Iron surrounding in CaO–FeO–2SiO₂ glass: EXAFS and molecular dynamics simulation

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EXAFS interpretation of iron-bearing glasses has been controversial. In order to get new information, the surrounding of iron in a synthetic Fe^{2+}-bearing glass (CaO-FeO-2SiO₂) has been investigated by combined use of EXAFS spectroscopy and Molecular Dynamics (MD) simulation. The radial distribution functions of oxygen atoms around Fe are compared. While MD simulation reveals the existence of 4-fold and 5-fold coordinated iron, EXAFS evidences a short Fe-O distance, classically attributed to 4-fold coordinated iron. An explanation for this apparent discrepancy is proposed.

keywords: EXAFS, Molecular dynamics, disorder, iron

1. Introduction

Iron is the main colouring impurity in technological glasses and can cause a deep color even at low concentrations. Understanding iron surrounding will help controlling its insertion during industrial processes. As technological glasses are multicomponents systems, their structure investigation needs the use of selective methods to focus on a peculiar element. In this work, we report the results obtained on a synthetic reduced glass, CaO-FeO-2SiO₂, by EXAFS spectroscopy and Molecular Dynamics (MD) simulations.

2. Experimental

The CaO-FeO-2SiO₂ glass has been synthesized at CRSCM (Orléans, France) starting from a gel precursor by mixing the required weights of standard solutions of calcium and ferric nitrates. Strongly reducing conditions were obtained by controlling the oxygen fugacity in a vertical oven under CO/CO_2 flux ($f_{O_2}=10^{-7}$, T=1075 K) (Creux, 1996). The resulting composition was 0.455 FeO-0.457CaO-SiO₂ as determined by microprobe analysis. The vitreous character of the sample has been confirmed by X-ray diffraction.

EXAFS data analysis has been performed using the GNXAS package (Filipponi & Di Cicco, 1995b; Filipponi *et al.*, 1995) over a large k range (2.5 to 14.3 Å^{-1}). The fit was performed on the raw absorption data without noise removal or Fourier filtering. Phase shifts have been calculated in the muffin-tin approximation starting from overlapped spherically averaged relativistic atomic charge densities. The Muffin-Tin radii were 1.03 Å, 0.87 Å, 0.95 Å and 1.58 Å for Fe, O, Si and Ca, respectively, according to the Norman

criteria (Norman, 1976). Theoretical EXAFS signals corresponding to single-scattering processes were generated. The background feature associated with the $[1s3p]$ double-electron excitation in Fe K-edge spectrum was taken into account. To account for possible asymmetry effects, the shells were modelled by a Gamma-like distribution depending on average distance R, variance σ^2 and asymmetry factor, β ($0 < \beta < 1$) (Filipponi & Di Cicco, 1995a). Standard error deviations were derived from correlation contours in the parameter space.

The MD simulations were performed using Born-Mayer-Huggins pair potential with a repulsive term and a Coulombian term. The potentials for Ca, Si and O were those sucessfully used by Delaye and Ghaleb, (1996) to simulate the glass structure of SiO₂-B₂O₃-Na₂O-ZrO₂-Al₂O₃-CaO glass. For the potential describing the pair FeO, we started from the repulsive term given by Belashchenko, 1996 (B=1900 eV), and we adjusted it to B=1712.5, so that the MD structure agrees with the EXAFS data.

Small deviations from this coefficient are acceptable and lead to adjustments of the value of the distance Fe-O without affecting the overall refined structure (nature and number of neighbors, distance of the next neighbors). Si-O-Si angles were constrained using a three body potential (Delaye & Ghaleb, 1996). A box of 1500 atoms was used to prepare the simulated glass. Starting from random positions, thermal equilibrium occured at 6000K. Quenching velocity was 5 10^{14} K/sec between 5000 K and 1500 K and 10^{14} K/sec until 300K.

3. Results and discussion

MD simulated structure around iron is composed of a first asymmetric shell of 4.3 oxygen atoms at an average distance of 2.00 Å (70% of 4-fold and 30% of 5-fold coordinated iron). Next-nearest neighbors are Fe, Ca and Si and appear in the range 3.0-3.5 Å.

