A relationship between electrical conductivity and structural relaxation of $10\text{SnO}_2\cdot10\text{Fe}_2\text{O}_3\cdot10\text{P}_2\text{O}_5\cdot x\text{AgI}\cdot(70-x)\text{V}_2\text{O}_5$ glass caused by heat-treatment

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A relationship between local structure, electrical conductivity ($\sigma$) and thermal property of $10\text{SnO}_2\cdot10\text{P}_2\text{O}_5\cdot10\text{Fe}_2\text{O}_3\cdot x\text{AgI}\cdot(70-x)\text{V}_2\text{O}_5$ glasses, respectively abbreviated as $\text{xAIVSPF}$, $\text{xAOVSPF}$ and $\text{xAAIVSPF}$ with $x$ between 0 and 40 mol% were investigated by $^{57}\text{Fe}$ and $^{119}\text{Sn}$-Mössbauer spectroscopies, X-ray diffractionmetry (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 $\text{xAIVSPF}$ glass with $x$ of 10, 20, 30 and 40 resulted in a marked increase in $\sigma$ from 2.2 $\times$ 10$^{-5}$, 9.4 $\times$ 10$^{-5}$, 3.2 $\times$ 10$^{-4}$ and 2.6 $\times$ 10$^{-4}$ cm$^{-1}$ to 2.6 $\times$ 10$^{-4}$, 2.1 $\times$ 10$^{-4}$, 5.2 $\times$ 10$^{-4}$ and 1.3 $\times$ 10$^{-3}$ S cm$^{-1}$, respectively. Similar increase in $\sigma$ caused by heat-treatment was also observed for $\text{xAOVSPF}$ and $\text{xAAIVSPF}$ 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 $\text{xAIVSPF}$ glass, whereas gradual decreases in $T_g$ from 277°C to 216°C and $T_c$ from 356°C to 283°C were confirmed for $\text{xAOVSPF}$ glass, implying that substitution of AgI for $\text{V}_2\text{O}_5$ didn’t affect the 3D glass network but that of AgO causes the cleavage of the 3D glass network. FT-IR study of the heat treated $\text{xAOVSPF}$ glass showed the dissappearance of bridging oxygen of $\text{P-O-P}$ and $\text{V-O-V}$ with the AgO content, indicating that cleavage of the 3D glass network caused the decrease of the electrical conductivity. It can be concluded that AgI-substitututed iron tin phosphovanadate glass is better than AgO-substituted iron tin phosphovanadate glass for achieving the higher electrical conductivity.

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1. Introduction

Semiconducting vanadate glass exhibits electrical conductivity ($\sigma$) of 10$^{-3}$ to 10$^{-5}$ S cm$^{-1}$ caused by a step-by-step electron (polaron) hopping from $\text{V}^{\text{VI}}$ to $\text{V}^{\text{V}}$ to $\text{V}^{\text{IV}}$.) Kubuki et al. discovered a remarkable increase in $\sigma$ from the order of 10$^{-5}$ to 10$^{9}$ S cm$^{-1}$ in 20BaO·10Fe$_2$O$_3$·70V$_2$O$_5$ glass after heat-treatment at temperatures higher than glass transition temperature ($T_g$) or crystallization temperature ($T_c$). This result showed that $\sigma$ 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$_2$O$_5$. Development of new vanadate glass has attracted much interest because some vanadate glasses have several industrial applications for electron-emitting needle for ionizer, cathode active material for Li-ion battery. Recently, an investigation of $15\text{Li}_2\text{O}\cdot10\text{Fe}_2\text{O}_3\cdot x\text{SnO}_2\cdot (70-x)\text{V}_2\text{O}_5$ glass revealed that introduction of Li$_2$O, SnO$_2$ and P$_2$O$_5$ into vanadate glass is effective for achieving higher conductivity caused by structural relaxation of the glass network.

