A relationship between electrical conductivity and structural relaxation of $10\text{SnO}_2 \cdot 10\text{Fe}_2\text{O}_3 \cdot 10\text{P}_2\text{O}_5 \cdot x\text{AgI} \cdot (70 - x)\text{V}_2\text{O}_5$ glass caused by heat-treatment

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A relationship between local structure, electrical conductivity (σ) and thermal property of $10\text{SnO}_2 \cdot 10\text{P}_2\text{O}_5 \cdot 10\text{Fe}_2\text{O}_3 \cdot x\text{AgI} \cdot (70 - x)\text{V}_2\text{O}_5$, $10\text{SnO}_2 \cdot 10\text{P}_2\text{O}_5 \cdot 10\text{Fe}_2\text{O}_3 \cdot x\text{Ag}_2\text{O} \cdot (70 - x)\text{V}_2\text{O}_5$ and $10\text{SnO}_2 \cdot 10\text{P}_2\text{O}_5 \cdot 10\text{Fe}_2\text{O}_3 \cdot x/2(\text{AgI} \cdot \text{Ag}_2\text{O}) \cdot (70 - x)\text{V}_2\text{O}_5$ glasses, respectively abbreviated as $x\text{AIVSPF}$, $x\text{AOVSPF}$ and $x\text{AIAOVSPF}$ with 'x' between 0 and 40 mol % were investigated by ^{57}Fe - and ^{119}Sn -Mössbauer spectroscopies, X-ray diffractometry (XRD), Scanning Electron Microscopy (SEM), Fourier transform infrared spectroscopy (FT-IR), differential thermal analysis (DTA) and DC two- and four-probe methods. Heat-treatment at 500°C for 100 min of $x\text{AIVSPF}$ glass with 'x' of 10, 20, 30 and 40 resulted in a marked increase in σ from 2.2×10^{-5} , 9.4×10^{-6} , 3.2×10^{-6} and $2.6 \times 10^{-6} \text{ S cm}^{-1}$ to 2.6×10^{-1} , 2.1×10^{-1} , 5.2×10^{-2} and $1.3 \times 10^{-2} \text{ S cm}^{-1}$, respectively. Similar increase in σ caused by heat-treatment was also observed for $x\text{AOVSPF}$ and $x\text{AIAOVSPF}$ glasses with 'x' being equal to or less than 20 mol %. From DTA study, glass transition temperature (T_g) of 248–298°C and crystallization temperature (T_c) of 362–379°C were observed for $x\text{AIVSPF}$ glass, whereas gradual decreases in T_g from 277 ± 5 to 216 ± 5 °C and T_c from 356 ± 2 to 283 ± 2 °C were confirmed for $x\text{AOVSPF}$ glass, implying that substitution of AgI for V_2O_5 didn't affect the 3D glass network but that of Ag_2O causes the cleavage of the 3D glass network. FT-IR study of the heat treated $x\text{AOVSPF}$ glass showed the disappearance of bridging oxygen of P–O–P and V–O–V with the Ag_2O content, indicating that cleavage of the 3D glass network caused the decrease of the electrical conductivity. It can be concluded that AgI-substituted iron tin phosphovanadate glass is better than Ag_2O -substituted iron tin phosphovanadate glass for achieving the higher electrical conductivity.

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1. Introduction

Semiconducting vanadate glass exhibits electrical conductivity (σ) of 10^{-7} – $10^{-5} \text{ S cm}^{-1}$ caused by a step-by-step electron (polaron) hopping from V^{III} or V^{IV} to V^{V} .¹⁾ Kubuki et al. discovered a remarkable increase in σ from the order of 10^{-7} to 10^0 S cm^{-1} in $20\text{BaO} \cdot 10\text{Fe}_2\text{O}_3 \cdot 70\text{V}_2\text{O}_5$ glass after heat-treatment at temperatures higher than glass transition temperature (T_g) or crystallization temperature (T_c).^{2,3)} This result showed that σ of vanadate glasses can be controlled by conditions of heat treatment. Since then, Kubuki and co-workers have been looking for the higher electrically conductive glass at room temperature by substituting various metallic oxides for V_2O_5 . Development of new vanadate glass has attracted much interest because some vanadate glasses have several industrial applications for electron-emitting needle for ionizer, conductive nanoparticle paste, host material for focused ion beam (FIB) processing, glass lining, cathode active material for Li-ion battery.⁶⁾ Recently, an investigation of $15\text{Li}_2\text{O} \cdot 10\text{Fe}_2\text{O}_3 \cdot x\text{SnO}_2 \cdot (70 - x)\text{V}_2\text{O}_5 \cdot 5\text{P}_2\text{O}_5$ glass revealed that introduction of Li_2O , SnO_2 and P_2O_5 into vanadate

glass is effective for achieving higher conductivity caused by structural relaxation of the glass network.^{4,5)}

