

D.c. conductivity of V_2O_5 –MnO–TeO₂ glasses

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Semiconductive oxide glasses in the system V_2O_5 –MnO–TeO₂ were prepared, and the mechanism of d.c. conduction was studied. The Seebeck coefficient measurements at temperatures from 375–475 K indicated the glasses to be *n*-type semiconducting. The d.c. conductivity ranged from 5×10^{-5} to $1.9 \times 10^{-6} \text{ S cm}^{-1}$ at 405 K for $V_2O_5 = 60 \text{ mol } \%$ and $\text{MnO} = 0\text{--}20 \text{ mol } \%$, and decreased with increasing MnO content. The conduction was confirmed to obey the adiabatic small polaron hopping model, and was due to mainly hopping between V-ions in the glasses. The polaron band width J was estimated to be $J = 0.10\text{--}0.20 \text{ eV}$. The electron–phonon interaction coefficient γ_p was very large (21–26). The hopping mobility evaluated as $2.3 \times 10^{-7}\text{--}2.7 \times 10^{-6} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ increased with increasing V_2O_5 content. The estimated carrier concentration was the order of 10^{19} cm^{-3} . The principal factor determining conductivity was the polaron hopping mobility in these glasses.

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1. Introduction

Semiconducting oxide glasses with transition metal (TM) oxide, e.g. V_2O_5 , have attracted much interest in the study of their conduction; extensive studies have been carried out [1–11] on their electrical conduction. The conduction mechanism was understood by the small polaron hopping model [12–14]. The conductivity has been studied for glasses containing two kinds of TM ions such as, Fe_2O_3 – V_2O_5 – P_2O_5 [15], TeO_2 – V_2O_5 – MoO_3 [16], TiO_2 – V_2O_5 – P_2O_5 [17], and Bi_2O_3 – V_2O_5 – Fe_2O_3 [18]. In these systems, the conductivity increased [15] or decreased [17] with increase in the concentration of the second TM oxide for a constant amount of V_2O_5 . Thus, contribution of the second TM ion to the conduction was indicated [15]. Previously we studied d.c. conduction of vanadium tellurite glasses such as V_2O_5 –ZnO–TeO₂ [19], V_2O_5 –Sb₂O₃–TeO₂ [20], and V_2O_5 –SnO–TeO₂ [21] glasses. These had relatively high d.c. conductivities of $\sim 10^{-4} \text{ S cm}^{-1}$ above 400 K [20, 21], and fitted the small polaron hopping model [12, 13].

In the present work, we report d.c. conductivity of V_2O_5 –MnO–TeO₂ system, because no earlier studies were found on vanadium mangan tellurite glasses. We expected, for this system, high conductivity on addition of MnO (the second transition metal ion with multivalency) to V_2O_5 –TeO₂ glasses [7].

2. Experimental procedure

Reagent grade chemicals, V_2O_5 (99.9%), MnO (99.9%) and TeO₂ (99.99%) were used for melting. After mixing in air a batch of 6 g with prescribed compositions, this was melted in an alumina crucible for 1 h at 1023 K in an electric furnace. The atmosphere for melting was pure Ar to avoid oxidation of MnO at high temperature. The melt then was poured on a cop-

per block plate and immediately quenched by pressing with another copper block plate, and we obtained a bulk glass sample of $2 \times 2 \text{ cm}$ size and 1 mm thickness.

The glass forming region was determined by X-ray diffraction analysis (Philips, PW1830/00). The glass transition temperature T_g and crystallization temperature T_c were measured by differential thermogravimetric analysis (DTA) (Rigaku, DSC8230/TAS300). The homogeneity of glass samples was checked by electron probe microanalysis (EPMA) (Shimadzu, EPMA-8024).

Density of glasses was determined by the Gay–Lussac method using toluene. The glass d.c. electrical conductivity σ was measured at temperatures from 330 to 475 K using the four-point probe technique, a constant d.c. current of 0.1 μA being applied between the electrodes with a spacing of 2 mm. The Seebeck coefficient Q for the glasses was determined at temperatures between 475 and 375 K by measuring thermoelectric power of the glasses with a temperature difference of 10 K between two electrodes caused by blowing N_2 gas on one side of electrodes.

