Verification of the "\( T_g - \Delta \) 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 \( (\Delta) \) 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 "\( T_g - \Delta \) 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 "\( T_g - \Delta \) 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\(_2\) 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, "\( T_g - \Delta \) 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 \( (\delta) \) \([1 - 4]\). Increase in the fraction of nonbridging oxygen \( (NBO) \), i.e., terminal oxygen in the covalently bonded skeleton structure, results in decrease in the \( \delta \) of Fe\(^{3+}\) because of the increased 4s-electron density (increased covalency) at the nuclear site \([1 - 4]\). Quadrupole splitting \( (\Delta) \) 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. \( \Delta \) 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 \( (T_g) \) or Fe\(^{3+}\)O\(_6\) octahedra \( (O_h) \) because "eq\(_{val}\)" produced by the valence electrons is negligible and \( \Delta \) is associated with "eq\(_{val}\)" produced by the negative charge of oxygen atoms.

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

\[
T_g = a\Delta + b,
\]

(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\(^{4+}\), 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 \( (\theta_D) \) \([2 - 4, 6]\). According to a simplified Debye model, which is usually valid at temperatures \( \geq \theta_D/2 \), \( \theta_D \) can be estimated from the equation

\[
\theta_D^2 \ M \ (-d \ln f / d T) = 3E^2 / kc^2,
\]

(2)
in which \( M \) and \( f \) are the mass of Mössbauer ions and the recoil-free fraction, respectively, and \( E \) is the \( \gamma \)-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, \( d \) \( \ln f/d T \) can be approximated by \( d \) \( \ln A/d T \), where \( A \) is the absorption area. \( \theta_d \) can be obtained from the slope of the straight line of the plot \( \ln A \) vs. \( T \). The \( \theta_d \)'s obtained from \({}^{57}\)Fe- and \({}^{119}\)Sn-Mössbauer measurements at lower temperatures proved to be higher than 280 K when \( \text{Fe}^{3+} \) and \( \text{Sn}^{4+} \) were covalently bonded to oxygen atoms at “substitutional” sites of NWF [2-4]. On the contrary, the \( \theta_d \)'s were lower than 270 K when \( \text{Fe}^{2+} \), \( \text{Fe}^{3+} \), \( \text{Sn}^{2+} \), and \( \text{Sn}^{4+} \) 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 \( \gamma \)-rays can be related to the structural role of \( \text{Fe}^{2+} \), \( \text{Fe}^{3+} \), \( \text{Sn}^{2+} \), and \( \text{Sn}^{4+} \) 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 [2-6]. 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 \( \text{Fe}^{3+} \)) when the iron is covalently bonded to oxygen at NWF sites. On the contrary, \( \gamma \)-ray irradiation will cause electron transfer from the lower level (3d- or 4s-orbital of \( \text{Fe}^{2+} \)) to the higher level (probably antibonding \( \pi \)-orbital of oxygen) when \( \text{Fe}^{2+} \) is ionically linked to oxygen at NWM sites.

It is known that silicate glasses are composed of distorted \( \text{SiO}_4 \) tetrahedra, whereas tungstate glasses are composed of distorted \( \text{WO}_4 \) tetrahedra and distorted \( \text{WO}_6 \) octahedra. In this paper, the “\( T_g-\Delta \) rule” was applied to \( x\text{K}_2\text{O}(99-x)\text{SiO}_2{\cdot}{}^{57}\text{Fe}_2\text{O}_3 \) and \( x\text{Na}_2\text{O}(99-x)\text{WO}_3{\cdot}{}^{57}\text{Fe}_2\text{O}_3 \) 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 “\( T_g-\Delta \) 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 (\( \theta_d \)) and the \(^{60}\)Co \( \gamma \)-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 (\( \nu_3 \)) is closely related to the CN of NWF.

**2. Experimental**

Potassium silicate glasses \( x\text{K}_2\text{O}(99-x)\text{SiO}_2{\cdot}{}^{57}\text{Fe}_2\text{O}_3 \) were prepared by melting mixtures of \( \text{K}_2\text{O}, \text{SiO}_2 \), and \( \text{Fe}_2\text{O}_3 \) 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, \( x\text{Na}_2\text{O}(99-x)\text{WO}_3{\cdot}{}^{57}\text{Fe}_2\text{O}_3 \), were prepared by melting mixtures of \( \text{Na}_2\text{CO}_3 \), \( \text{WO}_3 \), and \( \text{Fe}_2\text{O}_3 \) 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 (\( \alpha \)-Fe). A source of 10 mCi \(^{57}\)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 \( \alpha \)-Al\(_2\)O\(_3\) was used for calibrating the temperature.

