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Electrical properties of Sb_2O_3–CaO–V_2O_5 glasses and glass-ceramics

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The d.c. conductivity (σ) of (a) glasses prepared by the press-quenching method and (b) glass-ceramics (crystallized glass) produced by post-heat treatment was investigated in the system Sb_2O_3–CaO–V_2O_5 and their conduction mechanism was studied. The glasses were *n*-type semiconductors with $\sigma = 2.6 \times 10^{-6} \sim 2.8 \times 10^{-5}\ \mathrm{S\,cm^{-1}}$ at 333 K for varying glass compositions. The conduction was attributed to small polaron hopping in the adiabatic regime. The estimated carrier density was $1.7 \sim 3.8 \times 10^{21}\ \mathrm{cm^{-3}}$ for $V_2O_5 = 70 \sim 80$ mol % and the mobility was 3.5×10^{-9} to $6.9 \times 10^{-8}\ \mathrm{cm^2\,V^{-1}\,s^{-1}}$.

Crystallization raised the conductivity by a factor of 10^3. The crystalline product in the glass-ceramics was $Ca_{0.17}V_2O_5$. The glass-ceramics were *n*-type semiconductors, and the conduction was interpreted by a superposition of the small polaron hopping in the crystalline and glassy phases.

1. Introduction

Electrical conduction of oxide glasses with transition metal oxides (TMO), e.g. V_2O_5, as a major component has been understood by the small polaron hopping (SPH) model [1, 2]. This phonon-assisted hopping of electrons accompanies a valence change between V^{4+} and V^{5+} in glasses. In hopping, the V–O–V spacing (R) affects activation energy for conduction and thus electrical conductivity (σ).

Recently there has been a considerable interest in the study of electrical conduction in ternary vanadate glasses [3–7]. A high conductivity of $3.4 \times 10^{-3}\ \mathrm{S\,cm^{-1}}$ at 373 K was reported for $80V_2O_5$–12 PbO–8 P_2O_5 glass (mol %) [3].

Also, the conduction of vanadate glasses containing two transition metal oxides has been investigated [8–10].

Our previous study on Sb_2O_3–SrO–V_2O_5 glasses [11] without traditional network former prepared by press-quenching method, gave conductivities ranging from 7×10^{-7} to $10^{-5}\ \mathrm{S\,cm^{-1}}$ at 300 K. Hence, we expected more conductive glasses with more closely packed structures and lower basicity when substituted Ca for Sr. Ca^{2+} has a smaller ionic radius (0.099 nm) than Sr^{2+} (0.116 nm) in the Sb_2O_3–SrO–V_2O_5 system [11].

The present work aims at determining the electrical conductivity of Sb_2O_3–CaO–V_2O_5 glasses and clarifying the conduction mechanism. We were also interested in the conductivity of glass-ceramics (crystallized glasses) prepared by post-heat treatment of the as-quenched glasses, since from previous reports [11, 12], we observed that the crystallization raised remarkably the conductivity of the ternary antimony– and bismuth–vanadate glasses [11, 12].

2. Experimental procedure

Reagent grade (99.9%) chemicals V_2O_5, $CaCO_3$ and Sb_2O_3 were mixed in prescribed composition for 15 min in a mortar. Each glass batch (5 g) was melted in air in a porcelain crucible at 1000 °C for 1 h in an electric furnace. The melt was then poured onto copper blocks maintained at room temperature and quenched by pressing immediately with another copper block. Thus, the glass samples of about 1 mm in thickness and 5 $\mathrm{cm^2}$ in area were obtained by the melt-quench technique, similar to our earlier works [6, 11, 12].

The samples were used for various measurements without annealing. The amorphous nature of the samples were verified by X-ray diffraction (Philips PW 1830). Glass transition temperature, T_g, and crystallization temperature, T_c, were measured using differential thermal analysis–differential scanning calorimetry (DTA–DSC) apparatus (Rigaku, DSC 8230/DTAS 300). Density (d) of the glasses was measured by the Gay–Lussac method, the measurement error being within 2%. The fraction of the reduced V ion in the glass, i.e. $C_v = V^{4+}/V_{total}$, was determined by titration method using $KMnO_4$ and $FeSO_4(NH_4)_2SO_4$. Electrical conductivity (d.c.) was determined by the four-point probe technique with Ag paste electrodes with a spacing of 1 mm, a constant d.c. current of 0.1 μA being applied during measurements.

