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Characterization and Conduction Mechanism of Highly Conductive Vanadate Glass

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Abstract: This paper reviews recent studies of *highly conductive* barium iron vanadate glass with a composition of 20 BaO · 10 Fe_2O_3 · 70 V_2O_5 (in mol %). Isothermal annealing of the vanadate glass for several ten minutes at a given temperature, higher than glass transition temperature or crystallization temperature, caused an increase in σ. Substitution of Cu^I ($3d^{10}$), Zn^{II} ($3d^{10}$) and Cu^{II} ($3d^9$) for Fe^{III} ($3d^5$) was investigated to elucidate the effect of electron configuration on the conductivity (σ). A marked decrease in the activation energy of conduction (E_a) was also observed after the annealing. Values of E_a were correlated to the energy gap between the donor level and the conduction band (CB) in *the n-type semiconductor model*. Isothermal annealing of Zn^{II}-substituted vanadate glass (20 BaO · 5 ZnO · 5 Fe_2O_3 · 70 V_2O_5) at 450 °C for 30 min showed an increase in σ from 2.5×10^{-6} to 2.1×10^{-1} S cm^{-1}, which was one order of magnitude larger than that of non-substituted vanadate glass (3.4×10^{-2} S cm^{-1}). Under the same annealing condition, σ's of 2.0×10^{-1} and 3.2×10^{-1} S cm^{-1} were observed for 20 BaO · 5 Cu_2O · 5 Fe_2O_3 · 70 V_2O_5 and 20 BaO · 5 CuO · 5 Fe_2O_3 · 70 V_2O_5 glasses, respectively. These results demonstrate an increase in the carrier (electron) density in the CB, primarily composed of anti-bonding $4s$-orbitals.

Keywords: highly conductive vanadate glass, heat treatment, structural relaxation, small polaron hopping, n-type semiconductor.

INTRODUCTION

SILICATE (SiO_2-based) glass is generally known as an "insulator" having the resistivity (ρ) of the order of "terra" Ω cm. However, silicate glass, synthesized by using recycling fly ash (coal ash) containing ≥ 12 wt % Fe_2O_3 after isothermal annealing at 1100 °C for 1 h, showed ρ of "mega" Ω cm.[1,2] This iron-containing silicate glass had decrease in ρ or increase in conductivity (σ). A change in the property of fly-ash recycled glass was ascribed to the precipitation of magnetite (Fe_3O_4) particles in the matrix. Formation of Fe_3O_4 was due to the partial reduction of Fe_2O_3 caused by several weight percent of carbon atoms, which were originally presented in the fly ash.[1,2]

The presence of Fe_3O_4 particles was confirmed from the Mössbauer spectra of fly-ash recycled glass.[1,2] The fraction of magnetite particles increased after a prolonged annealing at 1100 ºC.[1,2] Fe_3O_4 are generally known as semiconductor and may have created a "pathway" of the electric conduction along the crystalline particles. Mössbauer spectra showed a decrease in δ of Fe^{III} (doublet) from 0.32 − 0.34 mm s^{-1} to 0.14 − 0.15 mm s^{-1} after the annealing. This indicates an increased covalency of the distorted $Fe^{III}O_4$ tetrahedra occupying the network forming (NWF) sites in the glass matrix. In the as-quenched glass, another doublet of Fe^{II} (δ = 1.02 − 1.09 mm s^{-1}) was also observed, which was assigned to octahedral species occupying network modifying (NWM) sites. After the annealing, Fe^{II} occupied tetrahedral NWF sites, as revealed from the values of δ (0.81 − 0.86 mm s^{-1}). This suggests distorted $Fe^{II}O_6$ octahedra were transformed to distorted FeO^{II}_4 tetrahedra during the annealing.

In the fly-ash recycled glass, increase in σ from the order of 10^{-8} S cm^{-1} to 10^{-6} S cm^{-1} was observed, which was ascribed to the promotion of electron hopping from Fe^{II} to Fe^{III} in the glass matrix. In other words, a "pathway" of the electron hopping was created in the glass-ceramics. Although the fly-ash recycled glass or glass-ceramic has

attracted much interest, it is noted that the value of ρ was at least of the order of "mega" Ω cm. This indicates limited industrial applications of glass-ceramic having conductivity (σ) ranging from "insulator" to "semiconductor". This leads to interest in as-quenched vanadate (V_2O_5-based) glass that originally has resistivity of "mega" Ω cm.

Small polaron hopping theory has been usually applied to describe the conduction mechanism of vanadate glass.[3] Isothermal annealing of alkali vanadate glass, 25 $K_2O \cdot 10 Fe_2O_3 \cdot 65 V_2O_5$ (composition in mol %), was carried out at 380 °C for 10 min. This temperature was higher than the glass transition temperature (T_g) (217 °C) and also than the crystallization temperatures of 284 °C ($T_c(1)$) and 344 °C ($T_c(2)$). Isothermal annealing at 380 °C caused a substantial decrease in ρ from 1.6×10^7 Ω cm ($\sigma = 6.3 \times 10^{-8}$ S cm^{-1}) to 2.3×10^3 Ω cm ($\sigma = 4.3 \times 10^{-4}$ S cm^{-1}).[4,5] Nishida *et al.* suggested that the lowering of ρ by four orders of magnitude was due to an increased probability of *the small polaron hopping* from V^{IV} (or V^{III}) to V^V. The decrease in quadrupole splitting (Δ) of Mössbauer spectra measured at room temperature (*RT*) confirmed a decrease in the distortion of *pseudo-1D* network structure of 25 $K_2O \cdot 10 Fe_2O_3 \cdot 65 V_2O_5$ glass.[4,5] Decrease of the distortion of network structure or "*structural relaxation*" became large after the annealing of several ten minutes. Prolonged isothermal annealing of 25 $K_2O \cdot 10 Fe_2O_3 \cdot 65 V_2O_5$ glass for more than 150 min resulted in a gradual decrease of σ in conjunction with the precipitation of "insulating" KV_3O_8 particles.[4,5] A Kissinger plot of T_c in the differential thermal analysis (DTA) of x $K_2O \cdot 10 Fe_2O_3 \cdot (90 - x) V_2O_5$ glasses ($x = 20 - 35$) showed that the crystallization was triggered by the cleavage of Fe^{III}–O bonds forming distorted FeO_4 tetrahedra with the Fe^{III}–O bond energy of 2.6 eV. These experimental results suggested that the crystallization of glass (precipitation of crystalline particles or phase in the glassy phase) was not related to the increase in σ, but to *the structural relaxation*. It was noted that ρ was decreased to the order of "kilo" Ω cm in 25 $K_2O \cdot 10 Fe_2O_3 \cdot 65 V_2O_5$ glass consisting of a *pseudo-1D* network structure.[6–8] It was also noted that the "pathway" of conduction was restricted to the *pseudo-1D* direction.

