X-ray absorption study of the local environment around Ca and Na in aluminosilicate glasses

L. Cormier
Laboratoire de Minéralogie-Cristallographie, Universités Paris 6 et 7, UMR CNRS 7590, Institut de Physique du Globe de Paris, 4 place Jussieu, 75005 Paris France

D.R. Neuville
Laboratoire des Géomatériaux, Institut de Physique du Globe de Paris, UMR CNRS 7046, 4 place Jussieu, 75005 Paris France

A.-M. Flanck, P. Lagarde, V. Briois
Laboratoire pour l'Utilisation du Rayonnement Electromagnétique, Bat. 209D, B.P. 34, 91898, Orsay Cedex France

X-ray Absorption Ca and Na K-edge have been recorded on aluminosilicate glasses. Ca and Na sites correspond to distorted polyhedra, with 7 oxygen neighbours in the case of Ca. We examine the influence of the Si/Al or Ca/Na substitution on the local environment of Ca and Na. The distortion of the Ca site decreases with the addition of SiO_2, while no effect is observed when replacing Ca by Na. On the contrary, Na XANES spectra present little variation with composition.

Introduction

Soda lime aluminosilicate glasses are important glasses in glass industry or for geological melt systems but there have been relatively few structural studies of glasses in this system and, in particular, on the environment around non-network former cations (Na and Ca). Calcium and sodium in aluminosilicate glasses have a double structural role either as modifier, participating to the network depolymerization, or as charge compensator, near the $(AlO_4)^-$ tetrahedra. The local and medium range environment may be affected by the structural role played in the network by these cations. Alkali and alkaline earth content are strongly affecting the physical properties (viscosity, electrical conductivity and heat capacity) and the microstructure of the glasses.

Previous studies have mainly concentrated on the aluminosilicate network by NMR[1,2] or Raman spectroscopy[3,4,5] indicating that Al and Si are present in tetrahedral coordination when $C_{Al}/C_{Na} \leq 1$ or when $2C_{Al}/C_{Ca} \leq 1$ (with C the mole fraction). Yet, to our knowledge, a detailed analysis of the environment of Ca and Na are lacking, which is important to understand the structural role of the alkali and alkaline earth component.

XAS technique is a powerful method for investigating the environment around one specific element in disordered multicomponent materials. Extended X-ray Absorption Fine Structure (EXAFS) give information on the atomic radial distribution around the central atom while X-ray Absorption Near Edge Structure (XANES) give more direct structural information on the site geometry.[6,7] XANES spectra are due to multiple scattering processes between the excited photoelectron from absorber and the neighboring atoms.

In this paper, we are presenting an extensive study on a wide range of composition of aluminosilicate glasses containing Ca and Na. The environment of Ca and Na are investigated by X-ray Absorption Spectroscopy (XAS) to highlight the influence of the substitution Ca/Na or Si/Al.

Sample preparation

Several glasses in the system were prepared by melting stoichiometric mixture of analytic reagent grade $CaCO_3$, Na_2CO_3, Al_2O_3 and SiO_2. The powders were melted at 1900 K for 4 hours in a Pt crucible and then quenched by immersion of the bottom of the crucible in water. This process was repeated four times to ensure glass homogeneity.Calcium aluminosilicate glasses belonging to the SiO_2-Al_2O_3-CaO ternary system (CAS glasses) were selected along the joins R= CaO/Al_2O_3=1 and 3. We use the notation Cax.y, where x and y refer to the molar percent of SiO_2 and Al_2O_3, respectively, and 1-x-y is the CaO molar content. Soda lime aluminosilicate glasses (NCAS glasses) were synthesized at constant Na_2O/CaO ratio and at constant SiO_2/Al_2O_3 ratio. We use the notation NCAx.y.z, where x, y and z refer to the molar percent of SiO_2, Al_2O_3 and Na_2O respectively, and 1-x-y-z is the CaO molar content.

XAS measurements

XAS measurements at the Ca K-edge (4038.1 eV) were performed in transmission mode on beam line D44 at the LURE-DCI storage ring (Orsay, France). The storage ring was operating at 1.85 GeV with an average current of about 300 mA. XAS spectra were recorded with step of 0.15 eV, in transmission mode at ambient temperature using two Si(111) crystals properly detuned to avoid high energy harmonics. Incident and transmitted intensities were measure with ionisation chambers filled with helium and neon gas. A was used. The energy scale was calibrated with reference to Ti (4966.8 eV).

