Verification of the "T_g-Δ Rule" in Potassium Silicate and Sodium Tungstate Glasses *

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A linear relationship exists in oxide glasses between glass transition temperature (T_g) and quadrupole splitting (Δ) of Fe^{3+}. DTA and Mössbauer measurements of silicate and tungstate glasses yielded large slopes of 680 and 260 °C/(mm s^{-1}) from the slope of the straight lines when Fe^{3+} occupied, as network former (NWF), distorted tetrahedral Si^{4+} and distorted octahedral W^{6+} sites, respectively. This linear relationship, named a "T_g-Δ rule", suggests that T_g is in proportion to the distortion of NWF-oxygen polyhedra and a higher activation energy is required for the fragments of glass to have a cooperative movement in the supercooled liquid state. The "T_g-Δ rule" was also valid in the case of potassium silicate glasses heat treated at the temperature close to T_g, indicating a distortion of SiO_4 and FeO_4 tetrahedra. Substitution of Fe^{3+} for individual NWF in silicate and tungstate glasses was confirmed from the Fourier transform infrared (FT-IR) spectra because only the absorption bands due to Si and W were respectively observed without the bands due to Fe.

Key words: Mössbauer effect, silicate glass, tungstate glass, glass transition temperature, quadrupole splitting, "T_g-Δ rule".

1. Introduction

^{57}Fe- and ^{119}Sn-Mössbauer effects are very effective for structural studies of oxide and halide glasses since the valency and coordination number (CN) of Mössbauer ions such as Fe^{3+}, Fe^{2+}, Sn^{4+}, and Sn^{2+} can be estimated from the isomer shift (δ) [1 - 4]. Increase in the fraction of nonbridging oxygen (NBO), *i. e.* terminal oxygen in the covalently bonded skeleton structure, results in decrease in the δ of Fe^{3+} because of the increased 4s-electron density (increased covalency) at the nuclear site [1 - 4]. Quadrupole splitting (Δ) is estimated from the peak separation of the doublet peak which is caused by the electric field gradient (*eq*) at the nuclear sites of Mössbauer ions. Δ of "high spin" Fe^{3+} with a symmetric electron configuration of $3d^5$ is directly related to the distortion of $Fe^{3+}O_4$ tetrahedra (T_d) or $Fe^{3+}O_6$ octahedra (O_h) because "eq_{val}" produced by the valence electrons is negligible and Δ is associated with "eq_{val}" produced by the negative charge of oxygen atoms.

A linear relationship, named "T_g-Δ rule", was discovered between Δ of Fe^{3+} and the glass transition temperature (T_g) of oxide, halide, and sulfate glasses [2 - 6]. The "T_g-Δ rule" is expressed by:

$$T_g = a\Delta + b, \tag{1}$$

which is effective for determining the structural role of iron, because the slope, a, of the straight line is closely related to the site occupation of Fe^{3+}, *i. e.* whether a network former (NWF) or network modifier (NWM). a was estimated to be 680 °C/(mm s^{-1}) when Fe^{3+} occupies four-fold coordinated NWF sites such as B^{3+}, Al^{3+}, Ga^{3+}, Si^{4+}, Ti^{4+}, Te^{4+}, and V^{5+}, whereas a was only 35 °C/(mm s^{-1}) when Fe^{3+} was ionically linked to oxygen or halogen atoms at six-fold coordinated NWM sites.

The site occupation of Mössbauer ions in glasses was also determined by comparing the Debye temperatures (θ_D) [2 - 4, 6]. According to a simplified Debye model, which is usually valid at temperatures $\geq \theta_D/2$, θ_D can be estimated from the equation

$$\theta_D^2\, M\,(-\mathrm{d}\ln f / \mathrm{d}T) = 3E^2 / kc^2, \tag{2}$$

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in which M and f are the mass of Mössbauer ions and the recoil-free fraction, respectively, and E is the γ-ray energy (14.4 keV in the case of ^{57}Fe-Mössbauer effect). In (2) k is Boltzmann constant and c the velocity of light. When a "thin" sample is measured, $\mathrm{d} \ln f / \mathrm{d} T$ can be approximated by $\mathrm{d} \ln A / \mathrm{d} T$, where A is the absorption area. θ_D can be obtained from the slope of the straight line of the plot $\ln A$ vs. T. The θ_Ds obtained from ^{57}Fe- and ^{119}Sn-Mössbauer measurements at lower temperatures proved to be higher than 280 K when Fe^{3+} and Sn^{4+} were covalently bonded to oxygen atoms at "substitutional" sites of NWF [2 - 4, 6]. On the contrary, the θ_Ds were lower than 270 K when Fe^{2+}, Fe^{3+}, Sn^{2+}, and Sn^{4+} were ionically linked to oxygen or halogen atoms at "interstitial" sites of the glass matrix, playing a role of NWM [2 - 4].