Mössbauer spectroscopy is a powerful tool for the local structural study of oxide glass in which Mössbauer atoms are incorporated as a probe. Oxidation number, coordination number and electronic structure of Mössbauer atoms are evaluated by isomer shift (δ), while local symmetry or distortion by quadrupole splitting (Δ). Nishida et al. reported that structural relaxation of $\text{Fe}^{\text{III}}\text{O}_4$ confirmed by Mössbauer spectra is also the case for $\text{V}^{\text{IV}}\text{O}_4$ and $\text{V}^{\text{V}}\text{O}_4$ tetrahedra since they share corner oxygen atoms with $\text{Fe}^{\text{III}}\text{O}_4$ tetrahedra.⁶⁾ It was reported that silver vanadate glass showed high electrical conductivity of $10^{-2} \text{ S cm}^{-1}$ due to electron hopping from V^{IV} or V^{III} to V^{V} together with ionic conduction caused by Ag^+ .^{7,8)} In the present study, a relationship between local structure, electrical and thermal properties of silver-substituted iron tin phosphovanadate glass was investigated in order to develop higher conductive vanadate glass than previously reported ones.

2. Experimental

Silver substituted iron tin phosphovanadate glass with the compositions of $10\text{SnO}_2 \cdot 10\text{P}_2\text{O}_5 \cdot 10\text{Fe}_2\text{O}_3 \cdot x\text{AgI} \cdot (70 - x)\text{V}_2\text{O}_5$,

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$10\text{SnO}_2 \cdot 10\text{P}_2\text{O}_5 \cdot 10\text{Fe}_2\text{O}_3 \cdot x/2(\text{AgI} \cdot \text{Ag}_2\text{O}) \cdot (70-x)\text{V}_2\text{O}_5$ and $10\text{SnO}_2 \cdot 10\text{P}_2\text{O}_5 \cdot 10\text{Fe}_2\text{O}_3 \cdot x\text{Ag}_2\text{O} \cdot (70-x)\text{V}_2\text{O}_5$, respectively of which was abbreviated as $x\text{AIVSPF}$, $x\text{AOVSPF}$ and $x\text{AIAOVSPF}$ were prepared by conventional melt-quenching method. Reagent chemicals of SnO , $(\text{NH}_4)_2\text{HPO}_4$, Fe_2O_3 , AgI , Ag_2O and V_2O_5 were well mixed in an agate mortar. The mixture with the total amount of 1 or 2 g was poured into a platinum crucible and melted at 1200°C for 1 h. Homogeneous dark brown glass samples could be obtained when the melt was quenched by dipping the crucible bottom into ice-cold water. The prepared glass samples were subjected to heat-treatment at 500°C for 100 min. DC two- and four-probe methods were used for the measurement of electrical conductivity (σ) between room temperature and 125°C ($25, 50, 75, 100$ and $125_{\pm 5}^\circ\text{C}$). For electrical conductivity measurements, as prepared samples were grind into the shape of $5\text{ mm}^2 \times 1\text{ mm}$. Either edge of rectangular glass samples were coated with silver paste. After silver paste was dried, two or four copper leads were attached to the silver paste with solder. The DC-current (I) was recorded by changing the voltage from -50 to 50 V in the former case, whereas voltage (V) was recorded by changing the current from -10 to 10 mA in the latter. Value of σ (S cm^{-1}) was estimated using the following equation, *i.e.*,

