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Citation	Transactions of JWRI. 1977, 6(2), p. 179-184
Version Type	VoR
URL	https://doi.org/10.18910/12286
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Mössbauer Studies on Iron in Calcium-Silicate Glasses[†]

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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 Fe_2O_3 , Fe^{2+} ion was always in octahedral site and Fe^{3+} 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 Fe_2O_3 , Fe^{2+} ion was in both sites of tetrahedral and octahedral although the coordinate state of Fe^{3+} ion was not sufficiently clear.

1. Introduction

It is generally recognized that in glass, acid cations such as Si^{4+} occupy tetrahedral site to be network-former while basic cations such as Ca^{2+} or Fe^{2+} are network-modifier in octahedral position and amphoteric cations such as Al^{3+} or Fe^{3+} can occupy both sites. Especially the structural behaviours of Fe^{2+} and Fe^{3+} ions in glass seem to be usefully studied by Mössbauer spectroscopy.

Since Pollack, DeCoster and Neuwirth applied the Mössbauer spectroscopy to fused quartz and Pyrex glass¹⁾, a number of glasses have been studied by this means.²⁻⁹⁾ It is reported from Mössbauer study that Fe^{3+} 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+} .¹⁰⁾ 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 $(CaO-SiO_2)-10$ mol % Fe_2O_3

glasses (Type I) were analyzed in more detail and $(CaO-SiO_2)-0.2$ mol % Fe_2O_3 glasses (Type II) produced in various partial oxygen pressure (P_{O_2}) were further studied by Mössbauer spectroscopy.

2. Experimental Procedures

The procedures of the experiment were almost same way as described in the previous paper.¹¹⁾ 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 ^{57}Fe in the form of Fe_2O_3 .

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 within experimental 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 $CO-CO_2$ mixed gas.

Each sample was quenched in a given atmosphere by raising out 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

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Table 1 Composition of the glass samples

Type	Sample No.	CaO/SiO ₂ (mol ratio)	P _{O₂} (atm.)	Fe ₂ O ₃ (mol%)
I	1	2/3		
	2	1/1	1	
	3	3/2		
	4	2/3		10.0
	5	1/1	0.21	
	6	3/2		
	7	2/3		3×10^{-7}
	8	1/1		
	9	3/2		
II	10	2/3		
	11	1/1	0.21	
	12	5/4		
	13	2/3		0.2 (⁵⁷ Fe ₂ O ₃ :90%)
	14	1/1	3×10^{-5}	
	15	5/4		
	16	2/3		3×10^{-7}
	17	1/1		
	18	5/4		

Most components of Mössbauer spectrometer were constructed by the cooperators in Kobe University. The γ -ray source was a Co⁵⁷ in palladium (about 5 m Ci) and driven with a constant velocity. The laser interferometer was used for measuring and controlling absolute velocity.¹²⁾ The absorption γ -ray was detected and stored by a multichannel analyzer up to larger than 2.5×10^5 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 Fe²⁺ ions are located. In order to get the Mössbauer parameters, every spectrum was analyzed by the iterative least square procedures¹³⁾ 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 method¹⁴⁾ was applied to the computer program so that the iteration converged rapidly.

3. Experimental Results

3-1 Type I glasses

Some features of the Mössbauer spectra depending on CaO content and partial oxygen pressure were described in previous paper.¹¹⁾

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 Fe²⁺ ions, respectively. The isomer shifts of Fe³⁺ and Fe²⁺ ions are shown in Fig. 1. That of Fe³⁺ ion becomes

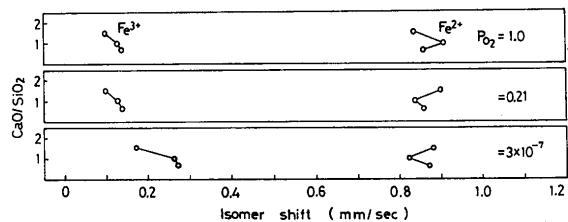
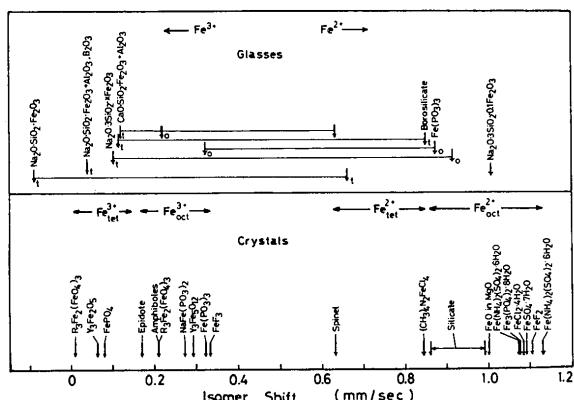


