JOURNAL OF MATERIALS SCIENCE 31 (1996) 1621–1624

Seebeck coefficient of V_2O_5–R_2O_3–TeO_2 (R = Sb or Bi) glasses

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The thermoelectric power of glasses in the systems V_2O_5–Sb_2O_3–TeO_2 and V_2O_5–Bi_2O_3–TeO_2 was measured at temperatures in the range 373–473 K. The glasses in both systems were found to be n-type semiconductors. The Seebeck coefficient, Q, at 473 K was determined as -192 to -151 $\mu V K^{-1}$ for V_2O_5–Sb_2O_3–TeO_2 glasses, and -391 to -202 $\mu V K^{-1}$ for V_2O_5–Bi_2O_3–TeO_2 glasses. For these glasses in both systems, Heikes' formula was satisfied adequately for the relationship between Q and $\ln[C_V/(1-C_V)]$ ($C_V = V^{4+}/V_{total}$, C_V is the ratio of the concentration of reduced vanadium ions), and discussions confirmed small polaron hopping conduction of the glasses in both systems. Mackenzie's formula relating to Q and V^{5+}/V^{4+} was also applicable to the glasses in both systems, and it was concluded that the dominant factor determining Q was C_V.

1. Introduction

Electrical conduction of glasses containing transition metal oxides (TMO) has been extensively studied [1–16], and the mechanism of conduction is now well understood by the small polaron hopping theory [1, 2]. TMO glasses containing V_2O_5 were recently investigated from the view points of acoustic and optical properties [3], and relationship between d.c. conductivity and the ratio of the concentration of reduced transition metal ions to that of total transition metal ions, C_V in the glass was also studied [4].

Studies of the Seebeck coefficient, Q, for TMO glasses were also carried out [12, 17–25]. In these works, binary glass systems such as V_2O_5–Bi_2O_3 [17] and V_2O_5–P_2O_5 [18] were discussed in relation to the temperature dependence of Q and its adaptation to Heikes' formula [19, 20], described as

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

where C is the ratio of the concentration of reduced transition metal ions to that of total transition metal ions ($C = C_V$). k is Boltzmann's constant, e is the electronic charge and α' is a constant of the proportionality between the heat of transfer and the kinetic energy of an electron.

With the aid of Heikes' formula, it is possible to discuss the mechanism of electrical conduction for semiconducting glasses with very low mobility ($\mu \ll 10^{-2}$ $cm^2 V^{-1} s^{-1}$ [26]). From discussions on the basis of Equation 1, the conduction was concluded to be due to small polaron hopping [1, 2] for V_2O_5–P_2O_5 and V_2O_5–Bi_2O_3 glasses [17, 18] because of the low mobility and $\alpha' < 1$. On the other hand, a relationship between Q and C_V was reported for V_2O_5–CaO–P_2O_5 and V_2O_5–CaO–B_2O_3 glasses [12, 25]. These glasses resulted because the dominant factor determining Q was found to be C_V values.

However, very few works on the Seebeck coefficient of ternary tellurite glasses have been found in the literature [5, 6]. Therefore, in the present work, we determined the Seebeck coefficient for V_2O_5–Sb_2O_3–TeO_2 and V_2O_5–Bi_2O_3–TeO_2 glasses in the temperature range 373–473 K, and discussed the conduction mechanism using Equation 1 and the relationship between Q and C_V.

2. Experimental procedure

The process for the preparation of glass samples and the determination of the ratio of V^{4+} concentration to total vanadium ion concentration, were described elsewhere [5, 6, 15, 16]. The thermoelectric power of the glass samples was measured in the temperature range 373–473 K in air. The temperature of the glass sample was measured using two copper–constantan thermocouples between hot and cold surfaces of the sample. The temperature was measured using a Keithley microvolt meter (196 system DMM). A temperature difference between the two surfaces (5–10 K) was established by moving the hot surface to the coil of an electric furnace. When the temperature difference exceeded 10 K, argon gas was flowed over the cold surface of the sample. In these measurements, the thermoelectric power of the same sample in different runs agreed within ±2% error.

3. Results and discussion

3.1. Effects of temperature on the Seebeck coefficient

Fig. 1 shows the relationship between the Seebeck coefficient, Q, at 473 K, and the V_2O_5 concentration. Q increases with decreasing V_2O_5 concentration for each system. The sign of Q was negative for different