**3. Results**

### 3.1. Potassium Silicate Glass

DTA curves of \( x\text{K}_2\text{O}(99-x)\text{SiO}_2{\cdot}{}^{57}\text{Fe}_2\text{O}_3 \) glasses (Fig. 1) indicated that \( T_g \) was decreased gradually from 419 (±5) °C to 409, 389, 371, and 352 °C when the \( \text{K}_2\text{O} \) 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 \( \text{SiO}_4 \) 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 \( \text{SiO}_4 \) 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 (\( \text{V}_2\text{O}_5 \)-based) glasses [8], because the degree of cross-linking or polymerization was increased due to
the higher charge and hence higher ionic potential of the NWM: Ba\(^{2+}\) and Mg\(^{2+}\).

The \(^{57}\)Fe-Mössbauer spectra of \(x\)K\(_2\)O-(99-x)SiO\(_2\)-Fe\(_2\)O\(_3\) glasses (Fig. 2) are composed of an intense doublet due to Fe\(^{3+}\)(\(T_d\)) with \(\delta\) values of 0.23 to 0.28 (±0.01) mm s\(^{-1}\) and a less intense doublet (shoulder) due to Fe\(^{2+}\)(\(T_d\)) with \(\delta\) of 0.83 to 0.94 (±0.01) mm s\(^{-1}\). All the Mössbauer parameters of \(x\)K\(_2\)O-(99-x)SiO\(_2\)-Fe\(_2\)O\(_3\) glasses are summarized in Table 1. The \(\delta\) of Fe\(^{3+}\) showed a gradual decrease from 0.28 to 0.23 mm s\(^{-1}\) with increasing K\(_2\)O content, whereas that of Fe\(^{2+}\) from 0.94 to 0.83 mm s\(^{-1}\). The decrease of \(\delta\) 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). \(\Delta\) of Fe\(^{3+}\) and that of Fe\(^{2+}\) showed a gradual decrease from 0.85 to 0.73 mm s\(^{-1}\) and from 2.10 to 1.98 mm s\(^{-1}\), respectively. \(\Gamma\) of Fe\(^{3+}\) was 0.73 to 1.15 mm s\(^{-1}\), and that of Fe\(^{2+}\) was 0.76 to 0.79 mm s\(^{-1}\). The former showed a marked decrease with increasing K\(_2\)O content due to a decreasing randomness of the steric configuration of Fe\(^{3+}\)(\(T_d\)).

The relative fraction of Fe\(^{2+}\)(\(T_d\)) decreased gradually from 20.4 % to 2.2 % with increasing K\(_2\)O content, as generally show several oxide glasses; increasing basicity brings about an oxidizing atmosphere and a resultant higher oxidation state of NWF.

Table 1. \(^{57}\)Fe-Mössbauer parameters of \(x\)Na\(_2\)O-(99-x)SiO\(_2\)-Fe\(_2\)O\(_3\) glasses measured at room temperature.

<table>
<thead>
<tr>
<th>(x)</th>
<th>Species</th>
<th>(\delta) [mm/s] (±0.01)</th>
<th>(\Delta) [mm/s] (±0.02)</th>
<th>(\Gamma) [mm/s] (±0.02)</th>
<th>(A^d) [%] (±0.5)</th>
</tr>
</thead>
<tbody>
<tr>
<td>10</td>
<td>Fe(^{3+})</td>
<td>0.28</td>
<td>0.85</td>
<td>1.15</td>
<td>79.6</td>
</tr>
<tr>
<td>10</td>
<td>Fe(^{2+})</td>
<td>0.94</td>
<td>2.09</td>
<td>0.79</td>
<td>20.4</td>
</tr>
<tr>
<td>20</td>
<td>Fe(^{3+})</td>
<td>0.27</td>
<td>0.84</td>
<td>1.09</td>
<td>87.0</td>
</tr>
<tr>
<td>20</td>
<td>Fe(^{2+})</td>
<td>0.93</td>
<td>2.10</td>
<td>0.78</td>
<td>13.0</td>
</tr>
<tr>
<td>30</td>
<td>Fe(^{3+})</td>
<td>0.27</td>
<td>0.80</td>
<td>0.90</td>
<td>90.8</td>
</tr>
<tr>
<td>30</td>
<td>Fe(^{2+})</td>
<td>0.92</td>
<td>2.07</td>
<td>0.78</td>
<td>9.2</td>
</tr>
<tr>
<td>40</td>
<td>Fe(^{3+})</td>
<td>0.25</td>
<td>0.75</td>
<td>0.85</td>
<td>93.8</td>
</tr>
<tr>
<td>40</td>
<td>Fe(^{2+})</td>
<td>0.88</td>
<td>2.02</td>
<td>0.76</td>
<td>6.2</td>
</tr>
<tr>
<td>50</td>
<td>Fe(^{3+})</td>
<td>0.23</td>
<td>0.73</td>
<td>0.73</td>
<td>97.8</td>
</tr>
<tr>
<td>50</td>
<td>Fe(^{2+})</td>
<td>0.83</td>
<td>1.98</td>
<td>0.76</td>
<td>2.2</td>
</tr>
</tbody>
</table>