Fig. 1 Dependence of isomer shift on composition and equilibrating oxygen pressure. (Type I glasses)

smaller with both the increase of CaO/SiO₂ ratio and P_{O₂}. 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 Fe²⁺ ion does not have clear dependence both on P_{O₂} and the composition of glass. If the isomer shifts in this study are compared with those from the literatures for crystalline^{2~4,15,16)} and vitreous materials^{2,8,7~9)} (Fig. 2), it seems that Fe³⁺ ion consists



of tetrahedral and octahedral ferric ions and the former ion increases with CaO/SiO_2 ratio and P_{O_2} . Therefore, the 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.⁸⁾ the iteration did not converge without this additional assumption. Their isomer shifts were $0.82 \sim 0.94 \text{ mm/sec}$, $-0.07 \sim 0.1 \text{ mm/sec}$ and $0.25 \sim 0.34 \text{ mm/sec}$, respectively. Their quadrupole splittings were $1.83 \sim 2.29 \text{ mm/sec}$, $1.05 \sim 1.61 \text{ mm/sec}$ and $1.03 \sim 1.25 \text{ mm/sec}$, respectively. It is assumed that the separated lines are attributed to octahedral ferrous ($\text{Fe}_{\text{oct}}^{2+}$), tetrahedral ferric ($\text{Fe}_{\text{tet}}^{3+}$) and octahedral ferric ($\text{Fe}_{\text{oct}}^{3+}$) ions, respectively.

For the glasses produced in atmosphere of $P_{\text{O}_2} = 0.21$ and 1 atm., the variation of $\text{Fe}_{\text{tet}}^{3+}/(\text{Fe}_{\text{tet}}^{3+} + \text{Fe}_{\text{oct}}^{3+})$ ratio was little around about 0.5 according to CaO/SiO_2 ratio. For the one produced in $P_{\text{O}_2} = 3 \times 10^{-7}$ atm., it changed from about 0.3 to 0.5 as CaO content increased. $\text{Fe}^{3+}/\text{Fe}^{2+}$ ratios calculated from the areas under the separated lines are shown in Fig. 3. It will be anticipated that $\text{Fe}^{3+}/\text{Fe}^{2+}$ ratio increases in any oxygen pressures as CaO content increases. Moreover the ratio decreases in any compositions as P_{O_2} does.

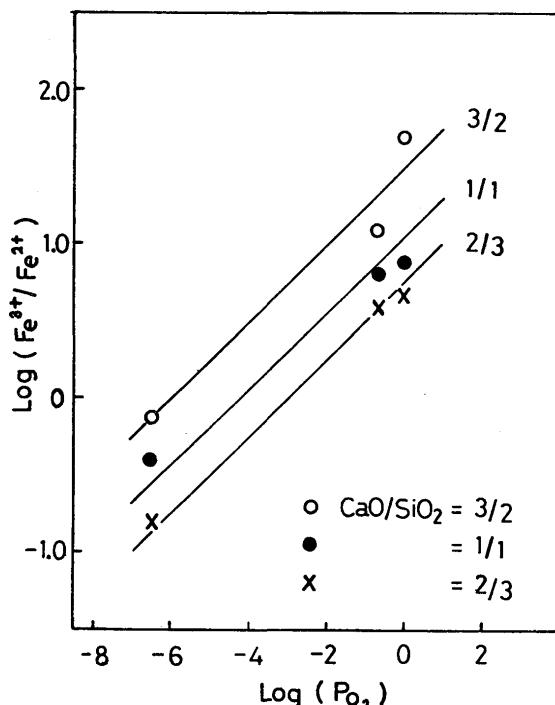


Fig. 3 Equilibrium dependence of $\log(\text{Fe}^{3+}/\text{Fe}^{2+})$ on $\log(P_{\text{O}_2})$ at various compositions. (Type I glasses) The slope of a quarter is shown with solid lines.

3-2 Type II glasses

The spectra for the glasses with various compositions produced in the atmosphere of $P_{\text{O}_2} = 0.21 \text{ atm.}$ are shown in Fig. 4. Figure 5 shows the spectra for the glasses with constant CaO/SiO_2 ratio of 2/3 produced in various oxygen partial pressures. Their spectra had different features from those of glasses having 10 mol % Fe_2O_3 as shown in Figs. 1 and 2 in previous paper.¹¹⁾ 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 $3 \times 10^{-5} \text{ atm.}$ However, the three peaks changed in almost same way according to both CaO/SiO_2 ratio and P_{O_2} as described in type I glasses. It will be anticipated that the peaks caused by Fe^{2+} ion appear dominantly in the spectra for type II glasses.

