<table>
<thead>
<tr>
<th>Title</th>
<th>Mossbauer Studies on Iron in Calcium-Silicate Glasses</th>
</tr>
</thead>
<tbody>
<tr>
<td>Author(s)</td>
<td>Iwamoto, Nobuya; Tsunawaki, Yoshiaki; Nakagawa, Hirotaka; Yoshimura, Takeaki; Wakabayashi, Nobuo</td>
</tr>
<tr>
<td>Citation</td>
<td>Transactions of JWRI. 6(2) P.179-P.184</td>
</tr>
<tr>
<td>Issue Date</td>
<td>1977-12</td>
</tr>
<tr>
<td>Text Version</td>
<td>publisher</td>
</tr>
<tr>
<td>URL</td>
<td><a href="http://hdl.handle.net/11094/12286">http://hdl.handle.net/11094/12286</a></td>
</tr>
<tr>
<td>DOI</td>
<td></td>
</tr>
<tr>
<td>rights</td>
<td>本文データはCiNiiから複製したものである</td>
</tr>
<tr>
<td>Note</td>
<td></td>
</tr>
</tbody>
</table>
Mössbauer Studies on Iron in Calcium-Silicate Glasses†

Nobuya IWAMOTO*, Yoshiaki TSUNAWAKI**, Hirotaka NAKAGAWA***, Takeaki YOSHIMURA**** and Nobuo WAKABAYASHI*****

Abstract

The behaviours of iron atom in calcium-silicate glasses depending on oxygen partial pressure and basic oxide content have been studied on the basis of Mössbauer spectra.

In the glasses containing a large amount of FeO, Fe⁺⁺ ion was always in octahedral site and Fe⁺⁺⁺ ion behaved as amphoteric one of which site change from octahedral to tetrahedral with increasing of CaO content. The same dependence on partial oxygen pressure as CaO content were observed. In the glasses having small content of FeO, Fe⁺⁺ ion was in both sites of tetrahedral and octahedral although the coordinate state of Fe⁺⁺ ion was not sufficiently clear.

1. Introduction

It is generally recognized that in glass, acid cations such as Si⁺⁺⁺⁺ occupy tetrahedral site to be network-former while basic cations such as Ca⁺⁺⁺ or Fe⁺⁺ are network-modifier in octahedral position and amphoteric cations such as Al⁺⁺⁺ or Fe⁺⁺ can occupy both sites. Especially the structural behaviours of Fe⁺⁺ and Fe⁺⁺⁺ ions in glass seem to be usefully studied by Mössbauer spectroscopy.

Science Pollack, DeCoster and Neuworth applied the Mössbauer spectroscopy to fused quartz and Pyrex glass, a number of glasses have been studied by this means.²⁻⁵ It is reported from Mössbauer study that Fe⁺⁺ ion appears to prefer tetrahedral coordination in silicate glass on the other hand octahedral one in phosphate glass and the both glasses indicate predominantly octahedral coordination for Fe⁺⁺⁺⁺.²⁻⁵ However, most of the silicate glasses which have been investigated were alkali-silicate glasses, and the behaviours of iron in glass depending on experimental circumstances have been scarcely studied by Mössbauer spectroscopy.

In this paper, the structural behaviours of iron in calcium-silicate glasses containing iron and the redox reaction were investigated, that is, the results obtained in previous paper¹¹ for (CaO-SiO₂)-10 mol.% Fe₂O₃ glasses (Type I) were analyzed in more detail and (CaO-SiO₂)-0.2 mol.% Fe₂O₃ glasses (Type II) produced in various partial oxygen pressure (P₀₂) were further studied by Mössbauer spectroscopy.

2. Experimental Procedures

The procedures of the experiment were almost same as described in the previous paper. The compositions of the glasses and the conditions of the production are, shown in Table 1. Type II glasses were enriched with resonant Mössbauer isotope ⁵⁷Fe in the form of Fe₂O₃.