$$\sigma = R^{-1} \cdot S^{-1} \cdot l, \quad (1)$$

where R , S and l are electrical resistivity (in Ω) obtained from a slope of straight line of V vs. I plot, surface area (in cm^2) and the distance between the electrodes (in cm), respectively. DTA measurements were performed from RT to 700°C with a heating rate of $10^\circ\text{C min}^{-1}$ under N_2 gas atmosphere with the amount of 100 mL min^{-1} . Ten milligrams of $\alpha\text{-Al}_2\text{O}_3$ was used as a reference. ^{57}Fe -Mössbauer measurements were conducted by a constant acceleration method with a source of ^{57}Co (Rh) and a reference of $\alpha\text{-Fe}$ foil for isomer shift (δ). ^{119}Sn -Mössbauer measurements were also carried out by a conventional acceleration method using $\text{Ca}^{119\text{m}}\text{SnO}_3$ and BaSnO_3 as a source and a reference, respectively. Both spectra were recorded at room temperature and analyzed into Lorentzian with *Mösswinn 3.0i XP*. XRD was measured between 2θ of 10 and 80° setting interval and scanning rate of 0.02 and 5°min^{-1} , respectively. X-rays ($\text{Cu K}\alpha$; $\lambda = 0.1541\text{ nm}$) were generated by setting the tube voltage and current to 50 kV and 300 mA , respectively. Detected crystal phases were identified with respect to standards compiled by the International Center for Diffraction Data (ICDD). SEM images of SEM were taken under the voltage of 2 kV . FT-IR spec-

tra were measured using KBr disk method between the wave-number of 370 and 4000 cm^{-1} under the resolution of 4 cm^{-1} .

3. Results and discussion

3.1 Electrical and thermal properties of new vanadate glass

3.1.1 Electrical conductivity

Homogeneous dark brown glasses were obtained for $x\text{AIVSPF}$, $x\text{AOVSPF}$ and $x\text{AIAOVSPF}$ glasses with ' x ' between 0 and $40\text{ mol } \%$. **Figure 1** shows electrical conductivity (σ) of $x\text{AIVSPF}$, $x\text{AOVSPF}$ and $x\text{AIAOVSPF}$ glasses measured at room temperature. σ of $4.6 \times 10^{-5}\text{ S cm}^{-1}$ was obtained for Ag-free vanadate glass, *i.e.* $10\text{SnO}_2 \cdot 10\text{P}_2\text{O}_5 \cdot 10\text{Fe}_2\text{O}_3 \cdot 70\text{V}_2\text{O}_5$, which is much higher than that of previously studied $15\text{Li}_2\text{O} \cdot 10\text{Fe}_2\text{O}_3 \cdot 70\text{V}_2\text{O}_5 \cdot 5\text{P}_2\text{O}_5$ glass having σ of $7.3 \times 10^{-7}\text{ S cm}^{-1}$.^{4),5)} Therefore, it can be considered that SnO_2 and P_2O_5 contents being equal or less than $10\text{ mol } \%$ is favourable for achieving higher electrical conductivity of vanadate glass. Before heat-treatment at 500°C for 100 min, decreasing σ s from $(2.2_{\pm 0.2}) \times 10^{-5}$ to $(2.6_{\pm 0.2}) \times 10^{-6}\text{ S cm}^{-1}$ for $x\text{AIVSPF}$ [Fig. 1(a)], from $(3.9_{\pm 0.5}) \times 10^{-4}$ to $(4.5_{\pm 2.0}) \times 10^{-8}\text{ S cm}^{-1}$ for $x\text{AOVSPF}$ glass [Fig. 1(b)] and from $(1.5_{\pm 0.1}) \times 10^{-5}$ to $(1.3_{\pm 0.1}) \times 10^{-8}\text{ S cm}^{-1}$ for $x\text{AIAOVSPF}$ glass [Fig. 1(c)] were observed with the increase of AgI or Ag_2O content from 10 to $40\text{ mol } \%$. These results imply that introduction of AgI or Ag_2O into vanadate glass causes decrease in σ . After heat-treatment at 500°C for 100 min, much higher σ s

Fig. 1. Electrical conductivity (σ) of $x\text{AIVSPF}$ (red circle), $x\text{AOVSPF}$ (blue circle) and $x\text{AIAOVSPF}$ (green circle) with different silver content before (open symbols) and after heat-treatment (closed symbols).