The Na K-edge (1070.8 eV) absorption spectra were collected at room temperature on the SA32 beam line at the Super ACO storage ring at the LURE (Orsay, France) operating at 800 MeV and 200 mA. A beryl (001) double-crystal monochromator was used. Powdered samples were uniformly spread on an adhesive graphite tape. The Na K-edge spectra were recorded over the photon energy range 1060-1160 eV, with 0.1 eV step and 1 s integration time using the total yield of photoelectrons (TEY). TEY was measured using the sample current for two or three scans. Spectra were calibrated using the inflection point of the absorption edge of NaCl (1070.8 eV) and energy calibration was periodically checked during the measurements.

A pre-edge victoreen fit was applied and the spectra were normalized relative to the atomic absorption above the absorption threshold. Such normalization was necessary to avoid effects deriving from differences in thickness in the samples studied.

Results and discussion

Ca K-edge XANES

Figure 1 shows the XANES spectra of the CAS and NCAS glasses. A first pre-edge transition is observed at 4040 eV and corresponds to a 1s->3d type transition.[8] The main resonance appears at 4051 eV, corresponding to the main 1s -> n p transition. There is a shift in energy position and an increase in intensity of the edge crest with increasing SiO_2 content in CAS and NCAS glasses. A bump is found at about 6 eV below the main feature. The intensity of the bump at 4045 eV increases markedly with addition of SiO_2 for the CAS glass while no such changes are observed for the mixed Ca-Na glasses.

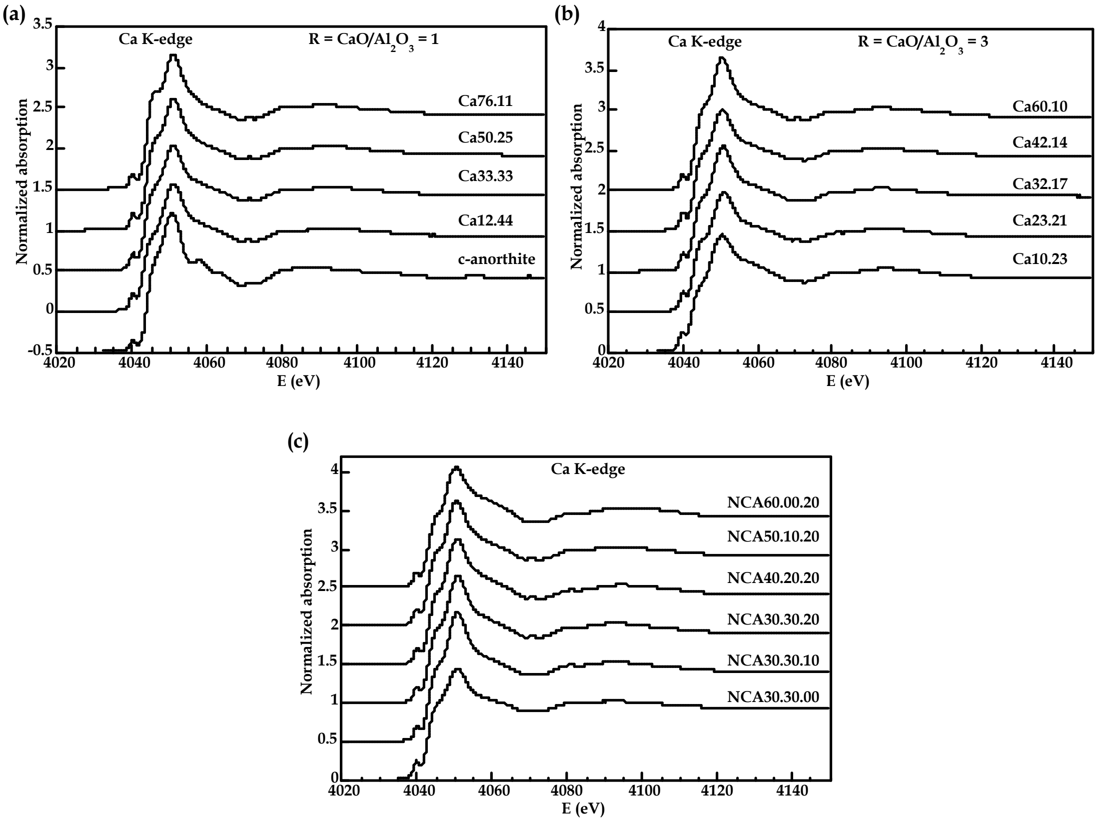

Figure 1: Ca K-edge XANES spectra for the CAS glasses along the join (a) R=CaO/Al$_2$O$_3$=1 and (b) R=3 and (c) for the NCAS glasses.

