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# MOESSBAUER SPECTRA OF IRON IN GLASS PREPARED BY THE GEL FORMATION REACTION OF WATER GLASS

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The gel formed by the reaction of water glass and $Fe^{3+}$ ion was dried at 150°C and the chemical state of iron was analyzed using Moessbauer spectroscopy as a function of heating temperature. Moessbauer spectra of these samples showed a well-resolved quadrupole-split doublet. The Moessbauer parameters indicated that iron entered into the silicate lattice as tetrahedrally coodinated $Fe^{3+}$. These results suggested that $Fe^{3+}$ ion reacted with silicate molecules in the water glass solution in the process of gel formation.

Recently, low temperature glass synthesis by the sol-gel method has attracted the attention of many researchers in the field of glass fabrication1)2). We have investigated an application of the sol-gel method using water glass (sodium silicate solution) to immobilize radioactive nuclides such as $^{90}Sr$, $^{106}Ru$ and $^{60}Co$ in high level radioactive liquid wastes produced during fuel reprocessing operations.

Since the water glass solution reacts with several metal elements to form a gel-precipitation, it is expected that the glass including metal ions can be synthesized at low temperature by heating this gel-precipitation. However, the reaction mechanism and product structure are not clear. In this communication, we report results for the gel-precipitation by the reaction of water glass with $Fe^{3+}$ ion. Iron was selected as a typical transition metal because it would allow product analysis using Moessbauer spectroscopy.

A 0.5M $Fe^{3+}$ solution was prepared by dissolving $Fe(NO_3)_3 \cdot 9H_2O$ in distilled water. Composition of the water glass solution was 23.3wt% $SiO_2$, 6.4wt% $Na_2O$, and 70.3wt% $H_2O$. On mixing 20ml of $Fe^{3+}$ nitrate solution and 20ml of water glass solution, a lightbrown gel immediately precipitated. This gel was dried at 150°C for 8h to produce a fine powder (sample A). Samples to investigate heating effect were prepared by heating this fine powder for 3h at 300°C (sample B) and 600°C (sample C). Moreover, for comparisons with the glass prepared by melting at high temperature, the fine powder was heated for 8h at 1100°C to melt and form an iron-silicate glass which was used as the fourth sample after being ground in an agate mortar (sample D).

Moessbauer spectra were measured at room temperature using 14.39 keV $\gamma$-ray from a $^{57}Co$ source of 25 mCi diffused into palladium.

The powder samples were mounted in copper rings (inner diameter : 12 mm ; thickness : 1mm) and then both sides of the rings were covered with cellophane tape. The velocity scale was calibrated with a pure iron foil at room temperature.

Measured spectra of the four samples are shown in Fig. 1. All these spectra showed a well-resolved quadrupole doublet with no magnetic spliting. Kurkjian and Sigety$^{3)}$ measured Moessbauer spectra of iron-silicate glasses and obtained values of 0.29 and 0.85 mms$^{-1}$ for isomer shift and quadrupole splitting, respectively. Moessbauer parameters calculated from the spectra shown in Fig. 1 are summarized in Table 1. Parameters of the melted sample (sample D) and other two samples (sample B and C) showed a good agreement with the values described above.

