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Highly conductive barium iron vanadate glass containing different metal oxides

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Abstract: $20BaO{\cdot}5ZnO{\cdot}5Fe_2O_3{\cdot}70V_2O_5$ glass annealed at 450 °C for 30 min showed a marked decrease in the electric resistivity (ρ) from 4.0×10^5 to 4.8 Ωcm, while $20BaO{\cdot}5Cu_2O{\cdot}5Fe_2O_3{\cdot}70V_2O_5$ glass from 2.0×10^5 to 5.0 Ωcm. As for the conduction mechanism, it proved that *n-type semiconductor model* in conjugation with the *small polaron hopping theory* was most probable. Since Zn^{II} and Cu^{I} have a $3d^{10}$-electron configuration in the outer-most orbital, Ga_2O_3- and GeO_2-containing vanadate glasses were explored in this study. $20BaO{\cdot}5Ga_2O_3{\cdot}5Fe_2O_3{\cdot}70V_2O_5$ glass showed a less remarkable decrease of ρ from 4.5×10^5 to 100 Ωcm, and $20BaO{\cdot}5GeO_2{\cdot}5Fe_2O_3{\cdot}70V_2O_5$ glass from 3.3×10^6 to 400 Ωcm. Activation energies for the conduction (E_a) of GeO_2- and Ga_2O_3-contaning glasses before the annealing were respectively estimated to be 0.42 and 0.41 eV. It proved that barium iron vanadate glass with a smaller E_a value could attain the higher conductivity after the annealing at temperaures higher than the crystalization temperature.

Keywords: activation energy; band gap; conductive glass; Mössbauer spectroscopy; *n*-type semiconductor; small polaron hopping; SSC-2016; structural relaxation.

Introduction

Highly conductive vanadate glasses have a lot of industrial applications such as cathode active material for LIB, solid state electrolyte, electric discharge needle, static electricity protecting material, conductive glass paste, hyperfine processing material with laser or FIB, etc. Some conductive vanadate glasses were reviewed in our previous paper [1], together with the results for semiconducting iron silicate glass prepared by recycling a mixture of fly ash (coal ash) and Fe_2O_3. *Small polaron hopping theory* has so far been applied to explain the conduction mechanism of semiconducting vanadate glass with a resistivity (ρ) of mega order (MΩcm) [2]. Highly conductive vanadate glass will be utilized as advanced materials because its conductivity (σ) is easily "tunable" in association with the heat treatment at a given temperature higher than glass transition temperature (T_g) or crystallization peak temperature (T_c) determined by differential thermal analysis (DTA) [1, 3–8].

Isothermal annealing of potassium iron vanadate glass, $25K_2O{\cdot}10Fe_2O_3{\cdot}65V_2O_5$ (composition in mol%), at 380 °C for only 10 min caused a substantial decrease in ρ from 1.6×10^7 Ωcm ($\sigma = 6.3\times10^{-8}$ Scm^{-1}) to 2.3 kΩcm (4.3×10^{-4} Scm^{-1}) [3, 4]. The annealing was conducted at 340–380 °C which was higher than T_g of 217 °C, $T_c(1)$

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of 284 °C and $T_c(2)$ of 344 °C. After the heat treatment at 340 °C for 10 min, *RT*-Mössbauer spectra showed a marked decrease in quadrupole splitting (Δ) of $\mathrm{Fe^{III}}$ from 0.61 to 0.55 $\mathrm{mms^{-1}}$, which reflected an increased symmetry or a decreased distortion of "distorted" FeO_4 and VO_4 tetrahedra that were involved with an increased *structural relaxation* of *pseudo-1D* network [3, 4]. Nishida et al. concluded that the lowering of ρ in potassium iron vanadate glass, amounting to several orders of magnitude, was ascribed to an increased probability of the *small polaron hopping* from $\mathrm{V^{IV}}$ to $\mathrm{V^{V}}$. In case of potassium iron vanadate glass, $25K_2O{\cdot}10Fe_2O_3{\cdot}65V_2O_5$, an isothermal annealing at 380 °C for more than 150 min resulted in an increase in ρ due to the precipitation of "insulating" KV_3O_8 particles. Finally, the ρ became comparable to that of the as-cast potassium iron vanadate glass [3, 4], indicating that the *structural relaxation* of the network was involved with the high conductivity, as confirmed by a decrease in Δ of $\mathrm{Fe^{III}}$ in the Mössbauer spectra.

In case of $15BaO{\cdot}15Fe_2O_3{\cdot}70V_2O_5$ glass (in mol%), further decrease of ρ was observed after heat treatment at temperatures close to $T_c(1)$ of 372 °C and $T_c(2)$ of 468 °C [5]. In this glass, ρ decreased from 1.0×10^7 Ωcm (before annealing) to 250 Ωcm (4.0×10^{-3} $\mathrm{Scm^{-1}}$) and 25 Ωcm (4.0×10^{-2} $\mathrm{Scm^{-1}}$) after the annealing at 370 °C for 120 min and at 460 °C for 30 min, respectively. It is noted that these ρ values are one- or two-orders of magnitude smaller than that of crystalline V_2O_5 [9]. It was reported that $15BaO{\cdot}15Fe_2O_3{\cdot}70V_2O_5$ glass has a *3D*-network structure in which several "pathways" or "route" were available for the *small polaron hopping* than in *pseudo 1D*-network of $25K_2O{\cdot}10Fe_2O_3{\cdot}65V_2O_5$ glass [3, 4]. After the heat treatment of $15BaO{\cdot}15Fe_2O_3{\cdot}70V_2O_5$ glass at 460 °C for 60 min, Δ of $\mathrm{Fe^{III}}$ decreased from 0.67 to 0.60 $\mathrm{mms^{-1}}$, reflecting decreased distortion of "distorted" FeO_4 and VO_4 tetrahedra or an increased *structural relaxation* of the *3D*-network [5]. Representative Δ values for highly conductive $BaO{-}Fe_2O_3{-}V_2O_5$ glasses are summarized in Table 1.

Heat treatment of $20BaO{\cdot}10Fe_2O_3{\cdot}70V_2O_5$ glass for 60 min at 500 °C, which was higher than T_g of 312 °C, $T_c(1)$ of 376 °C and $T_c(2)$ of 468 °C, resulted in a marked decrease in ρ from 3.6×10^5 Ωcm (2.8×10^{-6} $\mathrm{Scm^{-1}}$) to 23 Ωcm (4.3×10^{-2} $\mathrm{Scm^{-1}}$) [6, 7]. Mössbauer spectra showed a remarkable decrease in Δ of $\mathrm{Fe^{III}}$ from 0.68 to 0.50 (±0.02) $\mathrm{mms^{-1}}$ after the heat treatment. Heat treatment of this glass at 500 °C for 1000 min caused

Table 1: Resistivity (ρ), conductivity (σ), activation energy (E_a) and quadrupole splitting (Δ) of $\mathrm{Fe^{III}}$ obtained for conductive barium iron vanadate glasses containing different metal oxides.

