

Ca and Na environments in $\text{Na}_2\text{O}-\text{CaO}-\text{Al}_2\text{O}_3-\text{SiO}_2$ glasses: influence of cation mixing and cation-network interactions

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Abstract

X-ray absorption spectroscopy at Ca and Na K-edges and Molecular Dynamics (MD) simulations are used to investigate the Ca and Na environment in soda lime aluminosilicate glasses. Both X-ray Absorption Near Edge Structure (XANES) spectra and MD calculations indicate a coordination number of about 7 for Ca and 6 for Na, in a distorted polyhedron. Ca and Na XANES spectra are poorly affected either by the Si/Al substitution or the Ca/Na substitution while MD simulations present some variations in the cationic environment. We show an affinity for non-bridging oxygens (NBOs) to be connected with Ca rather than Na. Evidence of Ca–Na mixing is shown by the MD models and there is a tendency toward forming more regions enriched in (Ca, NBOs) for CaO-rich aluminosilicate glasses. Variations in the cationic mobility upon the Na/Ca substitution are correlated with the observed structural modifications.

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1. Introduction

Soda lime aluminosilicate glasses are an important system for commercial applications or in earth science as geological melts. The knowledge of their structure and properties is essential for better understanding magmatic processes. Nevertheless, 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) though alkali and alkaline earth contents strongly affect the physical properties (viscosity, electrical conductivity and heat capacity) and the structure of the glasses. Calcium and sodium in aluminosilicate glasses can play different structural roles either as modifiers, participating in network depolymerization and bonded with non-bridging oxygens (NBOs), or as charge compensators, near the $(\text{AlO}_4)^-$ tetrahedra and bonded with bridging oxygens (BOs). The local and medium range environment around these cations may be affected by their

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structural role in the glass network while, simultaneously, perturbing the polymerized network.

Previous structural studies have mainly concentrated on the aluminosilicate network (Mysen, 1988) and have shown that the glass framework is well described by Al and Si present in tetrahedral units when $C_{Al}/C_{Na} \leq 1$ or when $2C_{Al}/C_{Ca} \leq 1$ (with C the concentration of element in mole). Yet, to our knowledge, a detailed analysis of the environment of Ca and Na is lacking, which is important to understand the structural role of the alkali and alkaline earth component. The cationic environment, in terms of coordination number and cation-network interactions, is a key parameter to establish a predictive theory of ion transport.

The 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) gives information on the atomic radial distribution around the central atom while X-ray Absorption Near Edge Structure (XANES) gives more direct structural information on the site geometry (Davoli et al., 1987; Quartieri et al., 1995). XANES spectra are due to single and multiple scattering processes between the excited photoelectron from absorber and the neighbouring atoms. Complementary to experimental studies, recent Molecular Dynamics (MD) simulations on Ca or Na aluminosilicate glasses have shown that this technique is an appropriate tool to obtain further structural information, in spite of the difficulty in building interatomic potentials or the inability to obtain realistic quenching rates (Stein and Spera., 1995; Benoit et al., 2001; Cormier et al., 2003). The evolution of the glass structure with composition can be accessed with MD simulations at a level of detail that cannot be obtained in real experiments.

In this paper, we present an extensive study on a wide range of aluminosilicate glass compositions containing Ca and Na. The environments of Ca and Na are investigated by X-ray Absorption Spectroscopy (XAS) to highlight the influence of the substitution Ca/Na or Si/Al on the aluminosilicate structure. Molecular Dynamics simulations have been performed for glasses at constant Si/Al ratio in which Ca was substituted by Na. The local cationic environment compares favourably with experimental data. We investigate the influence of the cation on the

aluminosilicate network and show that Ca atoms perturb the polymerized network more than Na atoms.

2. Experimental procedure

2.1. Sample preparation

Soda lime aluminosilicate glasses (NCA glasses) were synthesized from analytical grade CaCO_3 , Na_2CO_3 , Al_2O_3 and SiO_2 . About 100 g of the dried stoichiometric mixtures was ground for 1 h under alcohol in an agate mortar. The powders were heated slowly to decompose the carbonates, and then melted for 4 h between 1900 K (Ca-rich aluminosilicate glasses) and 1750 K (Na-rich aluminosilicate glasses), in a covered Pt crucible, and then quenched by immersion of the bottom of the crucible in water. The heating was repeated until homogeneous glasses were obtained without crystallization detected by optical microscope and X-ray diffraction. Chemical compositions were obtained by electron microprobe analyses (with a Camebax SX100 at the Camparis Center, Paris). The analysis, reported in Table 1, indicates that no Na loss can be detected. We use the notation $\text{NCA}_{x,y,z}$, 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.

2.2. 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. Experimental details are reported in Neuville et al. (2004a). The energy scale was calibrated with reference to Ti (4966.8 eV).