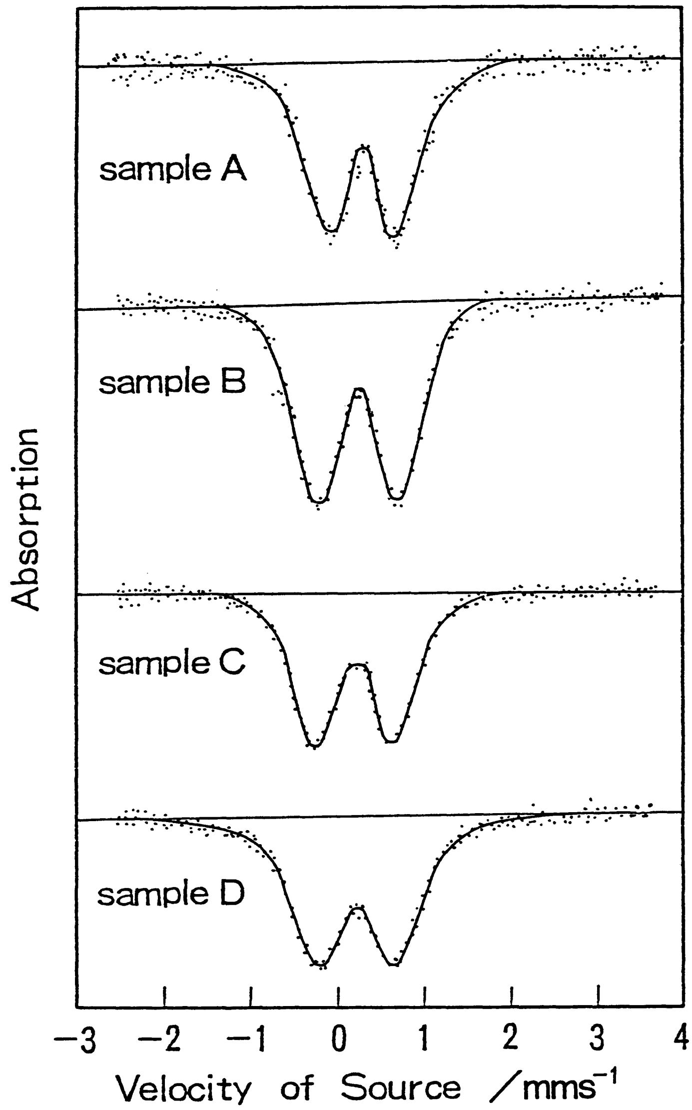

Fig.1. Moessbauer spectra of each sample

Moessbauer spectrum is very sensitive to chemical environments. Van Loef$^{4)}$ measured Moessbauer spectra of iron in ferrites and granets, and reported that isomer shift was correlated with valence and coordination number. Kurkjian and Buchman$^{5)}$ also found a similar correlation for iron phosphates and silicates. Taragin and Eisenstein$^{6)}$ reported that the quadrupole splitting of iron in oxides was related to valence and coordination number. These are summarized in Table 2. Comparing the values of Tables 1 and 2, it is seen that the iron species in samples A - D are present as tetrahedrally coordinated Fe$^{3+}$. Since the water glass solution is alkaline, it is assumed that most of the reaction product of water glass with metal ion is metal hydroxide. Iron hydroxide and oxide (formed by heating hydroxide) exist in several crystalline forms. However, irons in these compounds are known to be mainly present as octahedrally coordinated Fe$^{3+}$ and tetrahedrally coordinated Fe$^{3+}$ can't be present without octahedrally coordinated Fe$^{3+7)}$. Consequently, the reaction product of water glass with Fe$^{3+}$ ion can't be assigned to be a hydroxide or oxide.

The individual Moessbauer parameters shown in Table 1 are similar with each other. The chemical environment of iron in these samples is like that of silicate glass (sample D). But the values for sample A are slightly different from others. It is not sufficient to consider simply that this difference is caused by a diffusion of iron atom to the silicate lattice on heating, because the diffusion coefficient of iron in silicate glass is almost $10^{-14}$ $cm^2 s^{-1}$ at 300 °C8) and is too small for the reaction to proceed only by the atomic diffusion. Thus it can be concluded that iron combines with the silicate lattice even at 150 °C. The small difference in Moessbauer parameters of sample A is too small to assigned the result of the change of coordination number. This small difference may be caused by slight displacement of atoms keeping same coordination number.

Based on the above result, it is proposed that $Fe^{3+}$ ion reacts with the silicate molecule in the water glass and the gel formation reaction occurs. The chemical environment of iron changes slightly by low temperature heating, and becomes almost the same chemical environment as that in silicate glass. The spectral half width tends to become larger with rising heating temperature. This may be caused by difference in thermal history of the samples. The relatively large half width of sample D would be caused by quenching a highly disordered high temperature state.

Table 1. Moessbauer parameters for measured spectra

| Sample | Isomer Shift ($mms^{-1}$) | Quadrupole Splitting($mms^{-1}$) | Half Width ($mms^{-1}$) |
|---|---|---|---|
| Sample A | 0.33 | 0.75 | 0.66 |
| Sample B | 0.25 | 0.85 | 0.70 |
| Sample C | 0.25 | 0.85 | 0.70 |
| Sample D | 0.25 | 0.85 | 0.86 |

Table 2. Correlation of chemical state and Moessbauer parameters

| Chemical State | Isomer Shift ($mms^{-1}$) | Quadrupole Splitting ($mms^{-1}$) |
|---|---|---|
| Octahedrally Coordinated $Fe^{2+}$ | 1.0~1.2 | 1.5~3.5 |
| Tetrahedrally Coordinated $Fe^{3+}$ | 0.2~0.4 | 0.6~0.9 |
| Octahedrally Coordinated $Fe^{3+}$ | 0.4~0.6 | 0.1~0.5 |

As mentioned above, it is expected that low temperature synthesis of glass including $Fe^{3+}$ ion becomes possible using the gel formation reaction of water glass solution with $Fe^{3+}$ ion.

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