Composition (in mol%)	Annealing	ρ (Ωcm)	σ ($\mathrm{Scm^{-1}}$)	E_a (eV)	Δ ($\mathrm{mms^{-1}}$)
$15BaO{\cdot}15Fe_2O_3{\cdot}70V_2O_5$ [5]	Unannealed	1.0×10^7	1.0×10^{-7}	–	0.67
	460 °C, 30 min	25	4.0×10^{-2}	–	0.60 (1 h)
$20BaO{\cdot}10Fe_2O_3{\cdot}70V_2O_5$ [6, 7]	Unannealed	3.6×10^5	2.8×10^{-6}	0.38	0.68
	500 °C, 60 min	23	4.3×10^{-2}	0.13	0.50
$20BaO{\cdot}10Fe_2O_3{\cdot}70V_2O_5$ [8]	Unannealed	6.3×10^4	1.6×10^{-5}	–	0.77
	500 °C, 1000 min	0.91	1.1	–	0.53
$20BaO{\cdot}10Fe_2O_3{\cdot}20WO_3{\cdot}50V_2O_5$ [10]	Unannealed	2.6×10^5	3.9×10^{-6}	0.44[a]	0.82
	500 °C, 240 min	480	2.1×10^{-3}	0.24[a]	0.76
$20BaO{\cdot}10Fe_2O_3{\cdot}10WO_3{\cdot}60V_2O_5$ [11]	Unannealed	5.9×10^4	1.7×10^{-5}	–	0.73
	500 °C, 1000 min	10	1.0×10^{-1}	–	0.59
$20BaO{\cdot}10Fe_2O_3{\cdot}10MnO_2{\cdot}60V_2O_5$ [12]	Unannealed	2.2×10^6	4.5×10^{-7}	0.33	0.76
	500 °C, 1000 min	71	1.4×10^{-2}	0.11	0.49
$20BaO{\cdot}5CuO{\cdot}5Fe_2O_3{\cdot}70V_2O_5$ [13]	Unannealed	2.6×10^5	3.9×10^{-6}	0.16	0.66
	450 °C, 30 min	3.1	3.2×10^{-1}	0.10	0.54
$20BaO{\cdot}5Cu_2O{\cdot}5Fe_2O_3{\cdot}70V_2O_5$ [13]	Unannealed	2.0×10^5	5.1×10^{-6}	0.22	0.69
	450 °C, 30 min	5.0	2.0×10^{-1}	0.09	0.54
$20BaO{\cdot}5ZnO{\cdot}5Fe_2O_3{\cdot}70V_2O_5$ [1]	Unannealed	4.0×10^5	2.5×10^{-6}	0.23[b]	0.68
	450 °C, 30 min	4.8	2.1×10^{-1}	0.14[b]	0.61
$20BaO{\cdot}5Ga_2O_3{\cdot}5Fe_2O_3{\cdot}70V_2O_5$	Unannealed	4.5×10^5	2.2×10^{-6}	0.42[c]	0.69
	450 °C, 120 min	104	9.6×10^{-3}	0.18[c]	0.54
$20BaO{\cdot}5GeO_2{\cdot}5Fe_2O_3{\cdot}70V_2O_5$	Unannealed	3.3×10^6	3.0×10^{-7}	0.41[d]	0.77
	450 °C, 120 min	400	2.5×10^{-3}	0.21[d]	0.60

[a] I. Furumoto, Master thesis Kinki (Kindai) University (2013). [b] Present study. [c] Evaluated on $20BaO{\cdot}10Ga_2O_3{\cdot}70V_2O_5$ glass. [d] Evaluated on $20BaO{\cdot}10GeO_2{\cdot}70V_2O_5$ glass.

a marked decrease in ρ from 6.3×10^4 Ωcm (1.6×10^{-5} Scm^{-1}) to 0.91 Ωcm (1.1 Scm^{-1}) [8]. X-ray diffraction (XRD) study of the glass ceramic prepared by annealing at 450 °C for 2000 min showed the presence of small amounts of “insulating or semiconducting” $BaFe_2O_4$ and BaV_2O_6 particles. Crystal growth became maximal when annealed at temperatures around $T_c(1)$ and $T_c(2)$ [6, 7], at which the formation of $BaFe_2O_4$ and BaV_2O_6 particles were respectively detected, since the Fe^{III}–O bond energy was smaller than V^{V}–O bond energy of 3.9–4.9 eV [14, 15], and hence the precipitation of $BaFe_2O_4$ preceded that of BaV_2O_6. After the annealing at 500 °C for 1000 min, precipitation of “semiconducting” $FeVO_4$ particles which intrinsically had ρ of 1.5×10^6 Ωcm ($\sigma=6.7\times10^{-7}$ Scm^{-1}) was confirmed in “non-substituted” $20BaO\cdot10Fe_2O_3\cdot70V_2O_5$ glass and in $xR_2O\cdot10Fe_2O_3\cdot(90-x)V_2O_5$ glasses (R = Li, Na, K; $x=20$, 40) [16]. These results proved that the remarkable decrease of ρ in several vanadate glasses caused by the annealing was not ascribed to the crystalline particles precipitated in the glass matrix, but to *the structural relaxation* of the *3D*-network [1, 3–8, 10–13, 16, 17].