A preliminary sample of No. 5 was held at 1600°C for 2 hr, 6 hr and 8 hr. The analysis of the Mössbauer spectra showed that with extreme error the condition of the iron cation did not vary after 6 hr. Each batch of 2 g in a platinum crucible was melted at 1600°C for 8 hr in equilibrium pure oxygen or air or CO-ÇO₂ mixed gas.

Each sample was quenched in a given atmosphere by raising up from the hot zone of the furnace. After the sample ground to powder in acetone with mortar and pestle, pre-determined amount of the powder sample to obtain maximum resonant absorption was fixed with grease on a aluminum thin film.

† Received on November 1, 1977
* Professor
** Research Instructor
*** Graduate Student (Nippon Kokan K.K.)
**** Research Instructor, Faculty of Engineering, Kobe University
***** Professor, Faculty of Engineering, Kobe University
Table 1 Composition of the glass samples

<table>
<thead>
<tr>
<th>Type</th>
<th>Sample No.</th>
<th>CaO/SiO₂ (mol ratio)</th>
<th>P₀₂ (atm.)</th>
<th>Fe₂O₃ (mol%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>I</td>
<td>1</td>
<td>2/3</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>2</td>
<td>1/1</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>3</td>
<td>3/2</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>4</td>
<td>2/3</td>
<td>0.21</td>
<td>10.0</td>
</tr>
<tr>
<td></td>
<td>5</td>
<td>1/1</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>6</td>
<td>3/2</td>
<td>3 × 10⁻⁴⁷</td>
<td></td>
</tr>
<tr>
<td></td>
<td>7</td>
<td>2/3</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>8</td>
<td>1/1</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>9</td>
<td>3/2</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>10</td>
<td>2/3</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>11</td>
<td>1/1</td>
<td>0.21</td>
<td></td>
</tr>
<tr>
<td></td>
<td>12</td>
<td>5/4</td>
<td></td>
<td></td>
</tr>
<tr>
<td>II</td>
<td>13</td>
<td>2/3</td>
<td>3 × 10⁻⁵</td>
<td></td>
</tr>
<tr>
<td></td>
<td>14</td>
<td>1/1</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>15</td>
<td>5/4</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>16</td>
<td>2/3</td>
<td>3 × 10⁻⁷</td>
<td></td>
</tr>
<tr>
<td></td>
<td>17</td>
<td>1/1</td>
<td>(⁵⁷Fe₂O₃:90%)</td>
<td></td>
</tr>
<tr>
<td></td>
<td>18</td>
<td>5/4</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Most components of Mössbauer spectrometers were constructed by the cooperators in Kobe University. The γ-ray source was a Co⁷⁷ in palladium (about 5 mCi) and driven with a constant velocity. The laser interferometer was used for measuring and controlling absolute velocity. The absorption γ-ray was detected and stored by a multichannel analyzer up to larger than 2.5 × 10⁴ counts. All data quoted in this paper are with reference to a Co in Pd source.

Usually the Mössbauer spectrum of a glass consists of three peaks which are incompletely resolved in result of superposition of some symmetric doublets produced by quadrupole interaction at the places where the Fe³⁺+ and Fe⁴⁺ ions are located. In order to get the Mössbauer parameters, every spectrum was analyzed by the iterative least square procedures under the following assumptions; the line shape is Lorentzian and two peaks of a doublet have the same amplitude and the same width. With these assumptions Levenberg method was applied to the computer program so that the iteration converged rapidly.