3. Results and discussion

Glasses of V_2O_5 –MnO–TeO₂ system were able to be prepared. From an EPMA observation of V, Mn and Te elements in the glass sample (V_2O_5 :MnO:TeO₂ = 60:10:30 mol %), we found a homogeneous distribution of each element and no phase separation in the glasses prepared. The T_g and T_c for the glass were determined to be 517 and 577 K, respectively. Glasses with V_2O_5 more than 80 mol % could not be prepared.

Fig. 1 shows the glass formation region of V_2O_5 –MnO–TeO₂ glasses with $0 \leq V_2O_5 \leq 75 \text{ mol } \%$,

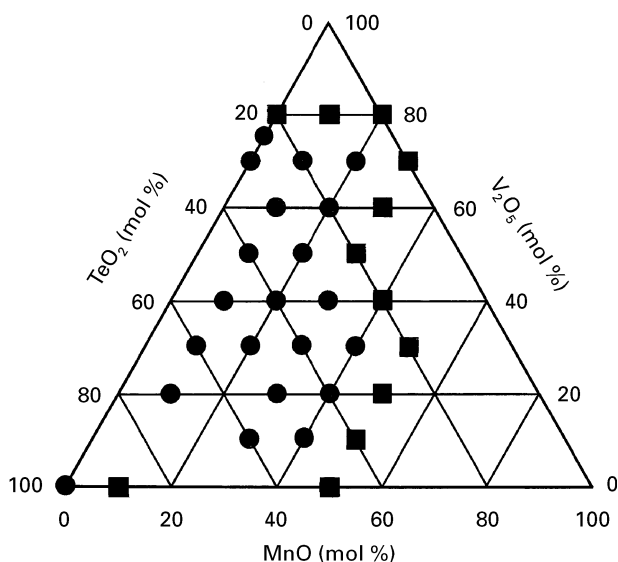


Figure 1 Glass formation region of the V_2O_5 -MnO- TeO_2 system. (●) glass; (■) crystallized.

$0 \leq MnO \leq 40$ mol %, and $25 \leq TeO_2 \leq 100$ mol %. V_2O_5 -ZnO- TeO_2 glasses [19] showed a larger glass forming region with $0 < V_2O_5 < 70$ mol %, $0 < ZnO < 60$ mol %, and $30 < TeO_2 < 100$ mol %, T_g and T_c for the glass $V_2O_5:ZnO:TeO_2 = 60:20:20$ mol % were 510 K and 585 K, respectively [19]. It is known that thermal stability of a glass depends upon $\Delta T = T_c - T_g$ of that glass [22]. So the fact that the value of $\Delta T = 60$ K for the present glasses is smaller than that for V_2O_5 -ZnO- TeO_2 glasses [19] ($\Delta T = 75$ K) explains the reason for glass formation region being narrower than that for the V_2O_5 -ZnO- TeO_2 glasses [19] and it being less stable as well.

Fig. 2 shows the Seebeck coefficient Q for glasses of different compositions as a function of temperature of measurements. No temperature dependence of Q was observed similar to ternary vanadate glasses [23, 24]. The value of Q decreased with increase in MnO content. No d.c. polarization was observed. The negative Q values indicated the glasses to be n -type semiconductors.

Q is expressed by the Heikes' formula [25]

$$Q = k/e \{ \ln[C/(1-C)] + \alpha' \} \quad (1)$$

where C is the ratio of the concentration of reduced transition metal ion to that of total transition metal ions, k the Boltzmann constant, e the electronic charge and α' a constant of proportionality between the heat transfer and the kinetic energy of an electron. For $\alpha' < 1$ small polaronic hopping conduction occurs [26, 27], but for $\alpha' \gg 2$ the conduction is due to large polaron [13, 28]. Equation 1 implies no temperature dependence. It was earlier reported that Q for some vanadium tellurite glasses [23, 24] obeyed the Heikes' formula [25]. Although the adaptability of this formula to vanadium tellurite glasses with two transition metal ions has not yet been examined, but assuming the Heikes' formula (Equation 1) for the present glasses and $\alpha' = 0.05$ from the previous ternary vanadium