Change of the resistivity caused by a heat treatment of barium iron vanadate glasses, in which Fe_2O_3 was partially replaced by different metal oxides, are summarized in Table 1. Heat treatment of $20BaO\cdot10Fe_2O_3\cdot20WO_3\cdot50V_2O_5$ glass at 500 °C for 240 min caused a decrease of ρ from 2.6×10^5 Ωcm (3.9×10^{-6} Scm^{-1}) to 480 Ωcm (2.1×10^{-3} Scm^{-1}) in conjunction with a decrease of Δ from 0.82 to 0.76 mms^{-1} [10]. In case of $20BaO\cdot10Fe_2O_3\cdot10WO_3\cdot60V_2O_5$ glass [11], an isothermal annealing at 500 °C for 1000 min caused a decrease of ρ from 5.9×10^4 Ωcm (1.7×10^{-5} Scm^{-1}) to 10 Ωcm (1.0×10^{-1} Scm^{-1}), simultaneously with a decrease in Δ of Fe^{III} from 0.73 to 0.59 mms^{-1}. XRD study of $20BaO\cdot10Fe_2O_3\cdot xWO_3\cdot(70-x)V_2O_5$ glasses revealed a precipitation of crystalline particles such as $FeVO_4$, $BaFe_2O_4$, $BaFe_{12}O_{19}$ and α-Fe_2O_3 [11]. It was concluded that these crystalline particles were not involved with the marked decrease of ρ, since the intrinsic resistivity of these compounds was much higher than that of WO_3-substituted vanadate glasses evaluated at *RT* after the annealing at 500 °C. It proved that cleavage of Fe^{III}–O bonds triggered the crystallization of WO_3-substituted glasses [11], as observed in $25K_2O\cdot10Fe_2O_3\cdot65V_2O_5$ glass [3]. Heat treatment of MnO_2-substituted vanadate glass, $20BaO\cdot10Fe_2O_3\cdot10MnO_2\cdot60V_2O_5$, at 500 °C for 1000 min resulted in a decrease in ρ from 2.2×10^6 Ωcm (4.5×10^{-7} Scm^{-1}) to 71 Ωcm (1.4×10^{-2} Scm^{-1}) in conjunction with a decrease in Δ of Fe^{III} from 0.76 to 0.49 mms^{-1} which evidently showed the *structural relaxation* [12] (see Table 1).

$20BaO\cdot5CuO\cdot5Fe_2O_3\cdot70V_2O_5$ and $20BaO\cdot5Cu_2O\cdot5Fe_2O_3\cdot70V_2O_5$ glasses showed a higher conductivity after the heat treatment at 450 °C for 30 min [13]. Resistivity (ρ) of the former decreased from 2.6×10^5 Ωcm (3.9×10^{-6} Scm^{-1}) to only 3.1 Ωcm (3.2×10^{-1} Scm^{-1}) after the annealing, and the latter glass showed a comparable decrease of ρ from 2.0×10^5 Ωcm (5.1×10^{-6} Scm^{-1}) to 5.0 Ωcm (2.0×10^{-1} Scm^{-1}) [13]. In 5 mol% CuO-substituted glass, Δ of Fe^{III} decreased from 0.66 to 0.54 mms^{-1}. In case of 5 mol% Cu_2O-substituted glass, Δ decreased from 0.69 to 0.54 mms^{-1} (see Table 1). It is noted that Cu^{II} and Cu^{I} in CuO-and Cu_2O-substituted glasses respectively have the electron configuration of $3d^9$ and $3d^{10}$ in the outer-most orbital.

Heat treatment of $20BaO\cdot5ZnO\cdot5Fe_2O_3\cdot70V_2O_5$ glass at 450 °C for 30 min, in which Zn^{II} has an electron configuration of $3d^{10}$ in the outer-most orbital, showed a marked decrease in ρ from 4.0×10^5 Ωcm (2.5×10^{-6} Scm^{-1}) to 4.8 Ωcm (2.1×10^{-1} Scm^{-1}), simultaneously with a decrease in Δ from 0.68 to 0.61 mms^{-1} [1]. It is noted that elevation of the conductivity was most remarkable in case of Cu_2O- [13], CuO- [13] and ZnO-substituted glasses [1], and that an electron configuration of $3d^{10}$ or $3d^9$ was preferable to attain the high conductivity. The present study was carried out in order to verify this idea in Ga_2O_3- and GeO_2-substituted vanadate glasses, since Ga^{III} and Ge^{IV} of “*p*-block” elements also have the electron configuration of $3d^{10}$ in the outer-most orbital.

Mössbauer spectroscopy has successfully been utilized as a powerful tool for the local structural study of oxide glasses. Mössbauer nuclides like ^{57}Fe and ^{119}Sn could play an effective role as a probe for the local structural study [1, 3–8, 10–13, 16–21]. A “T_g-vs-Δ plot”, applied to several inorganic glasses like silicates, borate, borosilicate, aluminates, tellurite and gallate glasses, is very effective to determine the structural role of Fe^{III} in these glasses, i.e. “substitutional” sites as the network former (NWF) or “interstitial” sites as the network modifier (NWM) [4, 8, 11, 12, 17, 18, 21]. When T_g’s of several oxide glasses, ranging from 180 to 770 °C, were plotted against the Δ of Fe^{III} (0.4–1.3 mms^{-1}), one “common” straight line with an identical slope of 680 K(mms^{-1})$^{-1}$ was drawn when Fe^{III} atoms occupied substitutional “tetrahedral” NWF sites [4, 8, 11, 12, 17, 18]. For example, “T_g-vs-Δ plot” applied to $xBaO\cdot10Fe_2O_3\cdot(90-x)V_2O_5$ glasses ($x=20$–40) and

$20BaO{\cdot}10Fe_2O_3{\cdot}xWO_3{\cdot}(70\text{-}x)V_2O_5$ glasses ($x=10$–50) yielded comparable slopes of 650 [8] and 680 $K(mms^{-1})^{-1}$ [11], respectively. These results proved that Fe^{III} atoms occupied substitutional "tetrahedral" sites of V^{IV} or V^{V} as NWF. Essentially the same results were obtained in $20BaO{\cdot}10Fe_2O_3{\cdot}xMnO_2{\cdot}(70-x)V_2O_5$ glasses ($x=0$–30) which yielded a slope of 707 $K(mms^{-1})^{-1}$ [12], and in $20R_2O{\cdot}10Fe_2O_3{\cdot}xWO_3{\cdot}(70-x)V_2O_5$ glasses (R = Na, K; $x=0$–50) with a slope of 670 or 680 $K(mms^{-1})^{-1}$ [17]. In contrast, Fe^{III} atoms in $xNa_2O{\cdot}Fe_2O_3{\cdot}(99-x)WO_3$ glasses ($30 \le x \le 42$) occupied substitutional "octahedral" sites of W^{VI} as NWF, in which a small slope of 260 $K(mms^{-1})^{-1}$ was obtained because of its longer bond length with a weaker bond energy [21].

Distortion or local symmetry at the Mössbauer nuclear sites could be deduced from the Δ of Fe^{III}. Mössbauer spectra of heat-treated vanadate glasses containing Fe^{III} showed a marked decrease in Δ, reflecting a decreased distortion or an increased symmetry of "distorted" $Fe^{III}O_4$ tetrahedra [1, 3–8, 10–13, 16–20]. This is also the case for "distorted" VO_4 tetrahedra in the *3D*-network, since one FeO_4 unit is randomly surrounded by three or four VO_4 units by sharing corner oxygen atoms. It is noted that the *electric field gradient* (*EFG*) caused by the valence electrons (eq_{val}) of high-spin Fe^{III} is "zero" since it has an isotropic electron configuration of $3d^5$ in the outer-most orbital. In this case, Δ of Fe^{III} reflects the *EFG* brought about by the lattice (eq_{lat}), i.e. by the steric configuration of oxygen atoms constituting the distorted FeO_4 and VO_4 tetrahedra.