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 current. A beryl (1010) double-crystal monochromator was used. Powdered samples were uniformly spread on graphite

Table 1
Chemical composition (mol%) of the investigated glasses verified by microprobe analysis

Sample	SiO ₂ (mol%)	Al ₂ O ₃ (mol%)	Na ₂ O (mol%)	CaO (mol%)	$f_{\text{NBO}}^{\text{a}}$	Density (g cm ³)	V_{m}^{b} (cm ³ mol ⁻¹)
NCA60.0.20	60	0	20	20	0.50	2.632	22.667
NCA50.10.20	50	10	20	20	0.35	2.647	24.126
NCA40.20.20	40	20	20	20	0.22	2.645	25.726
NCA30.30.20	30	30	20	20	0.11	2.656	27.198
NCA30.30.10	30	30	10	30	0.11	2.718	26.354
	30	30	0	40	0.11	2.823	25.169

Fraction of non-bridging oxygens, f_{NBO} , density and molar volume, V_{m} for the glasses.

$$^{\text{a}} f_{\text{NBO}} = 2 * (c[\text{Na}_2\text{O}] + c[\text{CaO}] - c[\text{Al}_2\text{O}_3]) / (2 * c[\text{SiO}_2] + 3 * [\text{Al}_2\text{O}_3] + [\text{Na}_2\text{O}] + [\text{CaO}]).$$

$$^{\text{b}} V_{\text{m}}: \text{theoretical molar volume calculated using the relation } V_{\text{m}} = M/d \text{ with } M \text{ the molecular mass of the glass.}$$

tape. The Na K-edge spectra were recorded over the photon energy range 1065–1165 eV, with 0.1-eV step using the total yield detection mode by measuring the drain current of the sample. Each spectrum was calibrated using the inflection point of the LIII absorption edge of Ge (1217 eV) and energy calibration was periodically checked during the measurements (Neuville et al., 2004b).

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.

3. Computational procedure

The structure of glasses corresponding to Na/Ca substitution (NCA30.30.10, NCA30.30.20, NCA30.30.30, NCA0.30.40) were simulated using Molecular Dynamics. It should be noted that the NCA30.30.40 has not been obtained experimentally with standard quenching techniques due to a high-crystallization rate. Born-Mayer Huggins potentials are used and the analytical formulas and adjustable parameters can be found in previously published papers (Delaye et al., 1997; Delaye et al., 2001; Cormier et al., 2003). The Coulombic interactions are based on the formal ionic charges and the covalent interactions are handled by three-body terms (applied on the angles O–Si–O, Si–O–Si and O–Al–O). The initial random configuration consists of 5184 atoms in appropriate proportions distributed in a cubic simulation cell. This configuration was thermalized at 4500 K for 5000 relaxation time steps of 10^{-15} s. The liquid

was quenched at a rate of 10^{15} K s⁻¹ from 4500 to 2000 K, and then at a lower quench rate of 4×10^{14} K s⁻¹ from 2000 K to room temperature. The final configuration was obtained by averaging over 2000 instantaneous configurations.

4. XAS results

4.1. Ca K-edge XANES

The Ca K-edge XANES spectra of the NCA glasses are presented in Fig. 1. A first pre-edge transition is observed at 4040 eV and corresponds to a 1s→3d type transition (Combes et al., 1991). The main resonance appears at 4050 eV, corresponding to

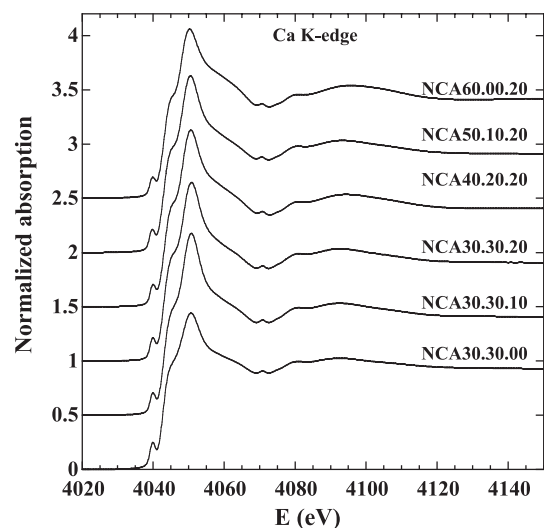


Fig. 1. Ca K-edge XANES spectra for the NCA glasses.

