

## Multiphonon tunneling conduction in vanadium-cobalt-tellurite glasses

H. Sakata and K. Sega

*Department of Applied Chemistry, Tokai University, 1117, Kitakaname, Hiratsuka, Kanagawa 259-1292, Japan*

B. K. Chaudhuri

*Indian Association for the Cultivation of Science, Jadavpur, Calcutta 700 032, India*

(Received 20 August 1998; revised manuscript received 4 February 1999)

Ternary vanadium oxide glasses in the system  $V_2O_5$ -CoO- $TeO_2$  are fabricated by press quenching of glass melts, and dc conductivities ( $\sigma$ ) are investigated at temperatures from 330 to 475 K for different glass compositions. From the study of the phase diagram, the glass formation region is found to be in the range of  $V_2O_5=0-85$  mol %,  $CoO=0-35$  mol %, and  $TeO_2=25-100$  mol %. These glasses contain microcrystalline clusters dispersed in the glass matrix. In the high-temperature regime above  $\Theta_D/2$  ( $\Theta_D$  is the Debye temperature), the small polaron hopping model is found to be applicable. In the low temperature (below  $\Theta_D/2$ ) regime, however, both Mott's variable-range hopping and the Greaves' intermediate range hopping models are found to be not applicable. The most probable transport for the entire range of temperature and compositions is concluded to be due to multiphonon tunneling of large polarons between the microclusters, supporting the model proposed by Shimakawa. [S0163-1829(99)03029-5]

### I. INTRODUCTION

The dc conductivities of transition metal oxide (TMO) glasses has been targeted for extensive studies<sup>1-9</sup> because of their interesting semiconducting properties as well as for their probable technological applications. The conduction mechanism in these glasses was understood by the small polaron hopping (SPH) model<sup>10,11</sup> based on strong electron-lattice interaction. The experimental results of conductivity and other transport properties of many binary<sup>1-3,4,6</sup> and ternary<sup>5,7-9</sup> vanadate glasses supported the SPH model.

At low temperatures (below  $\Theta_D/2$ ,  $\Theta_D$  is the Debye temperature) where polaron binding energy is less than  $kT$  ( $k$  is the Boltzmann constant and  $T$  is the absolute temperature), the three-dimensional (3D) variable-range hopping (VRH) (Ref. 12) with  $T^{1/4}$  dependence of conductivity ( $\sigma$ ) takes place. The VRH was reported for  $V_2O_5$ - $TeO_2$  (Ref. 3) or  $Bi_2O_3$  (Ref. 6) glasses and  $V_2O_5$ - $Bi_2O_3$ - $BaTiO_3$  (Ref. 13) and similar other vanadate glasses. We also reported VRH in  $V_2O_5$ - $SnO$ - $TeO_2$  glasses.<sup>14</sup> It should be mentioned that the above two models were based, in common, on a single phonon approach.

Recently Shimakawa,<sup>15</sup> assuming microclusters in a glass network, revealed that the dc and ac conduction of  $V_2O_5$ - $P_2O_5$  (Refs. 1,16) and  $V_2O_5$ - $TeO_2$  (Ref. 17) glasses could be interpreted by multiphonon tunneling of large polarons between microclusters in the glass. The conductivity in this model is given by  $\sigma \propto (T/T_0)^n$ , where  $n$  is a constant depending on glass composition<sup>15</sup> and  $T$  is temperature. This multiphonon tunneling model of Shimakawa<sup>15</sup> considering polaron hopping between microclusters in the glass network has not been well investigated. The multicomponent glasses that we have prepared are found to contain microcrystalline phases embedded in the glass matrix. So there is a good chance of verifying the Shimakawa's model<sup>15</sup> with samples of our present investigation.

Here it should be pointed out that compared to the TMO

glasses with single transition metal ion (TMI), conductivities of relatively small number of oxide glasses containing two TMI's have so far been thoroughly investigated.<sup>7,9,18,19</sup> The effect of the second transition metal ion on the overall conductivity is found to be different in different systems. That is, it decreases<sup>18</sup> or increases<sup>20</sup> with the addition of the second TMI. For  $Fe_2O_3$ - $V_2O_5$ - $P_2O_5$  glasses,<sup>20</sup> a SPH transport between Fe and V ions in addition to the SPH between V ions was suggested.

In the present work, we report the conductivity of a  $V_2O_5$ -CoO- $TeO_2$  type glassy system prepared by adding CoO to the  $V_2O_5$ - $TeO_2$  oxide mixtures. Interestingly, these glasses are found to contain microcrystalline clusters dispersed in the glass matrix. They also show some interesting features along with decreasing effect on conductivity with increase of Co content. The main objective of this work is to explain the accurately measured conductivity data of these glassy materials with two TM ions with an appropriate theoretical model.

### II. EXPERIMENT

Reagent grade  $V_2O_5$  (99.99%), CoO (99.99%), and  $TeO_2$  (99.99%) were used as raw materials. After mixing in air a batch of 6 g with prescribed compositions, the mixed mass of each glass composition was melted in alumina crucible for 1 h at 1023 K in an electric furnace. The melt was then poured on a thick copper block and immediately quenched by pressing with another similar copper block. Following this procedure we obtained bulk glass of  $2 \times 2$  cm<sup>2</sup> size and about 1 mm in thickness.