Mössbauer study of heat-treated vanadate glasses indicated that a remarkable decrease of ρ was observed in conjunction with a decrease of Δ, which reflected a decreased distortion of $Fe^{III}O_4$ tetrahedra and VO_4 tetrahedra [1, 3–8, 12–17]. It was also considered that Fe^{III} atoms having an isotropic symmetric electron configuration of $3d^5$ in the outermost orbital was preferable for the remarkable decrease of ρ since half-occupied 3d-orbitals could effectively accept the carriers (polaron) in the remaining unoccupied 3d-orbitals [5–8].

Experimental

Homogeneous glass samples with compositions of $20BaO{\cdot}xGa_2O_3{\cdot}(10\text{-}x)Fe_2O_3{\cdot}70V_2O_5$ and $20BaO{\cdot}xGeO_2{\cdot}(10\text{-}x)Fe_2O_3{\cdot}70V_2O_5$ (in mol%) were prepared by a melt-quenching method with weighed amounts of $BaCO_3$, Ga_2O_3, GeO_2, Fe_2O_3 and V_2O_5 of guaranteed reagent grade. Each reagent mixture placed in an alumina crucible was melted in an electric muffle furnace at 1300 °C for 2.5 h in Ga_2O_3-substituted glass, and at 1100 °C for 2 h in GeO_2-substituted glass. Glass samples of almost black color were prepared by quenching the melt in the air. Annealing of as-quenched glass sample was carried out at a given temperature using another electric furnace. For determining T_g and T_c values, DTA was conducted at a heating rate of 10 $Kmin^{-1}$ ranging from *RT* to 600 °C in an N_2 atmosphere. A fixed amount of α-Al_2O_3 powder was used as a reference of the temperature. Electrical resistivity (ρ) of a rectangular glass sample was determined by a conventional dc-four probe method, in which a linear relationship was obtained by plotting the voltage against the electric current applied by the electrometer. Mössbauer measurement was conducted at *RT* by a constant acceleration method with a source of $^{57}Co(Rh)$. Small amount of enriched isotope, $^{57}Fe_2O_3$, was used for the sample preparation of Mössbauer measurement. A foil of α-Fe was used as a reference of δ and for calibrating the velocity scale of the spectrometer. A software of Mösswinn 3.0i XP was used for the peak analysis of the Mössbauer spectrum.

Results

$20BaO{\cdot}xGa_2O_3{\cdot}(10-x)Fe_2O_3{\cdot}70V_2O_5$ glass

DTA of Ga_2O_3-substituted vanadate glass showed a gradual lowering of T_g from 351 °C ($x=0$) to 328 ($x=5$) and 324 °C ($x=10$), reflecting lowered heat resistivity. Nishida et al. reported that gallate (Ga_2O_3-based) glass had higher heat resistivity [4, 18–20]. When the coordination number (CN) of Ga^{III} was four, Ga^{III}–O bond was reported to have a single bond energy of 2.9 eV [14, 15], which was larger than the Fe^{III}–O bond energy of 2.6 eV [21, 22]. A gradual lowering of T_g observed in the present study will be ascribed to the structural role of Ga^{III}

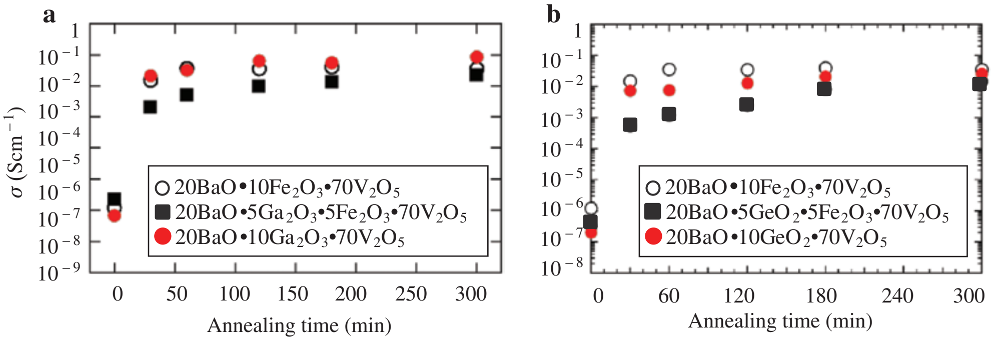

Fig. 1: (a) Electrical conductivity (σ) of $20BaO{\cdot}10Fe_2O_3{\cdot}70V_2O_5$ (open circle), $20BaO{\cdot}5Ga_2O_3{\cdot}5Fe_2O_3{\cdot}70V_2O_5$ (solid square) and $20BaO{\cdot}10Ga_2O_3{\cdot}70V_2O_5$ glasses (red solid circle) measured at *RT* after isothermal annealing at 450 °C. (b) Electrical conductivity (σ) of $20BaO{\cdot}10Fe_2O_3{\cdot}70V_2O_5$ (open circle), $20BaO{\cdot}5GeO_2{\cdot}5Fe_2O_3{\cdot}70V_2O_5$ (solid square) and $20BaO{\cdot}10GeO_2{\cdot}70V_2O_5$ glasses (red solid circle) measured at *RT* after isothermal annealing at 450 °C.

that plays a role of NWM like Ba^{2+} at the "interstitial" sites of *3D*-network of vanadate glass. In such case, six-fold coordinated Ga^{III} atoms have smaller single bond energy of 2.0 eV [14, 15]. Substitution of Ga_2O_3 for Fe_2O_3 will cause a lowering of T_g, since the increased fraction of NWM from 20 mol% BaO to 25 mol% (BaO + Ga_2O_3) is equivalent to a decreased degree of polymerization.

