Electrical properties of semiconducting amorphous copper-tellurite glasses

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Abstract. The temperature dependence of the electrical properties of the semiconducting amorphous copper–tellurite glasses is presented in a range of compositions. A polaronic model is shown to be generally applicable, and the variation of activation energy with the glass composition is found to dominate the conductivity. In particular, a strong pre-exponential factor containing a term $\exp(-2\alpha R)$, arising from electron tunnelling, is not observed. The results suggest that the theory of small polaron hopping in the adiabatic approximation may be most appropriate in the present system. In the intermediate temperature range, Greaves' variable range hopping analysis seems applicable. The glass forming oxide is shown to affect the activation energy for hopping conduction.

1. Introduction

Transition metal ion (TMI) glasses have important semiconducting properties, which arise due to the presence of TMIs in more than one valence state in the glass matrix [1–5]. In these glasses, the electron–phonon interaction is strong enough to form small polarons and the electrical conduction occurs by the hopping of small polarons from the ion of low valence state to the ion of high valence state of the TMIs [6]. Vanadium and iron oxide glasses [1–6] have been studied more extensively than the other TMI glasses, such as copper glasses [5, 7–12]. Drake and co-workers [7] first reported the DC conductivity and switching in the P_2O_5–CaO–CuO and B_2O_3–CaO–CuO glasses. The conduction processes in these copper oxide glasses are characterised by a high activation energy (~ 1 eV) [5, 7, 9, 11] which is mainly governed by an electron hopping mechanism between non-identical copper sites. The activation energy was too large to be explained by polaronic hopping conduction as observed in vanadium and iron oxide glasses [1–6]. Austin and Mott [6] pointed out that the ligand field environment is different for Cu^+ and Cu^{2+} ions and thus part of the activation energy can be a carrier excitation energy from one site to another. In addition, these glasses can be switched to a higher conduction state with a lower activation energy (~ 0.015 eV). In this state, the site environments are not identical. Moreover, it seems that polaron energy does not exist due to larger radial extension of the copper ion wavefunction [11].

Drake and Scanlan [8] proposed that Cu^+ and Cu^{2+} ions exist in different coordination spheres in copper phosphate glasses. They also supposed that the energy level extension of these states is enough to produce some overlapping, which provokes polaron hopping

Table 1. Chemical composition, density, glass transition temperatures, and average site spacing of $CuO–TeO_2$ glasses.

Starting compositions (mol% CuO)	Final compositions (mol% CuO)	Density (g cm^{-3})	N (10^{22} cm^{-3})	[Cu$^+$] (10^{22} cm^{-3})	C = [Cu$^+$]/N	R (Å)	T_g (°C)	T_c (°C)
60	64.14	5.15	1.80	1.33	0.74	3.82	320	410
50	56.36	4.92	1.41	0.96	0.68	4.11	280	380, 460
40	47.30	4.70	1.06	0.61	0.57	4.55	300	400
30	37.40	4.33	0.73	0.33	0.46	5.16	300	405

conduction in those overlapped levels. Some authors [10] postulated a mixed electronic and ionic conductivity in copper phosphate glasses and this behaviour is interpreted assuming that the Cu^+ ion exists in sites with different bonding forces.

The objective of the present work is to study the electrical conduction in the copper–tellurite glasses in a range of compositions over the temperature range 100–500 K. It is observed that the electrical conductivity of the copper–tellurite glasses is much higher than that of the copper phosphate glasses with similar copper oxide content and the electrical conduction is explained by the small polaron theory.

2. Experimental details

The glass samples were prepared from reagent grade CuO and TeO_2 (BDH Ltd, England). The appropriate mixtures (table 1) of these chemicals were melted in a lidded platinum crucible in air at 1000 °C for 45 min. The melts were poured on a stainless steel block and were immediately pressed by a similar stainless steel block. The samples were annealed for two hours at 200 °C, well below glass transition temperature (table 1) as determined from DTA.