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 ($\delta$), while local symmetry or distortion by quadrupole splitting ($\Delta$). Nishida et al. reported that structural relaxation of Fe$^{IV}$O$_4$ confirmed by Mössbauer spectra is also the case for V$^{IV}$O$_4$ and VO$_4$ tetrahedra since they share corner oxygen atoms with Fe$^{IV}$O$_4$ tetrahedra. It was reported that silver vanadate glass showed high electrical conductivity of 10$^{-2}$ S cm$^{-1}$ due to electron hopping from $\text{V}^{\text{IV}}$ to $\text{V}^{\text{III}}$ together with ionic conduction caused by Ag$^+$. 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 $10\text{SnO}_2\cdot10\text{P}_2\text{O}_5\cdot10\text{Fe}_2\text{O}_3\cdot x\text{AgI}\cdot(70-x)\text{V}_2\text{O}_5$. 
10SnO2·10P2O5·10Fe2O3·2/(AgI·Ag2O)·(70 – x)V2O5 and 10SnO2·10P2O5·10Fe2O3·xAgO·(70 – x)V2O5, respectively of which was abbreviated as xAIVSPF, xAOVSPF and xAIAOVSPF were prepared by conventional melt-quenching method. Reagent chemicals of SnO, (NH4)2HPO4, Fe2O3, AgI, Ag2O and V2O5 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°C). For electrical conductivity measurements, as prepared samples were grind into the shape of 5 mm2 x 1 mm. Either edge of rectangular glass samples were coated with silver paste and 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.,

\[ \sigma = \frac{R}{S} \cdot \frac{1}{L} \]

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 cm²) and the distance between the electrodes (in cm), respectively. DTA measurements were performed from RT to 700°C with a heating rate of 10°C min⁻¹ under N₂ gas atmosphere with the amount of 100 mL min⁻¹. Ten milligrams of α-Al₂O₃ was used as a reference. ⁵⁷Fe-Mössbauer measurements were conducted by a constant acceleration method with a source of ⁵⁷Co (Rh) and a reference of α-Fe foil for isomer shift (δ). ¹¹⁹Sn-Mössbauer measurements were also carried out by a conventional acceleration method using Ca¹¹⁹SnO₃ and BaSnO₃ as a source and a reference, respectively. Both spectra were recorded at room temperature and analyzed into Lorentzian with Mösswinn 3.0i program. XRD was measured between 2θ of 10 and 80° setting interval and scanning rate of 0.02 and 5°min⁻¹, respectively. X-rays (Cu Kα; λ = 0.1541 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 spectra 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 xAIVSPF, xAOVSPF and xAIAOVSPF glasses with ‘x’ between 0 and 40 mol %. Figure 1 shows electrical conductivity (σ) of xAIVSPF, xAOVSPF and xAIAOVSPF glasses measured at room temperature. σ of 4.6 × 10⁻⁵ S cm⁻¹ was obtained for Ag-free vanadate glass, i.e. 10SnO2·10P2O5·10Fe2O3·70V2O5, which is much higher than that of previously studied 15Li2O·10Fe2O3·70V2O5·5P2O5 glass having σ of 7.3 × 10⁻⁷ S cm⁻¹. Therefore, it can be considered that SnO2 and P2O5 contents being equal or less than 10 mol % is favourable for achieving higher electrical conductivity of vanadate glass. Before heat-treatment at 500°C for 100 min, decreasing σ from (2.2±0.2)×10⁻⁵ to (2.6±0.2)×10⁻⁶ S cm⁻¹ for xAIVSPF [Fig. 1(a)], from (3.9±0.5)×10⁻⁴ to (4.5±0.2)×10⁻⁸ S cm⁻¹ for xAOVSPF glass [Fig. 1(b)] and from (1.5±0.1)×10⁻⁵ to (1.3±0.1)×10⁻⁵ S cm⁻¹ for xAIAOVSPF glass [Fig. 1(c)] were observed with the increase of AgI or Ag2O content from 10 to 40 mol %. These results imply that introduction of AgI or Ag₂O 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 xAIVSPF (red circle), xAOVSPF (blue circle) and xAIAOVSPF (green circle) with different silver content before (open symbols) and after heat-treatments (closed symbols).](image)