DTA study of Ga_2O_3-substituted vanadate glass showed T_c values of 410, 422 and 405 °C when the Ga_2O_3 contents were 0, 5 and 10 mol%, respectively. Crystallization of oxide glass is closely related to the bond energy of NWF-oxygen polyhedra [3, 21–24]. For example, crystallization of Fe^{III}-containing aluminate glass [22] was triggered by a cleavage of Fe^{III}–O bonds, since the Al–O bond energy (3.4–4.4 eV [14, 15]) was much larger than the Fe–O bond energy of 2.6 eV [21, 22]. The same conclusion was drawn in vanadate [3] and tungstate glasses [21]. In the crystallization study of IR-transmitting gallate glass in combination with the heat treatment, Ar^+-laser and ^{60}Co-γ ray irradiations, FT-IR spectroscopy was effectively used to explore the kinetics and mechanism of crystallization [19, 23, 24]. Irradiation of Ga_2O_3-substituted vanadate glass with Ar^+-laser and ^{60}Co-γ rays will also show the "memory effect" as observed in the IR-transmitting gallate glass described above.

DTA study of $20BaO{\cdot}5CuO{\cdot}5Fe_2O_3{\cdot}70V_2O_5$ and $20BaO{\cdot}5Cu_2O{\cdot}5Fe_2O_3{\cdot}70V_2O_5$ glasses showed a small decrease in T_g along with an increasing CuO or Cu_2O content, together with a lowering of T_c amounting to *ca.* 30 K [13]. Similar lowering of T_g and T_c amounting to *ca.* 30 K was observed in $20BaO{\cdot}5ZnO{\cdot}5Fe_2O_3{\cdot}70V_2O_5$ glass [1]. In case of $20BaO{\cdot}10ZnO{\cdot}70V_2O_5$ glass, a decrease in T_g amounted to *ca.* 50 K and a decrease in T_c to *ca.* 30 K [1]. These DTA results proved that substitution of CuO, Cu_2O and ZnO for Fe_2O_3 was effective for the preparation of less heat-resistant vanadate glass with higher conductivity. Such conductive glass might be preferably utilized as sensors, electric discharge needle, conductive glass paste, static electricity-protecting material and hyperfine processing materials combined with FIB, electrons, laser, etc. This will be also the case for Ga_2O_3- and GeO_2-substituted glasses, if the conductivity were highly enough for each purpose.

Figure 1a depicts σ values of Ga_2O_3-substituted glasses measured at *RT* after the isothermal annealing at 450 °C, which was higher than the T_c's of 405–422 °C. *RT*-conductivity (σ) of 5 mol% Ga_2O_3-substituted vanadate glass measured after the heat treatment for 120 min (solid square) increased from 2.2×10^{-6} Scm^{-1} ($\rho = 4.5 \times 10^5$ Ωcm) to 9.6×10^{-3} Scm^{-1} (104 Ωcm), which was one-order of magnitude lower than that of "non-substituted" $20BaO{\cdot}10Fe_2O_3{\cdot}70V_2O_5$ glass measured in this study (3.5×10^{-2} Scm^{-1} or 28 Ωcm). If the heat treatment were made at temperatures higher than 450 °C, the conductivity will be enhanced. After the heat treatment at 450 °C, σ of 10 mol% Ga_2O_3-substituted vanadate glass (red solid circle) increased from 6.7×10^{-7} Scm^{-1} (1.5×10^6 Ωcm) to 6.2×10^{-2} Scm^{-1} (16 Ωcm), which was comparable to that of non-substituted vanadate glass, i.e. 3.5×10^{-2} Scm^{-1} (28 Ωcm).

All the σ values plotted in Fig. 1a are one- or two-orders of magnitude lower than those of 5 mol% CuO-substituted vanadate glass [13], which showed a marked increase of σ from 3.9×10^{-6} Scm^{-1} (2.6×10^5 Ωcm) to 3.2×10^{-1} Scm^{-1} (3.1 Ωcm) after the annealing at 450 °C for 30 min (see Table 1). After the same annealing, 5 mol% ZnO-substituted vanadate glass also showed a remarkable increase in σ from 2.5×10^{-6} Scm^{-1}

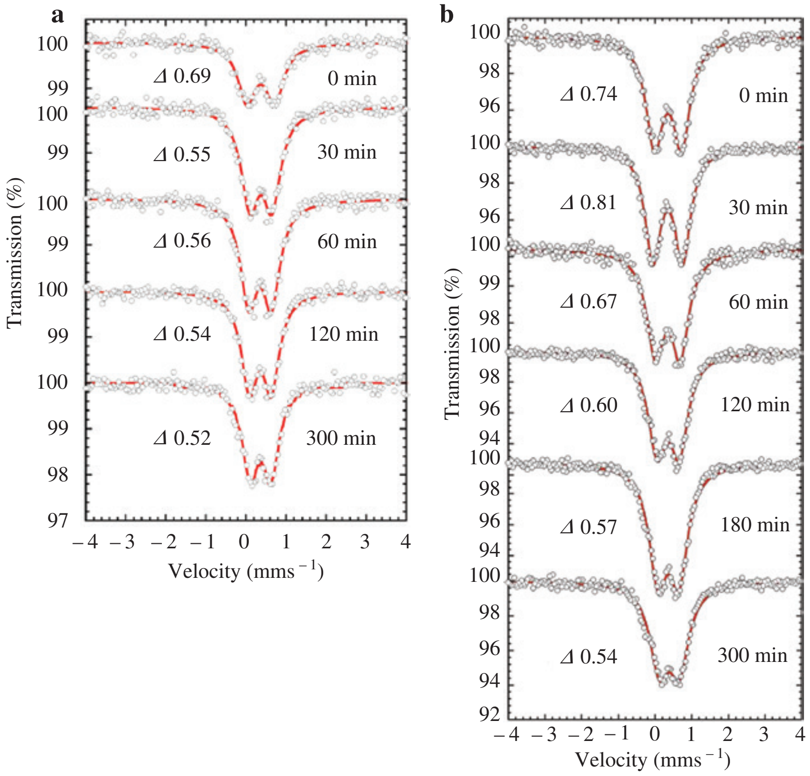

Fig. 2: (a) *RT*-Mössbauer spectra of $20BaO \cdot 5Ga_2O_3 \cdot 5Fe_2O_3 \cdot 70V_2O_5$ glass measured after isothermal annealing at 450 °C. (b) *RT*-Mössbauer spectra of $20BaO \cdot 5GeO_2 \cdot 5Fe_2O_3 \cdot 70V_2O_5$ glass measured after isothermal annealing at 450 °C.

(4.0×10^5 Ωcm) to 2.1×10^{-1} Scm^{-1} (4.8 Ωcm) [1]. Conductivities of related barium iron vanadate glasses are summarized in Table 1, together with the activation energy for the electrical conduction (E_a) and Δ values of Fe^{III} obtained from the Mössbauer measurement. As seen from Table 1, CuO-, Cu_2O- and ZnO-substituted vanadate glasses, in which Cu^{II} atom had an electron configuration of $3d^9$, and Cu^I and Zn^{II} atoms $3d^{10}$ configuration, were preferable for the preparation of highly conductive vanadate glass.

