(V_2O_5)_x$-$(ZnO)_{0.2}$ ($0.05 \leq x \leq 0.35$) 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 high-temperature experimental data. The temperature dependence of conductivity is found to be consistent with the predictions of Schnakenberg's model. [S0163-1829(97)04510-4]

I. INTRODUCTION

The electrical conduction in oxide glasses containing transition-metal oxide (TMO) occurs by thermally activated small polaron hopping from the low valence state to the high valence state of the TM ion (like between V^{+4} and V^{+5} ions in vanadate glasses). The oxide glasses containing vanadium have been extensively studied.[1–6] The dc electrical transport studies on glasses containing CuO (Refs. 7–10) and MoO_3 (Refs. 11 and 12) are also reported. TeO_2 in combination with modifiers like ZnO forms stable glasses at a cooling rate of ~ 1–10 K/min, typical of glass preparation.[13] The tellurite glasses are known to have low glass transition temperature, high refractive index, and high transmittance from ultraviolet to near infrared. These glasses consist of TeO_4 trigonal bipyramids, deformed TeO_4 groups, TeO_{3+1} units, and TeO_3 trigonal pyramids or a combination of these polyhedras.[13,14] TeO_2-rich glasses are characterized by TeO_4 building units.[13,14] Both Te-O_{ax} axial bonds in the TeO_4 polyhedra are strongly dynamic and easily attacked by the modifier. When a modifier oxide is introduced in the glass matrix, one of the Te-O_{ax} bonds in TeO_4 polyhedra undergoes elongation. The TeO_4 polyhedra with one elongated Te-O_{ax} bond is a TeO_{3+1} unit. Tellurium atoms take a $3+1$ coordination state for the Te-O_{ax} bond length from 0.208 to 0.298 nm. For a Te-O_{ax} bond length >0.298 nm the TeO_4 polyhedra is transformed into a TeO_3 unit.[13,14] The introduction of ZnO in the binary glass leads to a $TeO_4 \rightarrow TeO_{3+1}$ transition. The number of TeO_{3+1} units is limited by ZnO addition.[13]

In the present study we have investigated the glass formation range of the composition in the ternary system $(TeO_2)_{0.8-x}$-$(V_2O_5)_x$-$(ZnO)_{0.2}$ at cooling rates typical of glass preparation (1–10 K/min). The $(TeO_2)_{0.8}$-$(ZnO)_{0.2}$ glass has a chainlike structure of TeO_{3+1} and TeO_4 groups.[13] The substitution of V ions at the Te site is likely to create chainlike paths along which the polaron hopping conduction can take place. The objective of the present study is to examine the dc electrical conductivity as a function of composition and temperature of $(TeO_2)_{0.8-x}$-$(V_2O_5)_x$-$(ZnO)_{0.2}$ glasses. Moreover, there is no report on the synthesis and properties of V_2O_5-containing zinc tellurite 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[15] 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

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

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[16] have shown that

$$W = W_H + \frac{1}{2}W_D \text{ for } T > \theta_D/2, W = W_D \text{ for } T < \theta_D/4, \qquad (2)$$

where W_H is the polaron hopping energy and W_D is the disorder energy arising from energy differences 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 a $\log_{10}(\sigma)$ vs $1/T$ plot below a temperature $T = \theta_D/2$ indicating decrease in activation energy with the decrease in temperature.

Schnakenberg's theoretical model[17] predicts the temperature dependence of dc electrical conductivity. The activation energy in this model decreases with the decrease in temperature. 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

TABLE I. Various physical parameters of $(TeO_2)_{0.8-x}$-$(V_2O_5)_x$-$(ZnO)_{0.2}$ glasses.

Composition x (mol %)	Density (g cm^{-3})	N (10^{22} cm^{-3})	V^{+4} (10^{20} cm^{-3})	$c = V^{+4}/N$	R (Å)	r_p (Å)
0.05	5.24	0.22	6.76	0.311	7.72	3.11
0.15	5.02	0.61	7.77	0.126	5.46	2.20
0.25	4.51	0.91	8.32	0.092	4.79	1.93
0.35	4.09	1.14	9.19	0.081	4.45	1.79

making up the energy difference between sites. The conductivity expression in this model is given by

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

where the symbols have their usual meaning as defined in Mott's model.