Irradiation of oxide glasses with ^{60}Co γ-rays can be related to the structural role of Fe^{2+}, Fe^{3+}, Sn^{2+}, and Sn^{4+} in glasses because a reduction or oxidation of Mössbauer ions is observed due to electron transfer or scattering when they are present at NWF or NWM sites, respectively [2 - 4, 6]. The irradiation effect can be explained by the relative difference in the energy levels of NWF, NWM, and oxygen; electron transfer will take place from the lower energy level (2p-orbital of oxygen) to the higher level (3d- or 4s-orbital of Fe^{3+}) when the iron is covalently bonded to oxygen at NWF sites. On the contrary, γ-ray irradiation will cause electron transfer from the lower level (3d- or 4s-orbital of Fe^{2+}) to the higher level (probably anti-bonding π-orbital of oxygen) when Fe^{2+} is ionically linked to oxygen at NWM sites.

It is known that silicate glasses are composed of distorted SiO_4 tetrahedra, whereas tungstate glasses are composed of distorted WO_4 tetrahedra and distorted WO_6 octahedra. In this paper, the "T_g-Δ rule" was applied to $x K_2O \cdot (99-x) SiO_2 \cdot {}^{57}Fe_2O_3$ and $x Na_2O \cdot (99-x) WO_3 \cdot {}^{57}Fe_2O_3$ glasses. In addition, the "structural relaxation" of potassium silicate glass was investigated after heat treatment conducted at a temperature close to T_g, because it was expected that decreasing distortion of NWF-oxygen tetrahedra should accompany a decrease in T_g, if the "T_g-Δ rule" is actually associated with the distortion of NWF-oxygen polyhedra. Substitution of Mössbauer ions for each NWF was also investigated by using Debye temperatures (θ_D) and the ^{60}Co γ-ray irradiation effect. Fourier transform infrared (FT-IR) spectroscopy was used in order to confirm the site occupation of the Mössbauer ions in silicate and tungstate glasses. It is known that the peak position of the stretching band (ν_3) is closely related to the CN of NWF.

2. Experimental

Potassium silicate glasses $x K_2O \cdot (99-x) SiO_2 \cdot {}^{57}Fe_2O_3$ were prepared by melting mixtures of K_2CO_3, SiO_2, and $^{57}Fe_2O_3$ of guaranteed reagent grade, placed in a platinum crucible, at 1200 or 1300 °C for 2 or 3 h in an electric muffle furnace. Transparent, lightly yellow glasses were prepared in the compositional range $10 \leq x \leq 50$ when the platinum crucible was quickly immersed in ice-cold water. Sodium tungstate glasses, $x Na_2O \cdot (99-x) WO_3 \cdot {}^{57}Fe_2O_3$, were prepared by melting mixtures of Na_2CO_3, WO_3, and $^{57}Fe_2O_3$ of guaranteed reagent grade at 1000 °C for 2h. Transparent, lightly yellow glass samples were obtained in the small region of $30 \leq x \leq 42$. ^{57}Fe-Mössbauer spectra were measured with a source of 10 mCi ^{57}Co(Pd) and a reference of metallic iron (α-Fe). A source of 10 mCi $Ca^{119m}SnO_3$ and a reference of $BaSnO_3$ were used for ^{119}Sn-Mössbauer measurements. FT-IR spectra were measured by a conventional KBr method. T_g was estimated by differential thermal analysis (DTA), in which the glass sample was heated at a rate of 5 °C min^{-1}, and α-Al_2O_3 was used for calibrating the temperature.

3. Results

3.1. Potassium Silicate Glass

DTA curves of $x K_2O (99-x) SiO_2 \cdot Fe_2O_3$ glasses (Fig. 1) indicated that T_g was decreased gradually from 419 (±5) °C to 409, 389, 371, and 352 °C when the K_2O content (x) was increased from 10 to 20, 30, 40, and 50 mol%, respectively. A decrease in T_g of oxide glasses is generally observed when the alkali oxide content is increased. This decrease is due to the formation of NBO which is equivalent to a destruction or a depolymerization of the skeletal structure. Sprenger et al. [7] revealed the fraction of SiO_4 tetrahedra with one to four NBO(s) using X-ray photoelectron spectroscopy (XPS). The decrease in T_g observed in potassium silicate glasses (Fig. 1) is hence ascribed to the increase in the fraction of NBO in SiO_4 tetrahedra. It is noted that an increase in the BaO or MgO content resulted in an increase of T_g in the case of vanadate (V_2O_5-based) glasses [8], because the degree of cross-linking or polymerization was increased due to