3. Results and discussion

3.1. Glass-forming region and oxygen molar volume

Fig. 1 shows the glass formation region of Sb_2O_3–CaO–V_2O_5 glasses. Glasses could be obtained in the

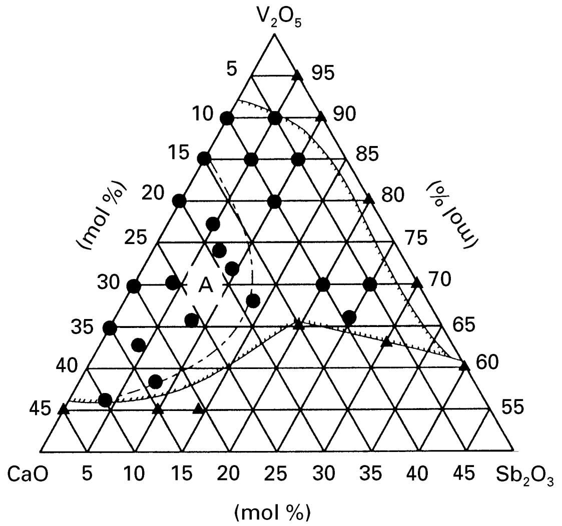

Figure 1 Glass-forming region for Sb_2O_3–CaO–V_2O_5 glasses. (●) glass, (▲) glass-crystal. (Zone A is the glass-forming region for Sb_2O_3–SrO–V_2O_5 glasses [11].)

composition range: $0 < Sb_2O_3 < 25$ mol %, $5 < CaO < 40$ mol %, and $60 < V_2O_5 < 90$ mol %. In the system Sb_2O_3–SrO–V_2O_5 [11], glasses were obtained for $0 < Sb_2O_3 < 10$ mol %, $15 < SrO < 45$ mol % and $55 < V_2O_5 < 80$ mol %, so the substitution of CaO for SrO extended the glass-forming region. This was reported also in another non-conventional bismuth-cuprite glasses added with $CaCO_3$ or $SrCO_3$ [13]. The T_g and T_c of the present glasses measured were $T_g = 310 \sim 330\,°C$ and $T_c \fallingdotseq 350\,°C$.

The oxygen molar volume V_0^* for the present glass-forming system is expressed as follows:

$$V_0^* = [M_{V205} - 16C_V)X + M_{CaO}Y + M_{Sb_2O_3}Z]/ \times d[5 - C_V)X + Y + 3Z] \qquad (1)$$

where M is the molecular weight, X, Y and Z are the mole fractions of V_2O_5, CaO and Sb_2O_3, d is the density of the glasses. The calculated results for V_0^* are shown in Fig. 2.

With an increase in V_2O_5 content, V_0^* decreased. It is known that V_0^* correlates with T_g [14]. In Fig. 2 $V_0^* = 13.0 \sim 13.8\ cm^3\ mol^{-1}$ for $V_2O_5 = 85 \sim 70$ mol %, which corresponded to $T_g = 330 \sim 310\,°C$. An increase in V_0^* means looser packing in the glass structure, resulting in a decrease in T_g, and as a result, a decrease in thermal stability of the glass [14]. The higher T_g of the present glasses than those for Sb_2O_3–CaO–V_2O_5 glasses [11] ($T_g = 280 \sim 282\,°C$ for $V_2O_5 = 87.5 \sim 70$ mol %) suggests larger V_0^* of the latter glasses. The decrease in V_0^*, in contrast, produces a decrease in V–O–V spacing, which causes an increase in conductivity for larger V_2O_5 content as shown in Fig. 3.

3.2. Reactions in glass melt

It is known that Sb_2O_3 can reduce V^{5+} to V^{4+}, resulting in conductivity in the solid glasses. Munakata *et al.* [15] reported that the reduction of V^{5+} to V^{3+} does not occur in the melts. Hence, assuming the following reactions in the glass melts for the present glasses

$$2V_2O_5 + Sb_2O_3 \rightarrow 4VO_2 + Sb_2O_5 \qquad (2a)$$

$$2V^{5+} + Sb^{3+} \rightarrow 2V^{4+} + Sb^{5+} \qquad (2b)$$

The fraction of the reduced-V ion, C_V was calculated ($C_{V\,cal}$) and compared with the experimental C_V. The experimental C_V values in Table I were $70 \sim 95\%$ of $C_{V\,cal}$ excepting those for three samples (Nos 8, 10 and 11). Accordingly the reactions (Equation 2a,b) are possible in the melts as well as in Sb_2O_3–TeO_2–V_2O_5 glasses [14]. Formation of VO_2 structural unit was also reported in V_2O_5–P_2O_5 glasses on adding Sb_2O_3 [16].