EXAFS signal is dominated by the first shell signal (peak A in Fig.1) but shows clearly a contribution from higher distance shells (peak B in Fig.1) as can be seen on the Fourier Transform (FT) (Fig. 1). EXAFS refinement has been done taking into account simultaneously the first oxygen shell and a contribution for Ca, Fe and Si at higher distance as was suggested by MD simulation. The comparison between experimental and theoretical signal is shown on figure 1. The residual curves show that the agreement in R and k spaces is good. The refined parameters of the fit are summarized in table 1 together with standard deviations. Although B parameter has been refined to obtain a good agreement between Fe-O distances resulting from MD simulation and from EXAFS data, some discrepancies are put in evidence for large distances when comparing the different radial distribution functions of oxygen atoms around Fe (Fig. 2). EXAFS $g(r)$, derived from the adjusted Gamma-like function, is slightly asymmetric (β=0.2) while that found by MD is greatly asymmetric ($\beta > 0.9$).

Table 1

Best fit parameters : The total fit has been performed with 18 free parameters : 4 for each shell (coordination number, distance, variance and asymmetry parameter β) and two non-structural parameters E_0 and S_0^2. The experimental resolution has been estimated to 4.0 eV, E_0 = 7119.23 eV and S_0^2 has been fitted to 0.67.

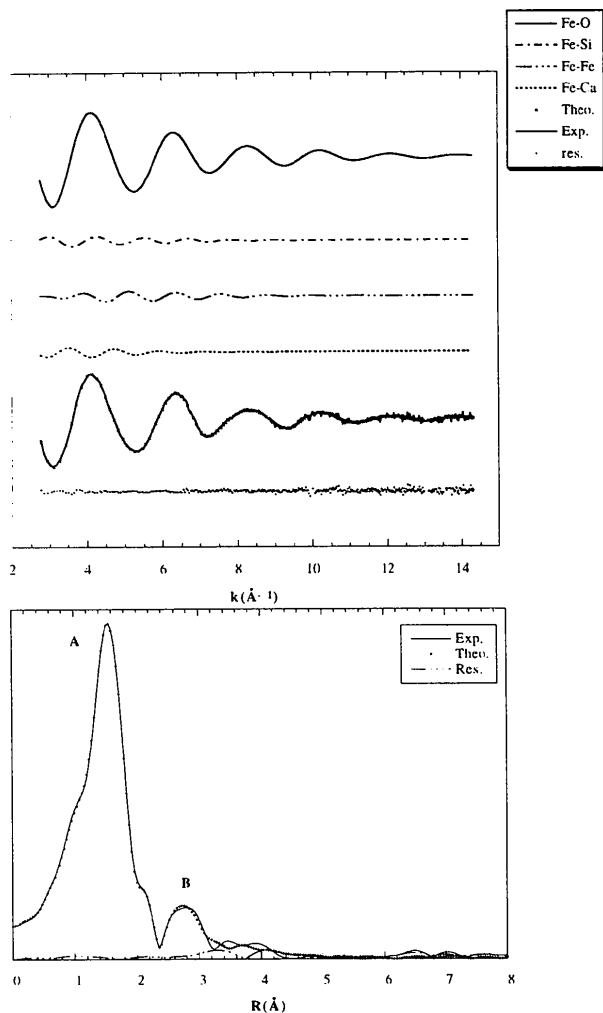|	N	R	σ^2	β
Fe-O	3.9 ± 0.3	1.99 ± 0.01	0.007 ± 0.002	0.2 ± 0.3
Fe-Si	2.0 ± 1.5	3.13 ± 0.06	0.022 ± 0.016	0.0 ± 0.8
Fe-Fe	1.8 ± 1.2	3.05 ± 0.06	0.023 ± 0.010	0.3 ± 0.6
Fe-Ca	3.5 ± 1.6	3.45 ± 0.08	0.045 ± 0.016	0.3 ± 0.7

Figure 1
Top: EXAFS signals for Fe-O, Fe-Si, Fe-Fe and Fe-Ca contributions. Total theoretical signal (Theo.) is compared to the experimental one (Exp.) and residual signal (res.) is shown. Bottom: Fourier transform of $k^2 \chi(k)$ superimposed with FT of theoretical signal and residual.