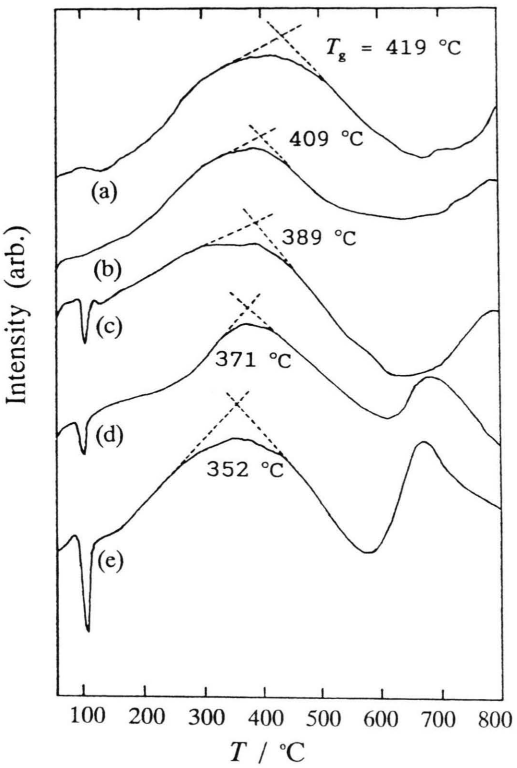

Fig. 1. DTA curves of $x\mathrm{K_2O}\cdot(99\text{–}x)\mathrm{SiO_2}\cdot\mathrm{Fe_2O_3}$ glasses recorded at a heating rate of 20 °C $\mathrm{min^{-1}}$; (a) x = 10, (b) x = 20, (c) x = 30, (d) x = 40, (e) x = 50.

the higher charge and hence higher ionic potential of the NWM: Ba^{2+} and Mg^{2+}.

The ^{57}Fe-Mössbauer spectra of $x\mathrm{K_2O}(99\text{–}x)\mathrm{SiO_2}\cdot{}^{57}\mathrm{Fe_2O_3}$ glasses (Fig. 2) are composed of an intense doublet due to $\mathrm{Fe^{3+}}(T_\mathrm{d})$ with δ values of 0.23 to 0.28 (±0.01) mm $\mathrm{s^{-1}}$ and a less intense doublet (shoulder) due to $\mathrm{Fe^{2+}}(T_\mathrm{d})$ with δ of 0.83 to 0.94 (±0.01) mm $\mathrm{s^{-1}}$. All the Mössbauer parameters of $x\mathrm{K_2O}\cdot(99\text{–}x)\mathrm{SiO_2}\cdot{}^{57}\mathrm{Fe_2O_3}$ glasses are summarized in Table 1. The δ of $\mathrm{Fe^{3+}}$ showed a gradual decrease from 0.28 to 0.23 mm $\mathrm{s^{-1}}$ with increasing $\mathrm{K_2O}$ content, whereas that of $\mathrm{Fe^{2+}}$ from 0.94 to 0.83 mm $\mathrm{s^{-1}}$. The decrease of δ indicates an increase in the 4s-electron density due to the formation of NBO which has shorter bond length and higher covalency than bridging oxygen (BO). Δ of $\mathrm{Fe^{3+}}$ and that of $\mathrm{Fe^{2+}}$ showed a gradual decrease from 0.85 to 0.73 mm $\mathrm{s^{-1}}$ and from 2.10 to 1.98 mm $\mathrm{s^{-1}}$, respectively. Γ of $\mathrm{Fe^{3+}}$ was 0.73 to 1.15 mm $\mathrm{s^{-1}}$, and that of $\mathrm{Fe^{2+}}$ was 0.76 to 0.79 mm $\mathrm{s^{-1}}$. The former showed a marked decrease with increasing $\mathrm{K_2O}$ content due to a decreasing randomness of the steric configuration of $\mathrm{Fe^{3+}}(T_\mathrm{d})$. The relative fraction of $\mathrm{Fe^{2+}}(T_\mathrm{d})$ decreased gradually from 20.4 % to 2.2 % with increasing $\mathrm{K_2O}$ content, as generally show several oxide glasses; increasing basicity brings about an oxidizing atmosphere and a resultant higher oxidation state of NWF.

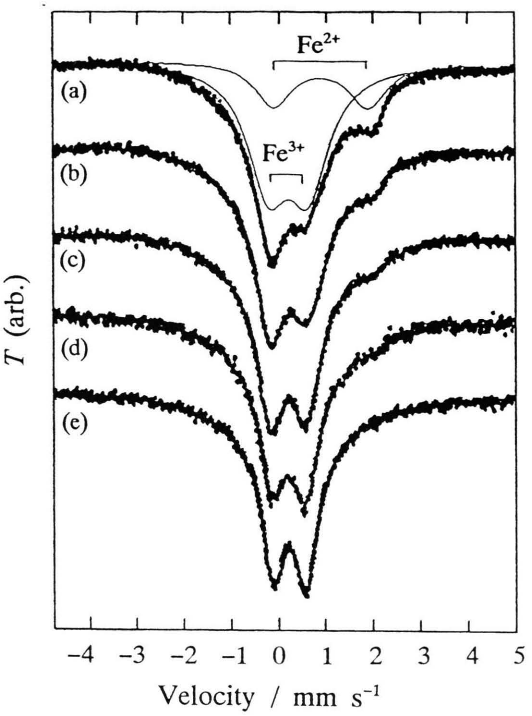

Fig. 2. ^{57}Fe-Mössbauer spectra of $x\mathrm{K_2O}\cdot(99\text{–}x)\mathrm{SiO_2}\cdot{}^{57}\mathrm{Fe_2O_3}$ glasses measured at room temperature; (a) x = 10, (b) x = 20, (c) x = 30, (d) x = 40, (e) x = 50.