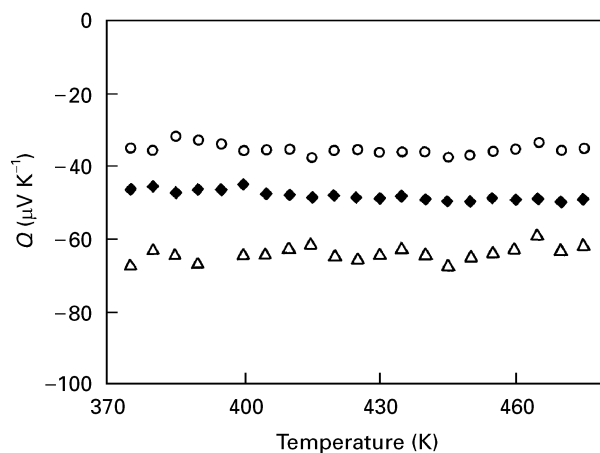


Figure 2 Seebeck coefficient of $xV_2O_5 \cdot 10MnO \cdot (90-x) TeO_2$ (mol %) glasses. (○) $x = 40$; (◆) $x = 50$; (△) $x = 60$.

tellurite glass study [24], we have estimated C values from the data in Fig. 2. The values were 0.385, 0.358, and 0.311 for $xV_2O_5 \cdot 10MnO \cdot (90-x) TeO_2$ ($x = 40, 50$ and 60 mol %), respectively, which were larger than those for V_2O_5 -ZnO- TeO_2 [19] glasses of the corresponding compositions ($C = 0.162$ – 0.118).

Figs 3 and 4 show the reciprocal temperature dependence of electrical conductivity, σ , for different glass compositions, which indicate that the relationship between $\log(\sigma T)$ and T^{-1} is almost linear and is apparently described in the measured temperature range (395–475 K) as

$$\sigma = (\sigma_0/T) \exp(-W/kT) \quad (2)$$

where σ_0 is the pre-exponential factor and W is activation energy for conduction.

The best fit of $\log(\sigma T)$ to T^{-1} gave $r^2 = 0.9996$ – 0.9997 (r : correlation coefficient) and $R = 4.26 \times 10^{-4} \text{ S cm}^{-1}$ (R : range) for the glasses with $V_2O_5 = 40$ – 60 mol % (R : range) (Fig. 3), indicating a satisfactory fit, similar to V_2O_5 -ZnO- TeO_2 [19] and V_2O_5 - Sb_2O_3 - TeO_2 [20] systems.

At 405 K, the glasses indicated σ to be 5.1×10^{-5} – $1.9 \times 10^{-6} \text{ S cm}^{-1}$ for $V_2O_5 = 60$ mol % and $MnO = 0$ – 20 mol % (Fig. 4). σ increased with an increase in V_2O_5 content (Fig. 5), but decreased with an increase in MnO content as shown in Fig. 6. This means that Mn ion seems to hinder electronic transport in the glass network.

Table I shows $\log \sigma_0$ and W values. σ_0 was estimated by extrapolation of $\log \sigma$ for T^{-1} by rearranging the experimental data in Fig. 3. W was obtained for the temperature range 395–475 K in Fig. 3. The mean V-ion spacing R was estimated from the formula $R = N^{-1/3}$ where N is the density of V-ion calculated from the measured density d .

We discuss then the adaptability of the Austin-Mott small polaron hopping model [12, 13] to the experimental relationship of the conductivity and temperature (Figs 3 and 4). The model predicts σ in non-adiabatic approximation as a function of