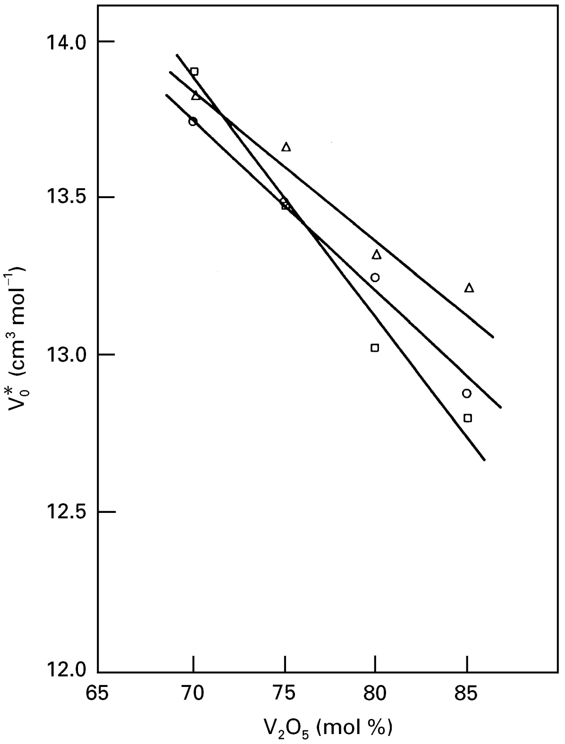

Figure 2 Oxygen molar volume, V_0^*, against V_2O_5 content. (△) 5 CaO, (○) 10 CaO, (□) 15 CaO (mol %).

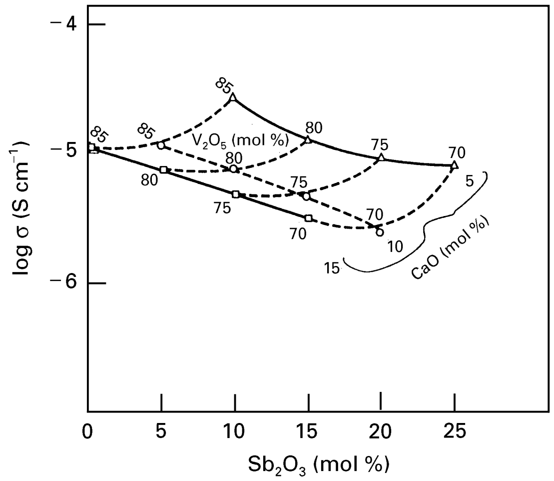

Figure 3 Compositional dependence on electrical conductivity σ at 333 K.

TABLE I Chemical composition and properties of glass samples

Sample no.	Nominal composition (mol %)			C_V	C_{Vcal}	d ($g\,cm^{-3}$)	W (eV)	$\log \sigma_{333\,K}$	N ($\times 10^{22}\,cm^{-3}$)	R ($\times 10^{-8}$ cm)	N_c ($\times 10^{21}\,cm^{-3}$)	μ ($\times 10^{-8}\,cm^2\,V^{-1}\,s^{-1}$)
	Sb_2O_3	CaO	V_2O_5									
1	25	5	70	0.477	0.714	3.60	0.385	−5.06	1.50	4.06	3.14	1.69
2	20	5	75	0.414	0.534	3.44	0.414	−5.04	1.57	3.99	3.81	1.45
3	15	5	80	0.319	0.375	3.31	0.416	−4.91	1.67	3.92	3.05	2.50
4	10	5	85	0.226	0.235	3.14	0.381	−4.54	1.73	3.87	2.54	6.93
5	20	10	70	0.447	0.571	3.48	0.440	−5.59	1.54	4.02	3.19	0.49
6	15	10	75	0.360	0.400	3.33	0.398	−5.32	1.62	3.95	3.13	0.93
7	10	10	80	0.241	0.250	3.17	0.398	−5.13	1.70	3.89	2.61	1.75
8	5	10	85	0.165	0.118	3.06	0.379	−4.93	1.80	3.82	2.08	3.45
9	15	15	70	0.368	0.429	3.28	0.425	−5.48	1.54	4.02	3.00	0.66
10	10	15	75	0.279	0.267	3.17	0.420	−5.27	1.65	3.93	2.78	1.16
11	5	15	80	0.138	0.125	3.05	0.396	−5.12	1.75	3.85	1.74	2.65
12	0	15	85	0.007	—	2.89	0.382	−4.95	1.82	3.80	0.10	6.93