\(^a\) Isomer shift; \(^b\) Quadrupole splitting; \(^c\) Linewidth (FWHM); \(^d\) Absorption area.
The decrease in $T_g$ of potassium silicate glasses obtained from DTA (Fig. 1) is consistent with the decrease in quadrupole splitting (Fig. 2), $\Delta$, which is associated with a decreasing distortion of Fe$^{3+}$. The plot of $T_g$ vs. $\Delta$ 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 ($\nu_3$) of SiO$_4$ tetrahedra [9] was observed in the FT-IR spectra of $x$K$_2$O-(99-)$x$SiO$_2$-$^{57}$Fe$_2$O$_3$ 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$_2$O 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$_2$O$_3$ reagent, used for the sample preparation, shows an absorption band due to Fe$^{3+}$($O_6$) 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$^{3+}$($O_6$) 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$_2$O-79SiO$_2$-Fe$_2$O$_3$ glasses heat treated at 450°C for (a) 0, (b) 300, (c) 600, (d) 900, and (e) 1500 min.

The Mössbauer spectra of 20K$_2$O-79SiO$_2$-$^{57}$Fe$_2$O$_3$ 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$^{2+}$($T_g$) (Figure 2b). $\Delta$ 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$_2$O-79SiO$_2$-Fe$_2$O$_3$ 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$_2$O-79SiO$_2$-Fe$_2$O$_3$ glasses (Fig. 4), in which the stretching mode of the SiO$_4$ tetrahedra shifted gradu-
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119Sn-Mössbauer study of 624 in 20K2O-79SiO2-3Fe2O3 glasses heat treated at 450 °C for 300 to 1500 min. The solid line is the same as that shown in Figure 3.

Figure 5 shows a plot of $T_g$ vs. $\Delta$ of Fe$^{3+}$ in 20K2O-79SiO2-3Fe2O3 glasses heat treated at 450 °C for 300 to 1500 min. The plot of $T_g$ vs. $\Delta$ 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 20K2O-79SiO2-3Fe2O3 glass is primarily determined by the distortion of SiO4 and FeO4 tetrahedra which share several bridging oxygen atoms with each other. It is concluded that distorted FeO4 tetrahedra have essentially the same structure as distorted SiO4 tetrahedra, and the steric configuration of the former is regulated by the latter because the number of SiO4 tetrahedra is much (79/2 times) larger than that of FeO4 tetrahedra.

3.2. Sodium Tungstate Glass

DTA curves of $x$Na$_2$O-(99-x)WO3-3Fe2O3 glasses showed a gradual decrease of $T_g$ from 354 (±5) °C to 315, 303, and 271 °C when the Na$_2$O content ($x$) was increased from 30 to 34, 38, and 42 mol%, respectively. The $T_g$s of iron-free $x$Na$_2$O-(100-x)WO3 glasses also decreased gradually from 365 to 315 °C when the Na$_2$O content was increased from 30 to 40 mol% [6]. This decrease in $T_g$ is ascribed to an increase in the fraction of WO$_6$ octahedra at the expense of WO$_5$ octahedra, as $T_g$ generally decreases with a decrease in CN of NWF and with a formation of NBO.

$^{57}$Fe-Mössbauer spectra of $x$Na$_2$O-(99-x)WO3-3Fe2O3 glasses were composed of a doublet due to Fe$^{3+}$($O_h$) with $\delta$ of 0.39 to 0.44 (±0.02) mm s$^{-1}$ and a weak doublet due to Fe$^{2+}$($O_h$) with $\delta$ of 1.11 to 1.18 (±0.02) mm s$^{-1}$. $\Delta$ 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. $\Gamma$ 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$^{3+}$ was in a range of 17.2 to 25.4 (±0.5) % in the Mössbauer spectra.