Barium, magnesium and phosphorus vanadate glasses have *3D*-network structures.[8,9] Fukuda *et al.* investigated 15 $BaO \cdot 15 Fe_2O_3 \cdot 70 V_2O_5$ glass (composition in mol %) in order to seek the higher possibility of "pathway" for *the small polaron hopping*.[10] Increase in the values of σ from 1×10^{-7} S cm^{-1} to 4×10^{-3} S cm^{-1} ($\rho = 250$ Ω cm) and to 4×10^{-2} S cm^{-1} ($\rho = 25$ Ω cm) were seen when this glass was annealed at 370 °C for 120 min and at 460 °C for 30 min, respectively. These annealing temperatures were based on $T_c(1)$ of 372 °C and $T_c(2)$ of 468 °C, which were appropriate for the precipitation of different crystalline particles.

Heat treatment of 20 $BaO \cdot 10 Fe_2O_3 \cdot 70 V_2O_5$ glass (composition in mol%) for 60 min at 500 °C, a temperature higher than T_g of 312 °C, $T_c(1)$ of 376 °C and $T_c(2)$ of 468 °C, resulted in an enhancement of σ from 2.8×10^{-6} to 4.3×10^{-2} S cm^{-1}.[11,12] After the heat treatment at 500 °C for 1000 min, 20 $BaO \cdot 10 Fe_2O_3 \cdot 70 V_2O_5$ glass showed an increase in σ from 1.6×10^{-5} S cm^{-1} to 1.1 S cm^{-1}.[13] X-ray diffraction (XRD) study of 20 $BaO \cdot 10 Fe_2O_3 \cdot 70 V_2O_5$ glass, annealed at 450 °C for 2000 min, showed precipitates of small amounts of $BaFe_2O_4$ and BaV_2O_6 particles of which crystalline growth became pronounced at $T_c(1)$ and $T_c(2)$, respectively.[11,12] Since the Fe^{III}–O bond energy (2.6 eV)[14] was smaller than the V^V–O bond energy (3.9 – 4.9 eV),[14] formation of $BaFe_2O_4$ would proceed to that of BaV_2O_6 particles. When 20 $BaO \cdot 10 Fe_2O_3 \cdot 70 V_2O_5$ glass and x $R_2O \cdot 10 Fe_2O_3 \cdot (90 - x) V_2O_5$ glasses (R = Li, Na, K; $x = 20$, 40) were annealed at 500 °C for 1000 min, precipitation of $FeVO_4$ particles was observed.[15] Kubuki *et al.* suggested that the isothermal annealing of alkaline iron vanadate glasses (x $R_2O \cdot 10 Fe_2O_3 \cdot (90 - x) V_2O_5$) at temperatures higher than 450 °C was not appropriate because $FeVO_4$ had σ of 6.7×10^{-7} S cm^{-1}, which was lower than that of the *highly conductive* vanadate glass.[15] It was noticed that 25 $K_2O \cdot 10 Fe_2O_3 \cdot 65 V_2O_5$ glass showed precipitation of "insulating" KV_3O_8 phase after isothermal annealing at 380 °C for more than 150 min.[4,5] Simultaneously, a decrease in σ was observed. These experimental results suggest that the increase in σ from 1.6×10^{-5} S cm^{-1} to 1.1 S cm^{-1}, recorded in 20 $BaO \cdot 10 Fe_2O_3 \cdot 70 V_2O_5$ glass after annealing at 500 °C for 1000 min,[13] was not due to the crystallization of the glass (formation of glass-ceramic), but to *the structural relaxation* of the glass network, observed in several vanadate glasses.[4,5,10–13,15–17]

In the case of 20 $BaO \cdot 10 Fe_2O_3 \cdot 70 V_2O_5$ glass, activation energy for the electrical conduction (E_a) showed a decrease from 0.38 eV to 0.13 eV when annealed at 500 °C for 60 min.[12] As described above, this glass showed a marked increase of σ from 2.8×10^{-6} to 4.3×10^{-2} S cm^{-1}.[11,12] These experimental results indicate that the less-distorted *3D*-network is more effective for fabricating *highly conductive* vanadate glass than less-distorted *pseudo-1D* network. On the basis of the discussion above, conductivity of *highly conductive* vanadate glass could be easily "tuned" by changing the temperature and the time of annealing.

20 $BaO \cdot 10 Fe_2O_3 \cdot x$ $WO_3 \cdot (70 - x) V_2O_5$ glasses ($x = 10 - 50$) were prepared in order to enhance the water- and chemical-durability of 20 $BaO \cdot 10 Fe_2O_3 \cdot 70 V_2O_5$ glass.[16] XRD study of these glasses showed precipitation of crystalline particles like $FeVO_4$, $BaFe_2O_4$, $BaFe_{12}O_{19}$ and α-Fe_2O_3, depending on the composition and the annealing temperature[17] These crystalline particles were not in

volved with the marked increase of σ values, recorded in the *highly conductive* vanadate glass. A Kissinger plot in the DTA study for 20 BaO · 10 Fe$_2$O$_3$ · x WO$_3$ · (70 − x) V$_2$O$_5$ glasses revealed that the crystallization was triggered by the cleavage of Fe^{III}–O bonds having bond energy of 2.6 eV.[17] This was also reported for 25 K$_2$O · 10 Fe$_2$O$_3$ · 65 V$_2$O$_5$ glass.[4]