III. EXPERIMENTAL

The glasses of composition $(TeO_2)_{0.8-x}$-$(V_2O_5)_x$-$(ZnO)_{0.2}$ ($x = 0.05$, 0.15, 0.25, 0.35, and 0.45) were synthesized using (99.99%) pure powders of tellurium oxide, zinc oxide, and vanadium oxide in the appropriate ratio. The mixture was calcined at 200 °C for 6 h and then melted in a platinum crucible at 850 °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 x-ray diffraction of the present glasses indicated that the samples with 5–35 mol % of V_2O_5 are fully amorphous and the sample with 45 mol % of V_2O_5 contains fine crystallites embedded in the amorphous matrix. The density of the glass samples was measured by the Archimedes principle. The EPR spectra show hyperfine structure characteristic of V^{+4} ions in these glasses. The reduced transition-metal ion concentration (V^{+4}) was estimated by the $KMnO_4$ titration method. 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 the 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 fully amorphous samples in the present glass system could be obtained with a maximum of 35 mol % of V_2O_5 content using the typical cooling rate of 1–10 K/min. Although the amorphous sample with higher V_2O_5 content could be prepared by a twin roller quenching apparatus, the sample size was too small to be used for conductivity measurements. The dc conductivity measurements were therefore carried out only on samples with 5 to 35 mol % V_2O_5 content. The samples with V_2O_5 content more than 25 mol % are very brittle and as a result, the samples with higher V_2O_5 were very small. Due to small sample size the lowest temperature for conductivity measurements was 140 K for the glass-containing 35 mol % V_2O_5. The dc electrical conductivity measurement 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.

Table I shows various physical parameters of the present glass system. The density and c value of the glass decreases with increase in V_2O_5 content. Figure 1 shows the variation of logarithm of electrical conductivity, σ as a function of inverse of temperature for various glass compositions. The nonlinearity of these plots implies a temperature dependence of activation energy. This kind of variation of $\log_{10}(\sigma)$ vs $10^3/T$ is characteristic of small-polaron hopping conduction mechanisms in TMO-containing glasses. The polaron radius r_p can be estimated from the equation given by Bogomolov, Kudinov, and Firsov[18] for a nondispersive system as

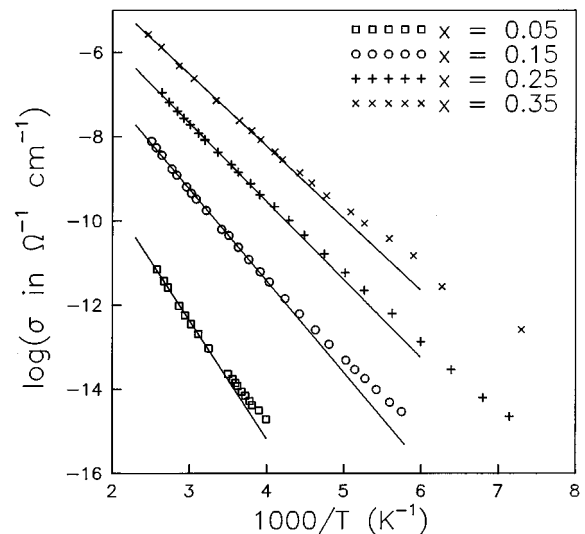$$r_p = \frac{1}{2}\left(\frac{\pi}{6N}\right)^{1/3}. \tag{4}$$

FIG. 1. Plot of logarithm (base 10) of conductivity vs temperature inverse for $(TeO_2)_{0.8-x}$-$(V_2O_5)_x$-$(ZnO)_{0.2}$ glasses. The solid lines are the best linear fits as per Mott's model.

TABLE II. Various electrical parameters of $(TeO_2)_{0.8-x}$-$(V_2O_5)_x$-$(ZnO)_{0.2}$ glasses.