Table 1. ^{57}Fe-Mössbauer parameters of $x\mathrm{Na_2O}(99\text{-}x)\mathrm{SiO_2}\cdot{}^{57}\mathrm{Fe_2O_3}$ glasses measurd at room temperature.

x	Species	δ^{a} [mm/s] (±0.01)	Δ^{b} [mm/s] (±0.02)	Γ^{c} [mm/s] (±0.02)	A^{d} [%] (±0.5)
10	$\mathrm{Fe^{3+}}$	0.28	0.85	1.15	79.6
10	$\mathrm{Fe^{2+}}$	0.94	2.09	0.79	20.4
20	$\mathrm{Fe^{3+}}$	0.27	0.84	1.09	87.0
20	$\mathrm{Fe^{2+}}$	0.93	2.10	0.78	13.0
30	$\mathrm{Fe^{3+}}$	0.27	0.80	0.90	90.8
30	$\mathrm{Fe^{2+}}$	0.92	2.07	0.78	9.2
40	$\mathrm{Fe^{3+}}$	0.25	0.75	0.85	93.8
40	$\mathrm{Fe^{2+}}$	0.88	2.02	0.76	6.2
50	$\mathrm{Fe^{3+}}$	0.23	0.73	0.73	97.8
50	$\mathrm{Fe^{2+}}$	0.83	1.98	0.76	2.2

[a] Isomer shift; [b] Quadrupole splitting;
[c] Linewidth (FWHM); [d] Absorption area.

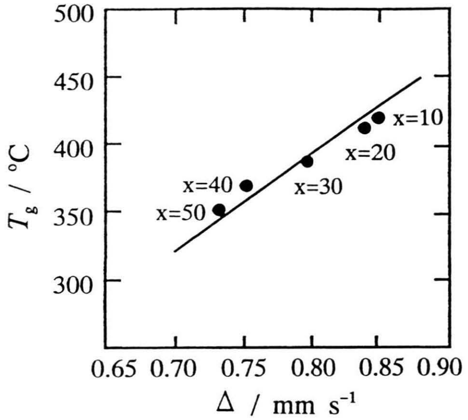

Fig. 3. Plot of glass transition temperature (T_g) vs. quadrupole splitting (Δ) of Fe^{3+} in $xK_2O{\cdot}(99{-}x)SiO_2{\cdot}{}^{57}Fe_2O_3$ glasses. The solid line was drawn by a least-squares method.

The decrease in T_g of potassium silicate glasses obtained from DTA (Fig. 1) is consistent with the decrease in quadrupole splitting (Fig. 2), Δ, which is associated with a decreasing distortion of Fe^{3+}. The plot of T_g vs. Δ of Fe^{3+} illustrated in Fig. 3 yielded a slope, a, of 680 °C/(mm s^{-1}). It is deduced from Fig. 3 that Fe^{3+} occupied tetrahedral Si^{4+} sites and played a role of NWF, because the slope is equal to that obtained for four-fold coordinated $Fe^{3+}(T_d)$ present at NWF sites of several oxide glasses studied so far, *e. g.* borate, aluminate, gallate, titanate, tellurite, and vanadate glasses [2 - 5].

An intense band ascribed to the stretching mode (ν_3) of SiO_4 tetrahedra [9] was observed in the FT-IR spectra of $xK_2O{\cdot}(99{-}x)SiO_2{\cdot}{}^{57}Fe_2O_3$ glasses, as shown in Figure 4(a). The peak position shifted gradually from 1074 to 1010, 1006, 1004, and 998 cm^{-1} when the K_2O content was 10, 20, 30, 40, and 50 mol%, respectively. This peak shift is ascribed to an increasing fraction of NBO which has a smaller binding energy and smaller force constant than BO, as Sprenger et al. [7] revealed using X-ray photoelectron spectroscopy (XPS). The FT-IR spectrum of Fe_2O_3 reagent, used for the sample preparation, shows an absorption band due to $Fe^{3+}(O_h)$ at 542 cm^{-1}. It is known that an absorption band due to $Fe^{3+}(T_d)$ is generally observed for wavenumbers larger than 550 cm^{-1} [10]. The absence of the absorption peak due to $Fe^{3+}(O_h)$ or $Fe^{3+}(T_d)$ revealed that $Fe^{3+}(T_d)$ substitutes $Si^{4+}(T_d)$ sites of potassium silicate glasses without essentially changing the intrinsic structure.

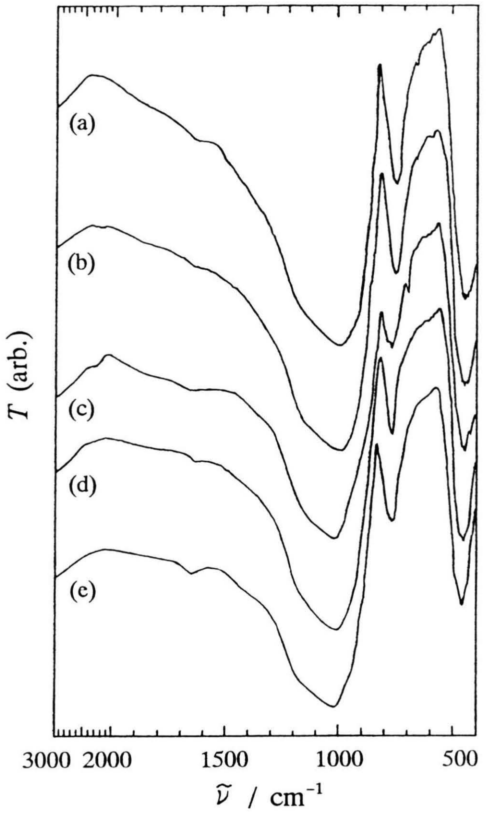

Fig. 4. FT-IR spectra of $20K_2O{\cdot}79SiO_2{\cdot}Fe_2O_3$ glasses heat treated at 450°C for (a) 0, (b) 300, (c) 600, (d) 900, and (e) 1500 min.