3.3. Effects of glass composition on conductivity

No d.c. polarization was observed in the present glasses. Seebeck coefficient measured for $20Sb_2O_3{\cdot}5CaO{\cdot}75V_2O_5$ (mol %) and $5Sb_2O_3{\cdot}10CaO{\cdot}85V_2O_5$ (mol %) glasses was -32 to $-39\,\mu V\,K^{-1}$ and -127 to $-101\,\mu V\,K^{-1}$ respectively for temperatures from 460 to 425 K, which indicates the glasses to be *n*-type semiconductors.

Fig. 3 shows the effect of glass composition on σ at 333 K. With an increase in V_2O_5 content for fixed Sb_2O_3 content, σ increased. However it decreased with an increase in Sb_2O_3 for fixed CaO content.

Fig. 4a shows the effect of the basicity of glass (CaO/Sb_2O_3) on σ. The conductivity decreased with an increase in CaO/Sb_2O_3 from 0 to 0.5 for $V_2O_5 = 80 \sim 85$ mol %. Similar results were also reported for P_2O_5–BaO–V_2O_5 glasses [15]. The decrease in σ with the increasing basicity of the glass corresponded to the decrease in V^{4+}; this was confirmed by the effect of CaO/Sb_2O_3 on C_V in Fig. 4b where C_V decreased for $CaO/Sb_2O_3 = 0.9$ to 3.

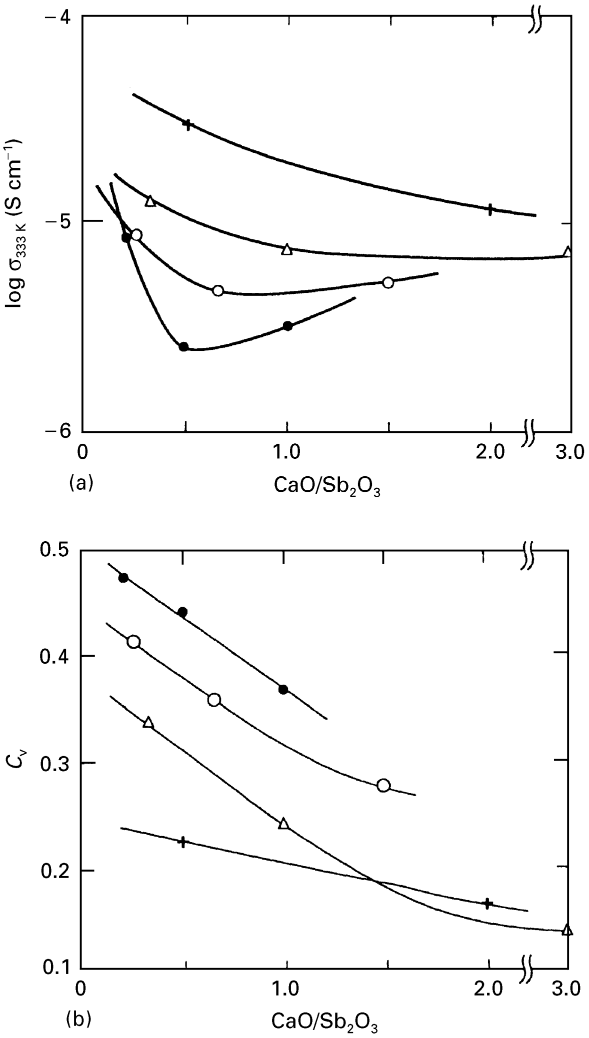

Figure 4 (a) Effect of the basicity of glass on conductivity. (●) $70\,V_2O_5$ mol %; (○) $75\,V_2O_5$ mol %; (△) $80\,V_2O_5$ mol %; (+) $85\,V_2O_5$ mol %. (b) Effect of the basicity of glass on C_V. (●) $70\,V_2O_5$ mol %; (○) $75\,V_2O_5$ mol %; (△) $80\,V_2O_5$ mol %; (+) $85\,V_2O_5$ mol %.

Thus we obtained the glasses with conductivities ($\sigma = 2.6 \times 10^{-6} \sim 2.8 \times 10^{-5}\,\mathrm{S\,cm^{-1}}$) which were higher than those for Sb_2O_3–SrO–V_2O_5 glasses [11].

