Article

Mössbauer Study of Water-Resistive Conductive Vanadate Glass

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Glass transition temperature (T_g) of $20 \text{ BaO} \cdot 10 \text{ Fe}_2\text{O}_3 \cdot x \text{ WO}_3 \cdot (70-x) \text{ V}_2\text{O}_5$ glasses showed a step-by-step increase from 339 to 470°C when x was increased from 0 to 50, together with a concordant increase in crystallization temperature (T_c) from 406 to 531°C. Plot of T_g against quadrupole splitting (Δ) of Fe^{III} in the Mössbauer spectra yielded a straight line with a slope of $680 \text{ K}(\text{mm s}^{-1})^{-1}$. This indicates that Fe^{III} atoms constitute distorted FeO_4 tetrahedra and play a role of network former in the 3D-glass network. Dissolution of vanadium ions from vanadate glass into boiling water was suppressed from 34 to 2 mg L^{-1} when x was modified from 0 to 50, reflecting that introduction of WO_3 into the 3D-network of vanadate glass is effective in the improvement of water resistivity. A gradual decrease of Δ was observed from 0.82 to 0.76 mm s^{-1} after isothermal annealing of vanadate glass ($x = 20$) at 500°C for 240 min, indicating structural relaxation of the glass network, and a marked increase in conductivity (σ) from 3.9×10^{-6} to $2.1 \times 10^{-3} \text{ S cm}^{-1}$ was observed at room temperature.

Key Words : Mössbauer spectroscopy, electrical conductivity, semiconducting glass, water resistivity, heat resistivity, structural relaxation

1. Introduction

Conduction mechanism of semiconducting vanadate glass was discussed by Mott with a small polaron hopping theory,¹⁾ i.e., a step-by-step electron hopping from V^{IV} or V^{III} to V^{V} . Semiconducting vanadate glass has attracted much interest in the field of advanced technology like nanotechnology, secondary battery, sensor, etc. Electrical conductivity (σ) of as-quenched vanadate glass is known to be of the order of 10^{-7} to $10^{-5} \text{ S cm}^{-1}$.^{2), 3)} Electrical conductivity of iron-containing vanadate glass is known to be increased by several orders of

magnitude after isothermal annealing at temperatures higher than glass transition temperature (T_g)³⁾⁻⁵⁾ or crystallization temperature (T_c).^{6), 7)} Vanadate glass has a lot of industrial applications like cathode-active material electrode for lithium-ion battery,⁸⁾ electron-emitting needle for ionizer, host material for hyperfine processing with focused ion beam (FIB), sensor, glass lining, etc.

Mössbauer spectroscopy has successfully been utilized for the local structural study of glass and amorphous materials which have interesting physical properties and a lot of applications. Mössbauer spectra provide several im-

portant chemical and physical information through the Mössbauer parameters of isomer shift (δ), quadrupole splitting (Δ), linewidth (FWHM : Γ) and internal magnetic field (H_{int}), which are observed as a result of nuclear interaction of Mössbauer atoms with neighboring atoms.

A linear relationship, named T_g - Δ rule,⁹⁾ was discovered between T_g of inorganic glass and Δ of Fe^{III} , being expressed by :

$$T_g = a\Delta + b. \quad (\text{eq. 1})$$

This experimental rule indicates that T_g of inorganic glasses like oxide glass and halide glass is in proportion to Δ of Fe^{III} , reflecting that distortion of network former (NWF)-oxygen polyhedra determines the heat-resistivity of inorganic glasses. Slope “ a ” of the straight line becomes $680 \text{ K}(\text{mm s}^{-1})^{-1}$ when Fe^{III} atoms occupy substitutional sites of tetrahedral NWF, while it becomes $260 \text{ K}(\text{mm s}^{-1})^{-1}$ when they occupy octahedral NWF sites.¹⁰⁾ T_g - Δ rule is also applicable to a structural study of inorganic glasses in which Fe^{III} atoms are present at interstitial network modifier (NWM) sites.⁹⁾ In such case, T_g vs. Δ plot gives a straight line with a slope “ a ” of only $35 \text{ K}(\text{mm s}^{-1})^{-1}$. It is noteworthy that T_g - Δ rule is very useful even when we are going to determine the structural role or sites of Fe^{III} atoms introduced into unknown glass.

Chemical durability of glass is primarily determined by its composition. This study was carried out in order to improve water-resistivity of barium iron vanadate glass, $20 \text{ BaO} \cdot 10 \text{ Fe}_2\text{O}_3 \cdot 70 \text{ V}_2\text{O}_5$, so that it could be applied to nanotechnology, secondary battery, sensor, etc. under severe environment: in the hot water and in the atmosphere of high temperature and humidity.