The Mössbauer spectra of $20K_2O{\cdot}79SiO_2{\cdot}{}^{57}Fe_2O_3$ glasses, heat treated at 450 °C for 300 to 1500 min, were similar to each other and were composed of an intense doublet due to $Fe^{3+}(T_d)$ and a weak doublet due to $Fe^{2+}(T_d)$ (Figure 2b). Δ of $Fe^{3+}(T_d)$ decreased linearly from 0.84 to 0.82, 0.81, 0.79, and 0.78 mm s^{-1} after the heat treatment at 450 °C for (a) 0, (b) 300, (c) 600, (d) 900, and (e) 1500 min, respectively. DTA curves of heat treated $20K_2O{\cdot}79SiO_2{\cdot}Fe_2O_3$ glasses showed a linear decrease of T_g from 409 to 386, 375, 346, and 316 °C after the heat treatment at 450 °C for (a) 0, (b) 300, (c) 600, (d) 900, and (e) 1500 min, respectively. Mössbauer and DTA studies of the heat treated silicate glasses suggest that they have essentially the same structure, and that only the distortion of the SiO_4 and FeO_4 tetrahedra was gradually reduced by the heat treatment. This conclusion was confirmed by the FT-IR spectra of heat treated $20K_2O{\cdot}79SiO_2{\cdot}Fe_2O_3$ glasses (Fig. 4), in which the stretching mode of the SiO_4 tetrahedra shifted gradu-

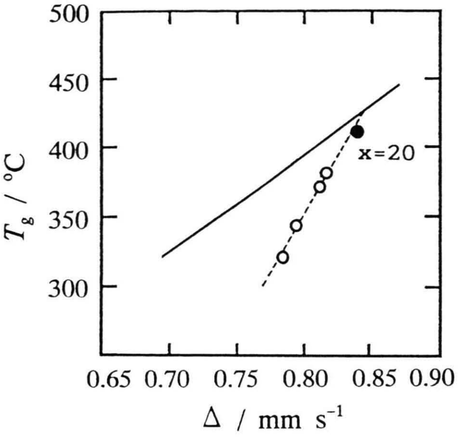

Fig. 5. Plot of glass transition temperature (T_g) vs. quadrupole splitting (Δ) of Fe^{3+} in $20K_2O{\cdot}79SiO_2{\cdot}{}^{57}Fe_2O_3$ glasses heat treated at 450 °C for 300 to 1500 min. The solid line is the same as that shown in Figure 3.

ally from 1010 cm^{-1} to 1013, 1015, 1019, and 1022 cm^{-1} when heat treated at 450 °C for (a) 0, (b) 300, (c) 600, (d) 900, and (e) 1500 min, respectively.

Figure 5 shows a plot of T_g vs. Δ of Fe^{3+} in $20K_2O{\cdot}79SiO_2{\cdot}{}^{57}Fe_2O_3$ glasses heat treated at 450 °C for 300 to 1500 min. The plot of T_g vs. Δ of Fe^{3+} in the heat treated glasses yielded a straight line with a slope larger than 680 °C/(mm s^{-1}). These results indicate that T_g of $20K_2O{\cdot}79SiO_2{\cdot}{}^{57}Fe_2O_3$ glass is primarily determined by the distortion of SiO_4 and FeO_4 tetrahedra which share several bridging oxygen atoms with each other. It is concluded that distorted FeO_4 tetrahedra have essentially the same structure as distorted SiO_4 tetrahedra, and the steric configuration of the former is regulated by the latter because the number of SiO_4 tetrahedra is much (79/2 times) larger than that of FeO_4 tetrahedra.

3.2. Sodium Tungstate Glass

DTA curves of $xNa_2O{\cdot}(99{-}x)WO_3{\cdot}Fe_2O_3$ glasses showed a gradual decrease of T_g from 354 (±5) °C to 315, 303, and 271 °C when the Na_2O content (x) was increased from 30 to 34, 38, and 42 mol%, respectively. The T_gs of iron-free $xNa_2O{\cdot}(100{-}x)WO_3$ glasses also decreased gradually from 365 to 315 °C when the Na_2O content was increased from 30 to 40 mol% [6]. This decrease in T_g is ascribed to an increase in the fraction of WO_4 tetrahedra at the expense of WO_6 octahedra, as T_g generally decreases with a decrease in CN of NWF and with a formation of NBO.