3. Experimental Results
3-1 Type 1 glasses

Some features of the Mössbauer spectra depending on CaO content and partial oxygen pressure were described in previous paper. Lorentzian functions were fitted to the spectra by assuming that the experimental points lie on two pairs of quadrupole split curves owing to Fe³⁺+ and Fe⁴⁺ ions, respectively. The isomer shifts of Fe³⁺+ and Fe⁴⁺ ions are shown in Fig. 1. That of Fe³⁺ ion becomes smaller with both the increase of CaO/SiO₂ ratio and P₀₂. Especially, the change of the isomer shift is large for the glasses produced in the atmosphere of oxygen partial pressure 3 × 10⁻⁷ atm. On the other hand, the isomer shift of Fe⁴⁺ ion does not have clear dependence both on P₀₂ and the composition of glass. If the isomer shifts in this study are compared with those from the literature for crystalline⁶⁻⁹ and vitreous materials⁷⁻⁹ (Fig. 2), it seems that Fe³⁺ ion consists
of tetrahedral and octahedral ferric ions and the former ion increases with CaO/SiO₂ ratio and P₀₂. Therefore, all spectra were separated again into three components caused by ferrous and tetrahedral and octahedral ferric ions under the additional assumption that the three doublets had the same width. As described by Pargamin et al., the iteration did not converge without this additional assumption. Their isomer shifts were 0.82 ~ 0.94 mm/sec, -0.07 ~ 0.1 mm/sec and 0.25 ~ 0.34 mm/sec, respectively. Their quadrupole splittings were 1.83 ~ 2.29 mm/sec, 1.05 ~ 1.61 mm/sec and 1.03 ~ 1.25 mm/sec, respectively. It is assumed that the separated lines are attributed to octahedral ferrous (Fe⁺₃₈⁶), tetrahedral ferric (Fe⁺₃₇⁶) and octahedral ferric (Fe⁺₃₈⁶) ions, respectively.

For the glasses produced in atmosphere of P₀₂ = 0.21 and 1 atm., the variation of Fe⁺₃₈⁶/(Fe⁺₃₇⁶ + Fe⁺₃₈⁶) ratio was little around about 0.5 according to CaO/SiO₂ ratio. For the one produced in P₀₂ = 3 × 10⁻⁷ atm., it changed from about 0.3 to 0.5 as CaO content increased. Fe⁺⁺/Fe⁺⁺ ratios calculated from the areas under the separated lines are shown in Fig. 3. It will be anticipated that Fe⁺⁺/Fe⁺⁺ ratio increases in any oxygen pressures as CaO content increases. Moreover the ratio decreases in any compositions as P₀₂ does.

3-2 Type II glasses

The spectra for the glasses with various compositions produced in the atmosphere of P₀₂ = 0.21 atm. are shown in Fig. 4. Figure 5 shows the spectra for the glasses with constant CaO/SiO₂ ratio of 2/3 produced in various oxygen partial pressures. Their spectra had different features from those of glasses having 10 mol% Fe₂O₃ as shown in Figs. 1 and 2 in previous paper. The right side peak was larger and the velocity of the left side peak was higher than those for type I glasses. The middle peak was smaller but was not observed for the glasses produced in lower oxygen pressure than 3 × 10⁻⁵ atm. However, the three peaks changed in almost same way according to both CaO/SiO₂ ratio and P₀₂ as described in type I glasses. It will be anticipated that the peaks caused by Fe⁺⁺ ion appear dominantly in the spectra for type II glasses.

Moreover, the optical absorption measurement was
done in the frequency range from 25000 to 4000 cm\(^{-1}\) using HITACHI 323 type spectrometer. The plate glasses ground and polished to about 1 mm thickness were prepared. The absorption spectra are shown in Fig. 6 which have the absorption bands at about 5500 and 10000 cm\(^{-1}\). These bands suggest that the glasses containing small Fe\(_2\)O\(_3\) amount of 0.2 mol\% have tetrahedral ferrous (Fe\(_{\text{tet}}^{2+}\)) and octahedral ferrous (Fe\(_{\text{oct}}^{2+}\)) ion, respectively, according to Bishay et al.\(^{17}\) and Goto et al.\(^{18}\).