RT-Mössbauer spectra of 5 mol% Ga_2O_3-substituted vanadate glass, measured after the isothermal annealing at 450 °C, are illustrated in Fig. 2a. A marked decrease in Δ from 0.69 to 0.55 (±0.01) mms^{-1} was observed after the annealing at 450 °C for only 30 min, and Δ showed a slight decrease from 0.55 to 0.52 (±0.01) mms^{-1} after the additional heat treatment up to 300 min. A larger decrease in Δ of 0.12–0.15 (±0.02) mms^{-1} was observed in CuO- and Cu_2O-substituted vanadate glasses after the annealing at 450 °C for 30 min [13]. In case of ZnO-substituted glass, the decrease in Δ was 0.06–0.07 (±0.01) mms^{-1} [1]. All the Mössbauer results are summarized in Table 1.

Figure 2a proved that the eq_{lat} at the nuclear sites of ^{57}Fe decreased as a result of heat treatment at 450 °C, reflecting a decreased distortion of FeO_4 tetrahedra. This is also the case for VO_4 tetrahedra since they are directly bonded to FeO_4 tetrahedra. In several vanadate glasses, decrease in the resistivity or an increase in the conductivity has been observed in conjunction with a decrease in Δ of Fe^{III} [1, 3–8, 10–13, 16, 17]. As shown in Fig. 1a with solid squares, σ values of 5 mol% Ga_2O_3-substituted glass were smaller than those of non-substituted vanadate glass (open circle) despite that the Mössbauer spectra showed a large decrease from 0.69 to 0.55–0.56 mms^{-1} after 30–60 min annealing (Fig. 2a). In case of CuO- and Cu_2O-substituted vanadate glasses, comparable decrease in Δ [0.12–0.15 (±0.02) mms^{-1}] was observed after the annealing at 450 °C for 30 min, and σ showed much more remarkable increase from 3.9×10^{-6} to 3.2×10^{-1} Scm^{-1} (3.1 Ωcm) [13]. In case of ZnO-substituted glass, a remarkable increase of σ was observed from 2.5×10^{-6} to 2.1×10^{-1} Scm^{-1} (4.8 Ωcm) in spite that the decrease in Δ was not so large [0.06–0.07 (±0.01) mms^{-1}] [1] (see Table 1). These results prove that elevation of the conductivity is partially related to the decrease in the distortion of FeO_4 and VO_4 units.

The conduction behavior of highly conductive barium iron vanadate glass should be discussed by combining the *small polaron hopping theory* and the *n-type semiconductor model*, as discussed below.

$20BaO{\cdot}xGeO_2{\cdot}(10-x)Fe_2O_3{\cdot}70V_2O_5$ glasses

DTA study of GeO_2-substituted vanadate glass revealed a gradual lowering of T_g from 354 °C ($x=0$) to 330 °C ($x=5$) and 318 °C ($x=10$), as observed in Ga_2O_3-substituted vanadate glasses. Substitution of 5 mol% GeO_2 for Fe_2O_3 resulted in an increase of T_c from 408 to 424 °C. It means that larger thermal energy was required for the rearrangement of each fragment when an equivalent amount of GeO_2 and Fe_2O_3 played a role of NWF in the *3D*-network. In case of 10 mol% GeO_2-substituted vanadate glass showed a lowering of T_c from 408 °C (non-substituted) to 389 °C, as also observed in 10 mol% Ga_2O_3-substituted glass.

RT-conductivities (σ) of 5 mol% GeO_2-substituted vanadate glass, measured after an isothermal annealing at 450 °C, are plotted with solid squares in Fig. 1b. After the heat treatment at 450 °C for 120 min, this glass showed an increase of σ from 3.0×10^{-7} Scm^{-1} ($\rho = 3.3\times10^6$ Ωcm) to 2.5×10^{-3} Scm^{-1} (400 Ωcm), which was one-order of magnitude smaller than that of non-substituted vanadate glass as plotted with open circles in Fig. 1b, i.e. 3.5×10^{-2} Scm^{-1} (28 Ωcm).

After the heat treatment at 450 °C, σ of 10 mol% GeO_2-substituted vanadate glass (red solid circles) increased from 2.0×10^{-7} Scm^{-1} (5.0×10^6 Ωcm) to 1.3×10^{-2} Scm^{-1} (77 Ωcm) which was still smaller than that of non-substituted vanadate glass plotted with open circles, 3.5×10^{-2} Scm^{-1} (28 Ωcm). Although the σ values of 10 mol% GeO_2-substituted vanadate glass plotted with red solid circles (Fig. 1b) were superior to those of 5 mol% GeO_2-substituted glass, they were still smaller than those of non-substituted vanadate glass (open circles). It is noted that σ's of GeO_2-substituted glasses were generally one or two-orders of magnitude smaller than those of 5 mol% CuO-substituted glass [13] that showed a marked increase in σ from 3.9×10^{-6} Scm^{-1} (2.6×10^5 Ωcm) to 3.2×10^{-1} Scm^{-1} (3.1 Ωcm) after the annealing at 450 °C for 30 min. Five mol% ZnO-substituted vanadate glass [1] also showed a remarkable increase in σ from 2.5×10^{-6} Scm^{-1} (4.0×10^5 Ωcm) to 2.1×10^{-1} Scm^{-1} (4.8 Ωcm), as summarized in Table 1.

As described above, CuO-, Cu_2O- and ZnO-substituted vanadate glasses showed higher conductivity, in which the electron configurations of $3d^9$ (Cu^{II}) and $3d^{10}$ (Cu^I and Zn^{II}) seemed to be preferable to attain the high conductivity [1, 13]. In case of Ga_2O_3- and GeO_2-substituted vanadate glasses, as described above, increase in the σ caused by the "common" heat treatment at 450 °C was less than that of Cu_2O- and ZnO-substituted glasses, despite Ga^{III} and Ge^{IV} atoms of "*p*-block elements" had $3d^{10}$ configuration. Conduction mechanism will be discussed in the following session by focusing the electron configuration, band gap of the metal oxides and the activation energy for the conduction (E_a).