Mössbauer spectroscopy has become a very powerful tool for studying the local structure of oxide glass, since Mössbauer nuclides like ^{57}Fe and ^{119}Sn could be easily incorporated into oxide glasses as a probe.[1,2,4–13,15–25] We could determine whether Fe^{III} atoms occupied NWF or NWM sites in oxide glasses like silicates, borate, borosilicate, aluminates, tellurite and gallate glasses by plotting the T_g values (*ca.* 180 – 770 °C) against the Δ of Fe^{III} (*ca.* 0.4 – 1.3 mm s^{-1}).[5,13,16,18–21] A slope of the straight line, obtained from the T_g *vs.* Δ plot, was 680 K (mm s^{-1})$^{-1}$ when Fe^{III} atoms occupied tetrahedral NWF sites.[18,19] However, the slope was 260 K (mm s^{-1})$^{-1}$ when Fe^{III} atoms occupied octahedral NWF sites, as in tungstate glass.[21] Significantly, the slope was only 35 K (mm s^{-1})$^{-1}$ when Fe^{III} atoms occupied NWM sites, as in phosphate glasses.[18,19] A calibration plot of T_g *vs.* Δ was very useful when we characterized unknown glass samples because the structural role of Fe^{III} atoms could be easily known. For example, a T_g *vs.* Δ plot for 20 BaO · 10 Fe$_2$O$_3$ · x WO$_3$ · (70 − x) V$_2$O$_5$ glasses (x = 10 – 50) yielded a slope of 680 K (mm s^{-1})$^{-1}$,[16] reflecting that Fe^{III} atoms occupied only tetrahedral NWF sites. It means that they substituted V^{IV} or V^{V} atoms,[18,19] not octahedral W^{VI} sites observed in tungstate glass.[21]

Isomer shift (δ) provides chemical information like oxidation number, coordination number and electronic structure of the Mössbauer atoms. Magnetic information is available from the internal magnetic field (H_{int}). The linewidth (Γ) offers useful information on the uniformity of the structural units in the materials of interest, *i.e.*, whether or not they are homogeneously distributed in the material or whether the material is crystalline or glassy.[18] Magnitude of Γ also gives information on the degree of crystallization of glass, *i.e.*, estimation of the crystalline phase and particles precipitated in the glass matrix.

Distortion or local symmetry of Mössbauer atoms could be deduced from the magnitude of Δ.[4–13,15–25] Mössbauer spectrum of heat-treated vanadate glasses [4,5,10–13,15–17,20,22–25] showed a substantial decrease of Δ for Fe^{III}, indicating a decreased distortion or an increased symmetry of "distorted" Fe^{III}O$_4$ tetrahedra. This was also the case for "distorted" VO$_4$ tetrahedra constituting the network of vanadate glass because they were directly bonded to "distorted" FeO$_4$ tetrahedra through corner oxygen atoms. Since high-spin Fe^{III} has an isotropic electron configuration of 3d^5, *the electric field gradient (EFG)* caused by valence electrons (eq_{val}) is "zero". In such a case, Δ reflects *the EFG*,

caused by lattice (eq_{lat}), *i.e.*, by the steric configuration of oxygen atoms constituting distorted Fe^{III}O$_4$ and VO$_4$ tetrahedra.[4–13,15–25] Mössbauer study of heat-treated vanadate glasses indicated that σ increased greatly when less-distorted Fe^{III}O$_4$ tetrahedra were bonded to less-distorted VO$_4$ tetrahedra.[4,5,10–13,15–17,20,22–25] Presence of Fe^{III} atoms having an isotropic symmetric electron configuration of 3d^5 in the outermost orbital was effective for the marked increase of σ, possibly due to the utilization of five half-occupied 3d-orbitals for accepting the carriers (electrons).

The present paper reviews *highly conductive* 20 BaO · x M$_m$O$_n$ · (10 − x) Fe$_2$O$_3$ · 70 V$_2$O$_5$ glasses (M = Cu, Zn; x = 5 & 10), in which substitution of Cu^{II} (3d^9), Cu^{I} (3d^{10}) and Zn^{II} (3d^{10}) for Fe^{III} (3d^5) was investigated focusing on the jump of the conductivity. These *highly conductive* vanadate glasses were prepared by heat treatment at 450 °C, a given temperature sufficiently higher than the T_g and T_c. Conduction mechanism for ZnO-substituted vanadate glass was discussed in conjunction with CuO- and Cu$_2$O-substituted vanadate glasses.[22]

EXPERIMENTAL

20 BaO · x M$_m$O$_n$ · (10 − x) Fe$_2$O$_3$ · 70 V$_2$O$_5$ glasses (M = Cu, Zn; x = 0, 5, 10) were prepared by a conventional melt-quenching method with BaCO$_3$, CuO, Cu$_2$O, ZnO, Fe$_2$O$_3$ and V$_2$O$_5$ of guaranteed reagent grade. Each reagent mixture placed in a platinum crucible or an alumina crucible was melted at 1100 °C for 2 h in the air using an electric muffle furnace. Homogeneous glass samples of almost black color were prepared by quenching the melt with ice-cold water or with air. Annealing of as-quenched glass sample was also carried out in an electric furnace. DTA study was conducted at a heating rate of 10 K min^{-1} from *RT* to 600 °C under N$_2$ atmosphere. Powder of α-Al$_2$O$_3$ was used as a reference of the temperature. Electrical conductivity (σ) was estimated by measuring the resistivity (ρ) of rectangular sample by a conventional DC-four probe method. A linear relationship was obtained by plotting the voltage against the electric current (*e.g.* 0 – 10 mA) that depended on the magnitude of ρ and the sample size. Mössbauer measurement was made by a constant acceleration method with a source of ^{57}Co(Rh). A foil of α-Fe was used as a reference of δ and also for calibrating the velocity scale of the spectrometer. Software, *Mösswinn* 3.0i XP, was used for the peak analysis of the Mössbauer spectra.