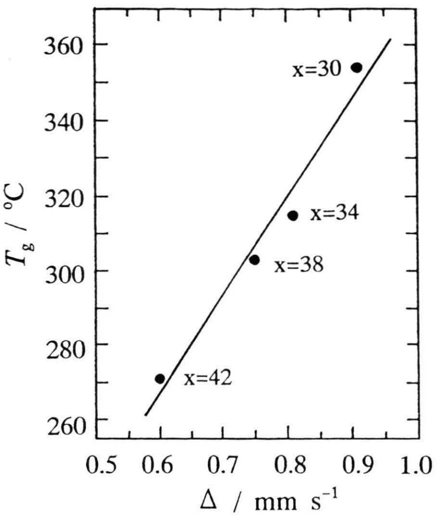

Fig. 6. Plot of glass transition temperature (T_g) vs. quadrupole splitting (Δ) of Fe^{3+} in $xK_2O{\cdot}(99{-}x)WO_3{\cdot}{}^{57}Fe_2O_3$ glasses. The solid line was drawn by a least-squares method.

^{57}Fe-Mössbauer spectra of $xNa_2O{\cdot}(99{-}x)WO_3{\cdot}{}^{57}Fe_2O_3$ glasses were composed of a doublet due to $Fe^{3+}(O_h)$ with δ of 0.39 to 0.44 (±0.02) mm s^{-1} and a weak doublet due to $Fe^{2+}(O_h)$ with δ of 1.11 to 1.18 (±0.02) mm s^{-1}. Δ of 0.60 to 0.91 and 1.88 to 2.03 (±0.02) mm s^{-1} were obtained for Fe^{3+} and Fe^{2+}, respectively. Γ of $Fe^{3+}(O_h)$ and that of $Fe^{2+}(O_h)$ were 0.74 to 0.85 and 0.49 to 0.79 (±0.02) mm s^{-1}, respectively, being characteristic of glassy phase. The relative absorption area of Fe^{2+} was in a range of 17.2 to 25.4 (±0.5) % in the Mössbauer spectra.

The plot of T_g vs. Δ of Fe^{3+} (Fig. 6) in $xNa_2O{\cdot}(99{-}x)WO_3{\cdot}{}^{57}Fe_2O_3$ glasses yielded a straight line with a slope, a, of 260 °C/(mm s^{-1}), which was smaller than half the slope obtained for four-fold coordinated Fe^{3+} occupying NWF sites described above: 680 °C/(mm s^{-1}) [2 - 5]. The simultaneous decrease of T_g and Δ of $Fe^{3+}(O_h)$ observed in sodium tungstate glasses indicates that T_g is directly related to the local distortion of NWF even when Fe^{3+} occupies six-fold coordinated $W^{6+}(O_h)$ sites.

^{57}Fe-Mössbauer spectra of $38Na_2O{\cdot}61WO_3{\cdot}{}^{57}Fe_2O_3$ glass at lower temperatures yielded a linear increase in the plot of ln A vs. T [6], from which θ_D of 580 K was obtained using the simplified Debye model of (2). In a ^{119}Sn-Mössbauer study of

$38Na_2O{\cdot}61WO_3{\cdot}^{119}SnO_2$ glass at low temperatures, θ_D of 360 K was obtained for $Sn^{4+}(O_h)$ occupying substitutional sites of $W^{6+}(O_h)$ as NWF [11]. The large θ_D of 580 K obtained for $38Na_2O{\cdot}61WO_3{\cdot}^{57}Fe_2O_3$ glass indicates that Fe^{3+} also occupied substitutional sites of $W^{6+}(O_h)$. ^{57}Fe-Mössbauer spectra of $38Na_2O{\cdot}61WO_3{\cdot}^{57}Fe_2O_3$ glass irradiated with ^{60}Co γ-rays showed a gradual increase in the absorption area of Fe^{2+} from 17.3 to 37.0 (±0.5) %, due to electron transfer from oxygen atoms of W–O and Fe–O bonds to Fe^{3+}. An irradiation-induced linear increase in the fraction of Fe^{2+} was previously observed in several $xK_2O{\cdot}(100\text{–}x)B_2O_3{\cdot}0.33^{57}Fe_2O_3$ glasses [12] when iron occupied tetrahedral boron sites as NWF.

FT-IR spectra of $xNa_2O{\cdot}(99\text{–}x)WO_3{\cdot}Fe_2O_3$ glasses showed an intense band between 860 and 884 cm^{-1} together with a weak band between 616 and 628 cm^{-1}. The former is ascribed to the ν_3 mode of WO_4 tetrahedra and the latter to ν_3 of WO_6 octahedra [9]. FT-IR spectra of iron-free $xNa_2O{\cdot}(100\text{–}x)WO_3$ glasses [6] were essentially the same as those of $xNa_2O{\cdot}(99\text{–}x)WO_3{\cdot}Fe_2O_3$ glasses and the ν_3 mode of WO_4 tetrahedra and that of WO_6 octahedra were observed between 856 and 884 cm^{-1} and between 616 and 644 cm^{-1}, respectively. An absorption peak due to iron was not observed in any FT-IR spectra, confirming the substitution of Fe^{3+} for W^{6+} in sodium tungstate glasses without an essential change of the intrinsic structure. The FT-IR study revealed that the relative fraction of tetrahedral WO_4 units became larger with increasing Na_2O content, indicating a gradual change of the glass matrix (skeleton) from WO_6 octahedra to WO_4 tetrahedra. The FT-IR result is well consistent with the DTA result described above, *i. e.*, increase in Na_2O content results in a gradual decrease of T_g from 354 (±5) °C to 271 °C due to a change of CN from 6 to 4.