The glass forming region was determined by X-ray diffraction analysis (Philips, X'pert System PW 3020). The glass transition temperature ( $T_g$ ) was determined by differential thermogravimetric analysis (DTA) (Rigaku, DSC8230/TAS300) of the glass samples at a heating rate of 10 °C min<sup>-1</sup>. The density ( $d$ ) of glasses were determined by

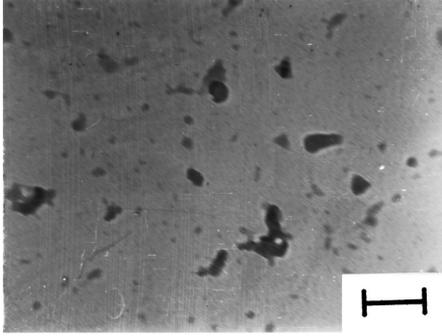


FIG. 1. Transmission electron micrograph of the 60V<sub>2</sub>O<sub>5</sub>-10CoO-30TeO<sub>2</sub>(mol %) glass (scale: 0.1  $\mu$ m).

the Gay-Lussac method using toluene as an immersion liquid.

The dc conductivity ( $\sigma$ ) of the as-quenched glasses was measured at temperatures between 330 and 475 K using the four-point probe technique, a constant dc current of 0.1  $\mu$ A being applied between the electrodes using silver paste with a spacing of 2 mm. The Seebeck coefficient ( $Q$ ) for the glasses was determined by measuring the thermoelectric power of the glass samples with a temperature difference of 10 K between the two electrodes as reported earlier.<sup>21</sup> To study the presence of microclusters in the glass, a transmission electron microscopic study of the fine glass powder on carbon-grids was made using an electron microscope (Hitachi: Model H6000).

### III. RESULTS

The x-ray diffraction (XRD) pattern of these glasses (with Cu  $K\alpha$  radiation) indicated homogeneous glassy character without showing any crystalline peak. However, a transmission electron microscopic study indicated the presence of microcrystalline grains (20 to 40 nm in size) (Fig. 1) uniformly distributed in the glass matrix. Their concentration is very small not detected from the XRD patterns of the glasses. So the glasses of our investigation are actually glass-nanocrystal composites. Similar behavior for all the V<sub>2</sub>O<sub>5</sub>-CoO-TeO<sub>2</sub> glassy system is observed. From an EPMA observation of V, Co, and Te elements in the glass, we found a homogeneous distribution of each constituent element and no phase separation was observed. Figure 2 shows the glass formation region:  $0 \leq V_2O_5 \leq 85$  mol % ,

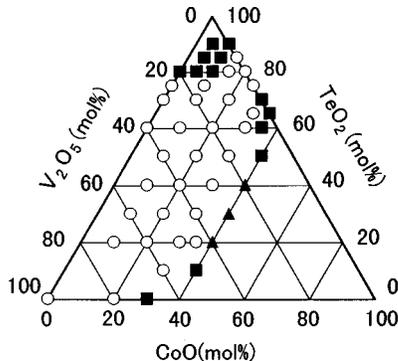


FIG. 2. Glass formation region of V<sub>2</sub>O<sub>5</sub>-CoO-TeO<sub>2</sub> glasses: ○, glass; ■, crystallized; ▲, not melted.

TABLE I. Chemical composition and physical properties of glasses.

Glass composition (mol %) <sup>a</sup>			$d^c$	$T_g^d$	$\sigma_0$	$W^b$	$R$
V <sub>2</sub> O <sub>5</sub>	CoO	TeO <sub>2</sub>	(g cm <sup>-3</sup> )	(K)	(S cm <sup>-1</sup> K)	(eV)	(nm)
70	10	20	3.095	513	$1.72 \times 10^5$	0.561	0.400
60	10	30	3.463	520	$3.79 \times 10^4$	0.538	0.404
50	10	40	3.832	529	$1.83 \times 10^4$	0.540	0.413
40	10	50	4.200	540	$7.71 \times 10^2$	0.511	0.429

<sup>a</sup>Nominal composition.

<sup>b</sup>475–435 K.

<sup>c</sup>Accuracy in the density measurement,  $\pm 1\%$ .

<sup>d</sup>Accuracy in the measurement of  $T_g$ ,  $\pm 2$  K.

$0 \leq \text{CoO} \leq 35$  mol % , and  $25 \leq \text{TeO}_2 \leq 100$  mol % . The density ( $d$ ) and  $T_g$  data are given in Table I.

The Seebeck coefficients ( $Q$ ) for these glasses with different compositions were measured. As shown in Table II, the negative values indicate  $n$ -type semiconducting behavior of these glasses. No temperature dependence of  $Q$  was observed, which is similar to many other vanadate glasses.<sup>22,23</sup> No dc polarization was observed.

Figure 3 shows the Arrhenius plot of  $\ln(\sigma T)$  between 475 and 395 K. Deviation from a linear curve occurs around  $\Theta_D/2$  ( $\sim 240$ – $190$  K, depending concentration), where  $\Theta_D$  is the Debye temperature. Figure 3 indicates a temperature dependent activation energy. The experimental conductivity data in such a situation is well described with an activation energy for conduction ( $W$ ) given by the Mott formula<sup>10,11</sup>

$$\sigma = (\sigma_0/T) \exp(-W/kT), \quad (1)$$

where  $\sigma_0$  is a temperature independent parameter as discussed below.  $W$  values obtained from fitting of the linear part of the curves in Fig. 3 (high-temperature regime, 475–435 K) are given in Table I together with the mean spacing ( $R$ ) for the V-O-V chains calculated from glass density ( $d$ ) using  $R = (1/N)^{1/3}$  (where  $N$  is the V-ion density). At temperatures lower than 395 K the linearity between  $\ln(\sigma T)$  and  $T^{-1}$  deviated appreciably as seen from Fig. 3.