The Mössbauer spectra were separated into three doublets based on the optical absorption results in the same method as for the type I glasses. As the amplitude of Fe\(^{3+}\) peak was very small, the accuracy of the calculated Mössbauer parameters of Fe\(^{3+}\) ion was not always enough and became smaller especially with decreasing of P\(_{\text{2O}}\). For the glasses produced in the atmosphere of P\(_{\text{2O}} = 3 \times 10^{-7}\) atm., the spectra were separated into two components consisting of Fe\(_{\text{tet}}^{2+}\) and Fe\(_{\text{oct}}^{3+}\) because the iteration did not converged. The isomer shift obtained from the computation were 0.22~0.30 mm/sec, 0.6~0.74 mm/sec and 0.9~1.1 mm/sec. Their quadrupole splitting were 0.8~1.1 mm/sec, 1.8~2.1 mm/sec and 1.9~2.1 mm/sec, respectively. The isomer shifts will correspond with Fe\(^{3+}\), Fe\(_{\text{tet}}^{2+}\) and Fe\(_{\text{oct}}^{3+}\), respectively, being compared with those of crystalline and other vitreous materials shown in Fig. 2. Fe\(^{3+}/Fe^{2+}\) ratios are shown in Fig. 7. The ratio decreased with reducing P\(_{\text{2O}}\) as well as for type I glasses.

4. Discussions

It is reported that generally, the site of Fe\(^{3+}\) ion is tetrahedral in a alkali silicate glasses and Fe\(^{2+}\) ion takes almost octahedral coordination.\(^{10}\) It seems, however, in this study that the calcium-silicate glass containing large amount of Fe\(_2\)O\(_3\) has octahedral ferric ion besides above mentioned sites, and for the glass having a little amount of Fe\(_2\)O\(_3\), Fe\(^{3+}\) ion takes the both coordinate sites. These phenomena coincide with some workers.\(^{8,15}\)

For the type I glasses, it is considered that the decreasing of P\(_{\text{2O}}\) or CaO content result in the reduction of Fe\(^{3+}/Fe^{2+}\) ratio and the change of Fe\(^{3+}\) ion site from tetrahedral to octahedral one. These phenomena might suggest the same effect of the decreasing of P\(_{\text{2O}}\) as that of CaO content. The effect caused by the CaO addition is remarkable for glasses produced in lower oxygen partial pressure.

For the type II glasses, the relation P\(_{\text{2O}}\) and CaO content is almost same for type I glasses. The quantitative discussions of Fe\(^{3+}/Fe^{2+}\) ratio is very difficult because of the unequal absorptivities of Fe\(^{3+}\) and Fe\(^{2+}\) ions for the glasses containing small Fe\(_2\)O\(_3\) amount.\(^{3,40}\) The coordinate states of Fe\(^{3+}\) ion remain unclear as the Mössbauer peak intensity caused by Fe\(^{3+}\) ion is very weak or not observed. If Fe\(^{3+}\) ion behaves in same way as Al\(^{3+}\) ion, it is expected that Fe\(^{3+}\) ion takes tetrahedral site. However, the isomer shift (0.22~0.30 mm/sec) of Fe\(^{3+}\) ion obtained in this study mean octahedral rather than tetrahedral. On the other hand, it is interesting that Fe\(^{3+}\) ion takes both tetrahedral and octahedral coordination. The appearence of Fe\(_{\text{tet}}^{3+}\) may mean the compensation of the lack of Fe\(_{\text{oct}}^{3+}\). Moreover, Fe\(_{\text{tet}}^{3+}/Fe_{\text{oct}}^{3+}\) ratio might have a minimum a certain CaO/SiO\(_2\) ratio; however, such a discussion is certainly premature without furthermore studies.