The amorphous nature of the annealed and unannealed samples was confirmed from x-ray diffraction (Philips PW 1050/1051) and SEM (Hitachi S-154) studies. SEM pictures were taken from the surfaces of polished samples etched with 1% HCl for one minute. A 200 Å gold coating was deposited by vacuum evaporation to serve as a conductive layer. DTA results were obtained from a Shimadzu DT-30 thermal analyser using a heating rate of 20 °C min^{-1}. Density was measured by Archimedes' principle. An estimate of refractive index was obtained from the measurement of the Brewster angle.

For electrical measurements, disc-shaped samples of diameter ~10 mm and thickness ~1 mm were cut and polished with very fine lapping papers. Gold electrodes were deposited on both faces of the samples by vacuum evaporation. To stabilise gold contacts, the samples were again annealed for two hours at 200 °C. The electrical conductivity of the samples was measured in a cryogenic unit described elsewhere [13] by a Keithley 640 electrometer. Measurements were also taken on the glass samples annealed for two hours at various temperatures up to 380 °C. The absence of barrier layers at the contacts was checked by observation of an accurately linear *I–V* characteristic. Thermopower was measured at room temperature to determine the nature of the charge carriers.

The final glass compositions and the concentrations of total Cu ions were determined from gravimetric chemical analysis [14]. The concentrations of Cu^{2+} ions were obtained
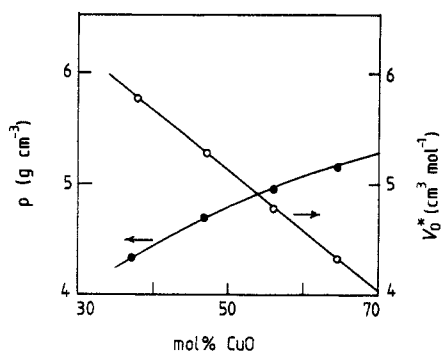
Figure 1. Variation of density ρ (●) and molar volume of oxygen V_0^* (○) with CuO content in the copper–tellurite glasses annealed at 200 °C for 2 h.
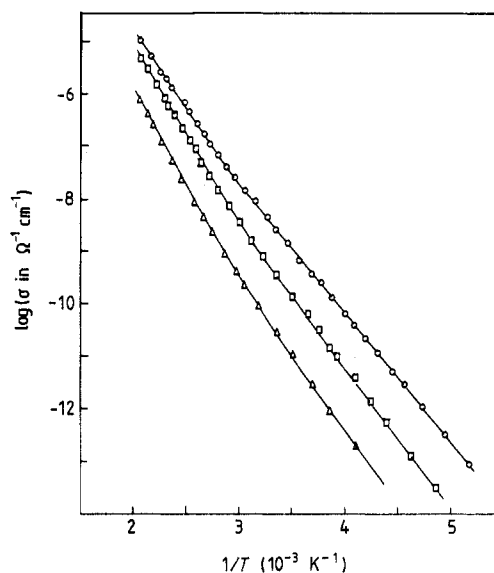

Figure 2. Plot of log σ versus $1/T$ for three compositions of the copper–tellurite glasses annealed at 200 °C for 2 h: 61.14 mol% CuO (○), 56.36 mol% CuO (□) and 47.30 mol% CuO (△).

from measurements of magnetic susceptibility [15] by an EG&G vibrating sample magnetometer (model 155).

3. Results and discussion

X-ray diffraction and SEM pictures confirmed the amorphous character of the samples. Annealing of the samples up to 380 °C (near crystallisation temperatures) did not induce any crystallinity in the samples. The crystallisation temperatures (T_c) and glass transition temperatures (T_g) (table 1), determined from DTA, did not show any systematic variation with the composition of the glasses.

The analysed compositions of the glasses, as shown in table 1, were markedly different from the batch compositions due to high evaporation loss of TeO_2 during melting. Table 1 also includes the estimated concentration of Cu^+ and total copper ions N. The concentrations of Cu^+ ions were calculated from the assumption that Cu^{2+} were the only ions contributing to the magnetic susceptibility [15]. The ratio C (table 1) of the concentration of Cu^+ to the concentration of total Cu ions increases with the increase of CuO content in the glasses. The average Cu–Cu spacings R were estimated from the relation $R = (1/N)^{1/3}$.