A fingerprint analysis based on the comparison with several Ca-bearing minerals indicates that the Ca XANES spectra of the glasses are very close to that observed for c-anorthite. In c-anorthite, Ca is localized in a distorted polyhedra with 7 oxygen neighbours localized at an average distance of 2.49 Å but with distances ranging from 2.29 to 2.83 Å. Such an environment agrees with Molecular Dynamics (MD) simulations obtained on various CAS glasses.[9] In the MD models, Ca atoms have 7 oxygens at a mean distance of 2.38 Å with a asymmetric distribution at high r-values. The shorter Ca-O distance in the glass compared to crystalline reference is in agreement with previous Ca K-edge XANES study.[3] The number of oxygen neighbours is difficult to evaluate by EXAFS due to high static disorder around Ca atoms. Furthermore, in the neutron or X-ray diffraction data, the high-r side of the Ca-O peak is partly overlapped by other contributions (O-O pair).[10] Using neutron diffraction on isotopically substituted samples,[11] the Ca-O contribution in the CaSiO$_3$ glass was deconvolved from the O-O pairs, giving a first Ca-O peak centred at 2.37 Å with an additional broad distribution stretching from 2.5 to 2.85 Å, in very good agreement with MD models.

The intensity of the pre-edge give information on the site geometry. In Figure 2, we present the pre-edge region for calcite, wollastonite and anorthite in which Ca is localized in a perfect octahedron, a distorted octahedron and a distorted polyhedra with 7 oxygens, respectively. We observe a decrease in the intensity of the pre-edge with increasing ordering of the Ca site. Compared to c-anorthite, the intensity of the pre-edge is higher in the CAS and NCA glasses, which suggests that the Ca environment is more distorted than in crystalline references. A slight decrease in intensity of the pre-edge is observed when the SiO_2 content increases in both CAS and NCAS glasses. This indicates that the Ca environment in SiO_2-rich glasses is less constraints than in poor-SiO_2 glasses.

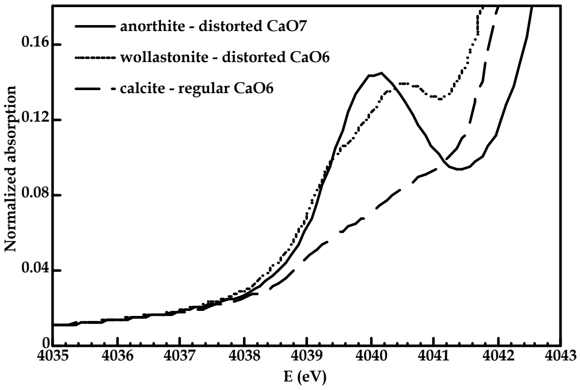

Figure 2: Pre-edge region for crystalline references presenting different Ca site geometry.

With increasing SiO_2 content, the intensity of the feature at 4045 eV becomes more important, which suggests that this peak may be associated with Ca-Si correlations. Considering CAS glasses along a constant CaO/SiO2 join (Figure 3), few differences are observed in the XANES spectra when Al_2O_3 is added in the network. In the Ca50.00 glass (wollastonite glass), Ca has a purely modifying role, associated with non-bridging oxygens, while in the Ca33.33 (Ca-Tschermakite glass), Ca are supposed to be charge compensating the $(AlO_4)^-$ tetrahedral. The lack of important changes with the addition of Al_2O_3 indicates that the structural role of the Ca in the network does not modify significantly its environment.

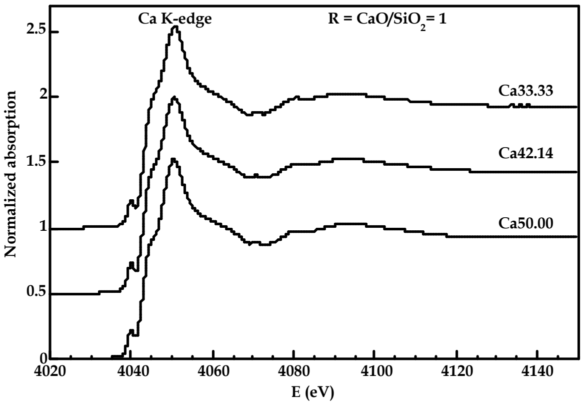

Figure 3: Ca K-edge XANES spectra for CAS glasses along the join R=CaO/SiO_2=1.