Composition x (mol %)	σ at 300 K (Ω^{-1} cm^{-1})	W (eV)	W at 390 K (eV)	ν_0 (adia) (Hz)	α (Å^{-1})
0.05	9.33×10^{-14}	0.56	0.60	1.38×10^7	0.87
0.15	1.78×10^{-10}	0.44	0.49	1.23×10^8	1.03
0.25	4.26×10^{-9}	0.37	0.42	6.54×10^8	1.00
0.35	7.24×10^{-8}	0.36	0.39	7.78×10^9	0.80

The r_p value is small and comparable to the reported values for other glass systems.[1–4,10–12] 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 2 orders of magnitude lower than that of tellurium vanadate glasses[4] containing similar amount of V_2O_5. This shows that TM-oxide content alone does not determine the magnitude of conductivity. The glass former and the modifier also play a role in fixing the magnitude of the conductivity. Figure 1 shows that $\log_{10}(\sigma)$ varies almost linearly in the temperature range above 250 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 the Mott's small-polaron hopping model. The temperature 240 K at which the departure from linearity in $\log(\sigma)$ vs $1/T$ plots occurs can give an estimate of θ_D (Debye temperature). The estimated $\theta_D/2 = 240$ K gives $\nu_0 = 1.0 \times 10^{13}$ Hz for the present glasses.

The high-temperature activation energy W listed in Table II is obtained from the linear least-squares fits for various glasses. A more precise measurement of activation energy at
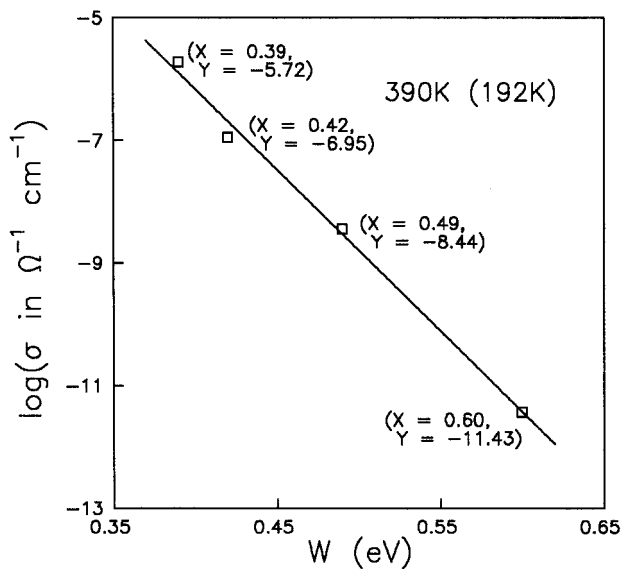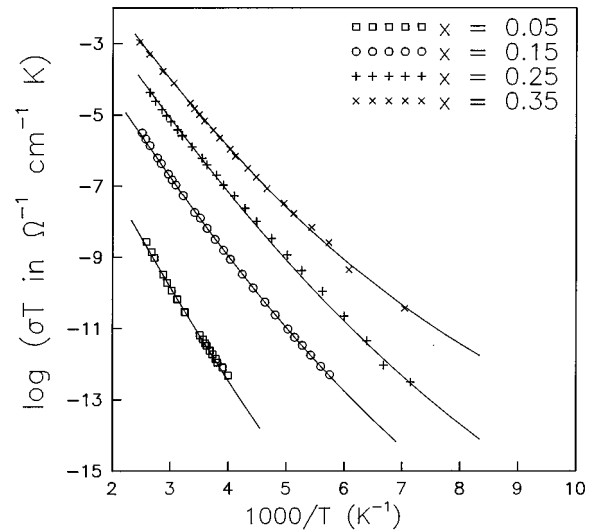

FIG. 3. Plot of $\log(\sigma T)$ vs $10^3/T$ of the experimental data of Fig. 1. The solid curves are the best fits to Schnakenberg's model [Eq. (3)].

a particular temperature was made by drawing tangent to $\log_{10}(\sigma)$ vs $1/T$ curve at that temperature. Table II also lists the activation energy at 390 K obtained by this method. These values are close to the activation energy obtained from the linear fits. The conductivity increases and the activation energy decreases with the increase in V_2O_5 content. The glass having the highest conductivity has the lowest activation energy. 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. A $\log_{10}(\sigma)$ vs W plot at a high temperature, say 390 K can ascertain the variation in the preexponential term. 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.

Substituting the values of various physical parameters from Table I in Eq. (1), the value of α can be estimated assuming $\nu_0 \sim 10^{13}$ Hz [estimated from $\log_{10}(\sigma)$ vs $1/T$ plots] 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[19] and the requirements of applying small-polaron theory viz. $\alpha^{-1} < r_p < R$ are fulfilled in all the compositions of this glass system.