Fig. 2. $\ln \sigma T$ vs. T^{-1} plot of (A) $x\text{AIVSPF}$ with ' x ' of 10 (circle), 20 (triangle) and 30 (square) and (B) $x\text{AOVSPF}$ with ' x ' of 10 (circle), 20 (triangle) and 30 (square) before (open symbols) and after heat-treatments (closed symbols).

of $(2.6_{\pm 0.1}) \times 10^{-1}$, $(2.1_{\pm 0.1}) \times 10^{-1}$, $(5.2_{\pm 0.1}) \times 10^{-2}$ and $(1.3_{\pm 0.4}) \times 10^{-2} \text{ S cm}^{-1}$ were observed for xAIVSPF glass with 'x' of 10, 20, 30 and 40 mol %, respectively [Fig. 1(d)]. It should be noted that high σ value was confirmed for xAIVSPF glass with larger AgI content, indicating that AgI contributes the increase in σ of vanadate glass. On the contrary, increase in σ becomes smaller in the case of annealed 40AOVSPF and 40AIAOVSPF glasses. These results indicate that increase in σ could not occur when Ag_2O is substituted for V_2O_5 .

Activation energy for electron hopping (W_H) is calculated by the following equation,^{9) i.e.,}

$$\ln \sigma T = \ln \sigma_0 - W_H/kT, \quad (2)$$

where σ , T , σ_0 and k are conductivity and measurement temperature, the extrapolation at infinite temperature ($T^{-1} = 0$) of the σT product and Boltzmann constant, respectively. Values of W_H can be calculated from the slope value of $\ln \sigma T$ vs. T^{-1} plot, as shown in Fig. 2. In Fig. 3, W_H values were plotted against "x" of xAIVSPF, xAOVSPF and xAIAOVSPF glasses before and after heat treatment. Stable W_H of $0.23_{\pm 0.02}$ ($x = 10$), $0.24_{\pm 0.04}$ ($x = 20$), $0.25_{\pm 0.03}$ ($x = 30$) and $0.25_{\pm 0.02}$ ($x = 40$) eV were obtained for xAIVSPF glasses (Fig. 3, open red circle), respectively of which decreased to $0.10_{\pm 0.02}$, $0.10_{\pm 0.01}$, $0.11_{\pm 0.01}$ and $0.02_{\pm 0.03}$ eV after the heat-treatment (Fig. 3, closed red circle). In

Fig. 3. Activation energy for electron hopping of xAIVSPF (red), xAOVSPF (blue) and xAIAOVSPF (green) glasses before (open symbols) and after heat-treatments (closed symbols).

the case of xAOVSPF glass, W_H slightly increased from $0.10_{\pm 0.01}$ to $0.25_{\pm 0.03}$, $0.31_{\pm 0.02}$ and $0.29_{\pm 0.02}$ eV with the increase of 'x' from 10 to 20, 30 and 40 mol % (Fig. 3, open blue circle). These results suggest that W_H of annealed xAOVSPF glass was increased by the introduction of Ag_2O , which inversely corresponds to the σ . An increase in W_H could also be observed for xAIAOVSPF glass (Figs. 3, open and closed green circles). It can be said that new vanadate glass with higher electron conductivity could be developed by introducing SnO_2 , P_2O_5 and AgI.

3.1.2 DTA curves

DTA curves of xAIVSPF and xAOVSPF glasses recorded under a heating rate (α) of $10^\circ\text{C min}^{-1}$ are illustrated in Fig. 4. In order to recognize glass transition temperature (T_g) clearly, focused DTA curves around the T_g are shown in Fig. 5. T_g of $248_{\pm 5}$, $285_{\pm 5}$, $289_{\pm 5}$ and $298_{\pm 5}^\circ\text{C}$ and crystallization temperature (T_c) of $376_{\pm 2}$, $363_{\pm 2}$, $362_{\pm 2}$ and $379_{\pm 2}$ were observed for xAIVSPF glass with 'x' of 10, 20, 30 and 40 mol %, respectively. In contrast, gradual decreases in T_g from $277_{\pm 5}$ to $273_{\pm 5}$, $258_{\pm 5}$ and $216_{\pm 5}^\circ\text{C}$ and T_c from $356_{\pm 2}$ to $329_{\pm 2}$, $332_{\pm 2}$ and $283_{\pm 2}$ were observed for xAOVSPF glass. Similar decreases in T_g from $293_{\pm 5}$ to $262_{\pm 5}^\circ\text{C}$ and T_c from $368_{\pm 2}$ to $332_{\pm 2}^\circ\text{C}$ could be observed for xAIAOVSPF glass. These results indicate that the thermal stability of xAIVSPF glasses is almost comparable irrespective of AgI, whereas that of xAOVSPF and xAIAOVSPF glass are decreased by the introduction of Ag_2O . By considering together with decreases in electron conductivity and thermal stability of xAOVSPF glass with the increase of 'x' after heat-treatment, it can be considered that Ag_2O acts as a network modifier (NWM) and cuts 3D glass network of vanadate glass composed by VO_3 and VO_4 units.