EXAFS data analysis of the glass structure leads to the determination of 4-fold coordinated iron (3.9 neighbors) at a distance of 2.00 Å. By contrast, the MD simulation reveals a broad Fe-O distance distribution. This latter can be decomposed into the contribution of mainly 4-fold and 5-fold coordinated sites for iron in the glass (Fig. 2). This result is compatible with Mössbauer spectroscopy of reduced glasses, where ferrous iron was found in two main coordination sites (Alberto et al., 1996; Rossano et al., 1998).

An analysis of the local environment of the iron atoms of our MD structural model was carried out. In most cases the iron atom is surrounded by three "touching" oxygen atoms (Fe-O < 2.1 Å), the other (one or two) oxygen atoms being spread over a broad range of distances (2.1 Å≤ Fe-O ≤ 2.6 Å). The contribution of the last atoms to the EXAFS signal is strongly damped by the ensuing destructive interference. Therefore, EXAFS spectroscopy is not sensitive to the high-R tail of the Fe-O $g(r)$ in our glass.

The partial blindness of EXAFS spectroscopy in CaO-FeO-2SiO₂ glass could be an explanation of the controversial results previously obtained for iron coordination in glasses.
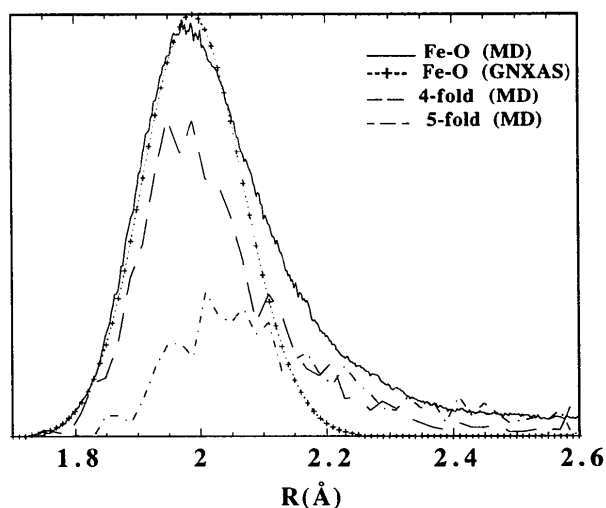

Figure 2
Radial distribution functions of oxygen atoms around Fe resulting from EXAFS spectroscopy fit (FWMH=0.2 Å)and Molecular Dynamics simulation (FWMH=0.24 Å). MD $g(r)$ has also been decomposed into 4-fold and 5-fold coordinated iron $g(r)$. These two contributions are characterized by mean distances of 1.99 Å and 2.15 Å respectively and Full-Width at Half-Maxima, FWHM₄ and FWHM₅ of around 0.2 Å and 0.3 Å respectively.

The next step will be to plug the structural model delivered by MD into GNXAS. Thus, the potential parameters of the MD calculation can be directly fitted to the EXAFS spectra, and EXAFS taken at different edges can be analyzed consistently. EXAFS is very sensitive to radial distances while MD simulation provides a good view of the glass structure. The combined use of these two techniques allows us to obtain a more realistic picture of the glass structure.

References

Alberto, H. V., da Cunha, J. L. P., Mysen, B. O., Gil, J. M. & de Campos, N. A. (1996). *Journal of non-crystalline solids*, **194**, 48–57.

Belashchenko, D. K. (1996). *J Non-cryst Solids*, **205-207**, 212–215.

Creux, S. (1996). Thèse de doctorat, université Paris 6.

Delaye, J.-M. & Ghaleb, D. (1996). *Materials Science and Engineering*, B37, 232–236.

Filipponi, A. & Di Cicco, A. (1995a). *Physical review B*, **7**(18), 12322–12336.

Filipponi, A. & Di Cicco, A. (1995b). *Physical review B*, **52**, 15135–15149.

Filipponi, A., Di Cicco, A. & Natoli, C. R. (1995). *Physical review B*, **52**, 15122–15134.

Norman, J. G. (1976). *Molecular physics*, **31**(4), 1191–1198.

Rossano, S., Balan, E., Morin, G., Bauer, J.-Ph., Calas, G. & Brouder, Ch. (1998). *Phys Chem Minerals (accepted)*.