The plot of $T_g$ vs. $\Delta$ of Fe$^{3+}$ (Fig. 6) in $x$Na$_2$O-(99-x)WO3-3Fe2O3 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 $\Delta$ 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$_2$O-61WO3-3Fe2O3 glass at lower temperatures yielded a linear increase in the plot of ln A vs. T [6], from which $\theta_D$ of 580 K was obtained using the simplified Debye model of (2). In a $^{119}$Sn-Mössbauer study of
38Na2O·61WO3·119SnO2 glass at low temperatures, \( \theta_D \) of 360 K was obtained for Sn4+(O6) occupying substitu-
tional sites of W6+(O6) as NWF [11]. The large \( \theta_D \) of 580 K obtained for 38Na2O·61WO3·57Fe2O3 glass indicates that Fe3+ also occupied substitu-
tional sites of W6+(O6). 57Fe-Mössbauer spectra of 38Na2O·61WO3·57Fe2O3 glass irradiated with 60Co γ-
rays showed a gradual increase in the absorption area of Fe2+ from 17.3 to 37.0 (±0.5) %, due to elec-
tron transfer from oxygen atoms of W-O and Fe-O bonds to Fe3+. An irradiation-induced linear increase in
the fraction of Fe2+ was previously observed in several xK2O·(100-\( x \))B2O3·0.3357Fe2O3 glasses [12] when iron occupied tetrahedral boron sites as NWF.

FT-IR spectra of 38Na2O·(99-x)WO3·Fe2O3 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 \( \nu_3 \) mode of WO4 tetrahedra and the latter to \( \nu_1 \) of WO6 octahedra [9]. FT-IR spectra of iron-free 38Na2O·(100-x)WO3 glasses [6] were essentially the same as those of 38Na2O·(99-x)WO3·Fe2O3 glasses and the \( \nu_3 \) mode of WO4 tetrahedra and that of WO6 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 Fe3+ for W6+ in sodium tungstate glasses without an essential change of the intrinsic structure. The FT-IR study revealed that the relative fraction of tetrahedral WO4 units became larger with increasing Na2O content, indicating a gradual change of the glass matrix (skeleton) from WO6 octahedra to WO4 tetrahedra. The FT-IR result is well consistent with the DTA result described above, i.e., increase in Na2O 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 dis-
tortion of Fe3+ (\( \Delta \)) proves that Mössbauer ions (Fe3+) 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 SiO4 and FeO4 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 rearrange-
ment” of fragments in the supercooled liquid state, in which two configurational sites of interest have dif-
frent Gibbs free energies of \( G \) and \( G' \). The \( E_a \) was expressed by the product of the size (z) and the differ-
ence in the potential energy \( (d \mu) \) of each fragment:

\[
E_a = G' - G = z \cdot d \mu.
\] (3)

Taking into account this molecular-kinetic theory, we speculate that the distortion of building units such as FeO4, SiO4, WO4, and WO6 brings about a higher re-
striction to the “cooperative movement” of fragments in the supercooled liquid state. The large slope, a, of 680 \(^{\circ}C/(mm \ \text{s}^{-1}) \) obtained in the plot of \( T_g \) vs. \( \Delta \) of Fe3+ in xK2O·(99-x)SiO3·57Fe2O3 glasses (Fig. 3) proves that Fe3+ is four-fold coordinated at NWF sites similarly to Si4+, as observed in several oxide glasses, e.g.,

- xCaO·(95-x)Al2O3·5Fe2O3 glasses [5],
- xCaO·(90-x)Ga2O3·10Fe2O3 glasses [5],
- xBaO·(90-x)Ga2O3·10Fe2O3 glasses [5],
- xCaO·(95-x)TiO2·5Fe2O3 glasses [14],
- xNa2O·(95-x)TeO2·5Fe2O3 glasses [15],
- xK2O·(95-x)TeO2·5Fe2O3 glasses [15],
- xMgO·(95-x)TeO2·5Fe2O3 glasses [15],
- and xBaO·(95-x)TeO2·5Fe2O3 glasses [15].

Several alkali and alkaline earth vanadate glasses also showed a simultaneous decrease of \( T_g \) and \( \Delta \) of Fe3+ [1, 8, 16]. It should be noted that the linear relationship is observed in several oxide glasses irrespective of the Fe2O3 content of 1 to 10 mol%.

