Sample Chambers, Detectors and Detection Methods

Collecting XAFS spectra at soft X-ray energies in a heated loop cell up to 1600 K

François Farges,[a] **Anne-Marie Flank, Pierre Lagarde and François Ténégal**[b]

[a]*Laboratoire des géomatériaux, Université de Marne-la-Vallée, 77454 Marne la Vallée cedex 2, France,*
[b]*LURE, Bât 209D, 91898 Orsay cedex. France. E-mail: farges@univ-mlv.fr*

A new device to collect in-situ-, high-temperature XAFS spectra is presented which runs at low x-ray energies (K edges from Na to Cl). XAFS data is collected in the fluorescence mode (Ge solid state detector) using a heated loop that contains the sample. The actual temperature is measured using an optical pyrometer and a thermocouple (temperatures are ± 20 K at 1500 K). The first XAFS spectra were collected at the Si K-edge, with 0.2 eV steps, on the ABS1 spectrometer at Super-ACO (LURE, Orsay). The study of the melting of a $Na_2Si_2O_5$ glass is an example of the possibilities offered by this new area of research.

Keywords : Si, glass, melt, high-temperature, XANES

1. Introduction

High temperature x-ray absorption fine structure (XAFS) spectroscopy has recently benefited from a wide number of technological progresses, because of the availability of new generation sources that allow to collect scans up to 2000 K or more in molten metals (Filipponi et al., 1994) or oxides (Farges et al., 1995). This method can also be used, for instance, to trace the evolution of the local structure in crystalline compounds during phase transitions induced by temperature, but also thermal expansion mechanisms. Theoretical limitations of the XAFS method due to thermal agitation are now overcome by the use of several theories that correct for thermal-induced anharmonicity. Among others, the cumulant expansion theory or comparison can be used together with atomistic simulations, either molecular dynamics (Rossano et al., 1998), Reverse Monte-Carlo or bond valence models (Farges et al., 1996).

In this study, a $Pt_{90}Rh_{10}$ loop technique has been developed to collect XAFS data from room to 1000 K in the fluorescence mode at the Si K-edge in glassy sodium disilicate ($Na_2Si_2O_5$). This relatively compact furnace takes advantage of the focusing properties of the beam delivered on second generation sources such as in Super-ACO (Orsay, France) which allow the study of relatively small samples (sample section of 3 mm in diameter).

2. Experimental

2.1. The heating loop

The heating wire cell was originally a 70-mm long $Pt_{90}Rh_{10}$ wire that has been flattened and given a shape of a loop that should contain the powdered sample (Fig. 1). Heating is provided by a stabilized power supply (we used a 5 V - 40 A device). The sample is placed in a vacuum of 10^{-5} atm. to avoid air absorption of the incoming x-rays and to reduce the heat losses due to convection. Therefore, the furnace is more efficient under vacuum than in air (the temperature of the furnace increases by 150 K when the vacuum is performed for a constant power delivered by the power supply).

2.2. In-situ, high-temperature measurement

The measurement of the actual temperature within the hole is done using two techniques: optical pyrometry and Pt: $Pt_{90}Rh_{10}$ thermocouple measurement (type S). In our experimental set-up, the optical pyrometer (working at 0.605 μm wavelength - emissivity of the $Pt_{90}Rh_{10}$ alloy 43 %) -is operating at 250 mm from the heating wire, through a window of the sample chamber. The presence of this window (in borosilicate glass) absorbs some of the infrared radiation. Thus, the temperature read on the pyrometer decreases by 40 K (for the same temperature in the furnace) when the window is present between the sample and the pyrometer. In order to check the temperature information derived from the pyrometer, the temperature inside the sample has been measured using a thermocouple set at the back of the sample. The difference in the temperature measurement was found to be 20 K at 1000 K on the average. The reproducibility and stability of the sample temperature (as read by the pyrometer) is better than 5 K at 1000 K. These values have also been cross-checked with that of the power delivered by the power supply for a heating element of a given resistance.