3.4. Conduction mechanism

The reciprocal temperature dependence of $\ln(\sigma T)$ is presented in Fig. 5. Good linearities are seen. The activation energy for conduction, W, obtained from the slope of the curves in Fig. 5 is given in Table I.

The conductivity of TMO containing oxide glasses is expressed by the small polaron hopping model [1, 2] as follows

$$\sigma = (\sigma_0/T)\exp(-W/kT) \tag{3}$$

$$\sigma_0 = [\nu_0 N e^2 R^2 C(1-C)/k]\exp(-2\alpha R) \tag{4}$$

with R as the mean V–O–V spacing, N the transition metal ion density ($= R^{-3}$), C the fraction of reduced transition metal ion [$C = C_V = V^{4+}/(V^{4+} + V^{5+})$], e the electron charge, k the Boltzmann constant, α the tunnelling factor, and ν_0 the phonon frequency.

It has been observed that small polaron hopping conduction in the adiabatic regime took place generally in vanadate glasses for $V_2O_5 > 50$ mol % [5–7], where σ_0 is unchanged for the variations in glass composition. In that case, the slope between $\log\sigma$ and W should be $-1/2.303kT$, since $\log\sigma = \log\sigma_0 - W/2.303kT$ from Equation 3. Fig. 6 shows the relationship between $\log\sigma$ and W at 333 K, indicating that the experimental slope for different CaO contents agrees with the theoretical slope. This confirms the adiabatic small polaron hopping for the present system of glasses. The values of activation energy (W) as estimated from the data in Fig. 5 are given in Table I.

Table I gives $W = 0.381 \sim 0.440$ eV at 333 K from the data in Fig. 5. For SPH, W is expressed by [1, 2],

$$W = W_H + W_D/2 \quad (\text{for } T > \theta_D/2) \tag{5}$$

where W_H is the hopping energy, W_D the disorder energy and θ_D the Debye temperature. Since $W_D < 0.1$ eV [7, 17], we have $W_H = 0.3 \sim 0.42$ eV for $W = 0.381 \sim 0.440$ eV (Table I) assuming $W_D = 0.05$ eV.

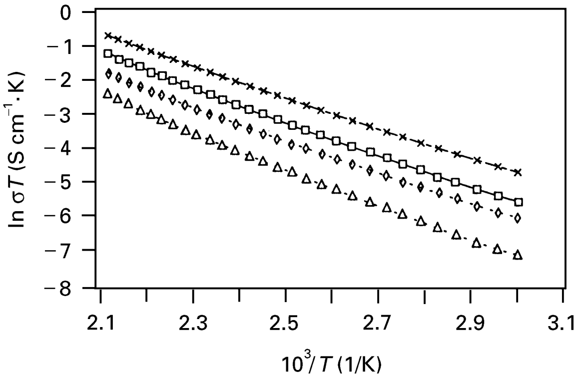

Figure 5 Temperature dependence of conductivity for glasses with different compositions (mol %). (×) $10Sb_2O \cdot 5CaO \cdot 85V_2O_5$; (□) $15Sb_2O_3 \cdot 5CaO \cdot 80V_2O_5$; (◇) $5Sb_2O_3 \cdot 15CaO \cdot 80V_2O_5$; (△) $20Sb_2O_3 \cdot 10CaO \cdot 70\,V_2O_5$.

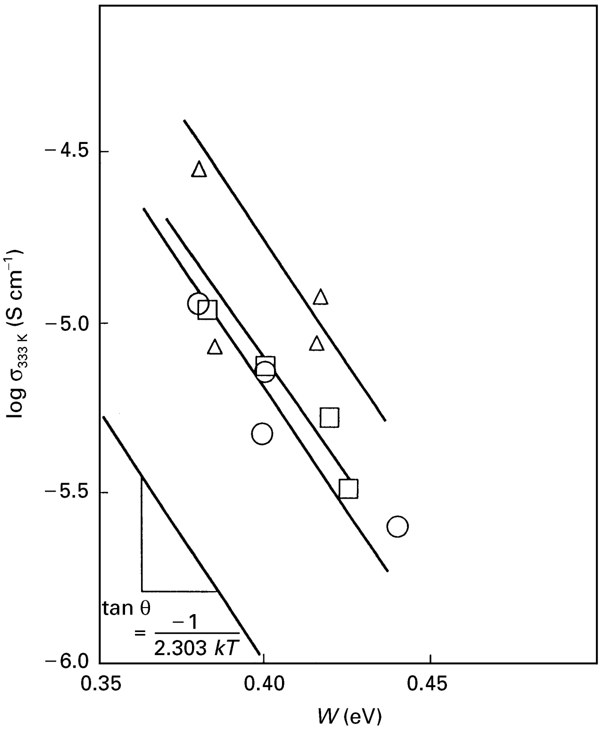

Figure 6 Relationship between $\log\sigma_{333\,\mathrm{K}}$ and activation energy W. (△) 5 CaO mol %; (○) 10 CaO mol %; (□) 15 CaO mol %.