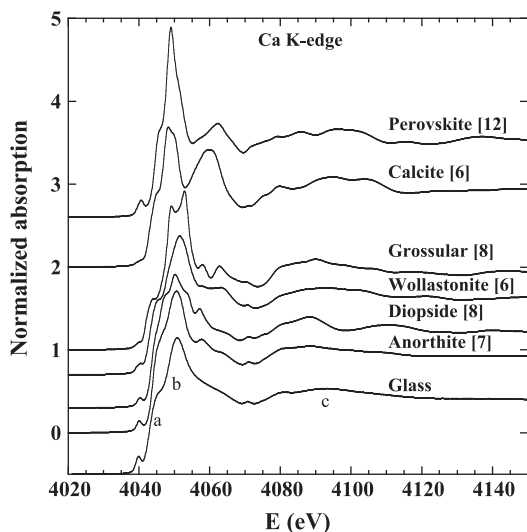


Fig. 2. Ca K-edge XANES spectra for various crystalline references: perovskite (CaTiO_3), calcite (CaCO_3), grossular ($\text{Ca}_3\text{Al}_2\text{Si}_3\text{O}_{12}$), wollastonite (CaSiO_3), diopside ($\text{CaMgSi}_2\text{O}_6$), anorthite ($\text{CaAl}_2\text{Si}_2\text{O}_8$). The corresponding Ca site is indicated in the brackets. The XANES spectra for the NCA30.30.20 is reported for comparison (lower curve).

the $1s \rightarrow n p$ transition. A shoulder is observed at about 6 eV below the main peak, whose intensity is not significantly affected by the addition of Al_2O_3 within the glass structure. Similarly, the Si/Al or Ca/Na substitution does not affect the main edge crest.

In order to interpret our Ca XANES spectra, we used the fingerprint technique based on the comparison between XANES spectra from crystalline references and XANES spectra from our glasses. In Fig. 2, the Ca XANES spectra for several Ca-bearing minerals are shown. These minerals correspond to various environment (coordination number, geometry) of Ca surrounded by O neighbours. The various coordination numbers are reported in brackets in Fig. 2. The features in the main edge are distinctly different for each mineral. Considering the two main peaks *a* and *b* and the first EXAFS oscillation (*c*) in the XANES spectra of the glass, we observe that anorthite ($\text{CaAl}_2\text{Si}_2\text{O}_8$) presents the XANES spectrum showing the closest agreement with that of our glasses. Some extra-features are present above peak *b* in the crystal which are probably smoothed in the glass. In anorthite, Ca is localized in a distorted polyhedron with seven oxygen neighbours localized at an average distance of 2.49 Å but with Ca–O

distances ranging from 2.29 to 2.83 Å. Such an environment agrees with Molecular Dynamics (MD) simulations obtained on various CAS glasses (Cormier et al., 2003) and with the simulations of some NCA glasses presented below. In the MD models, Ca atoms have about seven oxygens at a mean distance of 2.45 Å with an 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 (Combes et al., 1991). An exact determination of the number of oxygen neighbours is difficult to evaluate. For instance, EXAFS method is not precise due to high-static disorder around Ca atoms. Furthermore, in neutron or X-ray diffraction data, the high-*r* side of the Ca–O peak is partly overlapped by other contributions (O–O pair) (Cormier et al., 2000). Neutron diffraction associated with the isotopic substitution method has been performed on CaSiO_3 glass (Eckersley et al., 1988) and enabled the deconvolution of the Ca–O contribution from the O–O pairs. A first Ca–O peak centred at 2.37 Å was found but the Ca–O distances extend over a broad range from 2.5 to 2.85 Å, in very good agreement with MD models.

The intensity of the pre-edge gives complementary information on the cation site geometry. In Fig. 3, we present the pre-edge region for various crystalline

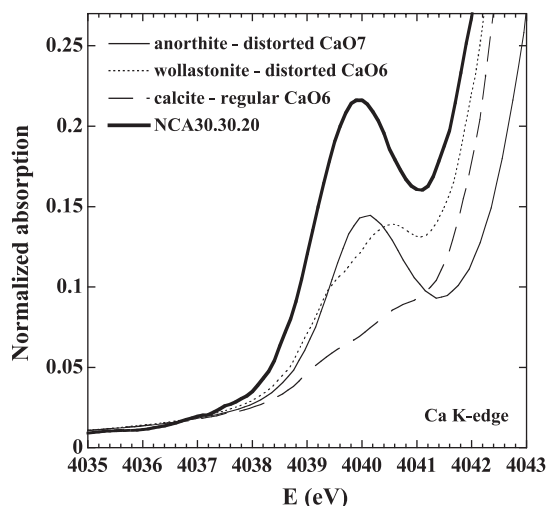


Fig. 3. Pre-edge region for crystalline references presenting different Ca site geometry, compared with that obtained for the NCA30.30.20 glass.

references, calcite, wollastonite and anorthite, in which Ca is localized in a perfect octahedron, a distorted octahedron and a distorted polyhedron with seven oxygens, respectively. We observe a decrease in the intensity of the pre-edge with increasing symmetry of the Ca site. Compared with anorthite, the intensity of the pre-edge is higher in the glasses, which suggests that the Ca environment is more distorted. When substituting Ca by Na, the pre-edge intensity and position of the Ca K-edge XANES spectra does not change significantly. This result indicates that the addition of an alkali in the glass does not modify the local Ca environment. In contrast to this result, a XANES study on pyroxenes (Al-free silicates) has shown that Ca is localized in more symmetric environment with increasing Na content (Davoli et al., 1987).