2. 3 Sample preparation

Glass of $Na_2Si_2O_5$ composition was previously prepared by mixing the appropriate amounts of reagents grade-, dehydrated Na_2CO_3 and SiO_2 powders in a Pt crucible for 2 hours at 1200 °C. Glass transition temperature for this glass is ~ 600 ± 50 K. Chip of this glass were set directly into the heating loop at high temperature to form a bubble and then quenched immediately by switching off the power supply of the heating loop. Then, in-situ experiments were conducted by collecting XANES spectra for each increasing temperature.
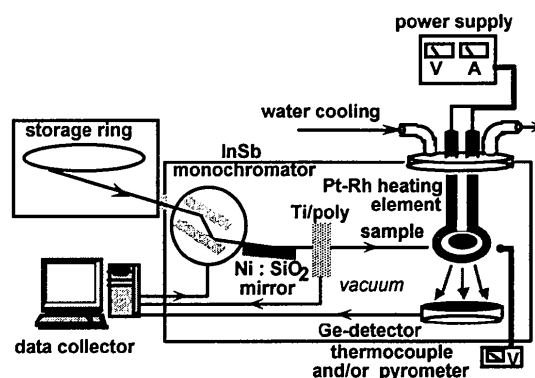

Figure 1

Principle of the high-temperature XANES experiment conducted at Super-ACO. The sample is set into a $Pt_{90}Rh_{10}$ heating loop, targeted by monochromatized x-rays and heated using a stabilized power supply. Temperature is measured simultaneously using an optical pyrometer and a Pt-Rh (type S) thermocouple.

2. 4 XANES data collection

Spectra were measured at the Super-ACO facility (Orsay, France), using the ABS 1 spectrometer (SA32) beamline. Electron beam current and energy are 200 mA and 0.8 GeV, respectively. A double crystal monochromator InSb(111) of (1-1) type, scanning energies with a step-by-step mode was used to collect Si K-edge XANES spectra (ca. 1.8 KeV). Energy resolution is 0.7 eV at the Si K-edge. Harmonics in the incident beam were rejected using a Ni-coated SiO_2 mirror (cutting energy : 3.5 KeV). I_0 was monitored by measuring the total electron yield (TEY) of a polyurethane film covered with 700 Å of Ti. XANES data was collected in the fluorescence mode (because of the high-T device) using a single element solid state Ge detector. We observed that the blackbody radiation does not perturb the Ge detector even at 1500 K, thanks to its Be window. Spectra were collected within 10 minutes at a given temperature, from 1830 to 1990 eV, with 0.2 eV steps. In order to increase the signal to noise ratio, 3 to 6 scans are averaged together for each temperature.

Spectra were background corrected by fitting a Victoreen function to the data, 50 eV prior the edge. Si K-edge XANES spectra were then normalized in absorbance using the 100 eV range after the edge.

3. Results

3.1 In-situ melting of $Na_2Si_2O_5$ glass to 900 K.

A glass of sodium disilicate ($Na_2Si_2O_5$) composition has been studied at the Si K-edge from 293 to 900 K (Fig. 2). At room temperature, the Si K-edge XANES spectrum for the glass shows mostly two features that are related to the short range environment of Si (similar as in quartz). Si is mostly 4-coordinated in this glass, in agreement with previous XANES studies at the Si K-edge, 29Si-Nuclear Magnetic Resonance (NMR), x-ray diffusion and Raman scattering studies (Stebbins, 1995).