Figures 4 and 5 present the effects of V<sub>2</sub>O<sub>5</sub> and CoO contents on  $\sigma$ . At 425 K,  $\sigma$  was found to be  $9.4 \times 10^{-5}$ – $2.3 \times 10^{-6}$  S cm<sup>-1</sup> for CoO=0–30 mol % . The conductivity increased with increasing V<sub>2</sub>O<sub>5</sub> content for a fixed CoO content (Fig. 4), while it decreased with an increase of CoO content (Fig. 5).

TABLE II. Seebeck coefficient of V<sub>2</sub>O<sub>5</sub>-CoO-TeO<sub>2</sub> glasses.

Glass composition (mol %) <sup>a</sup>			Temperature (K)			
V <sub>2</sub> O <sub>5</sub>	CoO	TeO <sub>2</sub>	405	430	445	455
			–Seebeck coefficient ( $\mu$ V K <sup>-1</sup> ) <sup>b</sup>			
60	0	40	556	547	546	547
60	10	30	596	583	600	605
60	20	20	635	638	611	634

<sup>a</sup>Nominal composition.

<sup>b</sup>Accuracy in the measurement,  $\pm 10$   $\mu$  V K<sup>-1</sup>.

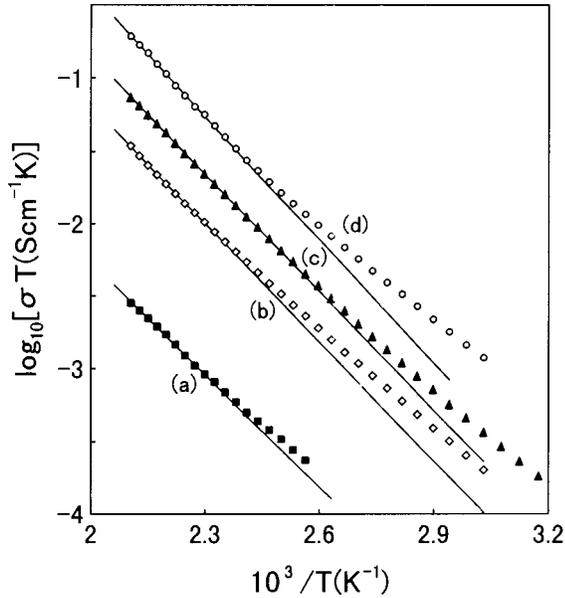


FIG. 3. Temperature dependence of dc conductivity for  $x\text{V}_2\text{O}_5$  10CoO (90- $x$ )TeO<sub>2</sub> (mol %) glasses: (a)  $x=40$ ; (b)  $x=50$ ; (c)  $x=60$ ; (d)  $x=70$ . The scale for  $\sigma T$  is  $\log_{10}(\sigma T)$ .

#### IV. DISCUSSION

The glass formation region of the glasses of the present investigation (Fig. 2) is similar to that of the  $\text{V}_2\text{O}_5$ -MnO-TeO<sub>2</sub> glasses.<sup>21</sup> The area of the region generally depends on  $\Delta T = T_c - T_g$  ( $T_c$  is crystallization temperature) and the values of  $\Delta T$  are similar to those of the  $\text{V}_2\text{O}_5$ -MnO-TeO<sub>2</sub> glasses (e.g.,  $\Delta T = 60$  K) studied earlier.<sup>21</sup>

With an increase of  $\text{V}_2\text{O}_5$  content in the glass, the conductivity increased (Fig. 4). This means a decrease in the V-O-V spacing  $R$  as indicated in Table I, which raises the hopping probability, providing that the activation energy ( $W$ ) and the fraction of reduced transition metal ion ( $C$ ) are almost unchanged for varying compositions, as seen later in the SPH model. In the  $\text{V}_2\text{O}_5$ -CoO-TeO<sub>2</sub> glasses of our present investigation, the CoO addition lowered the conductivity (Fig. 5). This means, Co ion in the glass hindered the carrier transport. Because CoO is not a glass network former, the Co ions are isolated in the glass network, which causes obstruction in the hopping of electrons due to the lack of oxygen bonds. A similar lowering of conductivity was also

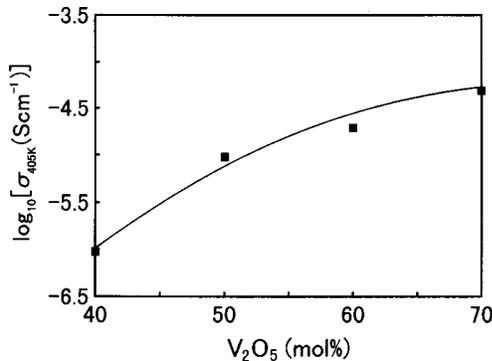


FIG. 4. Effect of  $\text{V}_2\text{O}_5$  content on dc conductivity of  $x\text{V}_2\text{O}_5$  10CoO (90- $x$ )TeO<sub>2</sub> (mol %) glasses at 405 K.