RESULTS AND DISCUSSION

A DTA study of 20 BaO · 5 CuO · 5 Fe$_2$O$_3$ · 70 V$_2$O$_5$ and 20 BaO · 5 Cu$_2$O · 5 Fe$_2$O$_3$ · 70 V$_2$O$_5$ glasses showed a slight lowering of T_g from 281 to 276 – 278 °C, compared to 20 BaO · 10 Fe$_2$O$_3$ · 70 V$_2$O$_5$ glass.[22] A lowering of T_c from 373 °C to 344

°C was also seen in these glasses. In the case of 20 BaO · 5 ZnO · 5 Fe$_2$O$_3$ · 70 V$_2$O$_5$ glass, a lowering of T_g from 307 to 276 °C was recorded, together with a lowering of T_c from 372 to 345 °C, compared to 20 BaO · 10 Fe$_2$O$_3$ · 70 V$_2$O$_5$ glass. In the case of 20 BaO · 10 ZnO · 70 V$_2$O$_5$ glass, decrease of T_g was observed from 307 to 259 °C, together with a noticeable decrease of T_c from 372 to 304 °C. These DTA results indicate that substitution of CuO, Cu$_2$O and ZnO for Fe$_2$O$_3$ in 20 BaO · 10 Fe$_2$O$_3$ · 70 V$_2$O$_5$ glass is effective to fabricate less heat-resistant vanadate glasses with high conductivity. They may have several applications like sensors, electron-emitting needle, conductive glass paste, static electricity protecting material and the hyperfine processing materials combined with FIB (focused ion beam), electrons and laser.

RT-conductivities (*σ*) of 20 BaO · 5 CuO · 5 Fe$_2$O$_3$ · 70 V$_2$O$_5$ and 20 BaO · 5 Cu$_2$O · 5 Fe$_2$O$_3$ · 70 V$_2$O$_5$ glasses, measured after isothermal annealing at 450 °C for 0 − 300 min, are illustrated in Figure 1.[22] It is noteworthy that 30 min-annealing caused an increase of *σ* from 3.9 × 10^{-6} to 3.2 × 10^{-1} S cm^{-1} (*ρ* = 3.1 Ω cm) in 20 BaO · 5 CuO · 5 Fe$_2$O$_3$ · 70 V$_2$O$_5$ glass (△), and from 5.1 × 10^{-6} to 2.0 × 10^{-1} S cm^{-1} (*ρ* = 5.0 Ω cm) in 20 BaO · 5 Cu$_2$O · 5 Fe$_2$O$_3$ · 70 V$_2$O$_5$ glass (□). These *σ* values are one order of magnitude higher than that of 20 BaO · 10 Fe$_2$O$_3$ · 70 V$_2$O$_5$ glass (○), which had an increase in *σ* from 1.9 × 10^{-6} to 3.4 × 10^{-2} S cm^{-1} (*ρ* = 29 Ω cm) under the same annealing condition (450 °C, 60 min). Figure 1 indicates that *σ* of CuO- and Cu$_2$O-containing vanadate glasses finally converged to 2.8 × 10^{-1} S cm^{-1} after

the annealing at 450 °C. It is likely that Cu$_2$O and CuO had equilibrium in the air. The gradual increase in *σ* from 2.0 × 10^{-1} to 2.8 × 10^{-1} S cm^{-1} observed for 20 BaO · 5 Cu$_2$O · 5 Fe$_2$O$_3$ · 70 V$_2$O$_5$ glass (□) was ascribed to slow oxidation of Cu$_2$O to CuO during the heat treatment in the air. As mentioned above, the increase of *σ* was observed in K$_2$O-Fe$_2$O$_3$-V$_2$O$_5$,[4,5] BaO-Fe$_2$O$_3$-V$_2$O$_5$[10–13] and BaO-Fe$_2$O$_3$-WO$_3$-V$_2$O$_5$ glasses[16,17] after isothermal annealing at temperatures higher than T_g or T_c. It is noteworthy that *σ* values of CuO- and Cu$_2$O-containing vanadate glasses were one order of magnitude higher than that of 20 BaO · 10 Fe$_2$O$_3$ · 70 V$_2$O$_5$ glass, in spite that they had essentially the same *3D*-network structure as 20 BaO · 10 Fe$_2$O$_3$ · 70 V$_2$O$_5$ glass. Figure 1 evidently demonstrated that the electron configurations of 3d^9 (Cu^{II}) and 3d^{10} (Cu^{I}) were involved in the high conductivity.

Similar result was recently observed in 20 BaO · 5 ZnO · 5 Fe$_2$O$_3$ · 70 V$_2$O$_5$ glass (Figure 2), which shows that *RT*-conductivity (*σ*) increased from 2.5 × 10^{-6} S cm^{-1} to 2.1 × 10^{-1} S cm^{-1} after isothermal annealing at 450 °C for 30 min (●). The latter conductivity was larger than that of 20 BaO · 10 Fe$_2$O$_3$ · 70 V$_2$O$_5$ glass (3.4 × 10^{-2} S cm^{-1}). This result further provides the evidence that substitution of ZnO for Fe$_2$O$_3$ is quite effective in improving the *RT*-conductivity of BaO-Fe$_2$O$_3$-V$_2$O$_5$ glass. It appears that 3d^{10}-configuration of Zn^{II} contributes to the increase in the conductivity. All the experimental results suggest that Zn^{II}, Cu^{I} and Cu^{II} atoms, having 3d^{10}- or 3d^9-electron configurations, are quite effective to fabricate *highly conductive* vanadate glass than the Fe^{III} atoms having 3d^5-configuration.[11,12]
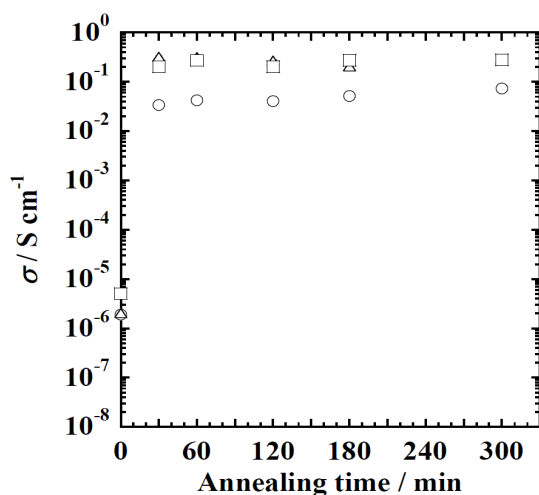