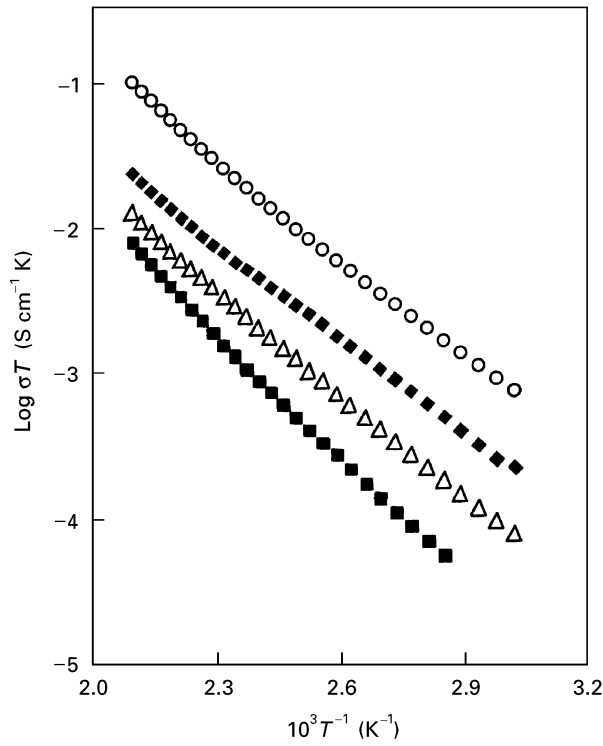


Figure 3 Temperature dependence of d.c. conductivity for $xV_2O_5 \cdot 10 MnO \cdot (90 - x) TeO_2$ (mol %) glasses. (■) $x = 30$; (△) $x = 40$; (◆) $x = 50$; (○) $x = 60$.

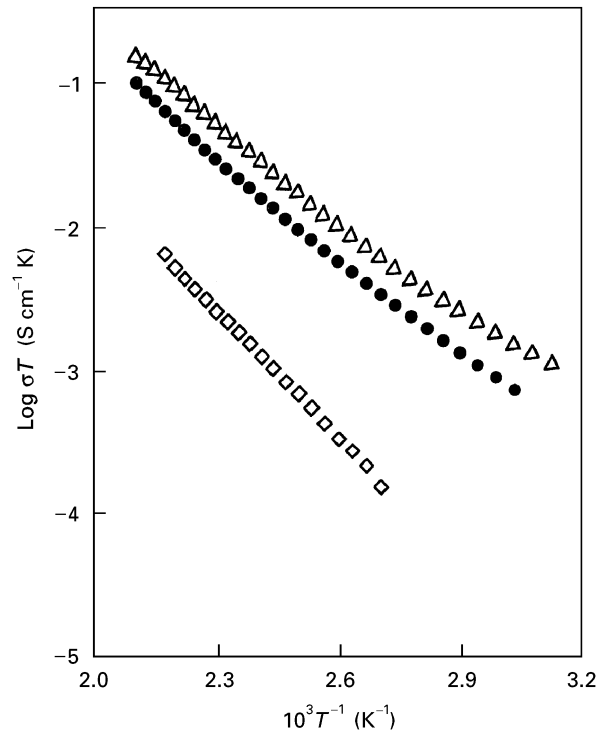


Figure 4 Temperature dependence of d.c. conductivity for $60 V_2O_5 \cdot x MnO \cdot (90 - x) TeO_2$ (mol %) glasses. (△) $x = 0$; (●) $x = 10$; (◇) $x = 20$.

temperature

$$\sigma = (\sigma_0/T) \exp(-W/kT) \quad (3)$$

$$W = W_H + W_D/2 \quad (\text{for } T > \Theta_D/2) \quad (4a)$$

$$W = W_D \quad (\text{for } T < \Theta_D/4) \quad (4b)$$

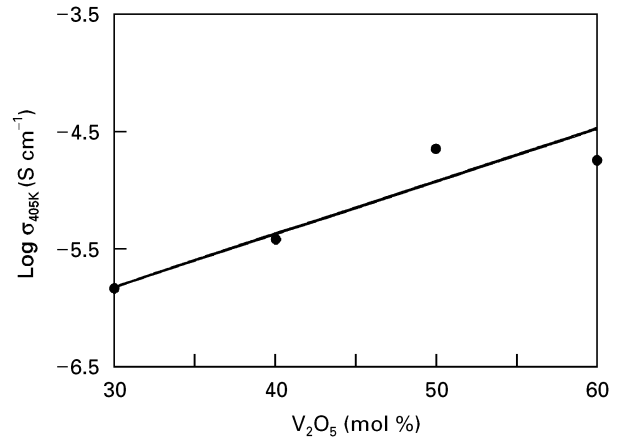


Figure 5 Effect of V_2O_5 content on d.c. conductivity of $xV_2O_5 \cdot 10 MnO \cdot (90 - x) TeO_2$ (mol %) glasses at $T = 405$ K ($x = 30-60$).