RT-Mössbauer spectra of 5 mol% GeO_2-substituted vanadate glass measured after the isothermal annealing at 450 °C are illustrated in Fig. 2b. In several vanadate glasses, the increase in the conductivity has so far been observed in conjunction with a decrease in $\varDelta$ of Fe^{III} [1, 3–8, 10–13, 16, 17]. The isothermal annealing illustrated in Fig. 2b showed a small increase of $\varDelta$ from 0.74 to 0.81 (±0.01) mms^{-1} after the annealing for 30 min. This will reflect a temporarily increased local distortion of FeO_4 and VO_4 tetrahedra of the *3D*-network on the way of the *structural relaxation*. It is considered that the *structural relaxation* could occur effectively if the heat treatment were conducted at temperatures higher than 450 °C. In Fig. 2b, a remarkable decrease in $\varDelta$ was observed from 0.81 to 0.54 (±0.01) mms^{-1} after the isothermal annealing for 60–300 min, which evidently demonstrated a decreased distortion or an enhanced *structural relaxation* of the FeO_4 and VO_4 units.

Figure 2b reveals that eq_{lat} at the nuclear sites of ^{57}Fe was decreased due to a decreased distortion of FeO_4 and VO_4 tetrahedra, since $eq=eq_{lat}$, as observed in 5 mol% Ga_2O_3-substituted vanadate glass (Fig. 2a). A decrease in $\varDelta$ amounted to 0.23 (±0.01) mms^{-1}, which was much larger than that of 5 mol% CuO- or Cu_2O-substituted vanadate glasses, 0.12–0.15 (±0.02) mms^{-1}, in which σ increased up to 3.2×10^{-1} Scm^{-1} (3.1 Ωcm) after the annealing at 450 °C for 30 min [12]. As describe above, 5 mol% ZnO-substituted glass showed a smaller decrease of $\varDelta$ [0.06–0.07 (±0.01) mms^{-1}], despite a remarkable elevation of σ was observed up to 2.1×10^{-1} Scm^{-1} (4.8 Ωcm) [1].

Discussion

Activation energy for the conduction (E_a) in the *small polaron hopping theory* [2] could be calculated with the following equation:

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

in which σ, T and k are the conductivity, measuring temperature (K) and the Boltzmann constant, respectively. Values of E_a could be calculated from the slope of the straight line obtained by plotting the natural logarithm of σT against the reciprocal of T, as illustrated in Fig. 3.

Non-substituted barium iron vanadate glass, $20BaO{\cdot}10Fe_2O_3{\cdot}70V_2O_5$, showed a marked increase of σ from 2.8×10^{-6} to 4.3×10^{-2} Scm^{-1} in conjunction with a decrease of E_a from 0.38 to 0.13 eV when annealed at 500 °C for 60 min [7, 8]. Conductivities of this glass showed a linear increase along with a decrease of E_a [8, 11]. The σ values increased significantly when annealed at higher temperatures, since the glass network was partially cleaved to cause the *structural relaxation* after prolonged annealing. Several E_a's obtained for a series of barium iron vanadate glasses are summarized in Table 1, in which latest results of Ga_2O_3-, GeO_2- and ZnO-substituted vanadate glasses are summarized together with those for non-substituted [7, 8], WO_3- [10], MnO_2- [12], CuO- [13] and Cu_2O- substituted glasses [13].

Figure 3a depicts the ln σT-vs.-T^{-1} plot for 10 mol% GeO_2-substituted vanadate glass, and Fig. 3b for 5 mol% ZnO_2-substituted glass. In these plots all the σT values were normalized with the σT obtained at *RT*. Ten mol% GeO_2-substituted vanadate glass had E_a's of 0.41 and 0.21 eV before and after the annealing at 450 °C for 120 min, respectively (Fig. 3a). Ten mol% Ga_2O_3-substituted vanadate glass also had comparable E_a's of 0.42 and 0.18 eV before and after the annealing, respectively (Table 1). In contrast, 5 mol% ZnO_2-substituted vanadate glass investigated for comparison (Fig. 3b) had much smaller E_a's of 0.23 and 0.14 eV before and after the annealing at 450 °C for 30 min, respectively. This glass had *RT*-conductivity of 2.1×10^{-1} Scm^{-1} (4.8 Ωcm) which was one-order of magnitude higher than that of non-substituted glass [1]. Smaller E_a's were also obtained in CuO- (0.16 and 0.10 eV) [13] and Cu_2O-substituted glasses (0.22 and 0.09 eV) [13], of which σ's after the heat treatment were 3.2×10^{-1} Scm^{-1} (3.1 Ωcm) and 2.0×10^{-1} Scm^{-1} (5.0 Ωcm), respectively.

These E_a values are significantly smaller than the band gap energy (E_g) 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) [7]. A photoluminescence study of $20BaO{\cdot}10Fe_2O_3{\cdot}70V_2O_5$ glass annealed at 500 °C for 60 min

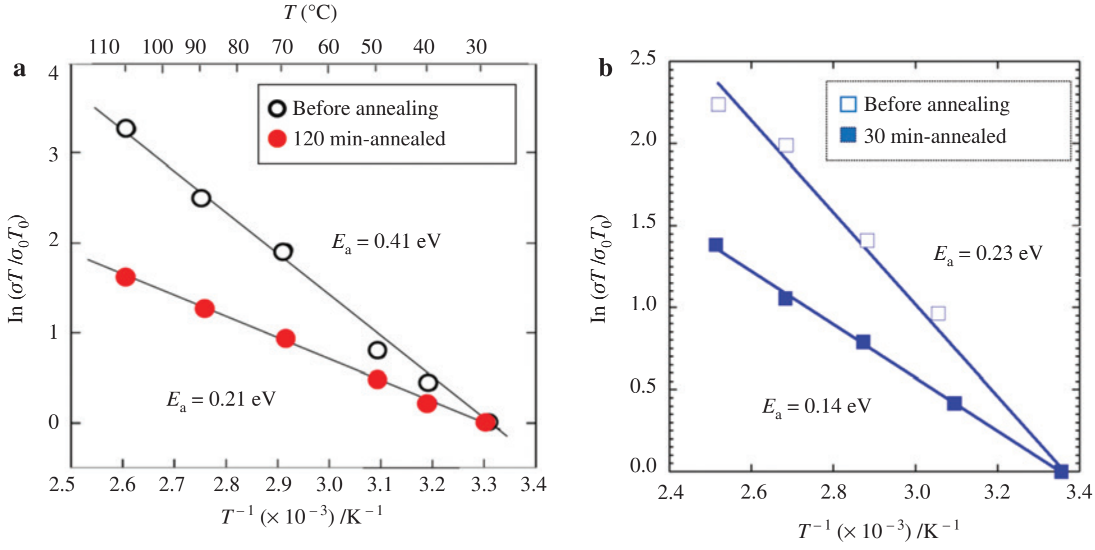

Fig. 3: (a) Natural logarithm of σT for $20BaO{\cdot}10GeO_2{\cdot}70V_2O_5$ glass plotted against the reciprocal of the measuring temperature (*T*) before and after the annealing at 450 °C for 120 min. (b) Natural logarithm of σT for $20BaO{\cdot}5ZnO_2{\cdot}5Fe_2O_3{\cdot}70V_2O_5$ glass plotted against the reciprocal of the measuring temperature (*T*) before and after the annealing at 450 °C for 30 min.