Figure 1 shows the density (ρ) and apparent molar volume of oxygen (V_0^*) of the glasses, calculated from the data of table 1 using the formula given by Drake and co-workers [16], as a function of CuO content in the glasses. The monotonic variation of V_0^* with compositions clearly indicates the homogeneous nature of the samples.

The analysis of time dependence of DC conductivity showed that the current intensity was constant with time. This implies that the electrical conduction in the copper–tellurite

glasses is predominantly electronic rather than ionic in contrast to the copper–phosphate glasses [10] in which mixed conduction was observed.

The thermopower measurements at room temperature indicated that all the samples were n-type semiconductors. Figure 2 shows the variation of DC conductivity (σ) of the copper–tellurite glasses with inverse temperatures. For all compositions of the glasses the conductivity above 300 K is almost linear with $1/T$. However, below 300 K it varies smoothly with $1/T$, showing a temperature dependent activation energy W. Such behaviour is typical of small polaron-hopping conduction in TMI glasses [5, 12]. The limitation in the temperature range utilised was the experimental difficulty of measuring currents of less than 10^{-14} A with the equipment available. The high-temperature activation energy (table 2) was computed from the slope of the graphs in the highest range of temperature measured. The dependence of the conductivity and the activation energy on CuO concentration in the glasses is shown in figure 3. It is observed that the conductivity increases with the increase of CuO content in the glasses similar to the vanadium glasses [5, 17] and that the activation energy is lower for those compositions of the glasses having the higher conductivity.

A most striking feature of the copper–tellurite glasses is that the conductivity of these glasses is about 3–4 orders of magnitude higher than that of the copper phosphate glasses [5, 6, 10, 11] with similar total Cu ion concentration. Similar higher conductivity was also observed in vanadium–tellurite glasses [18, 19] compared with that of the vanadium phosphate glasses [5]. Thus it appears that the glass forming oxide in the copper–tellurite glasses may not simply be the non-interacting solvent in the conduction processes as suggested by Ioffe and co-workers [20] for the vanadium phosphate glasses.

It was also observed that the electrical conductivity of the copper–tellurite glasses did not change significantly on annealing up to 380 °C.

Mott [6, 21] investigated theoretically the hopping conductivity of the TMI glasses and gave the following expression for the DC conductivity (σ) in the non-adiabatic approximation, $T > \theta_D/2$:

$$\sigma = \nu_0 (e^2 C(1 - C)/k_B TR) \exp(-2\alpha R) \exp(-W/k_B T) \qquad (1)$$

where ν_0 is the optical phonon frequency, R the average site spacing, C the ratio of the ion concentration in the low valence state to the total TMI concentration, α the wavefunction decay constant, k_B the Boltzmann constant and W the activation energy given by [6]

$$\begin{aligned} W &= W_h + W_d/2 \qquad & T > \theta_D/2 \\ &\simeq W_d \qquad & T < \theta_D/4 \end{aligned} \qquad (2)$$

where W_h is the polaron hopping energy and W_d is the disorder energy arising from the energy difference of the neighbouring sites θ_D is the Debye temperature given by $\theta_D = \eta\nu_0/k_B$.

In the case of the adiabatic mechanism, the tunnelling term $\exp(-2\alpha R)$ reduces to unity and the conductivity is given by

$$\sigma = \nu_0 (e^2 C(1 - C)/k_B TR) \exp(-W/k_B T). \qquad (3)$$

A plot of $\log(\sigma T)$ versus $1/T$ for the copper–tellurite glasses is shown in figure 4, which shows linear regions for each composition of the glasses above 300 K consistent with equation (1). The activation energy and the pre-exponential factor estimated from the least-squares fit of the linear part of figure 4 with equation (1) are shown in table 2. It is

Table 2. Physical parameters from log σ versus $1/T$ and log (σT) versus $1/T$ plots, and value of ν_0 from (3).