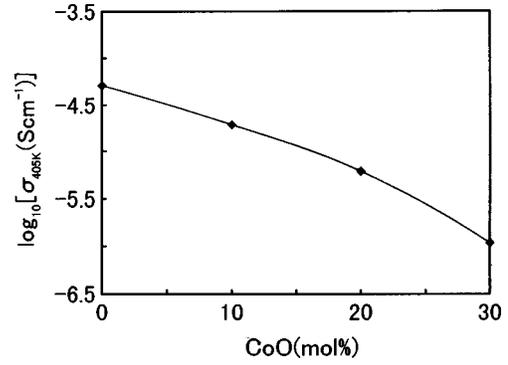


FIG. 5. Effect of CoO content on dc conductivity of  $60\text{V}_2\text{O}_5$   $x\text{CoO}$  (40- $x$ )TeO<sub>2</sub> (mol %) at 405 K.

observed in  $\text{TiO}_2$ - $\text{V}_2\text{O}_5$ - $\text{P}_2\text{O}_5$  (Ref. 18) and  $\text{V}_2\text{O}_5$ -MnO-TeO<sub>2</sub> (Ref. 21) glasses.

The logarithm of the conductivity (Fig. 3) shows a linear temperature dependence up to a critical temperature  $T_D$  ( $\sim \Theta_D/2$ ) and then the slope changes with deviation from linearity, and the activation energy is temperature dependent. Such a behavior is a feature of small polaron hopping.<sup>1</sup> So we first discuss the thermal variation of conductivity assuming the SPH model<sup>10,11</sup> based on a strong coupling of electron with the lattice by a single phonon. This model gives  $\sigma$  in the nonadiabatic regime for TM oxide glasses as given by Eq. (1) viz.

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

The activation energy  $W$  can be written as

$$W = W_H + W_D/2 \quad (\text{for } T > \Theta_D/2), \quad (3a)$$

$$W = W_D \quad (\text{for } T < \Theta_D/4). \quad (3b)$$

The temperature independent conductivity in Eq. (1) is given by

$$\sigma_0 = \nu_0 N e^2 R^2 C (1-C) \exp(-2\alpha R)/k, \quad (4)$$

where  $\nu_0$  is the optical phonon frequency ( $\sim 1 \times 10^{13}$  Hz) obtained from the Debye temperature given in Table III,  $R$  is the mean spacing between transition metal ions given by  $R = N^{-1/3}$ ,  $\alpha$  is the tunneling factor,  $W_H$  is the polaron hopping energy,  $W_D$  is the disorder energy, and  $C$  is the fraction of reduced transition metal ion. The values of  $W$  and  $\sigma_0$  shown in Table I are estimated from Fig. 3. The values of  $W$  increases from 0.511 to 0.561 eV for different glass compositions indicating an increase in conductivity (Fig. 3). Although the exact formula of  $C$  for TMO glasses with two TMI is not yet known, we assume  $C = 0.35, 0.315, 0.285, 0.25$  for the  $\text{V}_2\text{O}_5 = 40-70$  mol % (Table I), referring to the data from the  $\text{Fe}_2\text{O}_3$ - $\text{V}_2\text{O}_5$ - $\text{P}_2\text{O}_5$  glasses.<sup>20</sup> These values of  $C$  and other parameters shown in Table III were fitted to the linear part of the conductivity data in the high temperature regime (above  $\Theta_D/2$ ). The values of  $\alpha$  thus estimated from the fitting are given in Table III. These values are somewhat larger than those of the binary glasses<sup>3,6</sup> with single transition metal ions. This may be due to the effect of heterogeneity of the present glasses containing microclusters in the glass matrix.

TABLE III. Parameters for small polaron hopping conduction.

Glass composition (mol %) <sup>a</sup>			$N$	$C^b$	$\alpha$	$\nu_0$	$\sigma_0^c$	$\alpha'$	$\sigma_0$ (cryst)
$V_2O_5$	CoO	TeO <sub>2</sub>	( $10^{22} \text{ cm}^{-3}$ )		( $\text{nm}^{-1}$ )	( $10^{13} \text{ Hz}$ )	( $10^{-18}$ )	( $\text{nm}^{-1}$ )	( $\text{S cm}^{-1} \text{ K}$ )
70	10	20	1.650	0.250	64.1	1.70	7.7	0.25	$1.21 \times 10^5$
60	10	30	1.516	0.285	64.8	1.65	2.9	1.6	$4.24 \times 10^4$
50	10	40	1.419	0.315	65.0	1.67	0.78	1.9	$3.37 \times 10^4$
40	10	50	1.266	0.350	66.5	1.68	0.028	6.0	$9.62 \times 10^2$

<sup>a</sup>Nominal composition.<sup>b</sup>From Ref. 20.<sup>c</sup>In  $\text{S cm}^{-1} \text{ K}$  calculated from Eq. (4).

We examined the pre-exponential factor  $\sigma_0$  in Eq. (4) with the experimental data. Estimation using Eq. (4) gives  $\sigma_0 \sim 10^{-18}$  to  $10^{-20} \text{ S cm}^{-1} \text{ K}$  (Table III), a large difference between the experimental  $\sigma_0$  values (Table I) extrapolated from the data in Fig. 3. Such a large difference between the experimentally and theoretically observed values of the temperature independent conductivity ratio is considered to be a consequence of the presence of microcrystalline clusters in these glasses (Fig. 1). We then assume the conduction in microcrystallites to be due to also SPH as well as in the glassy matrix, and conduction is then expressed as

$$\sigma = \sigma(\text{glass}) + \sigma(\text{cryst}), \quad (5)$$

where  $\sigma(\text{glass})$  is  $\sigma$  in Eq. (2),  $\sigma(\text{cryst})$  is the conductivity of microcrystals and is given by

$$\sigma(\text{cryst}) = [\sigma_0(\text{cryst})/T] \exp(-W'/kT), \quad (6)$$

where  $W'$  is the activation energy of conduction.  $\sigma_0(\text{cryst})$  is described as

$$\sigma_0(\text{cryst}) = \nu_0' N' e^2 R'^2 C' (1 - C') \exp(-2\alpha' R') / k. \quad (7)$$

The parameters with primes are defined for microcrystals as the same as those in Eq. (4).