Above 800 K, the sample start to flow viscously and bubbles started to form due to vacuum. Bubbles become large above 1000 K, which favored important Na-losses. Therefore experiments were conducted below 1000 K. Increasing temperature resulted only in a progressive shift of feature C toward lower energy. Feature C is most likely due in a large part to the EXAFS signal associated with the Si-O pair correlation (Davoli et al., 1992). Then, we attribute the shift in feature C to the presence of a longer average Si-O bond length at higher temperatures thanks to the 1/R2 dependence of the EXAFS oscillations (R is the average Si-O distance here). This longer Si-O distance in the melt can be related to the thermal expansion of the Si-O bond. The average linear thermal expansion coefficient of the Si-O bond is 4 x 10-6 K-1; it corresponds to a lengthening of the Si-O bond of 0.005 Å at from 293 to 750 K. However, other factors can be responsible for this change in the position for feature C such as the presence of higher coordinations around Si in the melt (i.e., 5-, and 6-coordinated Si) as evidenced by 29Si-NMR experiments on similar systems (Stebbins, 1995).

4. Conclusions
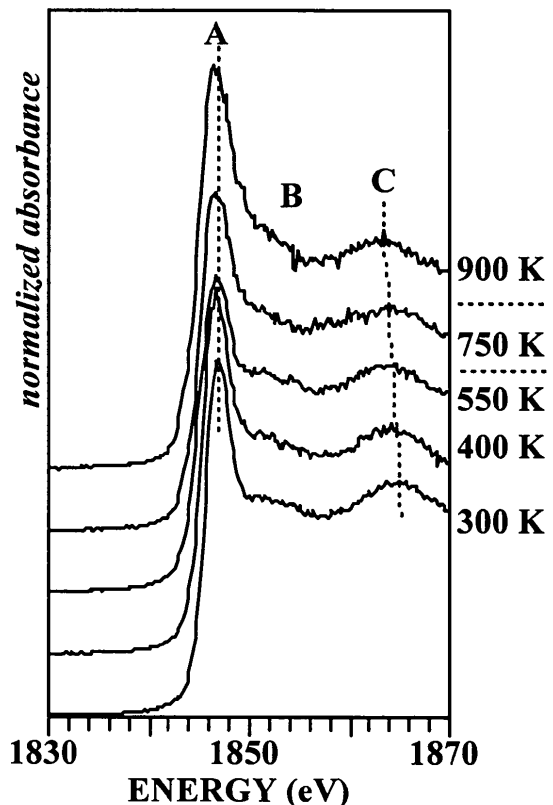
Figure 2 Si K-edge XANES spectra collected for glassy and molten sodium disilicate to 900 K. The spectra for the molten state recall that for the glass, suggesting the presence of dominantly tetrahedrally coordinated Si species in the melt.

We have shown that it is possible to collect XAFS data at high temperature at low energies using a fluorescence detection mode. Therefore, the study of a variety of complex amorphous oxides (radiation damaged ceramics, melts) containing relatively light elements (such as Mg, Na, Al, Si) can be undertaken.

XANES methods are particularly promising for the study of Fe-bearing melts at the Mg, Al and Si K-edges (such as natural melts) where NMR-methods are much less sensitive (due to the presence of paramagnetic nuclei such as Fe which strongly limit the signal to noise ratio collected from NMR spectrometers).

References

Davoli, I., Paris, E., Stizza, S., Benfatto, M., Fanfoni, M., Gargano, A., Bianconi, A., and Seifert, F. (1992) *Phys. Chem. Mineral.*, 19(3), 171-175.

Farges, F., Itié, J.-P., Fiquet, G. & Andrault, D. (1995) *Nucl. Instr. & Methods Phys. Res.* B101, 493-498.

Farges, F., Brown, G.E., Jr., Navrotsky, A., Gan, H. & Rehr, J.J. (1996) *Geochim. Cosmochim. Acta* 60, 3055-3065.

Filipponi, A. & Di Cicco, A. (1994). *Nucl. Instr. & Methods in Phys. Res.* B93, 302-307.

Rossano, S., Ramos A., Delaye, J.-M., Creux, S., Filipponi, A., Brouder, C., and Calas, G. (1998). *This volume.*

Stebbins, J.F. (1995). *Structure, Dynamics and Properties of Silicate Melts, Reviews In Mineralogy*, Vol. 32, edited by J.F. Stebbins, P.F. McMillan & D.B. Dingwell, pp. 191-246. Washington, DC: Mineralogical Society of America.