Next, we discuss carrier concentration, N_c, and hopping mobility, μ, of the glasses. For adiabatic hopping, μ is given by [1, 18]

$$\mu = \mu_0 \exp(-W_H/kT) \tag{6}$$

where $\mu_0 = \nu_0 e R^2/kT$. Also we know

$$\sigma = eN_c\mu \tag{7}$$

We calculated N_c and μ from Equations 6 and 7 with $\log\sigma$, R, and W_H values estimated from Equation 5 using W values in Table I assuming $W_D = 0.05$ eV.

Fig. 7 shows N_c and μ as a function of V_2O_5 concentration. N_c decreased with an increase in V_2O_5 concentration from 75 to 85 mol % while μ increased. Comparing these N_c and μ values with those for TeO_2–Sb_2O_3–V_2O_5 [6] and TeO_2–ZnO–V_2O_5 [19] glasses, we found the present glasses to have higher N_c and smaller μ values, and the increase in N_c caused higher conductivity. Very small $\mu \sim 10^{-8}\,\mathrm{cm^2\,V^{-1}\,s^{-1}}$ indicates a strong localization of d-electrons at V^{4+} ion; this satisfies the condition of electron localization ($\mu \ll 10^{-2}\,\mathrm{cm^2\,V^{-1}\,s^{-1}}$) [20].

In these glasses, $N_c \sim 10^{21}\,\mathrm{cm^{-3}}$ and μ changed by one order on varying glass compositions (Fig. 7). This indicates the dominant factor determining σ to be hopping mobility.

3.5. Formation and conductivity of glass-ceramics

The glass-ceramics were produced by crystallizing the glasses by heat treatments in air at 360 °C for 3 and 10 h. Fig. 8 gives the temperature dependence of conductivity for glass-ceramics obtained by the post-heat treatments of the as-quenched glasses. The

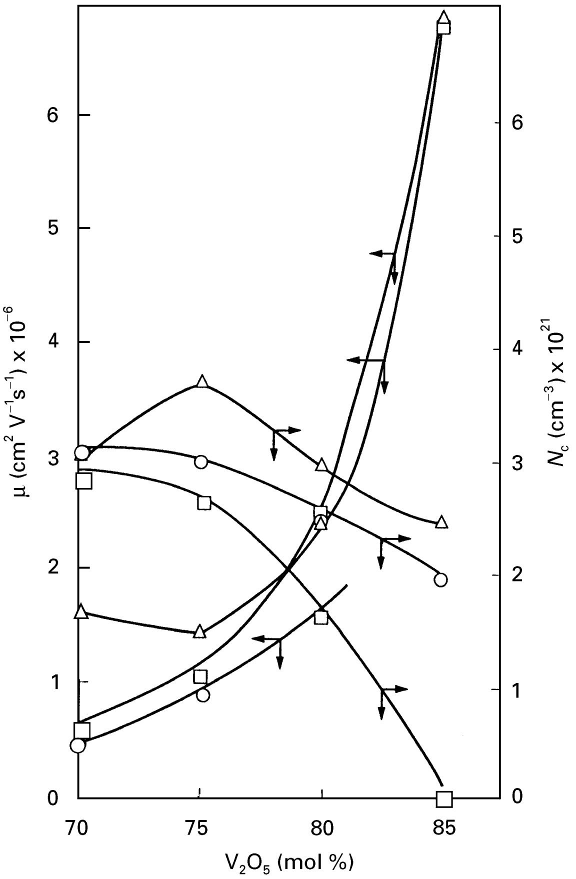

Figure 7 Compositional dependence of carrier density N_c and mobility μ at $T = 333$ K. (△) 5 CaO, (○) 10 CaO, (□) 15 CaO (mol %).

