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EXAFS and X-ray Diffraction Studies of Iron Ions in 0.2(Fe₂O₃) · 0.8(Na₂O · 2SiO₂) Glass †

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KEY WORDS: (Structure) (Iron Ion) (Sodium Disilicate Glass) (EXAFS) (X-ray Diffraction)

Silicate-based glasses are very interesting materials because of their broad applications as well as their remarkably high solubility for numerous metal oxides. Especially, the silicate glasses containing iron oxides play an important role in various fields such as slag or flux in metallurgical or welding process, and magnetic materials in glass industry. It is well known that trivalent iron ions can take two different coordination states in silicate crystals, i.e. tetrahedral and octahedral oxygen coordination states. Although the oxygen coordination states around trivalent iron ions in silicate glasses have been extensively studied by many investigators^{1)–10)} using various techniques, the coordination states have not been fully clarified. For instance, Bamford¹⁾ reported that the trivalent iron ions in sodium silicate glasses are in octahedral symmetry from his optical data, but Steele et al.²⁾ suggested that tetrahedral coordination is most consistent with their data. On the other hand, the conclusions drawn from Mössbauer data measured were also different: Pargamin et al.⁴⁾ concluded the ferric ions are tetrahedrally coordinated. Morinaga et al.⁶⁾ suggested that trivalent iron ions in sodium silicate glasses are in both octahedral and tetrahedral coordination.

The phenomenon of EXAFS (Extended X-ray Absorption Fine Structure) refers to the oscillatory modulation of the X-ray absorption coefficient as a function of the X-ray photon energy beyond the absorption edge. The existence of such as extended fine structure have been known and treated theoretically in 1930's by Kronig¹¹⁾. Recent developments initiated by the work of Sayers, Stern and Lytle¹²⁾ have led to the recognition of the structural content of this technique. The outstanding feature of EXAFS is that it can determine the structure of the local environment around a central atom in crystalline and/or noncrystalline materials. Many substances for which X-ray diffraction is not feasible can be probed by the EXAFS technique¹³⁾.

Therefore, we prepared a laboratory X-ray absorption

spectrometer consisting of a Johansson-cut bent crystal, a rotating anode X-ray generator and a scintillation counter. In order to study the oxygen coordination state of ferric ions in sodium silicate glasses, we have made a structural analysis of 0.2(Fe₂O₃) · 0.8(Na₂O · 2SiO₂) glass by EXAFS and X-ray diffraction techniques.

The starting materials used were reagent grade powders Na₂CO₃, SiO₂ and α-Fe₂O₃. 5-15 g batch was melted in a platinum crucible in air using an SiC electric furnace. Melting temperature was 1200°C and melting time was 2h. In order for glass sample to be obtained the melt had to be dipped in cold water using a platinum crucible.

The geometry of a focusing X-ray absorption spectrometer that has been developed in our laboratory adopted at this EXAFS' measurement. It is controlled by a micro computer including this equipment. Line-focus X-ray are produced in a Rigaku RU-200 12 kVA rotating anode generator.

Fe(K) edge EXAFS spectra of Fe, α-Fe₂O₃ and 0.2(Fe₂O₃) · 0.8(Na₂O · 2SiO₂) glass are shown in Fig. 1. Since in actual practice an EXAFS spectrum is taken over a fine energy range, the Fourier transform that is actually taken is

$$\begin{aligned} F(r) &= \int_{k_{\min}}^{k_{\max}} W(r) k^n \chi(k) \exp(-2ikr) dk \\ &= \int_{k_{\min}}^{k_{\max}} W(r) k^n \chi(k) \cos(2kr) dk - \\ &\quad \cdot i \int_{k_{\min}}^{k_{\max}} W(k) k^n \chi(k) \sin(2kr) dk - \end{aligned} \quad (1)$$

$$|F(r)| = \sqrt{(\text{Re}F(r))^2 + (\text{Im}F(r))^2} \quad (2)$$

where k_{\max} and k_{\min} are the maximum and minimum electron wave vector k values of the usable experimental data, $\chi(k) = [I(k) - I_0(k)] / I_0(k)$ is the fine structure part of the EXAFS spectrum, and $W(k)$ is a window function which when multiplied to the integrand converts our finite data set to an infinite set which is necessary for Fourier