Figure 1. *RT*-conductivity (*σ*) of 20 BaO · 10 Fe$_2$O$_3$ · 70 V$_2$O$_5$ (○), 20 BaO · 5 CuO · 5 Fe$_2$O$_3$ · 70 V$_2$O$_5$ (△) and 20 BaO · 5 Cu$_2$O · 5 Fe$_2$O$_3$ · 70 V$_2$O$_5$ glasses (□), measured after isothermal annealing at 450 °C[22] (left).
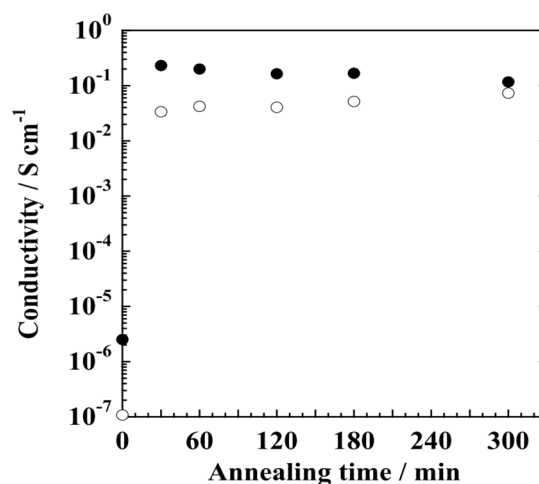
Figure 2. *RT*-conductivity (*σ*) of 20 BaO · 10 Fe$_2$O$_3$ · 70 V$_2$O$_5$ (○) and 20 BaO · 5 ZnO · 5 Fe$_2$O$_3$ · 70 V$_2$O$_5$ glasses (●), measured after isothermal annealing at 450 °C (right).
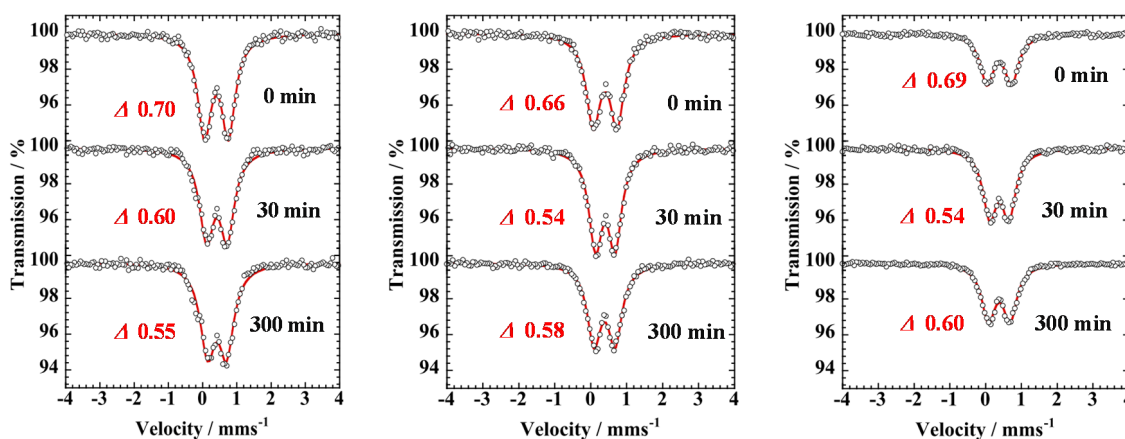
Figure 3. *RT*-Mössbauer spectra of 20 BaO · 10 Fe$_2$O$_3$ · 70 V$_2$O$_5$ (left), 20 BaO · 5 CuO · 5 Fe$_2$O$_3$ · 70 V$_2$O$_5$ (middle) and 20 BaO · 5 Cu$_2$O · 5 Fe$_2$O$_3$ · 70 V$_2$O$_5$ glasses (right), measured before and after isothermal annealing at 450 °C.[22]

Figure 3 illustrates *RT*-Mössbauer spectra of 20 BaO · 10 Fe$_2$O$_3$ · 70 V$_2$O$_5$ (left), 20 BaO · 5 CuO · 5 Fe$_2$O$_3$ · 70 V$_2$O$_5$ (middle) and 20 BaO · 5 Cu$_2$O · 5 Fe$_2$O$_3$ · 70 V$_2$O$_5$ glasses (right), measured before and after isothermal annealing at 450 °C.[22] A marked decrease of *Δ* was observed in 20 BaO · 10 Fe$_2$O$_3$ · 70 V$_2$O$_5$ glass (left) from 0.70 to 0.55 mm s^{-1} after the annealing at 450 °C for 300 min. Figure 3 indicates that both CuO- and Cu$_2$O-containing vanadate glasses showed a decrease of *Δ* by 0.12 – 0.15 mm s^{-1} after annealing at 450 °C for only 30 min. Decrease of *Δ* was not so large in the case of 20 BaO · 5 CuO · 5 Fe$_2$O$_3$ · 70 V$_2$O$_5$ (middle) and 20 BaO · 5 Cu$_2$O · 5 Fe$_2$O$_3$ · 70 V$_2$O$_5$ glasses (right) after the annealing for 300 min, probably because these glasses included Cu atoms in addition to Fe and V atoms. In this case, their complicated networks might be less effectively "*relaxed*" by the heat treatment.

All the Mössbauer spectra show a noticeable decrease in *Δ* values after the heat treatment, suggesting a decreased *eq*$_{lat}$ at the nuclear sites of ^{57}Fe, and hence a decreased distortion of FeO$_4$ tetrahedra. This is also the case for distorted VO$_4$ tetrahedra, since they are directly bonded to FeO$_4$ tetrahedra through corner oxygen atoms. These Mössbauer results are in good agreement with the marked increase of *σ*, observed after 30 min-annealing (*see* Figure 1).