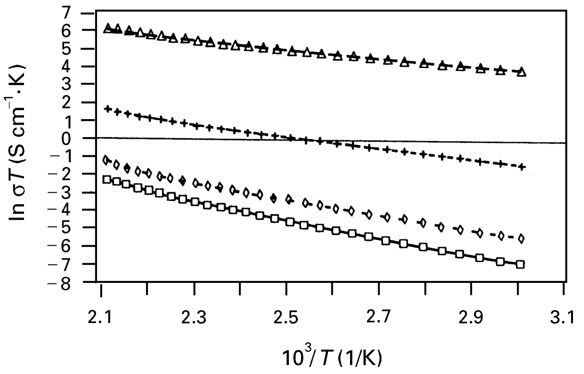

Figure 8 Temperature dependence for conductivity of glass-ceramics (crystallized glass). The glass-ceramics samples were prepared by heat treatment of the glass samples at 360 °C for 3 h. (△) $5Sb_2O_3 \cdot 10CaO \cdot 80V_2O_5$(mol %) glass-ceramics; (+) $20Sb_2O_3 \cdot 10CaO \cdot 70V_2O_5$(mol %) glass-ceramics; (◇) $5Sb_2O_3 \cdot 10CaO \cdot 85V_2O_5$(mol %) glass; (□) $20Sb_2O_3 \cdot 10CaO \cdot 70V_2O_5$ (mol %) glass.

crystallization confirmed by X-ray diffraction (XRD), raised σ by three orders, compared with those of the as-quenched glasses (Table I). Such remarkable increase in conductivity has been also reported in other ternary vanadate glasses [4, 11, 12]. The linear relationship between $\ln(\sigma T)$ and T^{-1} was found to be similar to Sb_2O_3–SrO–V_2O_5 [11], and Bi_2O_3–SrO–V_2O_5 [12] glasses.

With an increase in σ by crystallization, the activation energy for conduction was found to be $W = 0.206 \sim 0.275$ eV at 333 K, which was lower than those for the as-quenched glasses where $W = 0.381 \sim 0.440$ eV at 333 K.

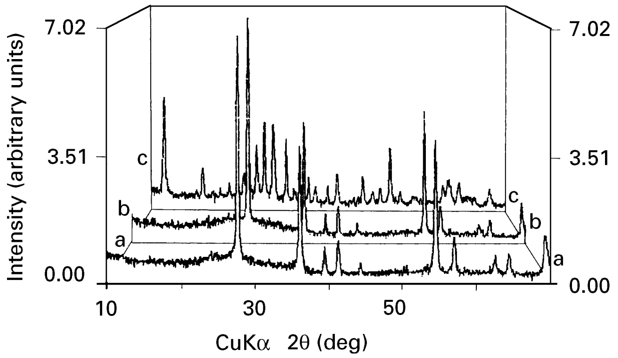

Figure 9 X-ray diffractograms (CuK$_\alpha$) for glass-ceramics. The samples were prepared by heat-treatment at 360 °C for 3 h. (a) Sb_2O_3:CaO:V_2O_5 = 20:10:70 (mol %); (b) Sb_2O_3:CaO:V_2O_5 = 15:10:75 (mol %); (c) Sb_2O_3:CaO:V_2O_5 = 5:10:85 (mol %).

The Seebeck coefficient measured for $5Sb_2O_3 \cdot 10CaO \cdot 85V_2O_5$ (mol %) glass-ceramics gave −0.19 to −0.17 μV K^{-1} between temperatures 460 and 425 K, indicating the glass-ceramics to be *n*-type semiconductors.

X-ray diffractograms for the glasses are shown in Fig. 9. Peaks due to a crystalline phase are seen. The peaks in the sample c are identified to be $Ca_{0.17}V_2O_5$ in reference with JCPDS card No. 26-1165. The samples a and b were considered to include $Ca_{0.17}V_2O_5$ and other crystalline compounds because some different peaks appeared. However, no peak due to Sb_2O_3 was observed.

We considered that the generation of $Ca_{0.17}V_2O_5$ in the glasses during the heat treatment was in accordance with the following reactions

$$Sb_2O_3 + 2CaO = Sb_2O_5 + 2Ca \qquad (8a)$$

$$V_2O_5 + 2Ca = Ca_2V_2O_5 \qquad (8b)$$

i.e. the Sb_2O_3 reduces CaO in the glass, resulting in generation of $Ca_2V_2O_5$ crystal which is almost similar to the $Ca_{0.17}V_2O_5$ crystal detected by XRD.

It is known that the conduction for $M_xV_2O_5$ was due to hopping of small polarons as reported for β-$Na_xV_2O_5$ [21]. Accordingly, the conduction as a whole of the glass-ceramics presenting the linearity of $\ln(\sigma T)$ against T^{-1} was considered to be due to a superposition of SPH in $Ca_{0.17}V_2O_5$ crystal and that of the glass phase, similar to antimony and bismuth vanadate glasses and glass-ceramics [11, 12].