The redox reaction according to Bodsworth were considered in the previous paper.\(^{11}\) This redox reaction will be continuously discussed using the results obtained for both type glasses. The redox reaction discussed by Johnston,\(^{10}\) Bodsworth,\(^{20}\) Douglas,\(^{21}\) Herring,\(^{22}\) and Budd\(^{23}\) is showed again as follows;
Mössbauer Studies in Calcium-Silicate Glasses

\[2\text{Fe}^{2+} \text{ (in glass)} + \frac{1}{2} \text{O}_2 \text{ (gas)}\]
\[= 2\text{Fe}^{3+} \text{ (in glass)} + \text{O}^{2-} \text{ (in glass)}\]  \hspace{1cm} (1)

The equilibrium constant for the reaction is as follows:

\[K = \frac{(a_{\text{Fe}^{2+}})^2 a_{\text{O}^{2-}}}{(a_{\text{Fe}^{3+}})(P_{\text{O}_2})^{1/2}} = \frac{(Fe^{3+})^2 (\tau_{Fe^{3+}})^2 a_{\text{O}^{2-}}}{(Fe^{2+})^2 (\tau_{Fe^{2+}})(P_{\text{O}_2})^{1/2}}\]  \hspace{1cm} (2)

where \(a_{\text{Fe}^{3+}}\) and \(a_{\text{Fe}^{2+}}\) are activity, activity coefficient and mole fraction of each ion, respectively. If \(\tau_{Fe^{3+}}\) and \(\tau_{Fe^{2+}}\) do not change depending on \(P_{\text{O}_2}\) for the fixed compositional glasses, the following equation can be derived.

\[\log \left( \frac{Fe^{2+}/Fe^{3+}}{Fe^{2+}/Fe^{3+}} \right) = \frac{1}{4} \log P_{\text{O}_2} - \log a_{\text{O}^{2-}} - C\]  \hspace{1cm} (3)

where \(C\) is constant. As shown in Figs. 3 and 7, each slope of \(\log(Fe^{2+}/Fe^{3+})\) to \(P_{\text{O}_2}\) for both type glasses seems to be approximately close to a quarter. Especially, this approximation seems to be better for type II glasses. This phenomenon might suggest the small dependence of \(a_{\text{O}^{2-}}\) on \(P_{\text{O}_2}\), though it is presumed from the dependences of isomer shift, \(\text{Fe}^{3+}/\text{Fe}^{2+}\) ratio and \(\text{Fe}^{2+}/\text{Fe}^{3+}\) on \(P_{\text{O}_2}\) and CaO/SiO\(_2\) ratio that the increase of \(P_{\text{O}_2}\) has same effect in glasses as the increase of CaO content.

On the other hand, for the various compositional glasses equation (1) shows that at constant partial oxygen pressure, \(a_{\text{Fe}^{3+}}/a_{\text{Fe}^{2+}}\) ratio varies inversely according to \(a_{\text{O}^{2-}}\). This phenomenon is interpreted by Bodworth as follows.\(^{20}\) The addition of the basic oxide (CaO) to the glass results in the decrease of \(a_{\text{Fe}^{3+}}\) caused by the creation of ferrite ion complex. On the other hand, ferrous ion activity \((a_{\text{Fe}^{2+}})\) does not change because ferrous oxide behaves as basic one. Therefore, the ratio of \(a_{\text{Fe}^{3+}}/a_{\text{Fe}^{2+}}\) decreases as basic oxide (CaO) increases. If this consideration is adaptable in this study, the activity coefficient ratio \((\tau_{Fe^{3+}}/\tau_{Fe^{2+}})\) should change more largely than the corresponding activity ratio \((a_{\text{Fe}^{3+}}/a_{\text{Fe}^{2+}})\) because \(\text{Fe}^{3+}/\text{Fe}^{2+}\) ratio increases as \(a_{\text{O}^{2-}}\) or CaO content does. Such large change of \(\tau_{Fe^{3+}}/\tau_{Fe^{2+}}\) may correspond to that of the isomer shift which means that the number of tetrahedral ferric ions becomes more as CaO content increases. It is, however, impossible to understand for the type II glasses \(\text{Fe}^{3+}/\text{Fe}^{2+}\) reduction with decreasing of CaO content using such a redox reaction as equation (1) because the change of \(\tau_{Fe^{3+}}/\tau_{Fe^{2+}}\) is considered to be little or almost zero for these glasses containing very small FeO\(_2\) amounts. In order to explain this apparent contradiction, Douglas assumed the variation of equilibrium constant according to composition of glass.\(^{21}\) However, Herring denied his considera-

tion.\(^{22}\) Perhaps, the redox reaction in which complex anions including \(\text{Fe}^{3+}\) ion are taken into account will be required in order to explain both the results for the glasses containing large and small FeO\(_2\) contents. For example, redox reaction indicated by Holmquist as following\(^{24}\) might give sufficient explanation to our results qualitatively at least.