4. Discussion

The consistent composition dependency observed between the physical properties (T_g) and the local distortion of Fe^{3+} (Δ) proves that Mössbauer ions (Fe^{3+}) can be utilized as a "probe" for local structural studies of glass. Figure 3 indicates that T_g of silicate glass increases/decreases with increasing/decreasing distortion of SiO_4 and FeO_4 tetrahedra. In the molecular-kinetic theory, Adam and Gibbs [13] asserted that T_g of polymers is proportional to the activation energy, E_a, which is required for the "cooperative rearrangement" of fragments in the supercooled liquid state, in which two configurational sites of interest have different Gibbs free energies of G and G'. The E_a was expressed by the product of the size (z) and the difference in the potential energy ($d\mu$) of each fragment:

$$E_a = G' - G = z\, d\mu. \tag{3}$$

Taking into account this molecular-kinetic theory, we speculate that the distortion of building units such as FeO_4, SiO_4, WO_4, and WO_6 brings about a higher restriction to the "cooperative movement" of fragments in the supercooled liquid state. The large slope, a, of 680 °C/(mm s^{-1}) obtained in the plot of T_g vs. Δ of Fe^{3+} in $xK_2O{\cdot}(99\text{–}x)SiO_2{\cdot}^{57}Fe_2O_3$ glasses (Fig. 3) proves that Fe^{3+} is four-fold coordinated at NWF sites similarly to Si^{4+}, as observed in several oxide glasses, *e .g.*,

$xCaO{\cdot}(95\text{–}x)Al_2O_3{\cdot}5Fe_2O_3$ glasses [5],
$xCaO{\cdot}(90\text{–}x)Ga_2O_3{\cdot}10Fe_2O_3$ glasses [5],
$xBaO{\cdot}(90\text{–}x)Ga_2O_3{\cdot}10Fe_2O_3$ glasses [5],
$xCaO{\cdot}(95\text{–}x)TiO_2{\cdot}5Fe_2O_3$ glasses [14],
$xNa_2O{\cdot}(95\text{–}x)TeO_2{\cdot}5Fe_2O_3$ glasses [15],
$xK_2O{\cdot}(95\text{–}x)TeO_2{\cdot}5Fe_2O_3$ glasses [15],
$xMgO{\cdot}(95\text{–}x)TeO_2{\cdot}5Fe_2O_3$ glasses [15],
and $xBaO{\cdot}(95\text{–}x)TeO_2{\cdot}5Fe_2O_3$ glasses [15].

Several alkali and alkaline earth vanadate glasses also showed a simultaneous decrease of T_g and Δ of Fe^{3+} [1, 8, 16]. It should be noted that the linear relationship is observed in several oxide glasses irrespective of the Fe_2O_3 content of 1 to 10 mol%.

The linear decrease in Δ observed for heat treated $20K_2O{\cdot}79SiO_2{\cdot}^{57}Fe_2O_3$ glasses (Fig. 5) indicates that a decrease in the distortion of SiO_4 and FeO_4 tetrahedra caused a decrease in eq_{lat}: an electric field gradient caused by oxygen atoms constituting the glass matrix (lattice). The large slope, a, obtained from the plot of T_g vs. T of heat treated $20K_2O{\cdot}79SiO_2{\cdot}^{57}Fe_2O_3$ glasses (Fig. 5) is associated with the "net" effect of local distortion of SiO_4 and FeO_4 tetrahedra on T_g, because the linear relationship was observed for glass pieces which had the same structure as each other originally. The linear relationship obtained for the potassium silicate glasses (Figs. 3 and 5) indicates that structural information on the NWF could be obtained because Fe^{3+} occupied NWF sites similarly to the tetrahedral Si^{4+}.

The small slope, a, of 260 °C/(mm s^{-1}) obtained in the plot of T_g vs. Δ of Fe^{3+} in

$x\mathrm{Na_2O}\cdot(99-x)\mathrm{WO_3}\cdot{}^{57}\mathrm{Fe_2O_3}$ glasses (Fig. 6) is ascribed to the six-fold coordination of NWF: $\mathrm{Fe^{3+}}(O_h)$ and $\mathrm{W^{6+}}(O_h)$. In the case of six-fold coordinated NWM-oxygen octahedra like $\mathrm{Fe^{3+}}(O_h)$ in phosphate glasses, a change of the local structure (distortion) will take place more easily than the NWF-oxygen tetrahedra, because the former has a longer bond length and weaker binding energy. Accordingly, a large change of Δ of $\mathrm{Fe^{3+}}$ will result in a small slope, *a*, of 35 °C/(mm $\mathrm{s^{-1}}$). The slope, *a*, of 260 °C/(mm $\mathrm{s^{-1}}$) obtained for six-fold coordinated NWF-oxygen octahedra in $x\mathrm{Na_2O}\cdot(99-x)\mathrm{WO_3}\cdot{}^{57}\mathrm{Fe_2O_3}$ glasses is located between the large "*a*" obtained for four-fold coordinated NWF-oxygen tetrahedra and the small "*a*" of six-fold coordinated NWM-oxygen octahedra. This means that the local structural change of $\mathrm{WO_6}$ and $\mathrm{FeO_6}$ octahedra is intermediate between those of NWF-oxygen tetrahedra and NWM-oxygen octahedra. Figure 6 proved that distortion of $\mathrm{WO_6}$- and $\mathrm{FeO_6}$-octahedra determines the T_g of tungstate glasses, although it is less effective than that of $\mathrm{WO_4}$ and $\mathrm{FeO_4}$ tetrahedra. If the $\mathrm{Fe^{3+}}(T_d)$ occupies $\mathrm{W^{6+}}(T_d)$ sites, the T_g-vs.-Δ plot will give a large slope of 680 °C/ (mm $\mathrm{s^{-1}}$).