When substituting Ca by Na, the pre-edge intensity does not change. This result indicates that the addition of an alkali in the glass do not modify the Ca local environment. In contrast to this result, a XANES study on pyroxenes have shown that Ca is localized in more symmetric environment with increasing Na content.[3] In the NCAS glasses, the bump at 4045 eV (Figure 1.c) do not change in intensity contrary to CAS glasses, which implies that the presence of Na may affect medium range order around Ca.

Na K-edge XANES

Na K edge XANES spectra are shown in Figure 4 for the NCAS glasses and compared with crystalline references (albite NaAlSi$_3$O$_8$, nepheline NaAlSiO$_4$ and jadeite NaAlSi$_2$O$_6$). The quality of the XANES spectra for the crystalline references is significantly improved compared to a previous study[12] and in agreement with more recent studies.[13] A weak pre-edge (peak *a*) at about 1069.4 eV is apparent on some samples. Absorption spectra present sharp features near threshold and broader resonances extending 60-90 eV above threshold. The sharp lines close to the threshold can be attributed to core-level excitons, i.e., an excitation of a core-level electron into an unoccupied bound level. The first sharp feature in the absorption spectra, peak *b*, can be associated with a localized transition from the 1s core level to the 3p state of Na$^+$.[14,15] Although the detailed interpretation of some peaks energetically close to the strong peak *b* is under discussion, there is a consensus that broad peaks above 1085 eV are due to photoelectron scattering resonances, i.e. the outgoing photoelectron wave from the absorbing atom and the single- or multiple-scattering from the surrounding atoms.

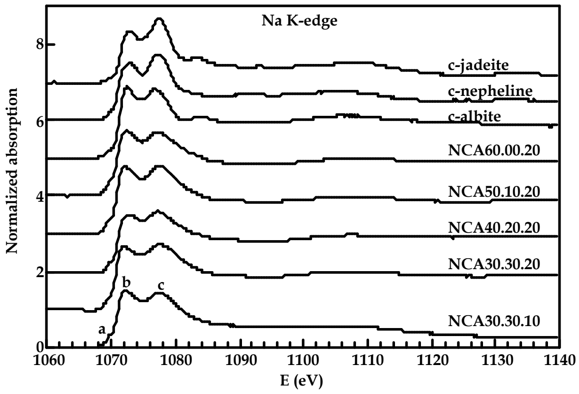

Figure 4: Na K-edge XANES spectra for the NCAS glasses compared with crystalline references.

We compared the XANES spectra of the NCAS glasses with several Na-aluminosilicate crystals. The positions of peak *b* and *c* are the same for the glasses and the references. Yet, the relative intensities of peak *b* and *c* change from jadeite to nepheline and albite. Peak *c* is more intense in jadeite that peak *b* and the reverse is observed for albite. XANES spectra for nepheline and albite have greater similitude with XANES spectra of glasses than the spectra of jadeite, in particular for the relative intensities of peaks *b* and *c*. The coordination number of Na in albite and nepheline corresponds to 9 oxygen neighbors with a wide range of Na-O distances between 2.5 and 3.15 Å. The Na site in jadeite is more regular with 8 oxygen neighbors. Peak *b* and *c* in glasses are broader which is likely due to a more disordered Na environment. Peak *c* in glasses present a broad tail at high energy which may overlap the feature present at 1084 eV in albite.

The positions, the relative intensities and the widths of peak *b* and *c* are not changed by substituting either Si by Al or Na by Ca. This indicates that the Na environment is poorly affected by such substitution or that the Na XANES spectrum is not sensitive to such changes.

Conlusions

We present X-ray absorption spectroscopy measurements at the Ca and Na K-edge on soda lime aluminosilicate glasses. Based on the Ca K-edge XANES spectra, the environment around Ca in the studied glasses is found to be close to the distorted site observed for c-anorthite, which corresponds to a coordination number of 7. The Ca XANES spectra is modify by the Si/Al substitution. The Ca site appears to be less distorted in the SiO_2-rich composition. By comparison with crystalline references, the Na environment correspond to a distorted polyhedron. The Na XANES is not change significantly when substituting Si by Al or Ca by Na.

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