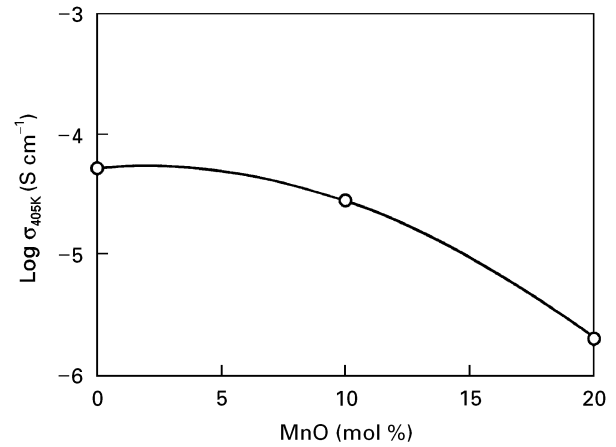


Figure 6 Effect of MnO content on d.c. conductivity of $60V_2O_5 \cdot x MnO \cdot (40 - x) TeO_2$ (mol %) glasses at $T = 405$ K ($x = 0-20$).

TABLE I Chemical compositions and physical properties of V_2O_5 - MnO - TeO_2 glasses

V_2O_5	MnO	TeO_2	$\log \sigma_0$	W	d	R
		(mol %) ^a	($S cm^{-1} K$)	(eV) ^b	($g cm^{-3}$) ^c	(nm)
60	10	30	3.44	0.433	3.997	0.384
50	10	40	2.95	0.435	4.121	0.403
40	10	50	3.04	0.473	4.349	0.424
30	10	60	3.38	0.532	4.541	0.456

^aNominal composition.

^bTemperature range 395–475 K.

^cGlass density at room temperature.

and

$$\sigma_0 = \nu_0 N e^2 R^2 C (1 - C) \exp(-2\alpha R)/k \quad (5)$$

where ν_0 is the optical phonon frequency ($\sim 10^{13}$ Hz), R the mean spacing between transition metal ions given by $R = N^{-1/3}$ with the density of transition metal ion (N), C , the fraction of reduced transition metal ion α , the tunnelling factor, W , the activation energy for hopping, W_H , the polaron hopping energy, W_D , the disorder energy, k the Boltzmann constant, and Θ_D , the Debye temperature.

In adiabatic hopping regime, αR in Equation 5 becomes negligible [3, 8, 20], and Equation 5 is described as

$$\sigma_0 = v_0 N e^2 R^2 C (1 - C) / k \quad (6)$$

Because Equation 6 was independent of V_2O_5 concentration in this regime and hardly varied with V_2O_5 content [20, 21], σ depends only on W in Equation 3 for adiabatic hopping mode [3]. Then, from Equation 3, $\log \sigma$ at a given temperature should be proportional to W , where the slope between $\log \sigma$ and W is equal to $-1/2.303 kT$ [8, 19–21].

Fig. 7 shows the relationship between $\log \sigma$ and W at $T = 405 K$. The linear relation between the two is seen, and the slope is the same as the predicted one, i.e. slope = $-1/2.303 kT$.

Fig. 8 presents the effect of V_2O_5 concentration on σ_0 , indicating almost unchanged value of σ_0 for $V_2O_5 = 30$ – 60 mol %.

From both these results, we conclude the conduction of the present glasses to be due to adiabatic small polaron hopping of electrons. The adiabatic hopping was reported for various vanadium tellurite glasses [19–21], and generally for $V_2O_5 > 50$ mol % [8, 19–21]. The present glasses showed this conduc-

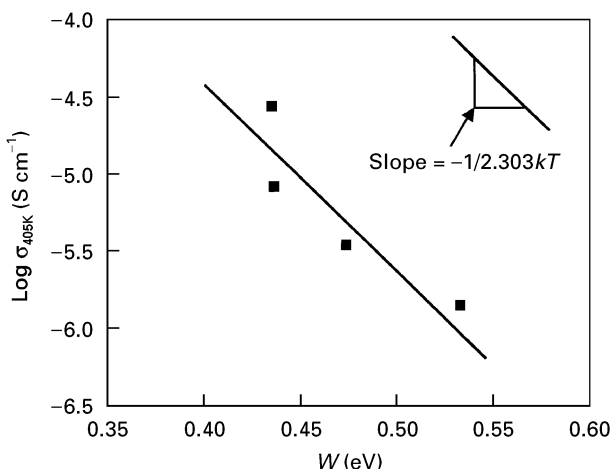


Figure 7 Effect of activation energy W on d.c. conductivity at $T = 405 K$ for different glass compositions.