4.2. Na K-edge XANES

Na K-edge XANES spectra are shown in Fig. 4 for the NCA glasses and compared with crystalline references (albite $\text{NaAlSi}_3\text{O}_8$, nepheline NaAlSiO_4 and jadeite $\text{NaAlSi}_2\text{O}_6$). The quality of the XANES spectra for the crystalline references is significantly improved compared to a previous study (McKeown et al., 1985) and in agreement with a more recent one (Neuville et al., 2004b). A weak pre-edge (peak *a*) at

about 1074.4 eV is clearly apparent on the glasses as a shoulder on the rising slope of the first feature and has been ascribed to $1s \rightarrow 3s$ transitions (Teodorescu et al., 2001). 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^+ (Teodorescu et al., 2001). Though, the origin of peak *c* is under discussion (Riedler et al., 2001), there is a consensus that broad peaks above 1090 eV are due to single or multiple photoelectron scattering resonances (Hudson et al., 1994). The XANES spectra of the glasses are characterized by a double peak at 1077.7 (peak *b*) and 1082.2 eV (peak *c*) of approximately equal amplitude, followed by a smooth resonance around 1111 eV corresponding to the first EXAFS oscillation. For these aluminosilicate glasses, the overall spectral shapes are very similar, which indicate similar short range ordering around Na.

The XANES spectra of the NCA glasses are compared in Fig. 4 with several Na-aluminosilicate crystals. The positions of peak *b* and *c* are the same for the glasses and the references but there is a change in the relative intensities of peaks *b* and *c*. The structure *c* is less intense in the NCA glasses than in jadeite and nepheline while the intensities of peaks *b* and *c* for the glasses and albite are of similar ratio. Beyond these two first peaks, the crystalline references present small features at about 1088 eV while the XANES spectra of the glasses present a broad tail for the peak *c* at high energy that may overlap the features present at 1088 eV. This lack of defined structure is in agreement with a higher disorder of the Na environment in the glasses. Based on the relative intensities of peaks *b* and *c*, the Na XANES spectra of the glasses provide an indication that the Na environment in our glasses is more similar to that in albite than in nepheline or jadeite. Na is surrounded by six close oxygen neighbours in nepheline (Henderson and Roux, 1977) and jadeite (Cameron et al., 1973) and five close oxygen neighbours in albite (Prewitt et al., 1976) with, in each case, two oxygen neighbours at higher distances between 2.8 and 3.0 Å. This gives a total coordination number of 7–8 with a wide range of Na–O distances between 2.35 and 3.15 Å. However, the Na environment in nepheline and jadeite is more ordered than in albite, which may influence the differences in the relative intensities of peaks *b* and *c*. The positions, the relative intensities and the widths

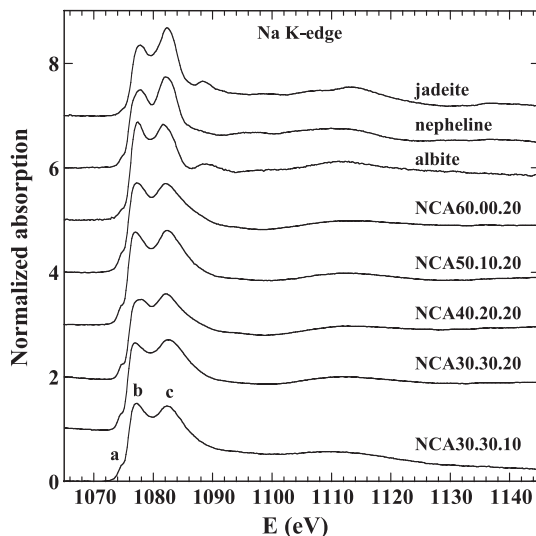


Fig. 4. Na K-edge XANES spectra for the NCA glasses compared with crystalline references.

of peaks *b* and *c* are not changed by substituting either Si by Al or Na by Ca in NCA glasses. This indicates that the Na environment is relatively unaffected by such substitution or that the Na XANES spectrum is not sensitive to such changes.