![Fig. 2. lnσT vs. T⁻¹ plot of (A) xAIVSPF with “x” of 10 (circle), 20 (triangle) and 30 (square) and (B) xAOVSPF with “x” of 10 (circle), 20 (triangle) and 30 (square) before before (open symbols) and after heat-treatments (closed symbols).](image)
of (2.6±0.1)×10⁻¹, (2.1±0.1)×10⁻¹, (5.2±0.1)×10⁻² and (1.3±0.4)×10⁻² 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 Ag₂O is substituted for V₂O₅.

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

\[ \ln(\sigma T) = \ln(\sigma_0) - \frac{W_H}{kT}, \]

where σ, T, σ₀ 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(σT) 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 0.25±0.02 (x = 10), 0.24±0.04 (x = 20), 0.25±0.03 (x = 30) and 0.25±0.02 (x = 40) eV were obtained for xAIVSPF glasses (Fig. 3, open red circle), respectively of which decreased to 0.10±0.02, 0.10±0.01, 0.11±0.01 and 0.02±0.01 eV after the heat-treatment (Fig. 3, closed red circle).

In the case of xAOVSPF glass, W_H slightly increased from 0.10±0.01 to 0.25±0.03, 0.31±0.02 and 0.29±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 Ag₂O, 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 SnO₂, P₂O₅ and AgI.

3.1.2 DTA curves

DTA curves of xAIVSPF and xAOVSPF glasses recorded under a heating rate (α) of 10°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±5, 258±5, 289±5 and 298±5°C and crystallization temperature (T_c) of 376±2, 363±2, 362±2 and 379±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±5 to 273±5, 258±5 and 216±5°C and T_c from 356±2 to 329±2, 332±2 and 283±2 were observed for xAOVSPF glass. Similar decreases in T_g from 293±5 to 262±5°C and T_c from 368±2 to 332±2°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 Ag₂O. 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 Ag₂O acts as a network modifier (NWM) and cuts 3D glass network of vanadate glass composed by VO₅ and VO₄ units.

3.2 Structural characterization of new vanadate glass

3.2.1 Mössbauer spectra

⁵⁷Fe-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 Fe⁷⁺O₄ tetrahedra with an identical isomer shift (δ) of 0.41±0.02 mm s⁻¹, a quadruple splitting (Δ) of 0.76±0.02 mm s⁻¹ and a line width (γ) of 0.52±0.03 mm s⁻¹ irrespective AgI content [Figs. 6(A) (a)–(d)], indicating that chemical environment of Fe³⁺ was not affected by the
introduction of AgI. On the other hand, constant $\delta$ of $0.44 \pm 0.02$ mm s$^{-1}$, $\Gamma$ of $0.57 \pm 0.04$ mm s$^{-1}$ and smaller or identical $\Delta$ 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 $x$AIVSPF glass, reflecting the structural relaxation of tetrahedral FeO₄ and VO₄ units[2-5] [Figs. 6(B) (a)-(d)]. In the case of $x$AOVSPF glass, $^{57}$Fe-Mössbauer spectra showed one doublet with identical $\delta$ of $0.42 \pm 0.02$ mm s$^{-1}$, $\Gamma$ of $0.51 \pm 0.04$ mm s$^{-1}$ and slightly decreasing $\Delta$s from $0.75 \pm 0.02$ to $0.70 \pm 0.01$, $0.61 \pm 0.03$ and $0.61 \pm 0.04$ 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 FeO₄ tetrahedra of $x$AOVSPF glass was decreased due to the introduction of Ag₂O. It is noted that drastic decreases in $\Delta$ from $0.86 \pm 0.01$ to $0.36 \pm 0.01$ mm s$^{-1}$ and $\Gamma$ from $0.58 \pm 0.02$ to
0.31\textpm0.01 \text{ mm s}^{-1} were observed from annealed xAOVSPF glass with the increase of Ag$_2$O content [Figs. 7(B) (a)–(d)]. These results suggest that substitution of AgI doesn’t affect Fe$_{IV}$O$_4$ or VO$_4$ and PO$_4$ forming glass network, while that of Ag$_2$O dramatically changes environment around the network former. These results are related to the reason why xAIVSPF glass showed higher \( \sigma \) and xAOVSPF glass didn’t.