5. Conclusions

1) The "T_g-Δ rule" was applied to potassium silicate glasses, $x\mathrm{K_2O}\cdot(99-x)\mathrm{SiO_2}\cdot{}^{57}\mathrm{Fe_2O_3}$, and a large slope, *a*, of 680 °C/(mm $\mathrm{s^{-1}}$) was obtained from the plot of T_g vs. Δ of $\mathrm{Fe^{3+}}$, as observed in several oxide glasses. This result indicates that T_g of oxide glass is most affected by the distortion of covalently bonded $\mathrm{SiO_4}$ tetrahedra.

2) The "T_g-Δ rule" was also valid in the case of $20\mathrm{K_2O}\cdot79\mathrm{SiO_2}\cdot{}^{57}\mathrm{Fe_2O_3}$ glasses, heat treated at a temperature close to T_g, and a large slope, *a*, larger than 680 °C/(mm $\mathrm{s^{-1}}$) was obtained.

3) The "T_g-Δ rule" indicates that highly distorted $\mathrm{SiO_4}$ and $\mathrm{FeO_4}$ tetrahedra have a higher restriction to the "cooperative movement" of fragments in the supercooled liquid state.

4) A slope, *a*, of 260 °C/(mm $\mathrm{s^{-1}}$) was obtained in the T_g-vs.-Δ plot of $x\mathrm{Na_2O}\cdot(99-x)\mathrm{WO_3}\cdot{}^{57}\mathrm{Fe_2O_3}$ glasses in which $\mathrm{Fe^{3+}}$ preferentially occupied six-fold coordinated $\mathrm{W^{6+}}$ sites as NWF than four-fold coordinated $\mathrm{W^{6+}}$ sites. The slope of 260 °C/(mm $\mathrm{s^{-1}}$) is ascribed to slightly longer $\mathrm{W^{6+}}$–O and $\mathrm{Fe^{3+}}$–O bond lengths and a weaker binding energy of NWF-oxygen octahedra, which is favorable for the change of local structure and distortion compared to four-fold coordinated NWF-oxygen tetrahedra.

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[1] T. Nishida, J. Non-Cryst. Solids **108,** 87 (1989).
[2] T. Nishida, J. Radioanal. Nucl. Chem. Articles **182,** 451 (1994).
[3] T. Nishida, J. Non-Cryst. Solids **177,** 257 (1994).
[4] T. Nishida, Hyperfine Interactions **95,** 23 (1995).
[5] T. Nishida, H. Ide, and Y. Takashima, Bull. Chem. Soc. Japan **63,** 548 (1990).
[6] T. Nishida, M. Suzuki, S. Kubuki, M. Katada, and Y. Maeda, J. Non-Cryst. Solids, **194,** 23 (1996).
[7] D. Sprenger, H. Bach, W. Meisel, and P. Gütlich, J. Non-Cryst. Solids **159,** 187 (1993)
[8] T. Nishida, S. Saruwatari, and Y. Takashima, Bull. Chem. Soc. Japan **61,** 2343 (1988).
[9] K. Nakamoto, in "Infrared and Raman Spectra of Inorganic and Coordination Compounds", John Wiley & Sons, New York 1986, p. 138 and p. 156.
[10] P. Tarte, in "Physics of Non-Crystalline Solids", ed J. A. Prins, North-Holland, Amsterdam 1965, p. 551.
[11] T. Nishida, T. Isobe, and M. Katada, Hyperfine Interactions **94,** 2113 (1994).
[12] T. Nishida, T. Shiotsuki, and Y. Takashima, J. Non-Cryst. Solids **41,** 161 (1980).
[13] G. Adams and J. H. Gibbs, J. Chem. Phys. **43,** 139 (1965).
[14] T. Nishida, Y. Yamaguchi, M. Yamada, and Y. Takashima, Bull. Chem. Soc. Japan **64,** 154 (1991).
[15] T. Nishida, M. Yamada, H. Ide, and Y. Takashima, J. Mater. Sci. **25,** 3546 (1990).
[16] T. Nishida, H. Ide, Y. Takashima, T. Yagi, S. Tomariguchi, S. Ishizuka, and A. Sakai, J. Mater. Sci. **24,** 1687 (1989).