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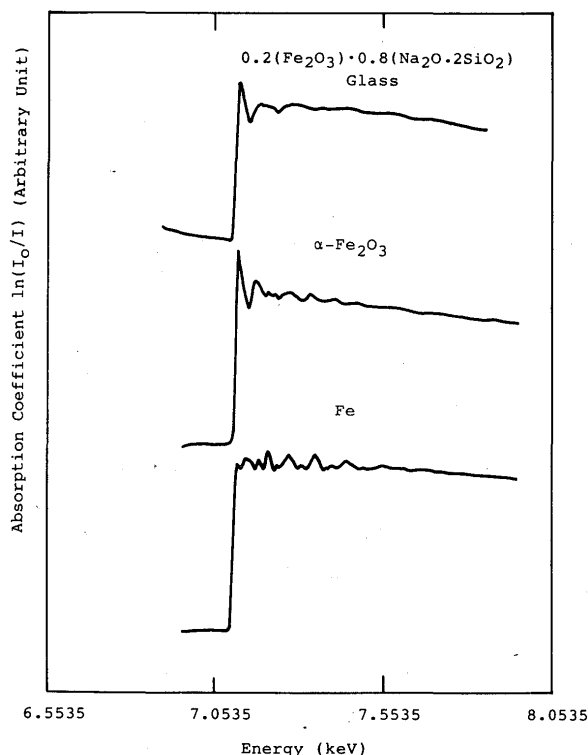


Fig. 1 EXAFS spectra for K Fe-edge in Fe, $\alpha\text{-Fe}_2\text{O}_3$ and $0.2(\text{Fe}_2\text{O}_3) \cdot 0.8(\text{Na}_2\text{O} \cdot 2\text{SiO}_2)$ glass.

transform, and k^n is a weighting function used to compensate for amplitude reduction as a function of k . Figure 2 shows the Fourier transform of the EXAFS spectrum of $0.2(\text{Fe}_2\text{O}_3) \cdot 0.8(\text{Na}_2\text{O} \cdot 2\text{SiO}_2)$ glass. As shown in this figure, the first peak is due to the nearest neighbor Fe-O pairs in this glass. Phase factor is not taken into account. The $\chi(k)$ pattern is represented by

$$\chi(k) = (m/4\pi\hbar^2 k) \sum (N_i/R_i^2) f_i(k) \exp(-R_i/\lambda_i) \cdot \sin[2kR_i + 2\delta_i(k)] \exp(-2k^2\sigma_i^2) \quad (3)$$

where m is the electron mass, \hbar is Planck's constant, N_i is the number of atoms in the i -th coordination sphere, R_i is the average distance from the absorbing atom to the i -th atom, $f_i(k)$ is the backscattering matrix element encountered by electrons, $\delta_i(k)$ is the mean free path of the electron, the second exponential term containing root-mean-square fluctuation σ_i the Debye-Waller type term and $\sin[2kR_i + 2\delta_i(k)]$ is the interference term, $\delta_i(k)$ being the phase shift. Therefore, as shown in Fig. 3, the atomic distance and coordination number of the nearest neighbor Fe-O pairs were determined in detail with using curve fitting of $k\chi(k)$ data. The extent of fitting were evaluated by the following equation:

$$R_{\text{factor}} = \frac{\sum |k\chi(k)_{\text{obs}}| - |k\chi(k)_{\text{cal}}|}{\sum |k\chi(k)_{\text{obs}}|} \quad (4)$$

By the use of modified phase shift and backscattering

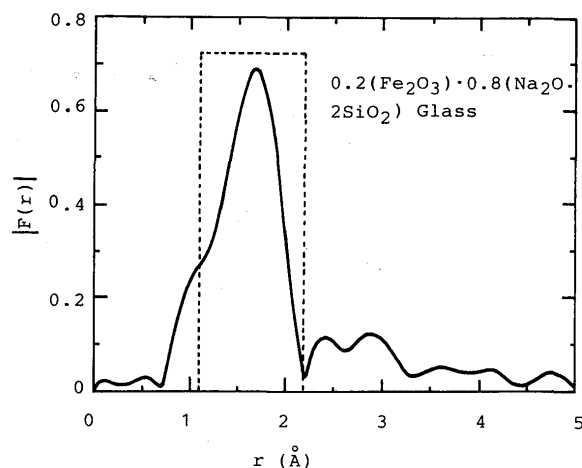


Fig. 2 Fourier transform of the Fe K-edge of $0.2(\text{Fe}_2\text{O}_3) \cdot 0.8(\text{Na}_2\text{O} \cdot 2\text{SiO}_2)$ glass.