5. Molecular Dynamics results

The partial pair distribution functions (PPDFs) corresponding to the Ca–O and Na–O pairs are shown in Fig. 5, for the NCA30.30.20 sample which is representative of all the different simulated compositions. The first peak is at 2.45 and 2.28 Å for the Ca–O and Na–O pairs, respectively. However, it should be noted that this peak is asymmetric toward high *r*-values. The cation–oxygen pairs have been deconvoluted into the contributions from bridging (BO) and non-bridging (NBO) oxygens. (An oxygen is considered as BO if it is connected with two T=Si,Al tetrahedra in a sphere of 2.2 Å, which corresponds to the minimum after the first peak in the T–O PPDF. An oxygen is labelled as NBO when it is connected to only one tetrahedra in the same sphere.) The cation–NBO bond lengths are smaller than the cation–BO bond lengths by about 0.1 Å. Since formal charges are used in these simulations, no charge differences

between BO and NBO should be detected in the models. Thereby, the observed variations in distances are likely due to steric effects. The contribution at low distances in the cation–O PPDF can be mainly attributed to NBO contributions with a well-defined peak. Conversely, the BO contributions appear at higher *r*-values and there is a constant distribution of cation–BO distances so that no well-resolved peak can be discerned. The consequence is that we cannot clearly define a first shell of O neighbours around Na and Ca cations.

A criteria generally taken to determine the coordination number (CN) is to use the minimum after the first peak as a cut-off radius to calculate the number of O. Taking this value (3.3 and 3.2 Å for Ca–O and Na–O, respectively), we report in Fig. 6, the Ca–O and Na–O coordination numbers for all compositions and the distribution between NBOs and BOs. The number of Ca atoms associated with either BOs or NBOs is a good indication of a charge-forming or modifying role. Cations are always associated with both BOs and NBOs so that a site is never purely modifying or charge compensating. The CN of Ca is close to seven oxygen neighbours while that of Na is slightly less with six to seven oxygen neighbours. There is a trend for increasing the CN of Ca as Na₂O is replaced by CaO, which is due to more BOs connected with Ca

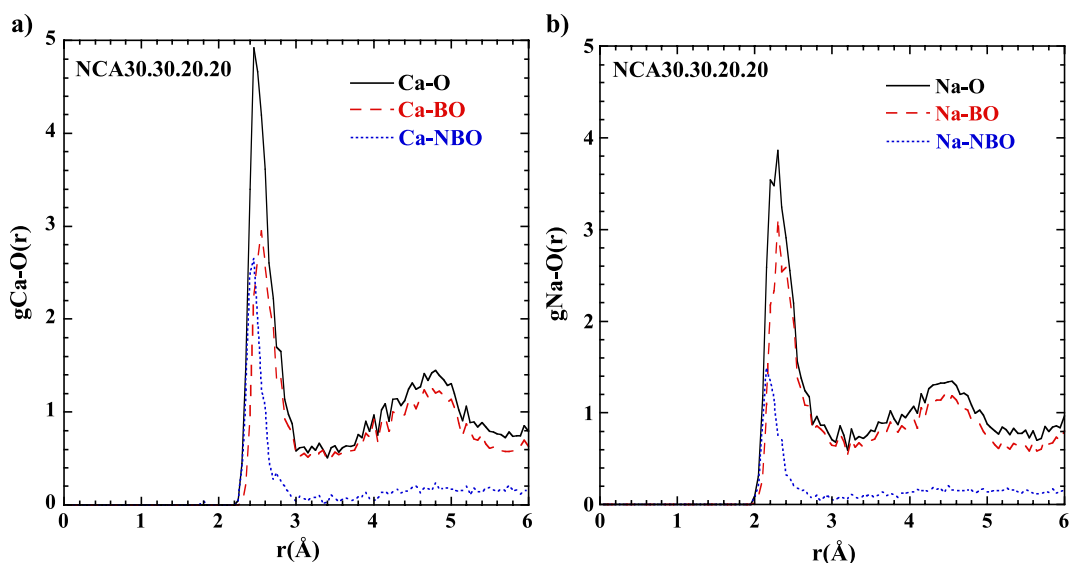


Fig. 5. Partial pair distribution functions for (a) Ca–O and (b) Na–O in the MD model of NCA30.30.20 glass. The total PPDFs (solid curve) have been decomposed into the contributions for the (Ca,Na)–BO (dashed curves) and (Ca,Na)–NBO (dotted curves).