3.2 Structural characterization of new vanadate glass

3.2.1 Mössbauer spectra

^{57}Fe -Mössbauer spectra of xAIVSPF glasses before and after heat-treatment for 100 min at 500°C are shown in Fig. 6. Before heat-treatment, all the spectra were analysed into one paramagnetic doublet due to distorted $\text{Fe}^{\text{III}}\text{O}_4$ tetrahedra with an identical isomer shift (δ) of $0.41_{\pm 0.02} \text{ mm s}^{-1}$, a quadruple splitting (Δ) of $0.76_{\pm 0.02} \text{ mm s}^{-1}$ and a line width (Γ) of $0.52_{\pm 0.03} \text{ mm s}^{-1}$ irrespective AgI content [Figs. 6(A) (a)–(d)], indicating that chemical environment of Fe^{III} was not affected by the

Fig. 4. DTA curves of (A) xAIVSPF and (B) xAOVSPF glasses with 'x' of (a) 10, (b) 20, (c) 30 and (d) 40 measured under a heating rate of $10^\circ\text{C min}^{-1}$.

Fig. 5. Focused DTA curves around the T_g of (A) $x\text{AIVSPF}$ and (B) $x\text{AOVSPF}$ glasses with 'x' of (a) 10, (b) 20, (c) 30 and (d) 40 measured under a heating rate of $10^\circ\text{C min}^{-1}$.

Fig. 6. ^{57}Fe -Mössbauer spectra of $10\text{SnO}_2 \cdot 10\text{P}_2\text{O}_5 \cdot 10\text{Fe}_2\text{O}_3 \cdot x\text{AgI} \cdot (70-x)\text{V}_2\text{O}_5$ glasses with 'x' of (a) 10, (b) 20, (c) 30 and (d) 40 (A) before and (B) after heat-treatment at 500°C for 100 min.

introduction of AgI. On the other hand, constant δ of $0.44_{\pm 0.02} \text{ mm s}^{-1}$, Γ of $0.57_{\pm 0.04} \text{ mm s}^{-1}$ and smaller or identical Δ of $0.66_{\pm 0.02}$ ($x = 10$), $0.76_{\pm 0.02}$ ($x = 20$), $0.70_{\pm 0.02}$ ($x = 30$) and $0.67_{\pm 0.01}$ ($x = 40$) mm s^{-1} were observed for annealed $x\text{AIVSPF}$ glass, reflecting the structural relaxation of tetrahedral FeO_4 and VO_4 units²⁾⁻⁵⁾ [Figs. 6(B) (a)–(d)]. In the case of $x\text{AOVSPF}$ glass, ^{57}Fe -Mössbauer spectra showed one doublet with iden-

tical δ of $0.42_{\pm 0.02} \text{ mm s}^{-1}$, Γ of $0.51_{\pm 0.04} \text{ mm s}^{-1}$ and slightly decreasing Δ s from $0.75_{\pm 0.02}$ to $0.70_{\pm 0.03}$, $0.61_{\pm 0.03}$ and $0.61_{\pm 0.04} \text{ mm s}^{-1}$ with the increase of 'x' from 10 to 20, 30 and 40 [Figs. 7(A) (a)–(d)]. This result indicates that the local distortion of FeO_4 tetrahedra of $x\text{AOVSPF}$ glass was decreased due to the introduction of Ag_2O . It is noted that drastic decreases in Δ from $0.86_{\pm 0.01}$ to $0.36_{\pm 0.01} \text{ mm s}^{-1}$ and Γ from $0.58_{\pm 0.02}$ to

Fig. 7. ^{57}Fe -Mössbauer spectra of $10\text{SnO}_2\cdot 10\text{P}_2\text{O}_5\cdot 10\text{Fe}_2\text{O}_3\cdot x\text{Ag}_2\text{O}\cdot (70-x)\text{V}_2\text{O}_5$ glasses with 'x' of (a) 10, (b) 20, (c) 30 and (d) 40 (A) before and (B) after heat-treatment at 500°C for 100 min.