Figure 4 shows *RT*-Mössbauer spectra of 20 BaO·5 ZnO · 5 Fe$_2$O$_3$ · 70 V$_2$O$_5$ glass in which a decrease of *Δ* was observed from 0.68 mm s^{-1} to 0.61 and to 0.62 mm s^{-1} after isothermal annealing at 450 °C for 30 and 300 min, respectively. The experimental error of *Δ* is estimated to be ± 0.01 – 0.02 mm s^{-1}. The decrease of *Δ* is ascribed to a decreased distortion of FeO$_4$ and VO$_4$ tetrahedra which are connected to each other through corner oxygen atoms to form distorted network structure.

Decrease of *Δ* value was observed when iron-containing vanadate glass was annealed for several ten minutes or more at temperatures higher than *T*$_g$ or *T*$_c$.[4,5,10–13,15–17,20,22,23] This behavior accompanied, without exception, significant increase or jump of the conductivity by several orders of magnitude, which primarily depended on the annealing temperature. It is interesting to correlate this behavior with the probability of *the small polaron hopping*,[3] which has successfully been utilized to understand the conduction mechanism of semiconducting vanadate glass with *σ* of *ca.* 10^{-5} to 10^{-7} S cm^{-1}. In the early study of 25 K$_2$O · 10 Fe$_2$O$_3$ · 65 V$_2$O$_5$ glass annealed at 380 °C, as described above, enhancement of *σ* was observed from 6.3 × 10^{-8} S cm^{-1} (*ρ* = 1.6 × 10^7 Ω cm) to 4.3 × 10^{-4} S cm^{-1} (*ρ* = 2.3 kΩ cm), which was ascribed to the increased probability of *the small polaron hopping* in the less-distorted FeO$_4$ and VO$_4$ tetrahedra.[4,5]
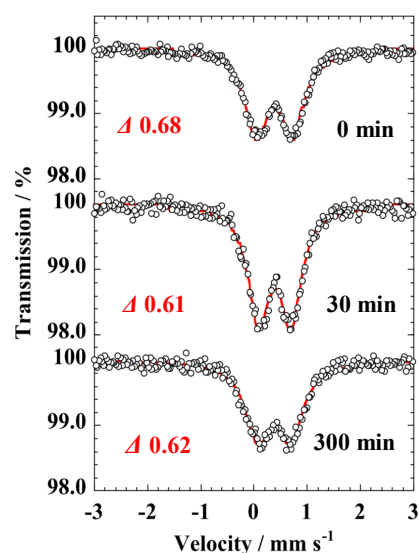

Figure 4. *RT*-Mössbauer spectra of 20 BaO · 5 ZnO · 5 Fe$_2$O$_3$ · 70 V$_2$O$_5$ glass, measured before and after isothermal annealing at 450 °C.

In such a case, 3d-orbitals of Fe^{III}, V^{IV} and V^V atoms would be effectively overlapped with the 2p-orbitals of oxygen atoms. It was concluded that less-distorted FeO_4 and VO_4 tetrahedra were favorable for *the small polaron hopping* from V^{IV} to V^V and Fe^{III} *via* oxygen atoms sharing VO_4 and FeO_4 tetrahedra. It was considered that the presence of Fe^{III} atoms, which have symmetric electron configuration of $3d^5$, was favorable for *the small polaron hopping* from V^{IV} to V^V and Fe^{III} *via* oxygen atoms.[4,5] All the Mössbauer results indicate that *the structural relaxation* of the glass network was well reflected as a decrease of Δ.[4–5,10–13,15–17,20,22,23] *The small polaron hopping* will be promoted as *the structural relaxatio*n of the network goes on.

If the electrical conduction of *highly conductive* vanadate glass with σ higher than *ca.* 10^{-4} S cm^{-1} were due to *the structural relaxation* of the network, increase in the σ value would be directly proportional to the decrease of Δ value. Mössbauer spectra revealed that the decrease of Δ was the most remarkable in the case of 20 BaO · 10 Fe_2O_3 · 70 V_2O_5 glass (Figure 3, left), while CuO-, Cu_2O- (Figure 3, middle and right) and ZnO-containing vanadate glasses (Figure 4) showed smaller decreases. Nevertheless, σ of the latter group was one order of magnitude larger than that of the former (*see* Figures 1 and 2). These results suggested that alternative mechanism to *the small polaron hopping* was necessary to explain the conduction behavior of *highly conductive* vanadate glasses.[4–5,10–13,15–17,20,22,23]

This authors' group introduced *n-type semiconductor model* to the conduction mechanism in conjunction with *the small polaron hopping theory*, because the carrier of vanadate glass was the valence electrons originating from V^{IV} atoms with $3d^1$-electron configuration.[12] In the case of 20 BaO · 10 Fe_2O_3 · 70 V_2O_5 glass, activation energy for the conduction (E_a) was calculated from the σ values obtained at different temperatures (T) between RT and 100 ºC.[12] For the calculation of E_a, *the small polaron hopping equation*[3] was used instead of the Arrhenius equation;

$$\sigma T = A \exp(-E_a / kT) \tag{1}$$

where T and k are the measuring temperature (K) and the Boltzmann constant, respectively. Conductivity (σ) of 20 BaO · 10 Fe_2O_3 · 70 V_2O_5 glass increased with an increasing temperature.[12] Natural logarithms of σT plotted against the reciprocal of the measuring temperature (T) showed a linear relationship with different slopes, which depended on the temperature and the time period of the isothermal annealing.[12] Activation energies (E_a) calculated from the slope of the ln σT *vs.* T^{-1} plot are shown in Figure 5, which indicates that E_a decreases when the annealing temperature is higher than T_c and when the annealing time is long. Figure 5 evidences that σ was linearly increased with
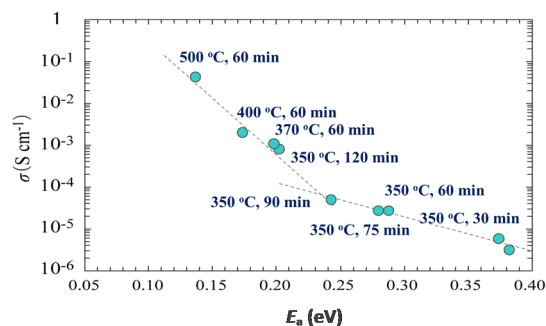