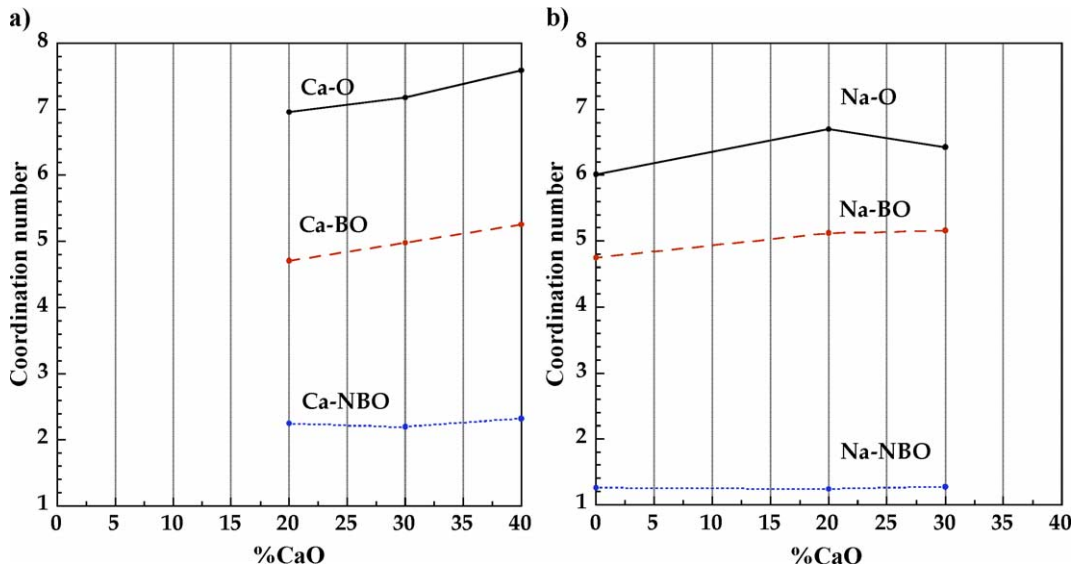


Fig. 6. Variation of the (a) Ca–O and (b) Na–O coordination numbers upon the Ca content. The total coordination numbers (solid curves) have been deconvoluted into the contributions for the BO (dashed curves) and NBO (dotted curves).

atoms. The intensity of the Ca–NBO pair (Fig. 5a) is much higher than that of the Na–NBO pair (Fig. 5b) which indicates a strong preference for NBOs to be associated with Ca rather than Na.

The number of BOs and NBOs was quantified in our MD models and the proportions NBO/(total O) and BO/(total O) were reported in Fig. 7 (right). The proportion of BOs and NBOs remains almost constant with the replacement of CaO by Na₂O as expected from stoichiometry (see the fraction of NBOs, *f*_{NBO}, reported in Table 1). Using this decomposition of O as BOs or NBOs, we calculated the BO–BO, BO–NBO and NBO–NBO coordination numbers that correspond to the numbers of BO or NBO surrounding each O (BO or NBO) in a sphere of 3.6 Å radius, which is the first minimum in the O–O PPDF. Important modifications with composition can be observed (Fig. 7, left). Indeed, when we substitute Na₂O by CaO, the NBO–NBO and BO–BO coordination numbers increase markedly which means that more BOs are associated with other BOs and more NBOs are associated with other NBOs. These variations in the coordination numbers illustrate that regions with enriched NBOs appear as Ca replaces Na (and conversely regions enriched in BOs are formed), though no phase separation can be observed either in the simulations or in the glasses.

The cation–cation distribution functions are shown in Fig. 8. Structural oscillations can be observed for both Ca–Ca and Na–Na PPDFs up to 10–12 Å, which suggests some kind of ordering even at low concen-

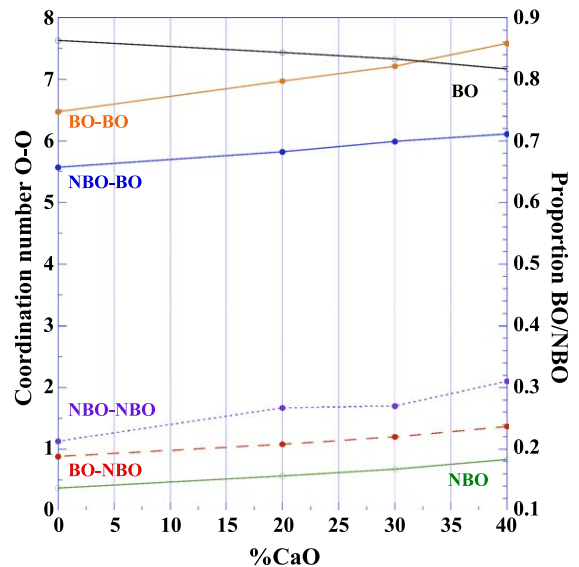


Fig. 7. Variation with the CaO content of the O–O coordination numbers, decomposed from the BO and NBO contributions (left) and variation with the CaO content of the proportion of BO and NBO (right).