If composition of the microcrystals is similar to that of the glass matrix, then  $W' \cong W$ . Assuming  $\nu_0' \cong \nu_0$ ,  $C' \cong C$ ,  $N' \cong N$ , and hence  $R' \cong R$ , we estimate  $\sigma_0(\text{cryst})$  for different  $\alpha'$  from Eq. (7). Estimation of gives  $\sigma_0(\text{cryst}) \sim 10^2$  to  $10^5 \text{ S cm}^{-1} \text{ K}$  (Table III), which is the same order of the  $\sigma_0$  values (Table I) obtained from the conductivity data (Fig. 3). Thus we conclude that SPH model is valid in the high temperature regime for these glasses containing microcrystals providing SPH in both glass matrix and microcrystalline clusters.

In Fig. 3 we notice that the temperature dependence of conductivity deviated from the linearity for temperatures less than 435 K (above which the SPH law is valid). We then attempted to apply variable-range hopping (VRH) (Refs. 10 and 12) as reported for binary or ternary vanadate glasses.<sup>3,6,14</sup> However, the validity of such a high temperature range is not beyond question. But it has been pointed out<sup>24</sup> that depending on the strength of Coulomb interaction the expression for the density of states at the Fermi level is modified and the VRH (Refs. 10 and 12) may be applied even at high temperatures  $\sim 300 \text{ K}$  and above, though the VRH should actually be applicable in the low temperature regime (below  $\Theta_D/4$ ) which is below 100 K. For these

glasses we, therefore, attempted to apply both the VRH models proposed by Mott<sup>10,12</sup> and Greaves<sup>25</sup> which is valid for the intermediate range of temperature. The expression for the conduction by the VRH model<sup>10,12</sup> is based on a single optical phonon approach. In this model  $\sigma$  is given by<sup>10,12</sup>

$$\sigma = B \exp(-A/T^{1/4}), \quad (8)$$

where

$$A = 4[2\alpha^3/9\pi kN(E_F)]^{1/4}, \quad (9)$$

$$B = [e^2/2(8\pi)^{1/2}] \nu_0 [N(E_F)/\alpha kT]^{1/2}, \quad (10)$$

$N(E_F)$  is the density of states at the Fermi level.  $A$  and  $B$  are obtained from the slopes of the  $\ln \sigma$  vs  $T^{-1/4}$  (Fig. 6). Then the mean hopping distance in VRH  $R_{\text{VRH}}$  and the hopping site energy ( $W_0 = W_D$ ) are evaluated from Eqs. (9) and (10) (Ref. 12),

$$R_{\text{VRH}} = 9^{1/4} / \{8\pi N(E_F) \alpha kT\}^{1/4}, \quad (11)$$

$$W_0 = 3 / \{4\pi R_{\text{VRH}}^3 N(E_F)\}. \quad (12)$$

The values of  $A$  and  $B$  are given in Table IV, which is of the order of  $10^{24} \text{ eV}^{-1} \text{ cm}^{-3}$ . This value of  $N(E_F)$  is found to be large compared with those of the TMO glasses with single

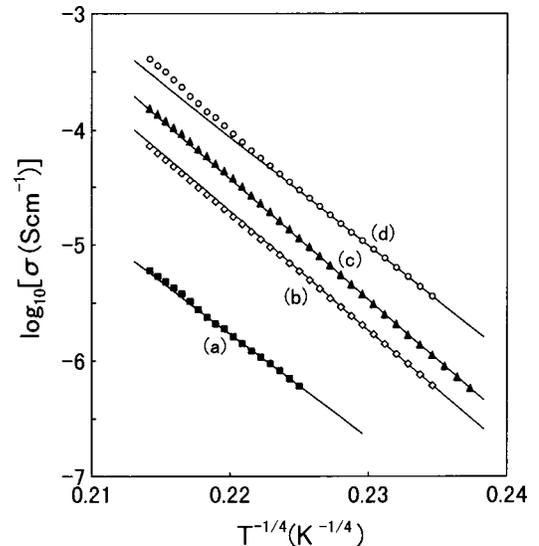


FIG. 6.  $\sigma$  vs  $T^{-1/4}$  for  $xV_2O_5 10CoO (90-x)TeO_2$  (mol %) glasses: (a)  $x=40$ ; (b)  $x=50$ ; (c)  $x=60$ ; (d)  $x=70$ . The scale for conductivity is  $\log_{10}\sigma$ .

TABLE IV. Mott parameters for variable-range hopping conduction.

Glass composition (mol %) <sup>a</sup>			A	B	$N(E_F)^b$	$R_{\text{VRH}}^b$	$W_D^b$
V <sub>2</sub> O <sub>5</sub>	CoO	TeO <sub>2</sub>	(K <sup>1/4</sup> )	(S cm <sup>-1</sup> )	(eV <sup>-1</sup> cm <sup>-3</sup> )	(nm)	(meV)
70	10	20	38.5	$5.43 \times 10^{16}$	$7.6 \times 10^{23}$	0.17	65
60	10	30	42.5	$3.11 \times 10^{18}$	$5.1 \times 10^{23}$	0.19	72
50	10	40	41.2	$7.90 \times 10^{17}$	$5.8 \times 10^{23}$	0.18	69
40	10	50	32.2	$9.83 \times 10^{13}$	$1.5 \times 10^{24}$	0.14	54

<sup>a</sup>Nominal composition.<sup>b</sup>Values calculated assuming  $\alpha = 20 \text{ nm}^{-1}$ .