Moreover, the optical absorption measurement was

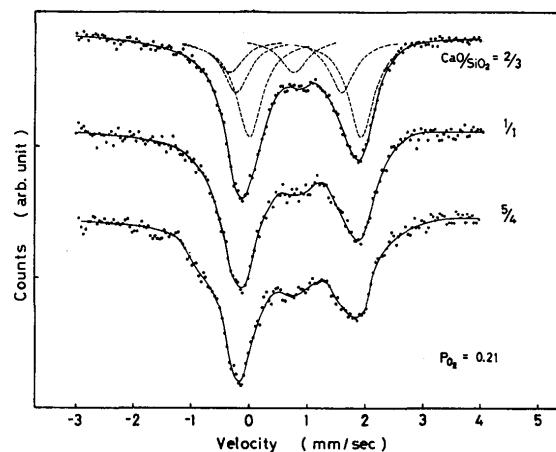


Fig. 4 Mössbauer spectra of glasses with various compositions produced in air. (Type II glasses)

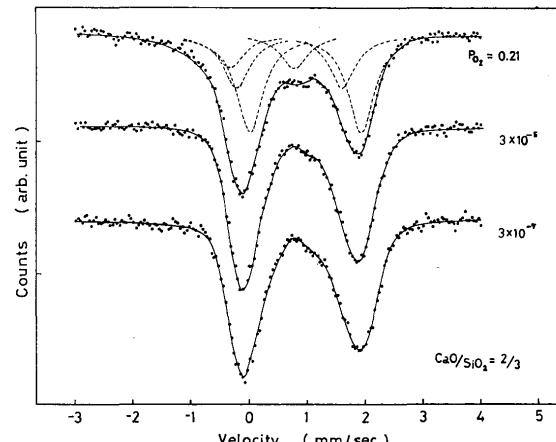


Fig. 5 Mössbauer spectra of glasses with constant composition ($\text{CaO}/\text{SiO}_2 = 2/3$) produced under various oxygen pressures. (Type II glasses)

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

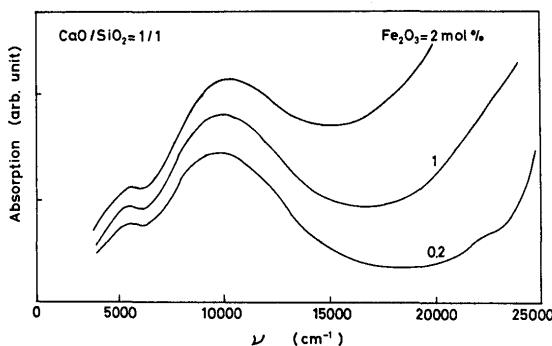


Fig. 6 Absorption spectra of glasses containing various Fe_2O_3 amount.

and 10000 cm^{-1} . These bands suggest that the glasses containing small Fe_2O_3 amount of 0.2 mol% have tetrahedral ferrous ($\text{Fe}_{\text{tet}}^{2+}$) and octahedral ferrous ($\text{Fe}_{\text{oct}}^{2+}$) 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_{O_2} . For the glasses produced in the atmosphere of $\text{P}_{\text{O}_2} = 3 \times 10^{-7}$ atm., the spectra were separated into two components consisting of $\text{Fe}_{\text{tet}}^{2+}$ and $\text{Fe}_{\text{oct}}^{2+}$ because the iteration did not converge. The isomer shifts 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+} , $\text{Fe}_{\text{tet}}^{2+}$ and $\text{Fe}_{\text{oct}}^{2+}$, respectively, being compared with those of crystalline and other vitreous materials shown in Fig. 2. $\text{Fe}^{3+}/\text{Fe}^{2+}$ ratios are shown in Fig. 7. The ratio decreased with reducing P_{O_2} 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_2O_3 has octahedral ferric ion besides above mentioned sites, and for the glass

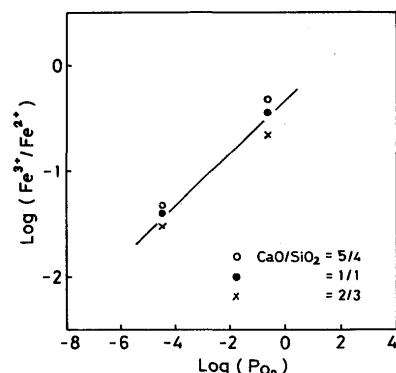


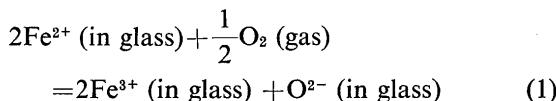
Fig. 7 Equilibrium dependence of $\log(\text{Fe}^{3+}/\text{Fe}^{2+})$ on $\log(\text{P}_{\text{O}_2})$ at various composition. (Type II glasses) The slope of a quarter is shown with a solid line.