The linear decrease in \( \Delta \) observed for heat treated 20K2O·79SiO2·57Fe2O3 glasses (Fig. 5) indicates that a decrease in the distortion of SiO4 and FeO4 tetrahe-
dra caused a decrease in \( E_{\text{int}} \); 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. \( T_h \) of heat treated 20K2O·79SiO2·57Fe2O3 glasses (Fig. 5) is associated with the “net” effect of local distortion of SiO4 and FeO4 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 Fe3+ occupied NWF sites similarly to the tetrahedral Si4+. 

The small slope, a, of 260 \(^{\circ}C/(mm \ \text{s}^{-1}) \) obtained in the plot of \( T_g \) vs. \( \Delta \) of Fe3+ in
\( \text{xNa}_2\text{O-(99-x)WO}_3^{57}\text{Fe}_2\text{O}_3 \) glasses (Fig. 6) is ascribed to the six-fold coordination of NWF: \( \text{Fe}^{3+}(O_h) \) and \( \text{W}^{6+}(O_h) \). In the case of six-fold coordinated NWM-oxygen octahedra like \( \text{Fe}^{3+}(O) \) 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 \( \Delta \) of \( \text{Fe}^{3+} \) will result in a small slope, \( a \), of \( 35 \text{°C}/(\text{mm s}^{-1}) \). The slope, \( a \), of 260 \( \text{°C}/(\text{mm s}^{-1}) \) obtained for six-fold coordinated NWF-oxygen octahedra in \( \text{xNa}_2\text{O-(99-x)WO}_3^{57}\text{Fe}_2\text{O}_3 \) 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 \( \text{WO}_6 \) and \( \text{FeO}_6 \) octahedra is intermediate between those of NWF-oxygen tetrahedra and NWM-oxygen octahedra. Figure 6 proved that distortion of \( \text{WO}_6 \) and \( \text{FeO}_6 \)-octahedra determines the \( T_g \) of tungstate glasses, although it is less effective than that of \( \text{WO}_4 \) and \( \text{FeO}_4 \)-tetrahedra. If the \( \text{Fe}^{3+}(T_g) \) occupies \( \text{W}^{6+}(T_g) \) sites, the \( T_g \)-vs.-\( \Delta \) plot will give a large slope of 680 \( \text{°C}/(\text{mm s}^{-1}) \).

5. Conclusions

1) The “\( T_g \)-\( \Delta \) rule” was applied to potassium silicate glasses, \( \text{xK}_2\text{O-(99-x)SiO}_2^{57}\text{Fe}_2\text{O}_3 \), and a large slope, \( a \), of 680 \( \text{°C}/(\text{mm s}^{-1}) \) was obtained from the plot of \( T_g \) vs. \( \Delta \) of \( \text{Fe}^{3+} \), as observed in several oxide glasses. This result indicates that \( T_g \) of oxide glass is most affected by the distortion of covalently bonded \( \text{SiO}_4 \) tetrahedra.

2) The “\( T_g \)-\( \Delta \) rule” was also valid in the case of \( \text{20K}_2\text{O-79SiO}_2^{57}\text{Fe}_2\text{O}_3 \) glasses, heat treated at a temperature close to \( T_g \), and a large slope, \( a \), larger than 680 \( \text{°C}/(\text{mm s}^{-1}) \) was obtained.

3) The “\( T_g \)-\( \Delta \) rule” indicates that highly distorted \( \text{SiO}_4 \) and \( \text{FeO}_4 \) tetrahedra have a higher restriction to the “cooperative movement” of fragments in the supercooled liquid state.

4) A slope, \( a \), of 260 \( \text{°C}/(\text{mm s}^{-1}) \) was obtained in the \( T_g \)-vs.-\( \Delta \) plot of \( \text{xNa}_2\text{O-(99-x)WO}_3^{57}\text{Fe}_2\text{O}_3 \) glasses in which \( \text{Fe}^{3+} \) preferentially occupied six-fold coordinated \( \text{W}^{6+} \) sites as NWF than four-fold coordinated \( \text{W}^{6+} \) sites. The slope of 260 \( \text{°C}/(\text{mm s}^{-1}) \) is ascribed to slightly longer \( \text{W}^{6+}-\text{O} \) and \( \text{Fe}^{3+}-\text{O} \) bond lengths and 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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