TMI for which  $N(E_F)$  is of the order of  $10^{19} - 10^{21} \text{ eV}^{-1} \text{ cm}^{-3}$  (Refs. 3, 6, and 14).

We shall now apply the Greaves law<sup>25</sup> of VRH which is valid for the intermediate range of temperature (below  $\Theta_D/2$ ). According to this model,<sup>25</sup> the expression for the conductivity can be written as

$$\sigma T^{1/2} = A \exp(-B/T^{1/4}), \quad (13)$$

where  $A$  and  $B$  are constants. The slope  $B$  of  $\ln(\sigma T^{1/2})$  vs  $T^{-1/4}$  (Fig. 7) is given by

$$B = 2.1[\alpha^3/kN(E_F)]^{1/4}. \quad (14)$$

Figure 7 shows the relationship of  $\ln(\sigma T^{1/2})$  against  $T^{-1/4}$  drawn by rearranging the data from Fig. 3. The linear relationship confirms the Greaves VRH (Ref. 25) in the intermediate temperature range. The values of the parameters  $A$  and  $B$  obtained from these curves are given in Table V. The  $N(E_F)$  values were estimated from Eq. (14) assuming  $\alpha = 20 \text{ nm}^{-1}$ . The values of the density of states at the Fermi level calculated from the parameter  $B$  of the Greaves model<sup>25</sup> given in Table V ( $\sim 10^{23} \text{ eV}^{-1} \text{ cm}^{-3}$ ) are also found to be very large, compared to the usual semiconducting oxide glasses. So none of these two VRH models is found suitable to explain the low temperature (below  $\Theta_D/2$ ) conductivity data of these multicomponent glass nanocomposites. Thus

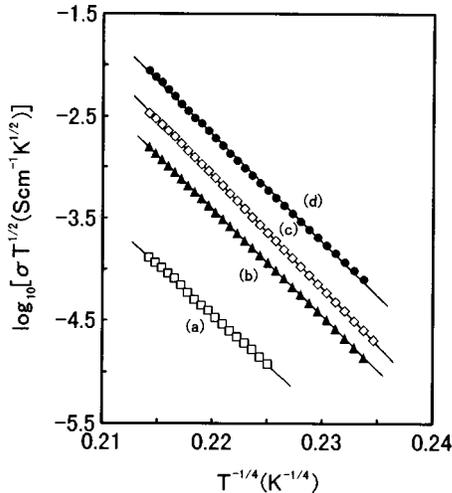


FIG. 7. Plots of  $\sigma T^{1/2}$  vs  $T^{-1/4}$  for  $x\text{V}_2\text{O}_5 10\text{CoO} (90-x)\text{TeO}_2$  (mol %) glasses: (a)  $x=40$ ; (b)  $x=50$ ; (c)  $x=60$ ; (d)  $x=70$ . The scale for  $\sigma T^{1/2}$  is  $\log_{10}(\sigma T^{1/2})$ .

TABLE V. Parameters for Greaves' variable-range hopping conduction.

Glass composition (mol %) <sup>a</sup>			B	A	$N(E_F)^b$
V <sub>2</sub> O <sub>5</sub>	CoO	TeO <sub>2</sub>	(K <sup>1/4</sup> )	(S cm <sup>-1</sup> K <sup>1/2</sup> )	(eV <sup>-1</sup> cm <sup>-3</sup> )
70	10	20	45.6	$2.62 \times 10^{20}$	$4.1 \times 10^{23}$
60	10	30	47.6	$1.11 \times 10^{21}$	$3.5 \times 10^{23}$
50	10	40	45.3	$3.46 \times 10^{19}$	$4.2 \times 10^{23}$
40	10	50	42.0	$6.82 \times 10^{16}$	$5.8 \times 10^{23}$

<sup>a</sup>Nominal composition.<sup>b</sup>Values calculated assuming  $\alpha = 20 \text{ nm}^{-1}$ .

we conclude that appearance of the VRH at  $T = 330 - 475 \text{ K}$  is rather unreasonable for the present glasses. So an alternative approach has been made to explain the experimental conductivity data for the entire range of temperature of our investigation.

Shimakawa,<sup>15</sup> assuming microclusters of the order of 8 nm in the glass network, explained dc and ac conductivities of  $\text{V}_2\text{O}_5\text{-P}_2\text{O}_5$  (Refs. 1 and 16) and  $\text{V}_2\text{O}_5\text{-TeO}_2$  (Ref. 17) glasses by a multiphonon tunneling model of large polarons (weak-coupled electron)<sup>26-28</sup> between microclusters. The conductivity of the present glasses presented  $T^{1/4}$  dependence (Fig. 6), and the structure may be similar to that for  $\text{V}_2\text{O}_5\text{-TeO}_2$  glasses. Hence we discuss the conductivity data (Fig. 3) using the multiphonon tunneling approach.<sup>15</sup>