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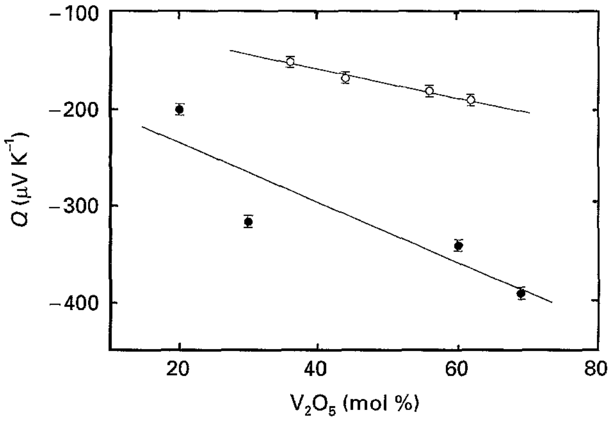

Figure 1 Variation of Q at 473 K with V_2O_5 concentration. (○) V_2O_5–Sb_2O_3–TeO_2 glasses ($x = 26$–62 mol %); (●) V_2O_5–Bi_2O_3–TeO_2 glasses ($x = 20$–69 mol %). (——) Regression lines calculated using the least square method.

concentrations of V_2O_5, indicating that the glasses in the present two systems were n-type semiconductors. Fig. 2 shows the relationship between Q and temperature from 373–473 K. In this figure, almost no temperature dependence of Q was observed. Equation 1 is indicated to be temperature independent, generally $T > 200$ K [17, 18]. The temperature invariance of Q in Equation 1 explains well the results in Fig. 2.

Next we discuss applicability of Equation 1 to the present Q data as a function of C_V of the glasses. Because Equation 1 is formally described by $Q = (k/e)\{\ln[C_V/(1 - C_V)]\} + (k/e)\alpha'$, the slope between Q and $\ln[C_V/(1 - C_V)]$ should be $k/e = 86.18\ \mu V\,K^{-1}$. Fig. 3 shows the experimental relationship between Q and $\ln[C_V/(1 - C_V)]$, together with the data from V_2O_5–SnO–TeO_2 [5] and using the least squares method gave $86.60\ \mu V\,K^{-1}$ for V_2O_5–Sb_2O_3–TeO_2 glasses and $89.00\ \mu V\,K^{-1}$ for V_2O_5–Bi_2O_3–TeO_2 glasses. These slopes agreed satisfactorily with $k/e = 86.18\ \mu V\,K^{-1}$. Accordingly, Heikes' formula holds adequately in the present ternary tellurite glasses.

In Equation 1, large polaron hopping conduction can take place when $\alpha' \gg 2$ [2, 24]. For $\alpha' \ll 1$ [13], however, the conduction is caused by small polaron hopping, because the polaron band width, j, is very much smaller than kT [18], and the mobility, μ, is $\mu \ll 10^{-2}\ cm^2\,V^{-1}s^{-1}$ [26], owing to the localization of electrons; this makes the heat transfer small compared with kT [18]. For $\alpha' \ll 1$, the term α' of Equation 1 can be neglected [2] only if the disorder energy, W_D, calculated from $W_D = 2(W - W_H)$ [2] with activation energy, W, and hopping energy, W_H, becomes nearly zero. Therefore, we discuss the conduction in terms of α' in Heikes' formula. First, assumng $\alpha' = 0$, calculated Q, Q_{cal}, was evaluated using Equation 1, to be -187 to $-148\ \mu V\,K^{-1}$ for V_2O_5–Sb_2O_3–TeO_2 glasses, and -380 to $-198\ \mu V\,K^{-1}$ for V_2O_5–Bi_2O_3–TeO_2 glasses, as shown in Tables I and II. Then, the relative difference exhibited an experimental error of ±2% in the measurements of Q, so α' could not be neglected. Tables I and II show that α', estimated from Q and C_V, is $\alpha' = 0.05$–0.02 (V_2O_5–Sb_2O_3–TeO_2 glasses, $V_2O_5 = 62$–26 mol %), and 0.12–0.02 (V_2O_5–Bi_2O_3–TeO_2 glasses, $V_2O_5 = 69$–20 mol %). In addition, α' in $(k/e)\alpha'$, estimated from the data from Fig. 3, was 0.09 for V_2O_5–Sb_2O_3–TeO_2 glasses and 0.08 for V_2O_5–Bi_2O_3–TeO_2 glasses, respectively. Thus this theoretical α' values and the above experimental ones were shown to be nearly equal.