Fig. 8. ^{119}Sn -Mössbauer spectra of (A) $10\text{SnO}_2\cdot 10\text{P}_2\text{O}_5\cdot 10\text{Fe}_2\text{O}_3\cdot x\text{AgI}\cdot (70-x)\text{V}_2\text{O}_5$ and (B) $10\text{SnO}_2\cdot 10\text{P}_2\text{O}_5\cdot 10\text{Fe}_2\text{O}_3\cdot x\text{Ag}_2\text{O}\cdot (70-x)\text{V}_2\text{O}_5$ glasses with 'x' of (a) 10 and (b) 40 (1) before and (2) after heat-treatment at 500°C for 100 min.

$0.31_{\pm 0.01} \text{ mm s}^{-1}$ were observed from annealed $x\text{AOVSPF}$ glass with the increase of Ag_2O content [Figs. 7(B) (a)–(d)]. These results suggest that substitution of AgI doesn't affect $\text{Fe}^{\text{III}}\text{O}_4$ or VO_4 and PO_4 forming glass network, while that of Ag_2O dramatically changes environment around the network former. These results are related to the reason why $x\text{AIVSPF}$ glass showed higher σ and $x\text{AOVSPF}$ glass didn't.

As shown in Fig. 8, identical ^{119}Sn -Mössbauer spectra with δ of $0.07_{\pm 0.01}$, Δ of $0.50_{\pm 0.02} \text{ mm s}^{-1}$ and Γ of $0.91_{\pm 0.02} \text{ mm s}^{-1}$ were observed for $x\text{AIVSPF}$ glass before and after the heat-treatments irrespective of silver content. These results show that starting material of SnO was oxidized to SnO_2 when incorporated into silver vanadate glass, and that the local structure was not

affected by the heat-treatment at 500°C . Similar results were also observed from the ^{119}Sn -Mössbauer spectra of $x\text{AOVSPF}$ glass before and after the heat-treatment (δ : $0.07_{\pm 0.02} \text{ mm s}^{-1}$, Δ : $0.50_{\pm 0.02} \text{ mm s}^{-1}$ and Γ : $0.91_{\pm 0.02} \text{ mm s}^{-1}$).

3.2.2 XRD patterns and SEM images

XRD patterns of $x\text{AIVSPF}$ glasses before and after heat-treatment at 500°C are shown in Fig. 9. Before heat-treatment, a halo pattern characteristic for glass amorphous and sharp intense peaks attributed to crystalline phase of SnO_2 ($2\theta = 26.5, 34.0, 37.9, 51.7$ and 54.8° etc., PDF No. 01-077-0447) could be observed [Figs. 9(A) (a)–(d)]. However, no grain boundaries derived from SnO_2 crystalline were observed from the SEM images of $x\text{AIVSPF}$ glass before heat treatment [Fig. 10(A)].

Fig. 9. XRD patterns of $10\text{SnO}_2\cdot 10\text{P}_2\text{O}_5\cdot 10\text{Fe}_2\text{O}_3\cdot x\text{AgI}\cdot (70-x)\text{V}_2\text{O}_5$ glasses with 'x' of (a) 10, (b) 20, (c) 30 and (d) 40 (A) before and (B) after heat-treatment at 500°C for 100 min.

Fig. 10. SEM images of 40AIVSPF glass (A) before and (B) after heat-treatment at 500°C for 100 min.