| Glass composition (mol% CuO) | log σ versus $1/T$ plot | | | log (σT) versus $1/T$ plot | | | | ν_0 from (3) with $C(1-C)$ replaced by $C(1-C)^5$ (10^{13} s^{-1}) |
	σ at 450 K (Ω^{-8} Ω^{-1} cm^{-1})	W at 300 K (eV)	W at 150 K (eV)	W at 300 K (eV)	log[$(\sigma T)_0$] (Ω^{-1} cm^{-1} K)]	α (Å^{-1})	ν_0 from (3) (10^{11} s^{-1})	
64.14	267	0.58	0.44	0.56	3.92	0.302	5.14	1.90
56.36	128	0.64	0.48	0.64	3.90	0.303	7.41	1.57
47.30	11.9	0.72	0.52	0.72	3.89	0.286	6.12	0.77
37.40	6.94	0.76	0.54	0.77	3.87	0.283	6.53	0.68
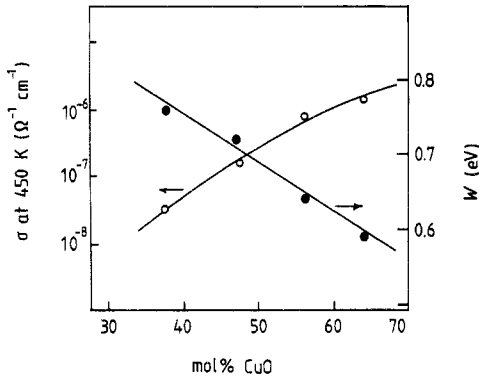
Figure 3. Variation of log σ ($\bigcirc$) and W ($\bullet$) with CuO content in copper–tellurite glasses.
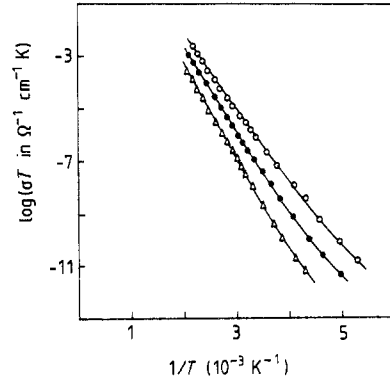
Figure 4. Plot of $\log(\sigma T)$ versus $1/T$ for three compositions of the copper–tellurite glasses annealed at 200 °C for 2 h: 61.14 mol% CuO ($\bigcirc$), 56.36 mol% CuO ($\bullet$) and 47.30 mol% CuO ($\triangle$).

observed that the pre-exponential factor is almost independent of glass compositions indicating that the tunnelling term $\exp(-2\alpha R)$ is essentially constant for all compositions of the glasses.

Another observation from figure 4 is that an appreciable break of linearity in the log (σT) versus $1/T$ curves occurs at $T = 300$ K. According to small polaron conduction model [6], this should happen at $T = \theta_D/2$. Thus small polaron model provides an estimate of $\theta_D/2 = 300$ K and hence $\nu_0 = 1.25 \times 10^{13}\,\mathrm{s}^{-1}$ for the copper–tellurite glasses. At this point it is worthwhile to mention that the infrared spectra of the different compositions of the copper–tellurite glasses [22] are similar, suggesting that optical phonon distribution does not appreciably differ in the different compositions of the copper glasses. From the infrared spectra [22], the characteristic phonon frequency is estimated to be $\sim 1.24 \times 10^{13}\,\mathrm{s}^{-1}$ corresponding to the observed infrared band at ~ 470 cm^{-1}. This value for the phonon frequency is very close to that estimated from the electrical data above.

It is interesting to estimate the decay constant α from the value of pre-exponential factor (as given in table 2). Employing $\nu_0 = 1.24 \times 10^{13}$ s^{-1} and the experimental data of table 1, estimated values of α are shown in table 2.

The values of α are almost independent of glass compositions and are within the range given in [23] for the TMI glasses.

It has been suggested [4, 5] that the nature of the hopping regime can be checked by plotting $\log(\sigma)$ versus W at a fixed temperature T. The temperature T_e estimated from the slope of such a plot will be very close to T if hopping is in the adiabatic regime, while it will be very different from T in the non-adiabatic case. Such a plot is shown in figure 5 for the present copper–tellurite glasses. It yields $T_e \simeq 498$ K for $T = 450$ K, suggesting that the polaron hopping in the copper–tellurite glasses is in the adiabatic regime.