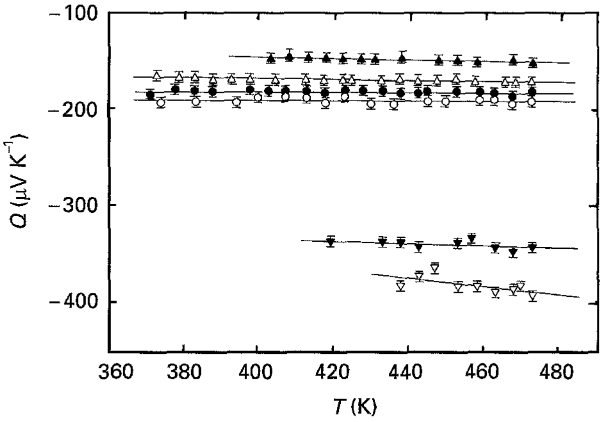

Figure 2 Seebeck coefficient of V_2O_5–Sb_2O_3–TeO_2 and V_2O_5–Bi_2O_3–TeO_2 glasses. (○, ●, △) xV_2O_5–$4Sb_2O_3$–$(96$-$x)TeO_2$ glasses, (○) $x = 62$, (●) $x = 56$, (△) $x = 44$ mol %; (▲) $26V_2O_5$–$3Sb_2O_3$–$71TeO_2$ glasses; (▽, ▼) xV_2O_5–$6Bi_2O_3$–$(94$-$x)TeO_2$ glasses, (▽) $x = 69$, (▼) $x = 60$ mol %. (——) Regression lines calculated using the least square method.

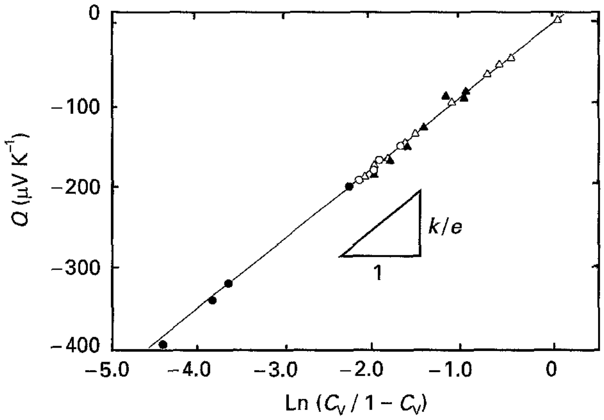

Figure 3 Relationship between Q and $\ln(C_V/1 - C_V)$ for V_2O_5–Sb_2O_3–TeO_2 and V_2O_5–Bi_2O_3–TeO_2 glasses at 473 K. (○) V_2O_5–Sb_2O_3–TeO_2 glasses ($V_2O_5 = 26$–62 mol %), (●) V_2O_5–Bi_2O_3–TeO_2 glasses ($V_2O_5 = 20$–69 mol %), (△) V_2O_5–SnO–TeO_2 glasses ($V_2O_5 = 20$–60 mol %) [5], (▲) V_2O_5–ZnO–TeO_2 glasses ($V_2O_5 = 20$–60 mol %) [6]. The slope of the theoretical line (solid line) is k/e. The slopes calculated from the least square method are $86.6\ \mu V\,K^{-1}$ for V_2O_5–Sb_2O_3–TeO_2 glasses and $89.0\ \mu V\,K^{-1}$ for V_2O_5–Bi_2O_3–TeO_2 glasses, respectively.

Accordingly, because $\alpha' \ll 1$, the electrical conductions of the present ternary tellurite glasses were concluded to be due to small polaron hopping. Apart from the above procedure, this small polaron hopping conduction was also confirmed by the analysis of d.c. conductivity for the glasses in the present systems [15, 16].

3.2. Relationship between Q and V^{5+}/V^{4+}

Apart from Heikes' formula [19, 20], Mackenzie [12, 25] proposed the following formula for semiconductive glasses with TMO

$$Q = (k/e)\ln[\text{high valence ions/low valence ions}] \qquad (2)$$

TABLE I Seebeck coefficient and other related parameters of V_2O_5–Sb_2O_3–TeO_2 glasses

Composition (mol %)			C_V [15]	Q at 473 K ($\mu V K^{-1}$) (exp.)	Q ($\mu V K^{-1}$) calc. from Eq. 1 with $\alpha' = 0$	α'
V_2O_5	Sb_2O_3	TeO_2				
62	4	33	0.102	−192	−187	0.05
56	4	40	0.117	−180	−174	0.06
44	4	52	0.124	−172	−168	0.01
26	3	71	0.152	−151	−148	0.02

TABLE II Seebeck coefficient and other related parameters of V_2O_5–Bi_2O_3–TeO_2 glasses

Composition (mol %)			C_V [16]	Q at 473 K ($\mu V K^{-1}$) (exp.)	Q ($\mu V K^{-1}$) calc. from Eq. 1 with $\alpha' = 0$	α'
V_2O_5	Bi_2O_3	TeO_2				
69	6	25	0.012	−391	−380	0.12
60	6	34	0.021	−340	−330	0.09
30	6	64	0.025	−317	−315	0.08
20	6	74	0.091	−202	−198	0.02