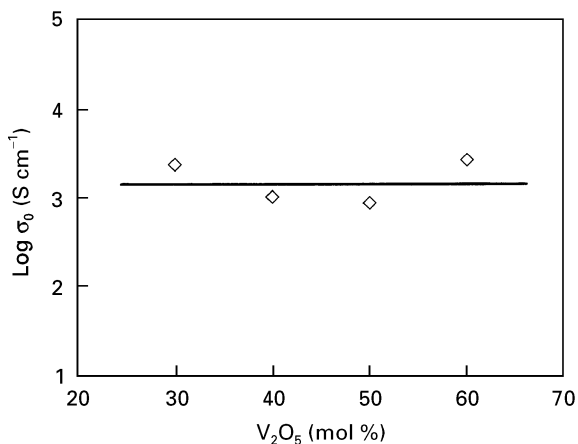


Figure 8 Effect of V_2O_5 content on pre-exponential factor σ_0 for V_2O_5 – MnO – TeO_2 glasses.

tion mode for $V_2O_5 > 30$ mol %. As the adiabatic regime occurs at shorter V ion spacing in high V_2O_5 concentration [8, 19–21], the above result may be due to the effect of Mn ion on hopping between V ions.

We estimated W_H from the W data (Table I), using Equation 4a. For V_2O_5 – TeO_2 glasses [7], $W_D < 0.05$ eV at room temperature, and normally W_D is less than 0.09 eV for V_2O_5 – Bi_2O_3 [9] glasses. Assuming $\Theta_D = 300$ – $500 K$ for our glasses, because $\Theta_D = 340$ – $500 K$ for V_2O_5 – P_2O_5 glasses [29], and $W_D \approx 0.01$ eV, we obtained $W_H = 0.428$ – 0.527 eV for different glass compositions in the temperature range 475–395 K.

Fig. 9 shows the relationship of W against R , i.e. V_2O_5 concentration. Here we regarded R as the V–V ion spacing calculated from $R = N^{-1/3}$, on the basis of the glass densities measured. W increases with an increase in R , which was admitted for various vanadate glasses [17, 19, 20, 30]. W depends on the distance between hopping sites [31, 32], and it is expressed as $W = W_0 + a(R - R_0)$ [30]. Our results nearly satisfy this relation (Fig. 9), and we have $a = 1.4$ eV nm $^{-1}$. Hirashima *et al.* [15] found that for Fe_2O_3 – V_2O_5 – P_2O_5 glasses with high Fe_2O_3 contents (more than 25 mol %), W was lowered notably than W for the glasses with lower Fe_2O_3 contents; they suggested hopping between V and Fe ions in addition to that between V ions. In the present study, we did not find such cases (Table I). Accordingly, so far as the present glasses with $MnO = 0$ – 20 mol % is concerned, the hopping is considered to be mainly that between V ions.

The polaron band width or the electron overlap integral J is related to W for adiabatic [33] and non-adiabatic [34] hopping as

$$W \approx W_H = W_p/2 = (W'_p/2) - J \quad (\text{adiabatic}) \quad (7)$$

$$W \approx W_H = W'_p/2 \quad (\text{non-adiabatic}) \quad (8)$$

where W_p is the polaron binding energy, W'_p the maximum polaron binding energy. J depends on R [30, 35, 36], so W_H depends on R for adiabatic hopping regime. From Equation 8 we can roughly estimate $W'_p/2$ by referring to the W data in Table I.

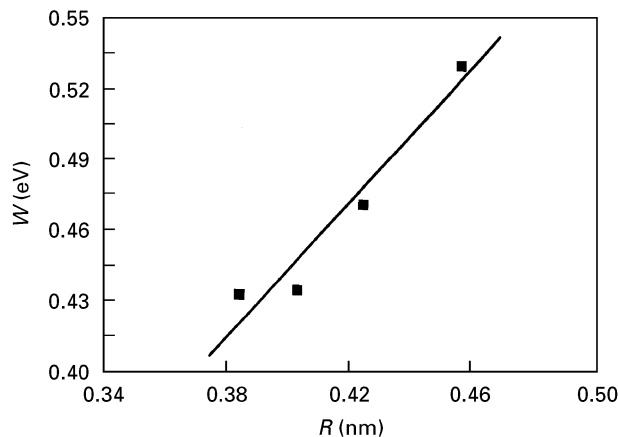


Figure 9 Effect of mean V ion spacing R on activation energy for conduction W .