For adiabatic hopping, values of ν_0 can be estimated from (3) using experimental values of the parameters listed in tables 1 and 2, and are themselves recorded in table 2. It is observed that the values of ν_0 do not vary much with glass compositions. This observation is also consistent with the infrared results which show that the structural arrangements of all glass compositions are similar [22]. However these values of ν_0 are one order of magnitude less than $\nu_0 = 1.24 \times 10^{13}$ s^{-1} obtained from infrared data. The
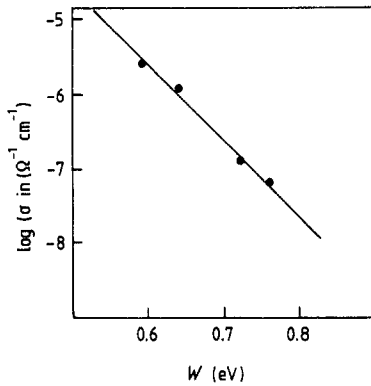
Figure 5. Log σ versus W for copper–tellurite glasses. The experimental temperature is 450 K; the temperature corresponding to the slope is 498 K.

Table 3. Refractive index n, polaron radius r_p and polaron hopping energy w_h calculated from (4).

Glass composition (mol% CuO)	n	r_p (Å)	W at 300 K (eV)	W_h (eV)	$(W$ at 300 K$) - W_h$ (eV)
64.14	1.97	1.53	0.58	0.36	0.22
56.36	1.82	1.67	0.64	0.38	0.26
47.30	1.64	1.82	0.72	0.43	0.29
37.40	1.58	2.06	0.76	0.46	0.30

discrepancy can be explained by taking the polaron correlation effect [5] into account. This fact would imply that the factor $C(1 - C)$ in (3) should be replaced by $C(1 - C)^{n'+1}$. Table 2 shows that an estimated ν_0 with $n' = 4$ is of the same order of magnitude as the characteristic phonon frequency obtained from the infrared spectra.

The polaron hopping energy W_h can be calculated from theory [6] and is given by

$$W_h = (e^2/4\varepsilon_p)(1/r_p - 1/R) \tag{4}$$

where

$$1/\varepsilon_p = 1/\varepsilon_\infty - 1/\varepsilon_0. \tag{5}$$

Here ε_∞ and ε_0 are the high frequency and static dielectric constants respectively. r_p is the polaron radius which can be estimated from the formula given in [24]:

$$r_p = 1/2(\pi/6N)^{1/3} \tag{6}$$

and the values of r_p are shown in table 3.

The estimated values of W_h from (4) and (5), under the approximations $\varepsilon_p \simeq \varepsilon_\infty = n^2$, where n is the refractive index of the glass and using the values of R and r_p from table 3, are also shown in table 3. According to (2) the difference between W and W_h arises from the disordering term $W_d/2$. An evaluation of W_d from Miller–Abrahams theory [25] gave $W_d/2 \simeq 0.05$ eV. It is seen from table 3 that $W - W_h$ values are much higher than the theoretically calculated values of $W_d/2$. Similar results were reported for
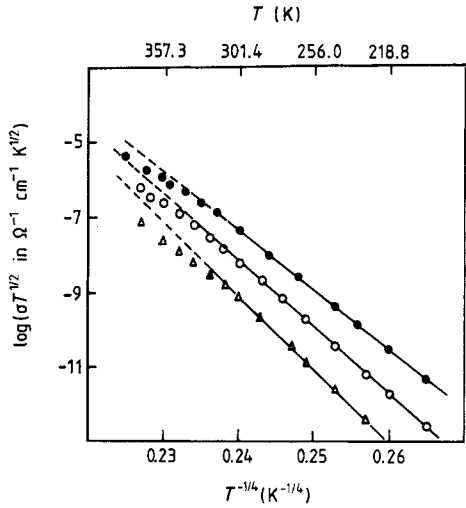
Figure 6. Plot of $\log(\sigma T^{1/2})$ versus $T^{-1/4}$ for three compositions of the copper–tellurite glasses: 61.14 mol% CuO (●), 56.36 mol% CuO (○) and 47.30 mol% CuO (△).