As shown in Fig. 8, identical $^{119}$Sn-Mössbauer spectra with $\delta$ of 0.07\textpm0.01, $\Delta$ of 0.50\textpm0.02 mm s$^{-1}$ and $I'$ of 0.91\textpm0.02 mm s$^{-1}$ were observed for xAIVSPF 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 xAOVSPF glass before and after the heat-treatment ($\delta$: 0.07\textpm0.02 mm s$^{-1}$, $\Delta$: 0.50\textpm0.02 mm s$^{-1}$ and $I'$: 0.91\textpm0.02 mm s$^{-1}$).

### 3.2.2 XRD patterns and SEM images

XRD patterns of xAIVSPF 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 $54.8^\circ$, 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 xAIVSPF glass before heat treatment [Fig. 10(A)].

![Fig. 7. $^{57}$Fe-Mössbauer spectra of 10SnO$_2$:10P$_2$O$_5$:10Fe$_2$O$_3$:xAg$_2$O:(70-x)V$_2$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.](image)

![Fig. 8. $^{119}$Sn-Mössbauer spectra of (A) 10SnO$_2$:10P$_2$O$_5$:10Fe$_2$O$_3$:xAgI:(70-x)V$_2$O$_5$ and (B) 10SnO$_2$:10P$_2$O$_5$:10Fe$_2$O$_3$:xAg$_2$O:(70-x)V$_2$O$_5$ glasses with ‘x’ of (a) 10 and (b) 40 (1) before and (2) after heat-treatment at 500°C for 100 min.](image)
These results suggest that Sn\textsuperscript{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 Ag\textsubscript{0.35}V\textsubscript{2}O\textsubscript{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 Ag\textsubscript{0.35}V\textsubscript{2}O\textsubscript{5} gradually decreased the intensity, and new peaks attributed to Ag\textsubscript{1.2}(VO\textsubscript{3})(2\(\theta\) = 12.5, 16.6, 25.9, 28.2, 29.0, 34.0, 44.7 and 50.7°, PDF No. 01-088-0686) and Sn\textsubscript{4}P\textsubscript{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 Ag\textsubscript{0.35}V\textsubscript{2}O\textsubscript{5}, SnO\textsubscript{2} and PSn were respectively confirmed from XRD patterns of annealed 10AOVSPF and 10AIAOVSPF glasses, both of which showed increase of \(\sigma\) after heat-treatment. In contrast, heat-treatment of 40AOVSPF and 40AIAOVSPF glasses resulted in precipitation of Ag\textsubscript{1.2}(VO\textsubscript{3})(2\(\theta\) = 12.5, 16.6, 25.9, 28.2, 29.0, 34.0, 44.7 and 50.7°, PDF No. 01-088-0686), AgVO\textsubscript{3} (2\(\theta\) = 17.2, 18.7, 28.2, 31.9, 32.7 and 33.7°, PDF No. 01-089-4396) and Fe\textsubscript{4}(PO\textsubscript{4})\textsubscript{2}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 Ag\textsubscript{0.35}V\textsubscript{2}O\textsubscript{5} precipitated in heat-treated silver vanadate glass contribute to the enhancement of conductivity because electrical conductivity of Ag\textsubscript{0.35}V\textsubscript{2}O\textsubscript{5} is reported to be high (0.5 S cm\textsuperscript{-1}).\textsuperscript{10) It is reasonable to consider that the slight decrease in \(\sigma\) from (2.6 ± 0.1)\(\times\)10\textsuperscript{-2} Sc m\textsuperscript{-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 Ag\textsubscript{0.35}V\textsubscript{2}O\textsubscript{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\textsuperscript{-1} were observed for all annealed xAIVSPF glasses irrespective of AgI content [Figs. 11(A) (a)-(d)]. The absorption peaks observed at 540 cm\textsuperscript{-1} is assigned to P–O–P bending\textsuperscript{11),12) and Fe–O stretching mode of Fe(\textit{T}d)O\textsubscript{4},\textsuperscript{13),14) at 680 