The dc hopping conductivity is generally given by<sup>26</sup>

$$\sigma = N_c (eR)^2 \Gamma / 6kT, \quad (15)$$

where  $N_c$  is the number of localized electron,  $R$  the hopping distance, and  $\Gamma$  is the hopping rate. The hopping rate in multiphonon tunneling of localized electrons with weak electron-phonon interaction is described by<sup>26-28</sup>

$$\Gamma = [C \exp(-\gamma p)] [1 - \exp(-h\nu_0/kT)]^{-p}, \quad (16)$$

where  $C \equiv \nu_0$ ,  $p = \Delta/h\nu_0$ ,  $\nu_0$  the acoustical phonon frequency,  $\Delta$  the difference of site energy ( $W_D$  in VRH), and  $\gamma$  is a constant and a measure of electron-phonon coupling. The electron overlapping term  $\exp(-2\alpha R)$  is implicitly incorporated in  $C$  (Ref. 15). For  $h\nu_0 < kT$ , Eq. (16) is approximated by

$$\Gamma = [C \exp(-\gamma p)] (T/T_0)^p, \quad (17)$$

with  $T_0 = h\nu_0/k$ . Since  $N_c$  must be  $N(E_F)kT$ ,<sup>29</sup> we have from Eqs. (15) and (17)

$$\sigma \propto (T/T_0)^p, \quad (18)$$

where  $p$  is integral number but becomes nonintegral number, providing distribution of hopping site distance is taken into consideration.<sup>29</sup>

Figures 8 and 9 represent the relationship between  $\ln \sigma$  and  $\ln T$  for different glass compositions. The linear relationship between these two quantities is clearly seen. According to the Shimakawa model<sup>15</sup> the experimental relationship between  $\sigma$  and  $T$  is expressed as  $\sigma = \sigma'_0 T^n$  using a constant  $\sigma'_0$  depending on glass composition and  $n$ , being nonintegral number. The best fit of the data gave  $n$  values for the glasses viz.  $n = 11.7 - 13.6$  (CoO = 10 mol %) and  $n = 12.2 - 14.5$

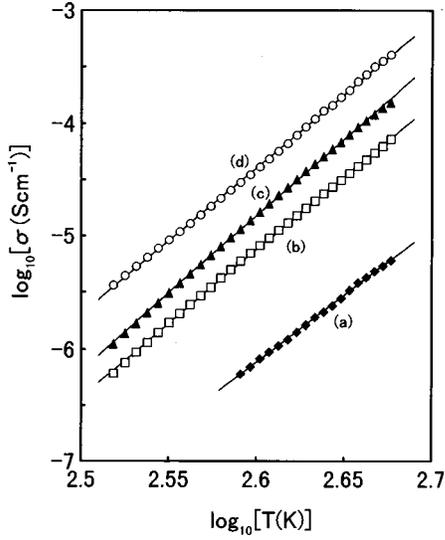


FIG. 8. Relationship between  $\sigma$  and  $T$  for  $x\text{V}_2\text{O}_5(10-x)\text{CoO}(90-x)\text{TeO}_2$  (mol %) glasses: (a)  $x=40$ ; (b)  $x=50$ ; (c)  $x=60$ ; (d)  $x=70$ . The scales for conductivity and temperature are  $\log_{10}\sigma$  and  $\log_{10}T$ .

( $\text{CoO}=20$  mol %) as shown in Table VI. These values of  $n$  are comparable with those obtained by Shimakawa for  $\text{V}_2\text{O}_5\text{-TeO}_2$  and  $\text{V}_2\text{O}_5\text{-P}_2\text{O}_5$  glasses.<sup>15</sup>

If we assume percolating microclusters in the glasses with mean size  $l_c$  (say,  $\sim 4$  nm), and  $\alpha^{-1}$  (the Bohr radius) which is larger than the mean V-O-V spacing ( $a \doteq 0.4$  nm =  $R$ , Table I), electron transfer occurs easily in the cluster. Assuming a mean separation of each cluster ( $R_c \doteq l_c$ ) and a difference of site energy  $\Delta$ , hopping of weakly coupled electron (large polaron) by tunneling is possible to occur between microclusters. Since  $\nu_0$  is given by  $(a/\alpha^{-1})\nu_D$  (Ref. 30) where  $\nu_D$  is the maximum phonon frequency (Debye frequency) and  $\nu_D = k\Theta_D/h$ ,  $\nu_0$  becomes smaller than normal  $\nu_D = 1.2 \times 10^{13}$  Hz.

Assuming  $R_c \doteq l_c \doteq \alpha^{-1} = 4$  nm and  $a = 0.4$  nm, we have  $\nu_0 = 1.2 \times 10^{12}$  Hz with  $\Theta_D \doteq 600$  K and  $T_0 = h\nu_0/k$

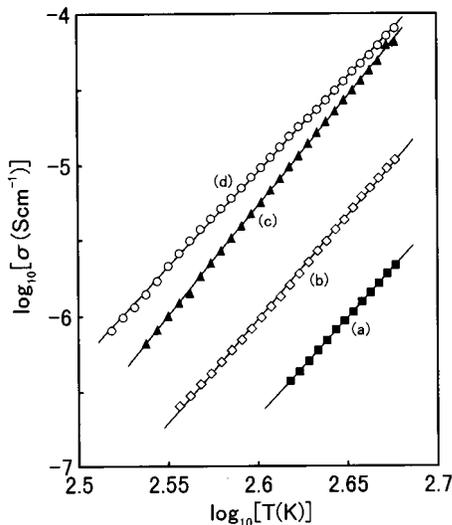


FIG. 9. Relationship between  $\sigma$  and  $T$  for  $x\text{V}_2\text{O}_5(20-x)\text{CoO}(80-x)\text{TeO}_2$  (mol %) glasses: (a)  $x=40$ ; (b)  $x=50$ ; (c)  $x=60$ ; (d)  $x=70$ . The scales for conductivity and temperature are  $\log_{10}\sigma$  and  $\log_{10}T$ .