Table 4. Greaves' $T^{1/4}$ analysis.

Glass composition (mol% CuO)	Slope B	α with $N(E_F)$ $\sim 10^{20}$ eV^{-1} cm^{-3} (Å^{-1})	W_d (eV)
64.14	160.0	0.67	10.03
56.36	180.0	0.77	8.26
47.30	200.0	0.89	6.23

vanadate glasses [15, 17]. This discrepancy is expected to be due to the effect of partial charge of cations of the glass forming oxides on the activation energy for hopping conduction similar to vanadate glasses [15, 17].

In the temperature range investigated (100–500 K) no $\log \sigma \sim T^{-1/4}$ dependence, as suggested in [26] for variable-range hopping, has been observed for the present glasses. However, it has been suggested [27] that the variable range may dominate even at intermediate temperatures and proposed the following expression for the DC conductivity:

$$\sigma T^{1/2} = A \exp(-B/T^{1/4}) \tag{7}$$

where A and B are constants, and B is given by

$$B = 2.1[\alpha^3/k_B N(E_F)]^{1/4} \tag{8}$$

where $N(E_F)$ is the density of states at the Fermi level.

The plot of $\log(\sigma T^{1/2})$ versus $T^{-1/4}$ is shown in figure 6 for copper–tellurite glasses. The linearity of the curves below ~ 250 K indicates that variable-range hopping may be valid in these glasses. The values of α can be estimated from the slope of the linear region of figure 6 using (8). Assuming a reasonable value of $N(E_F) \sim 10^{20}$ eV^{-1} cm^{-3} for localised states [26], (8) yields $\alpha \sim 0.7$–0.9 Å (table 4) which are somewhat higher than the values of α estimated earlier from the prefactor of the $\log(\sigma T)$ versus $1/T$ plot. However, these values are also within the range given in [23].

The disorder energy W_d can also be estimated from the following expression [26]

$$B = 2.4[W_d(\alpha R)^3/k_B]^{1/4}. \tag{9}$$

The estimated values of W_d shown in table 4 are much higher than the activation energies (table 2) measured at the lowest accessible temperature. Similarly higher values of W_d were also obtained from the variable-range hopping analysis for the vanadate glasses [17, 23].

A check of the nature of hopping can, in principle, be made using Holstein's condition [28, 29]. The polaron bandwidth J should satisfy the inequality

$$\begin{aligned} J &> (2k_B TW_h/\pi)^{1/4}(h\nu_0/\pi)^{1/2} && \text{adiabatic} \\ &< (2k_B TW_h/\pi)^{1/4}(h\nu_0/\pi)^{1/2} && \text{non-adiabatic} \end{aligned} \tag{10}$$

with the condition for the existence of a small polaron being $J < W_h/3$. The limiting values of J for all compositions of the copper glasses at 450 K are in the range 0.036–0.038 eV and therefore, the condition for the existence of small polaron in the adiabatic regime can be met. An unambiguous decision as to whether the polaron is actually in the adiabatic regime requires an estimate of J. An upper limit can be deduced by assuming that the entire concentration dependence of activation energy is due to variation in J. In the present glasses (table 2) this corresponds to a change in W from 0.58–0.76 eV, a possible variation in J of ~0.16 eV. However, since W is likely to change with composition, the true value is probably smaller than this, although it is large enough for the adiabatic hopping theory to be most appropriate to describe the polaronic conduction in the copper–tellurite glasses. Measurements of Hall mobility may be useful in finally resolving the matter.

4. Conclusions

Temperature dependence of the electrical conductivity of the copper–tellurite glasses is generally explained by small polaron theory. It is observed that polaron hopping occurs in the adiabatic regime. In the intermediate temperature range, Greaves' variable-range hopping analysis yields reasonable values of decay constant, but higher values of disorder energy. It is observed that the glass forming oxide affects the activation energy for hopping conduction.

Acknowledgments

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