\[2\text{Fe}^{3+} + \frac{1}{2} \text{O}_2 + (2x-1)\text{O}^{2-} = \text{Fe}^{2+}\text{O}_{x}^{2-}\]  \hspace{1cm} (4)

If \(P_{\text{O}_2}\) is fixed, \(a_{\text{Fe}^{3+}}/a_{\text{Fe}^{2+}}\) ratio changes in same way as \(a_{\text{O}^{2-}}\). Therefore, the increases of \(\text{Fe}^{3+}/\text{Fe}^{2+}\) ratio with CaO content can be explained successfully for both type glasses without considering the abrupt change of \(\tau_{Fe^{3+}}/\tau_{Fe^{2+}}\) ratio. On the other hand, if the glass composition is fixed, the same discussions as equation (1) is applicable in this case except for the sign of \(a_{\text{O}^{2-}}\). The consideration of ferrous complex anion based on the formation of tetrahedral ferrous ion in type II glasses might lead more precise redox reaction equation as indicated by Yoshiida et al. for phosphate glasses.\(^{23}\)

5. Conclusion

As mentioned above, the repartition of iron atom between ferrous and ferric cation and the coordinate states of their cations in calcium-silicate glasses depending on oxygen partial pressure and basic oxide content were studied on the basis of Mössbauer spectra.

For the type I glasses, \(\text{Fe}^{3+}/\text{Fe}^{2+}\) ratio increased as CaO content did. \(\text{Fe}^{2+}\) was always in octahedral site, on the other hand, \(\text{Fe}^{3+}\) ion behaved as amphoteric one of which site changed from octahedral to tetrahedral according to CaO content. The same dependence on \(P_{\text{O}_2}\) as CaO content was observed, that is, the increase of \(\text{Fe}^{3+}/\text{Fe}^{2+}\) ratio and the transfer of some octahedral \(\text{Fe}^{3+}\) ions to tetrahedral one with increasing of \(P_{\text{O}_2}\).

For the type II glasses, it is considered that \(\text{Fe}^{3+}/\text{Fe}^{2+}\) ratio had the same tendency as for the type I glasses according to \(P_{\text{O}_2}\) and CaO content. Although the coordinate state of \(\text{Fe}^{3+}\) ion was not sufficiently clear because of the weakness or lack of the Mössbauer peak. \(\text{Fe}^{2+}\) ion was in both sites of tetrahedral and octahedral.

Perhaps, the redox reaction in which ferric and ferrous complex anions are considered might interpret successfully the dependences of \(\text{Fe}^{3+}/\text{Fe}^{2+}\) ratio on \(P_{\text{O}_2}\) and CaO content for both two type glasses.

When the curve fitting procedure was done by iterative computation, the exclusion of some assumptions might present further precise Mössbauer param-
eters as analyzed for silicate minerals; for example, the assumptions that all peaks have the same width and two peaks of a doublet have the same amplitude and the same width. In fact, Frischat et al. shows in the Mössbauer spectra of soda-silicate glasses that $\text{Fe}^{2+}$ doublet does not have the equal amplitude and width peaks although the areas are equal. In order to analyze unresolved Mössbauer spectra containing many broad peaks, a lot of carefulness will be certainly necessary.

Acknowledgement
We wish to thank Prof. S. Minami and Dr. F. Zenitani for help of band fitting of Mössbauer spectra.

References
4) C.R. Kurkjian and E.A. Sigety: ibid, 9 (1968), p. 73.