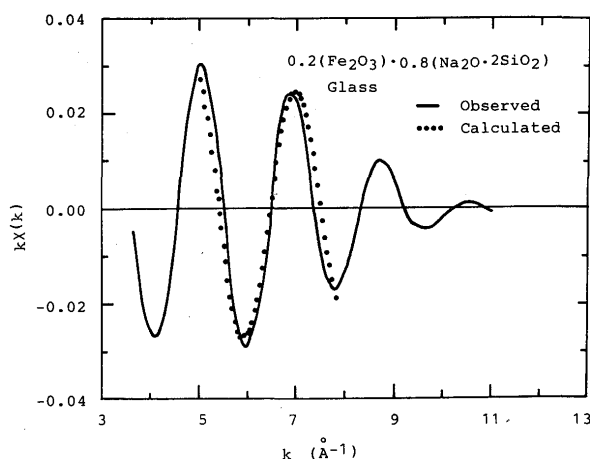


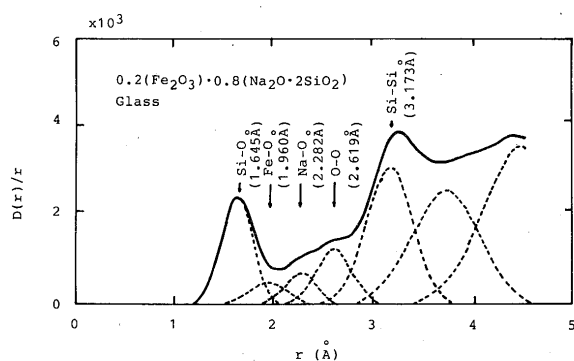
Fig. 3 Fit of the theory (dotted line) to the filtered experimental $k\chi(k)$ (solid line) for $0.2(\text{Fe}_2\text{O}_3) \cdot 0.8(\text{Na}_2\text{O} \cdot 2\text{SiO}_2)$ glass.

amplitude values ($R_{\text{factor}} = 0.26$), the structural parameters (bond length, coordination number and Debye-Waller factor) of the nearest neighbor Fe-O pairs were determined as indicated in Table 1. The obtained bond length and coordination number, 1.96 Å and 5.88, in $0.2(\text{Fe}_2\text{O}_3) \cdot 0.8(\text{Na}_2\text{O} \cdot 2\text{SiO}_2)$ glass suggested that the iron ions are almost in octahedral coordination. Fig. 4 shows RDF (Radial Distribution Function) $D(r)/r$ curve of $0.2(\text{Fe}_2\text{O}_3) \cdot 0.8(\text{Na}_2\text{O} \cdot 2\text{SiO}_2)$ glass. It is well known that the $D(r)/r$ curve can be described with symmetric Gaussian peaks. As shown in this figure, the $D(r)/r$ curve has been deconvoluted in several Gaussian peaks by curve fitting technique. The peaks at 1.645 Å, 1.960 Å, 2.282 Å, 2.619 Å and 3.173 Å are due to the bond lengths of the nearest neighbor pairs Si-O, Fe-O, Na-O, O-O and Si-Si, respectively. Therefore, the Fe-O bond distance of 1.96 Å obtained from EXAFS data was in good agreement with the value of 1.96 Å derived from the X-ray diffraction analysis.

Table 1 Structural parameters (bond length, coordination number and Debye-Waller factor) of nearest neighbor Fe-O pair.

Sample	Observed Fe-O distance (Å)	CN* (atoms)	σ^{**} (Å)	Measurement
α -Fe ₂ O ₃	1.91 2.06	6		X-ray ¹⁴⁾
0.2(Fe ₂ O ₃) 0.8(Na ₂ O 2SiO ₂) glass	1.96 1.96	5.88 —	0.06 —	EXAFS This work X-ray
0.2(Fe ₂ O ₃) 0.8(Na ₂ O 2SiO ₂) glass	1.96	6	0.061	EXAFS ¹⁰⁾
Oxidized sodium silicate glass (3wt%Fe)	1.91	—	—	EXAFS ¹⁵⁾
Oxidized sodium silicate crystal (3wt%Fe)	1.89 2.00	tetrahedral octahedral		EXAFS ¹⁵⁾

*CN: Coordination number

** σ : Debye-Waller factor**Fig. 4** Radial distribution function $D(r)/r$ curve of 0.2 (Fe₂O₃)·0.8(Na₂O·2SiO₂) glass.

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