yielded an E_g of 2.25 eV [1]. Carrier (electron) density in the CB would increase along with a decrease of E_g and also with the energy gap between the donor level and the CB of *n-type semiconductor*. It is considered that E_a is equivalent to the energy gap between the donor level and CB. All the experimental results obtained in different vanadate glasses [1, 6–8, 10–13, 17] proved that a decrease in E_a caused an increase in σ due to an increased carrier (electron) density in the CB. It is noted that *n-type semiconductor model* becomes predominant over the *small polaron hopping model* that has been utilized for the conduction mechanism of "semiconducting" vanadate glass of which σ is of the order of "mega" Ωcm [1, 13].

In the present study, as-quenched Ga_2O_3- and GeO_2-substituted vanadate glasses respectively had E_a's of 0.42 and 0.41 eV. After the annealing at 450 °C for 120 min, E_a's of Ga_2O_3- and GeO_2-substituted vanadate glasses were 0.18 and 0.21 eV, respectively. Conductivities of these glasses were 9.6×10^{-3} Scm^{-1} (104 Ωcm) and 2.5×10^{-3} Scm^{-1} (400 Ωcm), as shown in Fig. 1a and b. They were two-orders of magnitude lower than those of ZnO- [1], CuO- [13] and Cu_2O-substituted glasses [13]. All the E_a and σ values obtained for non-substituted, ZnO-, CuO, Cu_2O-, Ga_2O_3- and GeO_2-substituted vanadate glasses prove that smaller E_a's obtained before and after the annealing could attain the higher conductivity that was comparable to that of "metal heater" like Ni–Cr alloy.

As described above, electron configuration of $3d^{10}$ proved to be preferable for the preparation of highly conductive vanadate glass like ZnO-, CuO- and Cu_2O-substituted glasses [1, 13]. It is interesting to discuss the σ value in association with the band gap energy (E_g) of the substituents. The E_g of α-Fe_2O_3 is reported to be 2.2 eV [25], whereas CuO and Cu_2O, respectively have smaller E_g's of 1.2–1.5 [26, 27] and 2.1 eV [28]. It was reported that ZnO had comparable E_g of 3.3 [29] or 3.4 eV [30]. In contrast, much larger E_g of 5.3 eV was reported for α-Ga_2O_3 [31], and 4.7–4.9 eV for β-Ga_2O_3 [31, 32]. The former is known to be stable at relatively lower temperature like 470 °C, whereas the latter is stable at relatively higher temperatures of 550–630 °C [31]. In case of α-GeO_2, a large E_g of 5.95 eV was reported [33]. Larger E_a values obtained for Ga_2O_3- and GeO_2-substituted vanadate glasses before and after the heat treatment will be ascribed to the large E_g of Ga_2O_3 and GeO_2. These results prove that a partial replacement of Fe_2O_3 by metal oxide with small E_g is effective to attain the high conductivity of vanadate glass.

It was suggested that Fe^{III} atoms with a symmetric electron configuration of $3d^5$ were preferable for the *small polaron hopping* from V^{IV} to V^V (and Fe^{III}) via oxygen atoms. For example, $25K_2O{\cdot}10Fe_2O_3{\cdot}65V_2O_5$ glass annealed at 380 °C showed an increase of σ from 6.3×10^{-8} Scm^{-1} ($\rho=1.6\times10^7$ Ωcm) to 4.3×10^{-4} Scm^{-1} ($\rho=2.3$ kΩcm) as a result of an increased probability of the *small polaron hopping* among less-distorted FeO_4 and VO_4 tetrahedra [3, 4]. *Structural relaxation* of FeO_4 and VO_4 tetrahedra was confirmed as a marked decrease of $\varDelta$ in the Mössbauer spectra [1, 3–8, 10–13, 16, 17], and the conductivity was enhanced by the *structural relaxation*. This is also the case for the vanadate glasses in which Fe_2O_3 was replaced by metal oxides in which each metal had $3d^{10}$ configuration [1, 13].

Small polaron hopping theory [2] has generally been utilized to explore the conduction mechanism of semiconducting vanadate glass of which σ is $<10^{-4}$ Scm^{-1}. This authors' group suggested that *n-type semiconductor model* in conjunction with the *small polaron hopping theory* was most probable to explain the conduction mechanism of highly conductive vanadate glasses with σ higher than *ca.* 10^{-4} Scm^{-1} [1, 13]. In conductive barium iron vanadate glasses, increase in σ was directly proportional to the decrease in $\varDelta$ of Fe^{III} in the Mössbauer spectra. A marked decrease of $\varDelta$ was observed in non-substituted [5–8], WO_3- [10, 11], MnO_2- [12], CuO- [13], Cu_2O- [13] and Ga_2O_3- or GeO_2-substituted barium iron vanadate glasses (this study). In case of ZnO-substituted glass [1], a decrease in $\varDelta$ was not remarkable (Table 1), but σ of this glass was one order of magnitude larger than that of non-substituted glass. These results evidently prove that *n-type semiconductor model* in conjunction with the *small polaron hopping theory* is most probable for the conduction mechanism of highly conductive vanadate glass of which σ value is comparable to that of metal heater like Ni–Cr alloy.

Summary

1. As for the conduction mechanism of *highly conductive* vanadate glasses with σ value larger than 10^{-4} Scm^{-1}, *n-type semiconductor model* combined with the *small polaron hopping theory* is most probable.

2. Heat treatment of barium iron vanadate glass at a given temperature higher than T_c causes a marked increase in the conductivity in conjunction with a decrease in E_a, which could be correlated to the energy gap between the donor level and the CB.
3. Substitution of Ga_2O_3 or GeO_2 for Fe_2O_3 was less effective to increase the conductivity, despite that Ga^{III} and Ge^{IV} atoms had $3d^{10}$ configuration that was preferable to attain the higher conductivity.
4. This will be ascribed to the intrinsic large E_g's of Ga_2O_3 (5.3 eV) and GeO_2 (5.95 eV) which are much larger than that of Fe_2O_3 (2.2 eV).
5. All the experimental results suggest that replacement of Fe_2O_3 by the metal oxide with a small E_g is preferable to attain the higher conductivity, as recently discovered in CuO-, Cu_2O- and ZnO-substituted vanadate glasses.

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