TABLE II Polaron hopping parameters for V_2O_5 -MnO- TeO_2 glasses

Glass composition ^a			W_H (eV)	J (eV)	r_p (nm)	ϵ_p	$N(E_F)$ ($eV^{-1}cm^{-3}$)	μ ($cm^2V^{-1}s^{-1}$)	N_c (cm^{-3})	γ_p
V_2O_5	MnO	TeO_2								
60	10	30	0.428	0.20	0.1547	3.24	2.9×10^{18}	2.64×10^{-6}	8.9×10^{19}	21
50	10	40	0.430	0.20	0.1624	3.07	2.4×10^{18}	2.75×10^{-6}	2.4×10^{19}	21
40	10	50	0.468	0.16	0.1708	2.68	1.0×10^{18}	1.05×10^{-6}	2.8×10^{19}	23
30	10	60	0.527	0.10	0.1837	2.21	2.4×10^{17}	2.34×10^{-7}	5.5×10^{19}	26

^a Nominal composition (mol%). μ and N_c values at $T = 415$ K; J and $N(E_F)$ values at $T = 405$ K.

In the non-adiabatic regime, σ becomes lower than those extrapolated in adiabatic region for a fixed W [8, 19, 20]. The extrapolation of σ to a very low value of σ , i.e. $\log \sigma \simeq -7$ (lower V_2O_5 content, hence non-adiabatic) along the experimental curve (Fig. 7), yields $W_{max} - W_D \simeq W_H = W'_p/2 = 0.63$ eV assuming $W_D = 0.01$ eV. Note that, as for J , the following condition should be satisfied for small polaron hopping [36].

$$J < W_H/3 = (W'_p/2)/3 \quad (9)$$

From Equation 9 with $W_H \simeq 0.63$ eV, we have $J < 0.21$ eV. Next, J also satisfies [30, 33, 36, 37]

$$J > (2kTW_H/\pi)^{1/4} (h\nu_0/\pi)^{1/2} \quad (\text{adiabatic}) \quad (10)$$

$$J < (2kTW_H/\pi)^{1/4} (h\nu_0/\pi)^{1/2} \quad (\text{non-adiabatic}) \quad (11)$$

With $W_{min} = 0.433$ eV, we estimate, with Equation 10, $J > 0.036$ eV. As a result, we have 0.036 eV $< J < 0.21$ eV at 405 K for the present system. J values were obtained using Equation 7 for W_H values of different glass compositions in the temperature range 395–475 K. We had $J = 0.10$ – 0.20 eV, as given in Table II. From Tables I and II we find an increase in J with decreasing R , which is the same result for PbO - P_2O_5 - V_2O_5 glasses [8] and V_2O_5 - Sb_2O_3 - TeO_2 glasses [20].

The polaron radius r_p is given by [38]

$$r_p = (\pi/6)^{1/3} R/2 \quad (12)$$

r_p was then estimated to be $r_p = 0.1547$ – 0.1387 nm (Table II) from $R = 0.384$ – 0.456 nm (Table I). The polaron hopping energy given by $W_H = W_p/2$ is expressed by [13]

$$W_H = W_p/2 = (e^2/4\epsilon_p)(r_p^{-1} - R^{-1}) \quad (13)$$

where $\epsilon_p^{-1} = \epsilon_\infty^{-1} - \epsilon_0^{-1}$, and ϵ_0 and ϵ_∞ are the static and high-frequency dielectric constants of the glass, respectively, and ϵ_p the effective dielectric constant.

With W_H , r_p and R values, we had $\epsilon_p = 2.21$ – 3.24 (Table II) for $V_2O_5 = 30$ – 60 mol %, smaller than those of V_2O_5 - Bi_2O_3 doped with $BaTiO_3$ microcrystals [39]. J is expressed in terms of the state density at the Fermi level $N(E_F)$ as follows [7]

$$J \simeq e^3 N(E_F)^{1/2} / \epsilon_p^{3/2} \quad (14)$$

We obtained $N(E_F) = 2.4 \times 10^{17}$ – 2.9×10^{18} $eV^{-1}cm^{-3}$ at 405 K, as shown in Table II with the