These results suggest that Sn^{IV} occupy interstitial sites as a network modifier in the vanadate glass. Heat-treatment at 500°C for 100 min of 10AIVSPF glass resulted in appearance of sharp intense peaks attributable to $\text{Ag}_{0.35}\text{V}_2\text{O}_5$ ($2\theta = 12.1, 18.7, 22.8, 26.5, 29.0, 32.7, 33.7, 41.3$ and 45.5° , PDF No. 00-028-1027) and PSn ($2\theta = 27.8, 37.9, 50.7$ and 51.7° , PDF No. 03-065-9787) [Fig. 9(B) (a)]. On the other hand, peaks of $\text{Ag}_{0.35}\text{V}_2\text{O}_5$ gradually decreased the intensity, and new peaks attributed to $\text{Ag}_{1.2}(\text{VO}_3)$ ($2\theta = 12.5, 16.6, 22.4, 25.9, 28.2, 29.0, 34.0, 44.7$ and 50.7° , PDF No. 01-088-0686) and Sn_4P_3 ($2\theta = 31.3, 44.7$ and 45.7° , PDF No. 01-073-1820) were observed for XRD patterns of annealed xAIVSPF glass with 'x' of 20, 30 and 40 [Figs. 9(B) (b)–(d)]. Crystalline phases of $\text{Ag}_{0.35}\text{V}_2\text{O}_5$, SnO_2 and PSn were respectively confirmed from XRD patterns of annealed 10AOVSPF and 10AIAOVSPF glasses, both of which showed increase of σ after heat-treatment. In contrast, heat-treatment of

40AOVSPF and 40AIAOVSPF glasses resulted in precipitation of $\text{Ag}_{1.2}(\text{VO}_3)$ ($2\theta = 12.5, 16.6, 22.4, 25.9, 28.2, 29.0, 34.0, 44.7$ and 50.7° , PDF No. 01-088-0686), AgVO_3 ($2\theta = 17.2, 18.7, 28.2, 31.9, 32.7$ and 33.7° , PDF No. 01-089-4396) and $\text{Fe}_4(\text{PO}_4)_2\text{O}$ ($2\theta = 19.7, 28.1, 31.8, 33.1, 33.7$ and 42.4° , PDF No. 00-036-0114). These results prove that the crystalline phase of $\text{Ag}_{0.35}\text{V}_2\text{O}_5$ precipitated in heat-treated silver vanadate glass contribute to the enhancement of σ because electrical conductivity of $\text{Ag}_{0.35}\text{V}_2\text{O}_5$ is reported to be high (0.5 S cm^{-1}).¹⁰⁾ It is reasonable to consider that the slight decrease in σ from $(2.6 \pm 0.1) \times 10^{-1}$ to $(1.3 \pm 0.4) \times 10^{-2}\text{ S cm}^{-1}$ observed for annealed xAIVSPF glass with the increase of AgI content (x) from 10 to 40 mol % [see Fig. 1(d)] is due to the decrease in the fraction of conductive $\text{Ag}_{0.35}\text{V}_2\text{O}_5$ phase.

3.2.3 FT-IR spectra

FT-IR spectra of xAIVSPF and xAOVSPF glasses after heat-treatment at 500°C for 100 min are shown in Fig. 11. Absorption peaks at $540, 680, 750, 920, 970, 1020$ and 1100 cm^{-1} were observed for all annealed xAIVSPF glasses irrespective of AgI content [Figs. 11(A) (a)–(d)]. The absorption peaks observed at 540 cm^{-1} is assigned to P–O–P bending^{11),12)} and Fe–O stretching mode of $\text{Fe}(\text{T}_d)\text{O}_4$ ^{13),14)} at 680 cm^{-1} to V–O–V anti-symmetric stretching mode,^{14),15)} at 750 cm^{-1} to V–O stretching mode of $\text{V}(\text{T}_d)\text{O}_4$,¹⁶⁾ at 920 cm^{-1} to VO_3 terminal stretching mode of pyrovanadate ($\text{V}_2\text{O}_7^{4-}$) ion,^{14),15)} at 970 and 1020 cm^{-1} to $\text{V}=\text{O}$ stretching mode of VO_5 pyramid^{14),17)} and at 1100 cm^{-1} to P–O stretching mode.^{11),12)} Previous studies on AgI containing vanadate glass revealed that the addition of AgI caused no changes in FT-IR spectra,^{18),19)} evidently showing that the glass network structure of xAIVSPF glass is not affected by the addition of AgI and heat-treatment. Similar FT-IR spectra were obtained for annealed xAOVSPF glasses with 'x' of up to 20 mol % [Figs. 11(B) (a) and (b)]. In contrast, quite different FT-IR spectra were observed for heat-treated xAOVSPF glass with 'x' being equal to or larger than 30 mol % [Figs. 11(B) (c) and (d)]; the absorption bands of $\text{V}=\text{O}$ groups at $1000\text{--}970\text{ cm}^{-1}$ and P–O–P bending at 540 cm^{-1} disappeared, and new absorption bands appeared at 858 cm^{-1} corresponding to V–O–V bending of VO_5 ,^{14),20)} at 896 and 964 cm^{-1} to VO_3 terminal stretching of