To ascertain whether the preexponential term $e^{-2\alpha R}$ can be ignored, the ν_0 (adiabatic) for various glasses is estimated from Eq. (1) (taking $e^{-2\alpha R} = 1$) using physical parameters of these glasses from Table I. The ν_0 (adiabatic) is about 4–6 orders of magnitude smaller than the phonon frequency estimated from $\log_{10}(\sigma)$ vs $1/T$ plots. This discrepancy could be explained by taking into account the effect of the interaction between polarons, i.e., correlation effect.[2] 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 find any reasonable value of n to account for the large difference in ν_0 values. The value of ν_0 (adiabatic) can be made close to the optical-phonon frequency ($\approx 10^{13}$ Hz) by considering N to have values lower than than the actual measured values and assuming

FIG. 2. Plot of logarithm (base 10) conductivity vs activation energy for different compositions of $(TeO_2)_{0.8-x}$-$(V_2O_5)_x$-$(ZnO)_{0.2}$ glasses. The parameters of the points are $W = X$ and $\log_{10}(\sigma) = Y$. The points $(X = 0.60, Y = -11.43)$; $(X = 0.49, Y = -8.44)$; $(X = 0.42, Y = -6.95)$, and $(X = 0.39, Y = -5.72)$ are for the samples containing 5, 15, 25, and 35 mol % of V_2O_5, respectively.

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

Composition x (mol %)	ν_0 (10^{13} Hz)	W_H (eV)	W_D (eV)	$\gamma = W_H/h\nu_0$
0.05	1.0	0.60	0.03	14.50
0.15	1.0	0.49	0.04	11.84
0.25	1.0	0.41	0.08	9.91
0.35	1.2	0.40	0.08	8.05

that only a fraction of sites participates in conduction. However, the value of N needed would be of the order of 10^{17} and if such a small fraction of sites were to participate in conduction then the variation of conductivity with composition cannot be easily explained.

The nature of polaron hopping whether it is in the adiabatic or nonadiabatic regime can be ascertained from $\log_{10}(\sigma)$ vs W plot at a fixed temperature T for glasses of different compositions.[2,3] The estimated temperature T_c from the slope of such a plot will be close to T if the hopping is in the adiabatic regime [i.e., $e^{-2\alpha R} = 1$ in Eq. (1)] and will be different from T if the hopping is in the nonadiabatic regime and the term $e^{-2\alpha R}$ in Eq. (1) cannot be ignored. The temperature T_c (within brackets) is very much different from the temperature at which the $\log_{10}(\sigma)$ is plotted against W in Fig. 2. This further supports that the tunneling term $e^{-2\alpha R}$ in Eq. (1) cannot be ignored and the conduction in the present glasses is in the nonadiabatic regime.

The studies on molybdenum tellurite[11] glasses have shown that the tunneling term cannot be neglected. Similarly from the above analysis it is clear that the tunneling term in Eq. (1) cannot be neglected and the conduction in the present glass system takes place in the nonadiabatic regime.

The temperature dependence of conductivity as observed from the experimental data in Fig. 1 is consistent with prediction of the Schnakenberg model.[17] 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 V_2O_5 content and it is very close to the value of activation energy at 390 K listed in Table II. The ν_0 value is close to the value obtained from Mott's model. The disorder energy W_D is close to the prediction of the Miller-Abrahams theory.[20] 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 value of $\gamma > 4$ usually indicates strong electron-phonon interaction in solids.[16]

V. CONCLUSIONS

Glasses of composition $(TeO_2)_{0.8-x}$-$(V_2O_5)_x$-$(ZnO)_{0.2}$($x = 0.05$, 0.15, 0.25, 0.35, and 0.45) were obtained at cooling rates typical of glass formation. Fully amorphous glass samples were obtained with $x = 0.05$–0.35 of V_2O_5. The dc electrical conductivity of the synthesized glasses as a function of temperature were determined. The high-temperature conductivity data are explained in view of Mott's polaron model. The temperature dependence of electrical conductivity is consistent with the prediction 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.

ACKNOWLEDGMENT

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