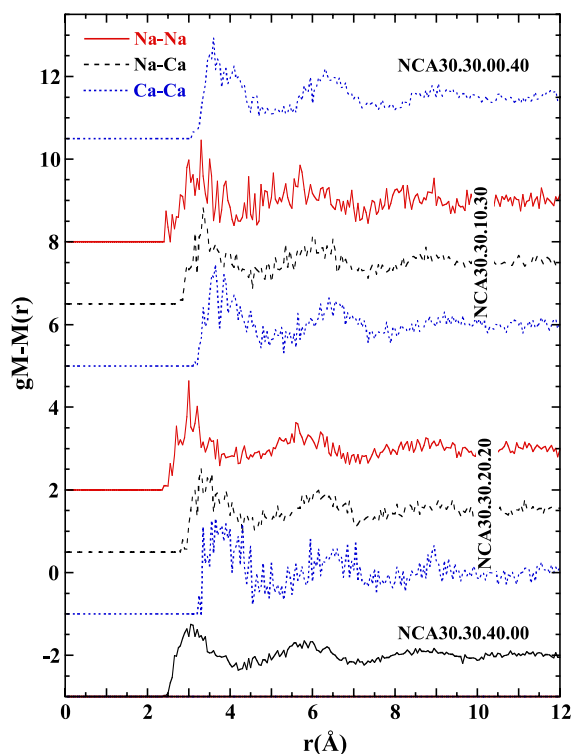


Fig. 8. Cation–cation partial pair distribution functions for the different simulated glass compositions.

tration (for example, noticeable Na–Na correlations are already seen for the NCA30.30.10 glass which contains only 10 mol% Na₂O).

6. Discussion

In pure silicate glasses (NCA60.00), Ca and Na are associated only with NBOs. Previous experimental and numerical studies (Brown et al., 1995) of the structure of Na–Ca silicate glasses indicate that Ca is surrounded by about six oxygen neighbours while Na has five oxygen neighbours. In Na–Ca silicate glasses, MD simulations (Yuan and Cormack, 1996; Cormack and Du, 2001) indicate that Ca and Na are present in modifier-rich regions with Ca having a greater propensity to be coordinated with NBOs than Na, and that Ca substitutes for Na randomly. However, a recent NMR study suggests that Na–Ca distribution is not random with preference for Na–Ca pairing around NBOs (Lee and Stebbins, 2003).

When we substitute Si by Al, aluminium acts as a network former substituting for Si in tetrahedral unit. Na and Ca are required to charge compensate the (AlO₄)[−] tetrahedra and are no longer available to create NBOs. Therefore, there is a decrease in the number of NBOs and a repolymerization of the network is observed (see the fraction of NBOs, fNBO, in Table 1). This also implies a change in the structural role of cations from modifiers to charge compensators. Based on the partial molar entropies, Richet et al. (1993) suggests few coordination changes around Ca between Al-free and Al-bearing glasses while the Na coordination must increase when Al polymerizes the network. However, XANES spectra do not reveal a significant change in the Ca or Na environment for the Si/Al substitution. Similarly, EXAFS measurements shows that the Na environment in NaAlSiO₄ and Na₂Si₂O₅ (McKeown et al., 1985) glasses is similar. An exact determination of the CN using EXAFS is difficult due to the asymmetric part in the distribution of Na–O distances (Fig. 5) and XANES resolution probably precludes detection of small coordination changes. Nevertheless, both techniques agree for the lack of significant change in the Na environment between silicate and aluminosilicate glasses.

For the Ca/Na substitution, the degree of network polymerization does not change and the proportion of NBOs remains constant (see the fraction of NBOs, fNBO, in Table 1). The Ca and Na XANES spectra appear to be insensitive to this substitution. The MD simulations find that Ca is surrounded by about seven oxygens neighbours as in anorthite (Fig. 6). The average coordination number around Na determined by MD is about six oxygens which is slightly lower than albite where the Na-coordination number is 7 (Prewitt et al., 1976). However, the numerical models are in agreement with a distorted Na polyhedra. The first coordination shell determined by the MD simulations is slightly better defined for Ca than for Na as indicated by the deeper minimum beyond the first cation–O peak in Fig. 5. A similar observation has been previously made in a MD simulation study of Ca–Na silicate glasses (Cormack and Du, 2001). A greater distortion of the Na polyhedra compared to that of Ca is in agreement with the broad features characteristics of the XANES spectra at the Na K-edge. The Ca and Na coordination numbers in the

present MD simulations of aluminosilicate glasses are slightly greater than those determined in Na–Ca silicate glasses (Cormack and Du, 2001). This difference can be explained by use of a different cut-off radius, different modelling conditions or differences in the glass structure itself between silicate and aluminosilicate network. The determination of coordination number for alkali and alkaline-earths is also not straightforward by diffraction or EXAFS methods. In fact, the PPDF derived from simulations (Cormack and Du, 2001; Cormier et al., 2003) or experiments (Eckersley et al., 1988) indicate that there is a continuous distribution of Ca–O or Na–O distances and no clear definition exists to estimate the coordination number. An exact coordination number cannot be strictly defined for Ca and Na contrary to network formers (Si, Al or B) or some intermediate elements (Ti; Cormier et al., 1998) for which the first peak in experimental or simulated PPDF goes to zero and correspond thus to a well-defined and finite number of oxygen neighbours.