Fig. 11. FT-IR spectra of (A) x AIVSPF and (B) x AOVSPF glasses heat-treated at 500°C for 100 min with ' x ' of (a) 10, (b) 20, (c) 30 and (d) 40.

pyrovanadate ions, and at 760 cm^{-1} to V–O bending of $\text{V}(\text{Td})\text{O}_4$. From these results, it can be said that introduction of Ag_2O into x AOVSPF glass results in the cleavage of glass network composed by VO_4 and VO_5 units and production of non-bridging oxygen of V=O bond of VO_5 or VO_3 terminal bond of $\text{V}_2\text{O}_7^{4-}$. And the production of non-bridging oxygen causes the decreases in thermal stability and electrical conductivity of x AOVSPF glasses. These results indicate that Ag_2O acts as a network modifier in x AOVSPF glass as likely to be observed in the previous studies.^{21)–24)} It is concluded that introduction of AgI is preferable for achieving the higher electrical conductivity of vanadate glass because it doesn't cleave network of vanadate glass composed by VO_4 and VO_5 units.

4. Summary

A relationship between local structure and physical properties of AgI and/or Ag_2O substituted tin iron phospho-vanadate glasses were investigated by ^{57}Fe - and ^{119}Sn -Mössbauer spectra, XRD, SEM, FT-IR, DTA, and DC-two and -four probe method. After heat-treatment at 500°C for 100 min, a larger σ between 2.6×10^{-1} and $1.3 \times 10^{-2} \text{ S cm}^{-1}$ was observed for annealed x AIVSPF glass irrespective of AgI content. These σ values are larger than 2 orders of magnitude higher than those of previously reported phospho-vanadate glasses.^{4),5)} On the other hand, decrease in σ from 2.9×10^{-1} to $1.8 \times 10^{-7} \text{ S cm}^{-1}$ was observed for annealed x AOVSPF glass with the increase of Ag_2O content. From DTA study, T_g around 280°C and T_c of 370°C were observed for x AIVSPF glass irrespective of AgI content, whereas gradual decreases in T_g from 277 to 216°C and T_c from 356 to 283°C were confirmed for x AOVSPF glass with the increase of Ag_2O content, respectively. From ^{57}Fe -Mössbauer study, decrease in quadrupole splitting (Δ) was observed for annealed x AIVSPF glass, indicating that the reduction of local distortion of FeO_4 tetrahedra occurred due to the structural relaxation. Precipitation of conductive $\text{Ag}_{0.35}\text{V}_2\text{O}_5$ phase having σ of $5.0 \times 10^{-1} \text{ S cm}^{-1}$ was identified from XRD patterns of heat-treated x AIVSPF glass with ' x ' of equal to or less than 30 mol %. From FT-IR study of heat-treated x AIVSPF glass, existence of

bridging oxygen (BO) was confirmed in the form of bending modes of O–P–O at 540 cm^{-1} and V–O–V at 680 cm^{-1} proving that 3D glass network was composed by VO_4 , VO_5 and PO_4 units. On the other hand, the above described absorption mode proving the existence of BO disappeared and non-bridging oxygen (NBO) was detected as VO_3 terminal stretching mode of $\text{V}_2\text{O}_7^{4-}$ in the case of annealed x AOVSPF with ' x ' of equal to or larger than 30 mol %. These results indicate that introduction of AgI into iron tin phosphovanadate glass doesn't cleave the 3D glass network and resulted in the enhancement of electrical conductivity due to the structural relaxation and precipitation of conductive $\text{Ag}_{0.35}\text{V}_2\text{O}_5$ phase, whereas introduction of Ag_2O causes cleavage of the glass network and resulted in the decrease in the electrical conductivity and thermal stability. It is concluded that AgI-substituted iron tin phosphovanadate glass is the most favourable material with high electron conductivity among the studied vanadate glasses.

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