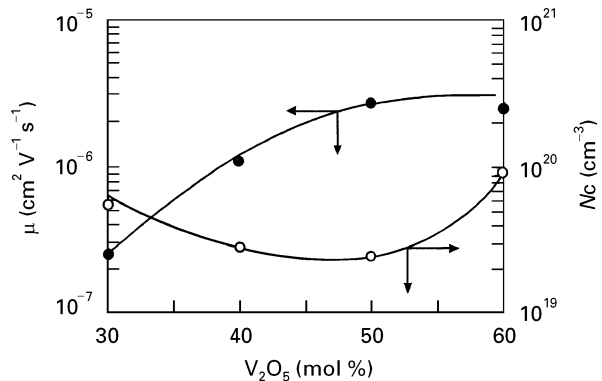


Figure 10 Effect of V_2O_5 content on hopping mobility μ and carrier concentration N_c .

estimated J and ϵ_p data (Table II), which are smaller than $N(E_F) = 7.33 \times 10^{19}$ – 8.45×10^{20} $eV^{-1}cm^{-3}$ at 230 K for V_2O_5 - SnO - TeO_2 glasses [40] obtained from the analysis of variable-range hopping [41].

The values of small polaron coupling constant γ_p , a measure of the electron-phonon interaction, given by the formula $\gamma_p = 2W_H/h\nu_0$ [42] were also evaluated for the present glasses. The estimated value of γ_p is 21–26 (Table II), which is larger than those for V_2O_5 - Bi_2O_3 glasses doped with $BaTiO_3$ (7.05–7.60) [39]. Such large values are indicative of a strong electron-phonon interaction of the present glasses.

The hopping carrier mobility, μ , and concentration, N_c were estimated for the present glasses. For adiabatic hopping regime, μ is given by [43]

$$\mu = (v_0 eR^2/kT) \exp(-W_H/kT) \quad (15)$$

Then, μ values were calculated for $T = 416$ K using the experimental data of R and W_H evaluated for different V_2O_5 concentrations (Table I and II) and assuming $v_0 = 10^{13}$ Hz. Also N_c values were evaluated using the formula $\sigma = eN_c\mu$.

The results are shown in Fig. 10 and Table II, indicating that the hopping mobility increases with V_2O_5 increase. The increase is expressed by the experimental relation $\mu \sim \mu_0 \exp[V_2O_5]$, similar to V_2O_5 - Bi_2O_3 - TeO_2 glasses [44]. μ values were evaluated to be 2.34×10^{-7} – 2.75×10^{-6} $cm^2V^{-1}s^{-1}$ and N_c values 2.4×10^{19} – 8.9×10^{19} cm^{-3} , being the same order as those for V_2O_5 - Sb_2O_3 - TeO_2 glasses [20]. Because the localization condition for hopping

electrons is $\mu \ll 0.01 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ [43], the results mean that electrons in the present glasses are localized mainly at V ion site. Further, the nearly constant $N_c \sim 10^{19} \text{ cm}^{-3}$ indicates that the conductivity of the glasses is primarily determined by the hopping mobility.

4. Conclusions

We have prepared semiconductive glasses in the system $\text{V}_2\text{O}_5\text{-MnO-TeO}_2$ and the d.c. conduction mechanism was investigated on the basis of temperature dependence of conductivity. The glasses were *n*-type semiconducting with d.c. conductivity of 5×10^{-5} – $1.9 \times 10^{-6} \text{ S cm}^{-1}$ for $\text{V}_2\text{O}_5 = 60 \text{ mol } \%$ and $\text{MnO} = 0\text{--}20 \text{ mol } \%$ at 405 K.

The conduction was confirmed to obey the adiabatic small polaron hopping model, and was due to mainly electronic hopping between V ions.

The polaron band width J was estimated to be $J = 0.10\text{--}0.20 \text{ eV}$. The electron–phonon interaction coefficient γ_p was very large (21–26). The estimated hopping mobility was very low (2.3×10^{-7} – $2.7 \times 10^{-6} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$) and increased with increasing V_2O_5 concentration.

Nearly invariable values of the estimated carrier concentration ($\sim 10^{19} \text{ cm}^{-3}$) indicated the principal factor determining conductivity to be the polaron hopping mobility.

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Received 15 November 1996

and accepted 24 July 1997