Figs. 5 and 6 reflect a greater affinity for Ca to be associated with NBOs than Na. This is not too surprising since the double charge of Ca requires more negative charge in its surrounding to ensure the neutrality of the structure. Ca and Na are always surrounded by both BOs and NBOs so that it is more appropriate to describe the cationic environment in terms of modifying or charge compensating character rather than modifying or charge compensating sites.

The cation–cation PPDFs (Fig. 8) present a first nearest neighbour cation separation that is shorter than the one expected for a homogeneous distribution. The presence of well-defined oscillations in these PPDFs is also an indication of some kind of cationic ordering (Gaskell et al., 1991; Cormier et al., 2001). The structural oscillations for the Ca–Ca pair are better defined than for the Na–Na pairs. This suggests a better ordering of Ca in regions where they are associated with NBOs. The Na–Ca PPDFs presents also similar oscillations which suggest that Ca is substituted more or less randomly by Na and that Na–Ca pairs are present in the mixed aluminosilicate glasses. These results confirm previous studies on mixed cations silicate glasses (Ali et al., 1995, Gee et al., 1997; Lee and Stebbins, 2003) concluding that cations are intimately mixed within the glass structure

rather than segregated in separate alkali-rich regions and alkali-earth-rich regions. However, this cation mixing does not imply a homogeneous cation distribution. MD models suggest that regions enriched with Ca and NBOs are favoured with the introduction of CaO. This agrees with thermodynamic data that indicates that Ca perturbs the aluminosilicate network more than Na and that an excess enthalpy is correlated with the formation of a non-random distribution of the cations (Navrotsky et al., 1982; Roy and Navrotsky, 1984).

The cation distribution in the glass network can have important implications for transport properties such as ion transport and viscosity. It was observed in mixed Na–Ca silicate glasses (Roling and Ingram, 2000) that the mobility of Ca^{2+} cation is enhanced when Ca^{2+} is replaced by Na^+ , which therefore has a positive coupling effect on the movement of divalents cations. Conversely, the activation energy related to movement of Na is changed slightly but remains lower than that for Ca. Results from tracer diffusion studies seem to indicate a similar trend in aluminosilicate glasses (Roselieb and Jambon, 2002). The cation mobility is strongly dependent on the glass composition, and structural changes during the Ca/Na substitution take place that facilitates the displacements of Ca^{2+} . The major change in the aluminosilicate network could be a reduction of the ring statistics in CaO-rich glasses. Indeed, the number of small-membered rings has been shown to increase from pure Na-aluminosilicate glasses to pure Ca-aluminosilicate glasses (Cormier et al., 2003). This modification in network topology would provide new types of empty sites that could be used for Ca movements. The formation of smaller rings in CaO-rich glasses is consistent with the increase in density (or the decrease of molar volume) as Na_2O is replaced by CaO (Table 1) and is a further evidence of the strong influence of the Ca ions on the network topology. This increase in density (decrease in molar volume) is related to a decrease in the free volume, which is a key parameter for describing the transport of cations (Ingram, 1999). However, further investigation of the network are required to define more clearly the modifications induced by the Ca/Na substitution.

The mobility of the divalent cation is then assisted by positive coupling from the more mobile

monovalent cation. The mobility of Ca^{2+} ions will favour the softening of the network and explains any decrease in T_g or in viscosity as CaO is replaced by Na_2O (unpublished data). The detailed description of both the local Ca and Na environment and the cationic influence on the network given here will have important implications for the theory of transport in glasses and melts and for understanding the configurational thermodynamic properties.

7. Conclusions

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 anorthite, which corresponds to a coordination number of 7. By comparison with crystalline references, the Na environment corresponds to a distorted polyhedron with CN=6. The Ca and Na XANES spectra are not change significantly when substituting Si by Al or Ca by Na. Molecular Dynamics simulations on $x\text{CaO} \cdot (1-x)\text{Na}_2\text{O} \cdot 3\text{Al}_2\text{O}_3 \cdot 3\text{SiO}_2$ glasses ($x=0.4, 0.3, 0.2, 0$) confirm a first asymmetric coordination shell around cations with about seven oxygen neighbours for Ca and six oxygen neighbours for Na. NBOs are preferentially associated with Ca and more regions enriched in (Ca,NBO) are formed when Na_2O is substituted by CaO. The Na/Ca substitution has an influence on the cationic mobility.

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