having a little amount of Fe_2O_3 , Fe^{2+} ion takes the both coordinate sites. These phenomena coincide with some workers.^{8,18)}

For the type I glasses, it is considered that the decreasing of P_{O_2} or CaO content result in the reduction of $\text{Fe}^{3+}/\text{Fe}^{2+}$ 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_{O_2} 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_{O_2} and CaO content is almost same for type I glasses. The quantitative discussions of $\text{Fe}^{3+}/\text{Fe}^{2+}$ ratio is very difficult because of the unequal absorptivities of Fe^{3+} and Fe^{2+} ions for the glasses containing small Fe_2O_3 amount.^{3,9)} 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^{2+} ion takes both tetrahedral and octahedral coordination. The appearance of $\text{Fe}_{\text{tet}}^{2+}$ may mean the compensation of the lack of $\text{Fe}_{\text{tet}}^{2+}$. Moreover, $\text{Fe}_{\text{tet}}^{2+}/\text{Fe}_{\text{oct}}^{2+}$ ratio might have a minimum at 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,¹⁹⁾ Bodsworth,²⁰⁾ Douglas,²¹⁾ Herring,²²⁾ and Budd²³⁾ is showed again as follows;



The equilibrium constant for the reaction is as follows;

$$K = \frac{(a_{\text{Fe}^{3+}})^2 a_{\text{O}^{2-}}}{(a_{\text{Fe}^{2+}})^2 (P_{\text{O}_2})^{\frac{1}{2}}} = \frac{(\text{Fe}^{3+})^2 (\gamma_{\text{Fe}^{3+}})^2 a_{\text{O}^{2-}}}{(\text{Fe}^{2+})^2 (\gamma_{\text{Fe}^{2+}})^2 (P_{\text{O}_2})^{\frac{1}{2}}} \quad (2)$$

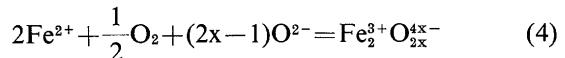
where a , γ , and Fe^{m+} are activity, activity coefficient and mole fraction of each ion, respectively. If $\gamma_{\text{Fe}^{3+}}$ and $\gamma_{\text{Fe}^{2+}}$ do not change depending on P_{O_2} for the fixed compositional glasses, the following equation can be derived.

$$\text{Log}(\text{Fe}^{3+}/\text{Fe}^{2+}) = \frac{1}{4} \text{Log} P_{\text{O}_2} - \text{Log} a_{\text{O}^{2-}} - C \quad (3)$$

where C is constant. As shown in Figs. 3 and 7, each slope of $\text{Log}(\text{Fe}^{3+}/\text{Fe}^{2+})$ to P_{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_{O_2} , though it is presumed from the dependences of isomer shift, $\text{Fe}^{3+}/\text{Fe}^{2+}$ ratio and $\text{Fe}_{\text{tet}}^{3+}/\text{Fe}_{\text{oct}}^{3+}$ on P_{O_2} and CaO/SiO_2 ratio that the increase of P_{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 various 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 reduction 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 ($\gamma_{\text{Fe}^{3+}}/\gamma_{\text{Fe}^{2+}}$) 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 $\gamma_{\text{Fe}^{3+}}/\gamma_{\text{Fe}^{2+}}$ may corresponds 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 $\gamma_{\text{Fe}^{3+}}/\gamma_{\text{Fe}^{2+}}$ is considered to be little or almost zero for these glasses containing very small Fe_2O_3 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 Fe^{3+} ion are taken into account will be required in order to explain both the results for the glasses containing large and small Fe_2O_3 contents. For example, redox reaction indicated by Holmquist as following²⁴⁾ might give sufficient explanation to our results qualitatively at least.



If P_{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 $\gamma_{\text{Fe}^{3+}}/\gamma_{\text{Fe}^{2+}}$ 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 Yoshida et al. for phosphate glasses.²⁵⁾

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. Fe^{2+} was always in octahedral site, on the other hand, Fe^{3+} ion behaved as amphoteric one of which site changed from octahedral to tetrahedral according to CaO content. The same dependence on P_{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 Fe^{3+} ions to tetrahedral one with increasing of P_{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_{O_2} and CaO content. Although the coordinate state of Fe^{3+} ion was not sufficiently clear because of the weakness or lack of the Mössbauer peak. 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_{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 minerals¹⁵⁾; 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 Fe^{2+} doublet does not have the equal amplitude and width peaks although the areas are equal.⁶⁾ 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.

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