2. Experimental

$20 \text{ BaO} \cdot 10 \text{ Fe}_2\text{O}_3 \cdot x \text{ WO}_3 \cdot (70 - x) \text{ V}_2\text{O}_5$ glass was prepared by melting mixture of BaCO_3 , Fe_2O_3 , WO_3 and V_2O_5 of guaranteed reagent grade, placed in alumina crucible, at 1200°C for 90 min in electric muffle furnace. Each melt was poured into a stainless mold, and was annealed at a given temperature for 0–240 min. Values of T_g and T_c were determined by DTA conducted at a heating rate of 10 K min^{-1} with a standard of $\alpha\text{-Al}_2\text{O}_3$. Mössbauer spectra were measured by a constant acceleration method with a ^{57}Co (Rh) source and a reference of $\alpha\text{-Fe}$ foil, which was also used for calibrating the velocity scale of the spectrometer. For the Mössbauer measurement, each glass powder was diluted with boron nitride (BN).

Electrical conductivity (σ) was measured at room temperature by a DC four-probe method with a rectangular glass sample of which each end was coated with silver paste. Copper lead wires were attached to each end with silver-containing SnO_2 solder. Electrical resistivity (R) was calculated from the slope of the straight line obtained by plotting the potential against the current. Specific conductivity (σ) was calculated with R and size of the glass sample, i.e.,

$$\sigma = R^{-1} \cdot S^{-1} \cdot l, \quad (\text{eq. 2})$$

in which S is the cross section (in cm^2) of the glass sample and l the length (in cm).

Water-resistivity was estimated by determining the concentration of vanadium, tungsten and iron ions dissolved into boiling water (15 mL), in which each glass sample (1.0 g) was immersed for 2 h. Atomic absorption spectroscopy was used for determining the metal

Fig. 1 Mössbauer spectra of 20 BaO · 10 Fe₂O₃ · x WO₃ · (70 - x) V₂O₅ glasses measured at room temperature before and after isothermal annealing at 500°C for 240 min.

ions in the boiling water before and after the leaching test.

3. Results and Discussion

Figure 1 shows Mössbauer spectra of 20 BaO · 10 Fe₂O₃ · x WO₃ · (70 - x) V₂O₅ glasses, measured at room temperature before and after isothermal annealing. Each spectrum was analyzed into one paramagnetic doublet due to distorted Fe^{III}O₄ tetrahedra. As-quenched 20 BaO · 10 Fe₂O₃ · 70 V₂O₅ glass (x = 0) has δ and Δ values of 0.38 ± 0.01 and 0.68 ± 0.02 mm s⁻¹, respectively. Value of Δ decreased from 0.68 ± 0.02 to 0.55 ± 0.02 mm s⁻¹ after isothermal annealing at 500°C for 240 min, while δ showed a very slight increase from 0.38 ± 0.01 to 0.42 ± 0.01 mm s⁻¹. This indicates that mean Fe^{III}-O bond length and the coordination number of Fe^{III} are scarcely changed by the isothermal annealing.

The decrease of Δ is ascribed to a decreased distortion or an increased local symmetry of Fe^{III}O₄ tetrahedra, as has been observed in tungsten-free barium iron vanadate glasses^{(4)–(7)}, in which structural relaxation of 3D-glass net-

work brought about a marked increase in the conductivity, as illustrated in Fig. 2. Distortion of Fe^{III}O₄ tetrahedra can be explained in relation to the electric field gradient, eq , at the nuclear site of Mössbauer atoms, i.e.,

$$eq = eq_{\text{val}} + eq_{\text{lat}}, \quad (\text{eq. 3})$$

in which eq_{val} and eq_{lat} are the electric field gradient caused by valence electrons and neighboring atoms, respectively. Since high-spin Fe^{III} has five valence electrons equally occupied five 3d-orbitals, eq_{val} can be ignored, and hence eq is equal to eq_{lat} . Hence, we can directly estimate the distortion of Fe^{III}O₄ tetrahedra from the decrease of Δ value.

In case of 20 BaO · 10 Fe₂O₃ · x WO₃ · (70 - x) V₂O₅ glasses with “x” of 20, 35 and 50, comparable δ values of $0.36 - 0.40 \pm 0.01$ mm s⁻¹ were obtained irrespective of the heat treatment, indicating identical mean Fe^{III}-O bond length. Quadrupole splitting of tungsten-containing vanadate glass with “x” of 20 showed a decrease from 0.82 ± 0.02 to 0.76 ± 0.02 mm s⁻¹ after the isothermal annealing conducted at

500 °C for 240 min.