TABLE VI. Physical parameters for multiphonon tunneling conduction. ( $\nu_0 = 1.2 \times 10^{12}$  Hz and  $T_0 = 57.6$  K are used for calculation).

Glass composition (mol %)							$\Delta$
$\text{V}_2\text{O}_5$	$\text{CoO}$	$\text{TeO}_2$	$n$	$-\log_{10}\sigma'_0$	$\gamma$	$G$	(meV)
70	10	20	13.00	38.2	2.76	1.5	64
60	10	30	13.65	40.3	2.79	1.5	68
50	10	40	12.97	38.9	2.89	1.3	64
40	10	50	11.72	36.6	3.19	0.9	58
70	20	10	12.29	36.9	2.92	1.2	61
60	20	20	14.53	43.1	2.81	1.6	72
50	20	30	13.69	41.6	2.99	1.3	68
40	20	40	12.98	40.4	3.16	1.0	64

$= 57.6$  K. A single-phonon process such as VRH cannot take place under the small  $\nu_0$ , provided the site energy  $\Delta$  is comparable or larger than  $h\nu_0$ , and this is possible because  $\Delta/h\nu_0 = n = 11-14$  from the data in Table VI. Using the experimental  $p$  values combined with Eqs. (15) and (17), we estimated  $\gamma$  and  $\Delta$  for the present glasses [assuming  $N(E_F) = 2.9 \times 10^{20} \text{ eV}^{-1} \text{ cm}^{-3}$  (Ref. 14)]. For a  $50\text{V}_2\text{O}_5\text{-}10\text{CoO}\text{-}40\text{TeO}_2$  (mol %) glass, for example, we obtained  $\gamma = 2.87$ ,  $\Delta = 64$  meV, and  $\Gamma = 7.706 \times 10^{-5} (T/57.6)^{12.97}$  (Hz).

The condition of occurring multiphonon tunneling process is  $\gamma = 2-3$  (Ref. 26). In the weak electron-lattice interaction,  $\gamma = \ln(\Delta/E_M) - 1$ , where  $E_M$  is the measure of the electron-lattice coupling strength.<sup>15</sup> The weak-coupling condition is that  $G = (E_M/h\nu_0)(kT/h\nu_0)$ , nearly less than 1 (Ref. 31). From  $\gamma$ , we have  $\Delta/E_M = p h \nu_0 / E_M$ , which gives  $E_M/h\nu_0$  with  $p (=n)$  values. The values for  $\Delta$ ,  $\gamma$ , and  $G$  thus estimated are presented in Table VI. These  $\gamma$  and  $G$  values satisfy the condition  $\gamma = 2-3$  (Ref. 26) or  $G < 1$  (Ref. 31). Accordingly, we conclude that the multiphonon tunneling conduction of weakly coupled electrons is the most probable carrier transport in the present glasses.

## V. CONCLUSION

Semiconducting  $\text{V}_2\text{O}_5\text{-CoO-TeO}_2$  glasses were prepared by the press-quenching technique from the melts and the dc conduction mechanism was investigated in terms of different physical models. The glass formation region was found to be  $0 \leq \text{V}_2\text{O}_5 \leq 85$  mol %,  $0 \leq \text{CoO} \leq 35$  mol % and  $25 \leq \text{TeO}_2 \leq 100$  mol %. The x-ray diffraction patterns of the glasses exhibited amorphous character, but transmission electron microscopic study of the glass together with electron diffraction revealed microcrystallites in the glass matrix. Glasses were found to be  $n$ -type semiconducting. The inverse temperature dependence of  $\ln(\sigma T)$  in the range 330–475 K gave linearity but deviated from linearity for temperatures less than about 435 K.

The high temperature (above  $\Theta_D/2$ ) dependence of conductivity could be qualitatively explained by the small polaron hopping model. Moreover, the low temperature (below  $\Theta_D/2$ ) conductivity data could not be explained either by Mott's or Greaves' variable-range hopping model giving rise to unusually large values of the density of states at the Fermi

level compared to those of transition metal oxide glasses. These are special features observed in the multicomponent semiconducting glasses with two transition metal ions and containing microcrystalline clusters. Presence of such a microcrystalline or nanocrystalline phase in the glass matrix also effects the frequency dependent conductivity and dielectric constant as in the case of  $V_2O_5$ - $Bi_2O_3$  (Ref. 32) and  $V_2O_5$ - $PbO$  (Ref. 33) glasses containing a  $BaTiO_3$  phase. These glasses show very high dielectric permittivity. Recently we have also observed (unpublished) a very large dielectric constant in  $V_2O_5$ - $P_2O_5$  glasses containing a nano-

crystalline  $TiO_2$  phase. The ac conductivity is also similarly effected since ac conductivity and the imaginary part of the dielectric constant are related to each other.

Finally, considering microclusters present in these glasses, the multiphonon tunneling conduction between microclusters by large polarons (weakly coupled electron) was found to be the possible mechanism of conduction in the  $V_2O_5$ - $CoO$ - $TeO_2$  glasses with two transition metal ions. Similar approach could be extended to many other multicomponent TMO glasses containing microcrystalline or nanocrystalline clusters.

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