Figure 5. A relationship between the electrical conductivity (σ) and the activation energy (E_a) estimated for 20 BaO · 10 Fe_2O_3 · 70 V_2O_5 glass after isothermal annealing.[12]

decreasing value of E_a. The plot is composed of two components: one relationship obtained after isothermal annealing at 350 °C and the other obtained after the isothermal annealing conducted at temperatures of 350 – 500 °C. The increase of σ was promoted by the annealing at higher temperatures probably because the glass network was significantly cleaved to induce recombination of the fragments for the "partial" crystallization or precipitation of crystalline particles. In the case of as-quenched 20 BaO · 10 Fe_2O_3 · 70 V_2O_5 glass with σ of 2.8×10^{-6} S cm^{-1}, E_a was calculated as 0.38 eV, whereas it decreased to 0.13 eV ($\sigma = 4.3 \times 10^{-2}$ S cm^{-1}) after the annealing at 500 °C for 60 min.[12]

As shown in Figure 1, 20 BaO · 5 CuO · 5 Fe_2O_3 · 70 V_2O_5 glass showed σ of 3.2×10^{-1} S cm^{-1} after isothermal annealing at 450 °C for 30 min, while 20 BaO · 5 Cu_2O · 5 Fe_2O_3 · 70 V_2O_5 glass had σ of 2.0×10^{-1} S cm^{-1}. Both glasses showed identical σ value of 2.8×10^{-1} S cm^{-1} after annealing at 450 °C for 300 min. It was noted that E_a's of copper-containing vanadate glasses annealed at 450 °C for 60 min were 0.09 – 0.10 eV,[22] smaller than that of 20 BaO · 10 Fe_2O_3 · 70 V_2O_5 glass (0.13 eV) in which σ was reported to be 3.4×10^{-2} S cm^{-1} after the same annealing. Conductivities of Li$^+$- and Na$^+$-containing iron vanadate glasses, measured after the isothermal annealing at 400 – 450 °C for 100 min, were respectively estimated to be 1.0×10^{-1} and 2.6×10^{-2} S cm^{-1}, together with the E_a's of 0.10 and 0.13 eV.[15] Alkaline iron tungsten vanadate glasses showed σ values of 6.2×10^{-4} – 4.5×10^{-3} S cm^{-1} and E_a's of 0.15 – 0.21 eV.[20] Barium iron manganese vanadate glasses exhibited σ of 1.4×10^{-2} S cm^{-1} after annealing at 500 °C for 1000 min, and the E_a was calculated as 0.11 eV.[23] These results suggest that the conductivity of *highly conductive* vanadate glasses, prepared by the annealing at temperatures higher than T_g, favorably at temperatures higher than T_c, is closely related to the magnitude of E_a.

These E_a values are significantly smaller than the band gap (ΔE) between the valence band (VB) and the conduction band (CB), reported for typical semiconductors like

GaSb (0.23 eV), Ge (0.68 eV) and Si (1.16 eV).[12] A photoluminescence study of 20 BaO · 10 Fe$_2$O$_3$ · 70 V$_2$O$_5$ glass annealed at 500 °C for 60 min showed the ΔE of 2.25 eV. ΔE of as-quenched vanadate glass was too large to be estimated. Figure 6 is a schematic view of 20 BaO · 10 Fe$_2$O$_3$ · 70 V$_2$O$_5$ glass in which E_a was correlated to the energy difference between the donor level and the CB, since it was much smaller than the band gap (ΔE). As described above, a decrease of E_a was recorded from 0.38 to 0.13 eV in 20 BaO · 10 Fe$_2$O$_3$ · 70 V$_2$O$_5$ glass after the isothermal annealing at 500 °C for 60 min.[12] Carrier (electron) density in the CB would increase along with a decrease of the energy gap between the donor level and the CB, hence giving high possibility of producing *highly conductive* vanadate glass.

Electron configurations of $3d^{10}$ and $3d^9$ in Zn^{II}, Cu^I and Cu^{II} cause the valence electrons to occupy the CB, which is primarily composed of anti-bonding 4s-orbitals. This will result in an increase in the carrier density of the CB and hence an increase in the electrical conductivity. In such a case, shielding of nuclear charge by nine or ten 3d-electrons will be effective for the "smooth" carrier (electron) flow in the CB. Figures 1 and 2 indicate that the number of 3d-electrons was closely related to the *highly conductive* vanadate glass. If the 3d-orbitals were almost or fully occupied, valence electrons originating from V^{IV} ($3d^1$) would occupy the CB primarily composed of anti-bonding 4s-orbitals. Figures 1 and 2 indicate that the transition metal oxides having $3d^{10}$- and $3d^9$-configurations are favorable for the fabrication of *highly conductive* vanadate glass. Substitution of "*3d-block elements*" having the electron configurations of $3d^{10}$ (Cu^I, Zn^{II}) and $3d^9$ (Cu^{II}) for $3d^5$ (Fe^{III}) is very effective, as 20 BaO · 5 ZnO · 5 Fe$_2$O$_3$ · 70 V$_2$O$_5$ glass annealed at 450 °C for 30 min proved a marked increase of σ from 2.5 × 10^{-6} S cm^{-1} to 2.1 × 10^{-1} S cm^{-1}, one order of magnitude larger than that of 20 BaO · 10 Fe$_2$O$_3$ · 70 V$_2$O$_5$ glass (3.4 × 10^{-2} S cm^{-1}). This was also the case for 20 BaO · 5 CuO · 5 Fe$_2$O$_3$ · 70 V$_2$O$_5$ and 20 BaO · 5 Cu$_2$O · 5 Fe$_2$O$_3$ · 70 V$_2$O$_5$ glasses of which σ values increased from 3.9 × 10^{-6} S cm^{-1} to 3.2 × 10^{-1} S cm^{-1} and from 5.1 × 10^{-6} S cm^{-1} to 2.0 × 10^{-1} S cm^{-1}, respectively, by the isothermal annealing at 450 °C for 30 min.[22] All the experimental results for several vanadate glasses[4–5,10–13,15–17,20,22,23] demonstrated that decrease of E_a accompanied an increase of carrier (electron) density in the CB, and the formation of *highly conductive* vanadate glasses. In other words, *n-type semiconductor model* is predominant over *the small polaron hopping*, which has been generally utilized to carry out the conduction mechanism of "semiconducting" vanadate glass with resistivity of "mega" Ω cm.