By contrast, isothermal annealing caused no change of Δ when “ x ” was 35 ($\Delta = 0.80 \pm 0.02$ mm s⁻¹) and 50 ($\Delta = 0.86 - 0.87 \pm 0.02$ mm s⁻¹). Mössbauer spectra shown in Fig. 1 indicate that *structural relaxation of glass network is intrinsic of vanadate glass* and that introduction of WO₃ into vanadate glass suppresses the structural relaxation of 3D-network of the vanadate glass.

Figure 2 depicts a relationship between σ of 20 BaO · 10 Fe₂O₃ · 70 V₂O₅ glass and Δ of Fe^{III} measured before and after isothermal annealing at temperatures ranging from 350 to 500 °C. Figure 2 indicates that increase in σ is observed along with a decrease of Δ for Fe^{III} which directly reflects an increased symmetry of Fe^{III}O₄ tetrahedra. Figure 3 shows a relationship between σ and Δ of Fe^{III} obtained for 20 BaO · 10 Fe₂O₃ · x WO₃ · (70 - x)V₂O₅ glasses with “ x ” of 20 and 35, measured before and after isothermal annealing at 450, 500 and 550 °C. Plot for vanadate glass with “ x ” = 20 indicates that σ is increased along with a decrease of Δ for Fe^{III}. This reflects that decreased distortion of Fe^{III}O₄, V^{IV}O₄ and V^VO₄ tetrahedra causes an increase in the conductivity, as observed in 20 BaO · 10 Fe₂O₃ · 70 V₂O₅ glass (Fig. 2). It is noted that isothermal annealing of iron-containing vanadate glass causes a decrease of Δ for Fe^{III} together with a marked decrease in the activation energy (E_a) for the conduction from 0.37 to 0.13 (± 0.01) eV.¹¹ Similar decrease of E_a from 0.33 (± 0.07) to 0.11 (± 0.01) eV was observed in 20 BaO · 10 Fe₂O₃ · x MnO₂ · (70 - x) V₂O₅ glasses.¹² We can understand from Figs. 2 and 3 that the correlation between σ and Δ becomes weaker when more V₂O₅ was replaced by WO₃. These results evidently show that the increase of σ associated with a decrease in the

Fig. 2 A relationship between electrical conductivity (σ) of 20 BaO · 10 Fe₂O₃ · 70 V₂O₅ glass and Δ of Fe^{III} measured before and after isothermal annealing at different temperatures ranging from 350 to 500 °C.

Fig. 3 A relationship between electrical conductivity (σ) of 20 BaO · 10 Fe₂O₃ · x WO₃ · (70 - x) V₂O₅ glasses (“ x ” = 20 and 35) and Δ of Fe^{III} measured before and after isothermal annealing at 450, 500 and 550 °C; ● : “ x ” = 20, ▲ : “ x ” = 35.

distortion of Fe^{III}O₄, V^{IV}O₄ and V^VO₄ tetrahedra is intrinsic of vanadate glass matrix, and that introduction of WO₃ causes no essential effect to the conduction mechanism of vanadate glass.

Glass transition temperatures (T_g) of 20 BaO · 10 Fe₂O₃ · x WO₃ · (70 - x) V₂O₅ glasses with “ x ” of 0, 20, 35 and 50 are plotted against Δ of Fe^{III} in Fig. 4, together with corresponding plots obtained earlier for aluminate, gallate, borosilicate and vanadate glasses.⁹ A linear re-

Fig. 4 T_g vs. Δ plot for $20 \text{ BaO} \cdot 10 \text{ Fe}_2\text{O}_3 \cdot x \text{ WO}_3 \cdot (70-x) \text{ V}_2\text{O}_5$ glasses with “ x ” of 0, 20, 35 and 50. Corresponding plot for tungstate glass, $x \text{ Na}_2\text{O} \cdot \text{Fe}_2\text{O}_3 \cdot (99-x) \text{ WO}_3$, with a slope of $260 \text{ K} (\text{mm s}^{-1})^{-1}$ is given for comparison.¹⁰⁾ Plots for alkali vanadate glass (●, ○), borosilicate glass (◆), gallate glass (▲, △) and aluminate glass (■, □) yield a straight line with a “common” slope of $680 \text{ K} (\text{mm s}^{-1})^{-1}$.⁹⁾

relationship is observed in these glasses with an identical slope of $680 \text{ K} (\text{mm s}^{-1})^{-1}$, indicating that distorted $\text{Fe}^{\text{III}}\text{O}_4$ tetrahedra occupy NFW sites, as do AlO_4 , GaO_4 , BO_4 , SiO_4 and VO_4 tetrahedra in aluminate, gallate, borosilicate and vanadate glasses.⁹⁾ In a recent study of $20 \text{ BaO} \cdot 10 \text{ Fe}_2\text{O}_3 \cdot x \text{ MnO}_2 \cdot (70-x) \text{ V}_2\text{O}_5$ glasses,¹²⁾ slope of $707 \text{ K} (\text{mm s}^{-1})^{-1}$ was obtained from the straight line. We can evidently exclude another possibility that Fe^{III} atoms oc-