cm\textsuperscript{-1} to V–O–V anti-symmetric stretching mode,\textsuperscript{14),15) at 750 cm\textsuperscript{-1} to V–O stretching mode of V(\textit{T}d)O\textsubscript{4},\textsuperscript{16) at 920 cm\textsuperscript{-1} to VO\textsubscript{3} terminal stretching mode of pyrovanadate (V\textsubscript{2}O\textsubscript{7})\textsuperscript{4–} ion,\textsuperscript{14),15) at 970 and 1020 cm\textsuperscript{-1} to V=O stretching mode of VO\textsubscript{3} pyramid\textsuperscript{14),17) and at 1100 cm\textsuperscript{-1} to P–O–P bending mode.\textsuperscript{14),20) Previous studies on AgI containing vanadate glass revealed that the addition of AgI caused no changes in FT-IR spectra,\textsuperscript{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 equal to or larger than 30 mol% [Figs. 11(B) (c) and (d)]; the absorption bands of V=O groups at 1000-970 cm\textsuperscript{-1} and P–O–P bending at 540 cm\textsuperscript{-1} disappeared, and new absorption bands appeared at 858 cm\textsuperscript{-1} corresponding to V–O–V bending of VO\textsubscript{3}\textsuperscript{14),20) at 896 and 964 cm\textsuperscript{-1} to VO\textsubscript{3} terminal stretching of VO\textsubscript{3}.
pyrovanadate ions, and at 760 cm\(^{-1}\) to V–O bending of V(T\(\text{II}\))O\(_4\). From these results, it can be said that introduction of Ag\(_2\)O into xAOSVSPF glasses 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\(_4\) or VO\(_5\) terminal bond of V\(_2\)O\(_7\). And the production of non-bridging oxygen decreases in thermal stability and electrical conductivity of xAOSVSPF glasses. These results indicate that Ag\(_2\)O acts as a network modifier in xAOSVSPF glass as likely to be observed in the previous studies.\(^{21-25}\) 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\(_2\)O 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 \(\sigma\) between 2.6 \(\times\) 10\(^{-1}\) and 1.3 \(\times\) 10\(^{-2}\) S cm\(^{-1}\) was observed for annealed xAIVSPF glass irrespective of AgI content. These \(\sigma\) 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 \(\sigma\) from 2.9 \(\times\) 10\(^{-1}\) to 1.8 \(\times\) 10\(^{-1}\) S cm\(^{-1}\) was observed for annealed xAOVSPF glass with the increase of Ag\(_2\)O content. From DTA study, \(T_g\) around 280°C and \(T_c\) of 370°C were observed for xAIVSPF 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 xAOVSPF glass with the increase of Ag\(_2\)O content, respectively. From \(^{57}\)Fe-Mössbauer study, decrease in quadrupole splitting (\(\Delta\)) was observed for annealed xAIVSPF glass, indicating that the reduction of local distortion of FeO\(_4\) tetrahedra occurred due to the structural relaxation. Precipitation of conductive Ag\(_{0.35}\)V\(_2\)O\(_7\) phase having \(\sigma\) of 5.0 \(\times\) 10\(^{-3}\) S cm\(^{-1}\) was identified from XRD patterns of heat-treated xAIVSPF glass with ‘\(x\)’ of equal to or less than 30 mol \%. From FT-IR study of heat-treated xAIVSPF 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 V\(_2\)O\(_7\) in the case of annealed xAOSVSPF 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 Ag\(_{0.35}\)V\(_2\)O\(_7\) phase, whereas introduction of Ag\(_2\)O 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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