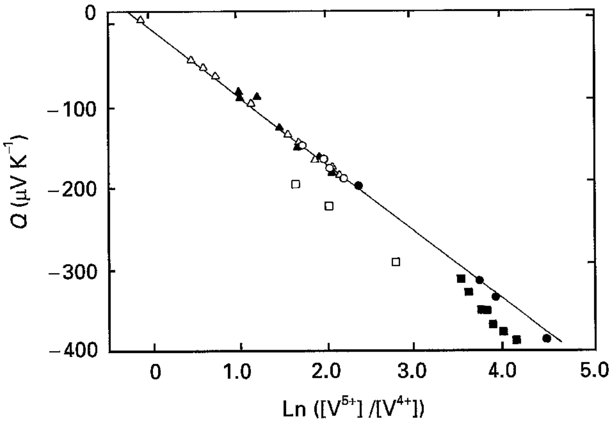

Figure 4 Relationship between Q and $\ln([V^{5+}]/[V^{4+}])$ for V_2O_5–Sb_2O_3–TeO_2 and V_2O_5–Bi_2O_3–TeO_2 glasses. (○) V_2O_5–Sb_2O_3–TeO_2 glasses (V_2O_5 = 26–62 mol %), (●) V_2O_5–Bi_2O_3–TeO_2 glasses (V_2O_5 = 20–69 mol %), (△) V_2O_5–SnO–TeO_2 glasses (V_2O_5 = 20–60 mol %) [5], (▲) V_2O_5–ZnO–TeO_2 glasses (V_2O_5 = 20–60 mol %) [6], (■) V_2O_5–Bi_2O_3 glasses (V_2O_5 = 70–95 mol %) [17], (□) V_2O_5–P_2O_5 glasses (V_2O_5 = 65–82 mol %) [18]. (——) The theoretical relationship, with the slope $-86.18\ \mu V K^{-1}$.

where e is the charge of an electron. So if Equation 2 is valid for the present glasses, it is possible to predict n- or p-type semiconductive glass from C_V. In vanadate glasses, the term [high valence ions/low valence ions] is formally represented by $[V^{5+}]/[V^{4+}]$. Hence, in the glasses with $[V^{5+}]/[V^{4+}] > 1$, Q becomes negative, indicating n-type semiconducting glasses [12, 25], but for $[V^{5+}]/[V^{4+}] < 1$, Q is positive, meaning p-type semiconductors [12, 25]. Also, provided that Equation 2 is applicable to the glasses, the slope of Q versus $\ln[V^{5+}]/[V^{4+}]$ is expected to be k/e from Equation 2.

Fig. 4 shows the experimental relationship between Q and $\ln[V^{5+}]/[V^{4+}]$. The slope of Q versus $\ln[V^{5+}]/[V^{4+}]$ obtained from the figure gave $-85.28\ \mu V K^{-1}$ for V_2O_5–Sb_2O_3–TeO_2 and V_2O_5–Bi_2O_3–TeO_2 glasses, respectively. This value ($-85.28\ \mu V K^{-1}$) was approximately equal to the theoretical slope ($-86.18\ \mu V K^{-1}$). Accordingly, we concluded that Mackenzie's formula (Equation 2) was applicable to the present glass systems. In addition, in Tables I and II, Q increased with increasing C_V, so we confirmed that the factor determining Q was C_V. However, examining the applicability of Equation 2 to the cases of V_2O_5–Bi_2O_3 [17] and V_2O_5–P_2O_5 glasses [18] by replotting their Q data and $\ln[V^{5+}]/[V^{4+}]$ in Fig. 4, the Q–C_V relationship was seen to clearly deviate from the slope value of k/e. So we found that Equation 2 is no longer applicable to these binary vanadate glass systems [17, 18].

4. Conclusion

The Seebeck coefficient, Q, was determined for ternary vanadium tellurite glasses in the systems V_2O_5–Sb_2O_3–TeO_2 and V_2O_5–Bi_2O_3–TeO_2 at temperatures ranging from 373–473 K. At 473 K, $Q = -192$ to $-151\ \mu V K^{-1}$ for the former and -391 to $-202\ \mu V K^{-1}$ for the latter glasses of different compositions. The glasses in these two systems were found to be n-type semiconductors and the experimental relationship between Q and C_V ($= V^{4+}/V_{total}$) satisfied the theoretical Heikes' formula. Because the parameter α' in Heikes' formula was estimated to be $\alpha' \ll 1$, namely $\alpha' = 0.035 \pm 0.015$ for V_2O_5–Sb_2O_3–TeO_2 glasses, and 0.070 ± 0.05 for V_2O_5–Bi_2O_3–TeO_2 glasses, the small polaron hopping conduction was confirmed to occur between 373 and 473 K for the glasses in both systems.

The relation between Q and $\ln[V^{5+}]/[V^{4+}]$ of the glasses in those two systems was also explained adequately by Mackenzie's formula, and the dominant factor determining Q was found to be the fraction of the reduced ion concentration, C_V.

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Received 9 May 1994
and accepted 17 October 1995