cupy octahedral NFW sites in $20 \text{ BaO} \cdot 10 \text{ Fe}_2\text{O}_3 \cdot x \text{ WO}_3 \cdot (70-x) \text{ V}_2\text{O}_5$ glasses at the substitutional sites of distorted WO_6 octahedra, as earlier observed in $x \text{ Na}_2\text{O} \cdot \text{Fe}_2\text{O}_3 \cdot (99-x) \text{ WO}_3$ glasses in which T_g vs. Δ plot yielded a straight line with a slope of $260 \text{ K} (\text{mm s}^{-1})^{-1}$.¹⁰⁾ Structural information obtained from T_g vs. Δ plot is that we can know the local structure of $\text{Fe}^{\text{III}}\text{O}_4$ tetrahedra that are connected to VO_4 tetrahedra or VO_5 pyramids by sharing corner oxygen atoms in the 3D-glass network.

Chemical durability of $20 \text{ BaO} \cdot 10 \text{ Fe}_2\text{O}_3 \cdot x \text{ WO}_3 \cdot (70-x) \text{ V}_2\text{O}_5$ glasses, estimated from a 2h-leaching test in boiling water, is summarized in Table 1. It is understood from the leaching test that introduction of WO_3 into iron-containing vanadate glass results in an increased water-resistivity, e.g., dissolution of vanadium ions were suppressed from 30 to 11 and 10 mg L^{-1} when “ x ” were 20 and 35, respectively. Higher water-resistivity was achieved in $20 \text{ BaO} \cdot 10 \text{ Fe}_2\text{O}_3 \cdot 50 \text{ WO}_3 \cdot 20 \text{ V}_2\text{O}_5$ glass in which only a few mg L^{-1} of vanadium ions were detected after the leaching test. This leaching test suggests that introduction of 20 mol% of WO_3 is effective in the preparation of vanadate glass with higher water-resistivity, and that 50 mol% of WO_3 could satisfactorily suppress the dissolution of vanadium ions. It is obvious from Table 1 that dissolution of iron

Table 1 Concentration of metal ions dissolved into boiling water after 2h-leaching

Composition	(mg/l)		
	V	W	Fe
$20 \text{ BaO} \cdot 10 \text{ Fe}_2\text{O}_3 \cdot 70 \text{ V}_2\text{O}_5^*$	30 (34)	—	ND (1)
$20 \text{ BaO} \cdot 10 \text{ Fe}_2\text{O}_3 \cdot 20 \text{ WO}_3 \cdot 50 \text{ V}_2\text{O}_5^*$	11 (21)	1 (4)	ND (ND)
$20 \text{ BaO} \cdot 10 \text{ Fe}_2\text{O}_3 \cdot 35 \text{ WO}_3 \cdot 35 \text{ V}_2\text{O}_5^*$	10 (16)	3 (8)	ND (ND)
$20 \text{ BaO} \cdot 10 \text{ Fe}_2\text{O}_3 \cdot 50 \text{ WO}_3 \cdot 20 \text{ V}_2\text{O}_5^*$	3 (2)	4 (8)	ND (ND)

*All the samples annealed at 500°C for 1h. Value in parenthesis for non-annealed sample. ND: non-detected.

was nearly zero, although only a small amount of tungsten ions were detected when WO_3 content was 35 or 50 mol%.

4. Summary

Iron(III) atoms constitute distorted FeO_4 tetrahedra at substitutional sites of VO_4 and WO_4 tetrahedra, constituting 3D-network structure of barium iron tungsten vanadate glass. Isothermal annealing at temperatures higher than T_c results in a marked decrease in Δ due to decreased distortion of FeO_4 tetrahedra. This is also the case for VO_4 and WO_4 tetrahedra since they share corner oxygen atoms with FeO_4 tetrahedra. Decrease in the local distortion of 3D-network causes an increase in σ , which is in proportion to the content of V_2O_5 . This indicates that *the increase in σ , generally observed together with a structural relaxation of glass network, is intrinsic of vanadate glass*. Substitution of WO_3 for V_2O_5 is effective in the improvement of water-resistivity of conductive barium iron vanadate glass. We can design and prepare new iron-containing conductive vanadate glass with desired conductivity and water-resistivity by regulating the content of WO_3 and V_2O_5 .

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