Silver- or lithium-ion containing iron vanadate glass exhibited ionic conduction due to mobile Ag$^+$ and Li$^+$ ions[15,24–28] in addition to the electronic conduction described above. Mössbauer and DTA study of 40 AgI · x Ag$_2$O · (59 – x) V$_2$O$_5$ · Fe$_2$O$_3$ and x Ag$_2$O · (90 – x) V$_2$O$_5$ · 10 Fe$_2$O$_3$
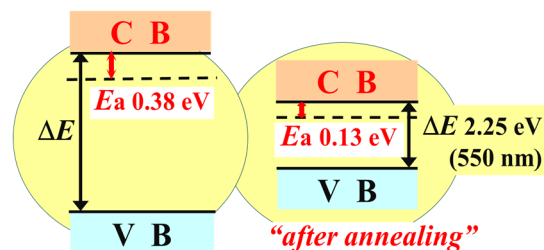

Figure 6. Schematic image of the energy level for 20 BaO · 10 Fe$_2$O$_3$ · 70 V$_2$O$_5$ glass before and after the isothermal annealing conducted at 500 °C for 60 min.

glasses revealed that the structural change caused by Ag$_2$O content was essentially the same as that by alkali ions in alkali vanadate glasses. Structural change was confirmed from *2D-* to *pseudo-1D* with an increasing Ag$_2$O content when the Ag$_2$O/V$_2$O$_5$ ratio was less than unity, while the change occurred from *pseudo-1D- to 3D* when the ratio exceeded unity.[24] Electrical conductivity of "superionic conducting" AgI-containing vanadate glass showed a concordant change with the change of Δ values for Fe^{III} in the Mössbauer spectra and with the T_g values, determined by DTA. These results suggest that the macroscopic physical properties of the "superionic conducting" vanadate glass (σ and T_g) were determined by the local distortion of the structural units (FeO$_4$ and VO$_4$ tetrahedra),[24] evidenced by the "T_g-Δ rule".[5,13,16,18–21] The electrical conduction of *superionic conducting* AgI-containing vanadate glass originated from the migration of mobile Ag$^+$ ions surrounded by I$^-$ ions, whereas Ag$^+$ ions originating from Ag$_2$O played a role NWM, similar to several alkali and alkaline-earth ions. Low-temperature Mössbauer study of 5 Ag$_2$O · 10 Fe$_2$O$_3$ · 85 V$_2$O$_5$ and 45 Ag$_2$O · 10 Fe$_2$O$_3$ · 45 V$_2$O$_5$ glasses[25] was consistent with the structural change of the glass matrix described above.

In studying x AgI · (75 – x) Ag$_2$O · Fe$_2$O$_3$ · 24 V$_2$O$_5$ and x LiI · (38 – x) Li$_2$O · 6 Fe$_2$O$_3$ · 56 V$_2$O$_5$ glasses, Ikeda *et al.* calculated the fractions of ionic conduction and electronic conduction by combining the results of AC and DC measurements.[26] In the Mössbauer study of alkali iron vanadate glasses, x R$_2$O · 10 Fe$_2$O$_3$ · (90 – x) V$_2$O$_5$ glasses (R = Li, Na, K; x = 20, 40), cationic conduction was effective in increasing the conductivity.[15] Li$^+$-containing conductive vanadate glass, LiFeVPO$_x$, was developed as a cathode active material for lithium ion battery (LIB).[12,27,28] LiFeVPO$_x$ glass annealed at 450 °C for 60 min showed an increase of σ from 1.3 × 10^{-6} to 1.0 × 10^{-3} S cm^{-1}, together with a marked increase of the specific discharge- and charge-capacities from 50 mAhg^{-1} to 150 mAhg^{-1}.[27] Mössbauer study of LiFeVPO$_x$ glass showed a decrease of Δ for Fe^{III} from 0.99 mm s^{-1} to 0.50 mm s^{-1}, reflecting *the structural relaxation* of the network composed of distorted FeO$_4$ and VO$_4$ tetrahedra. These

experimental results suggested that *the structural relaxation*, caused by the heat treatment, was effective even when the ionic conduction coexisted with the electronic conduction.

Highly conductive vanadate glasses have a lot of industrial applications, such as cathode active material for LIB, solid state electrolyte, sensor, electron-emitting needle, static electricity protecting material, conductive glass paste and the hyperfine processing material combined with FIB, electrons and laser. For these applications, vanadate glass is a very suitable material because of its flexibility in "tuning" the conductivity by the heat treatment. The authors wish this functional material could contribute to the development of science and technology all over the world.

SUMMARY

1. Electrical conductivity of conductive vanadate glass is promoted by *the structural relaxation* of the network composed of the structural units like VO_4, FeO_4 and VO_5 units, causing an increased probability of *the small polaron hopping*.

2. In the case of *highly conductive* vanadate glasses with σ higher than 10^{-4} S cm^{-1}, *n-type semiconductor model* becomes predominant over *the small polaron hopping*.

3. Heat treatment of vanadate glasses at temperatures higher than T_g or T_c resulted in a systematic decrease in the E_a for the conduction, which could be correlated to the energy gap between the donor level and the CB, mainly composed of anti-bonding 4*s*-orbitals.

4. Electron configurations of 3d^{10} and 3d^9 are favorable for the *highly conductive* vanadate glass because the carriers (electrons) necessarily have to occupy the 4*s*-orbitals which form isotropic chemical bonds.

5. Valence electrons in the fully or almost fully occupied 3*d*-orbitals could effectively shield the nuclear charge. This might be effective for the smooth carrier flow in the CB.

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