4. Conclusions

Glasses in the system Sb_2O_3–CaO–V_2O_5 were prepared by a press-quenching method and their d.c. conductivity was investigated. The glass-ceramics from these glasses were obtained by post-heat treatment of these glasses, and the conductivity was determined. With decreasing V_2O_5 content, the oxygen molar volume V_0^* of the glasses increased. The glasses were *n*-type semiconductors, and the conductivity at 333 K was from 2.6×10^{-6} to 2.8×10^{-5} S cm^{-1}. The conduction was due to adiabatic small polaron hopping of electrons. The estimated carrier concentration was $1.7 \sim 3.8 \times 10^{21}\,\mathrm{cm}^{-3}$ for $V_2O_5 = 70 \sim 80$ mol % and the hopping mobility was $3.5 \times 10^{-9} \sim 6.9 \times 10^{-8}\,\mathrm{cm}^2\,\mathrm{V}^{-1}\,\mathrm{s}^{-1}$. The factor determining the conductivity was hopping mobility. The relatively high conductivity was due to high carrier concentration.

Crystallization by heat treatment of the glasses raised the conductivity by an order of 10^3. The crystalline product was $Ca_{0.17}V_2O_5$. The conduction of the glass-ceramics, which are *n*-type semiconductors, was interpreted by a superposition of small polaron hopping in $Ca_{0.17}V_2O_5$ crystal and that in the glass.

References

1. N. F. MOTT, *Adv. Phys.* **16** (1967) 49.
2. I. G. AUSTIN and N. F. MOTT, *ibid.* **18** (1969) 41.
3. A. FELTZ and R. WOLLENHAUPT, *Z. anorg. allg. Chem.* **466** (1980) 41.
4. V. M. KALYGINA, V. I. GAMAN, L. D. BOGOMOLOVA, V. I. KOSINTSEV and O. E. MODEBADZE, *Fiz. Khim. Stekla* **10** (1984) 555.
5. H. HIRASHIMA, H. KUROSAWA, K. MIZOBUCHI and T. YOSHIDA, *Glastech. Ber.* **61** (1988) 151.
6. H. MORI, T. KITAMI and H. SAKATA, *J. Non-Cryst. Solids* **168** (1994) 157.
7. H. HIRASHIMA, D. ARAI and T. YOSHIDA, *J. Amer. Ceram. Soc.* **68** (1981) 486.
8. L. D. BOGOMOLOVA, T. F. DOLGOLENKO, V. N. LAZUKIN and I. V. FILATOVA, *Sov. Phys. Solid State* **15** (1974) 2477.
9. H. HIRASHIMA, K. NISHII and T. YOSHIDA, *J. Amer. Ceram. Soc.* **66** (1983) 704.
10. R. SINGH and K. SETHUPATHI, *J. Phys.* **D22** (1989) L709.
11. H. SAKATA, M. AMANO, T. ISHIGURO and T. HIRAYAMA, *J. Ceram. Soc. Jpn* **100** (1992) 1398.
12. M. AMANO, H. SAKATA, K. TANAKA and T. HIRAYAMA, *ibid.* **102** (1994) 424.
13. F. MIYAJI, T. YOKO and S. SAKKA, *J. Non-Cryst. Solids* **126** (1990) 170.
14. H. HIRASHIMA and H. TANAKA, *Seramikkusu-Ronbun-Shi* **97** (1989) 1150.
15. M. MUNAKATA, S. KAWAMURA, J. ASAHARA and M. IWAMOTO, *Yougyo-Kyokai-Shi* **67** (1959) 344.
16. T. NAITO, T. NAMEKAWA, A. KATOH and K. MAEDA, *J. Ceram. Soc. Jpn* **100** (1992) 685.
17. M. SAYER and A. MANSINGH, *Phys. Rev.* **B6** (1972) 4629.
18. L. MURAWSKI, C. H. CHUNG and J. D. MACKENZIE, *J. Non-Cryst. Solids* **32** (1979) 91.
19. H. MORI, J. IGARASHI and H. SAKATA, *J. Ceram. Soc. Jpn* **101** (1993) 1351.
20. M. H. COHEN, *J. Non-Cryst. Solids* **4** (1970) 391.
21. J. H. PERLSTEIN and M. J. SIENKO, *J. Chem. Phys.* **48** (1968) 174.

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