

## Structural evidence by NMR for the preference of Na<sup>+</sup> for the charge compensation of AlO<sub>4</sub> in aluminosilicate glasses

**E. Antoni<sup>(1,2)</sup>, L. Montagne<sup>(1)</sup>, G. Tricot<sup>(1)</sup>, G. Palavit<sup>(1)</sup>, J.L. Bernard<sup>(2)</sup>**

(1) Laboratoire de Cristallographie et Physicochimie du Solide, UMR CNRS 8012 ENSC-Lille, Université des Sciences et Techniques de Lille, France

(2) CRIR Isover Saint-Gobain, Rantigny, France

### Introduction

When the molar quantity of modifying oxides (e.g. Na<sub>2</sub>O, K<sub>2</sub>O, CaO) is larger than the Al<sub>2</sub>O<sub>3</sub> content in an aluminosilicate glass, aluminium is tetraordinated with oxygens. A charge compensation is then necessary to maintain the electrical neutrality of the AlO<sub>4</sub> tetrahedra. Several experiments have been carried out to show that the charge balance is preferentially assumed by cations with low electrostatic field strength: K<sup>+</sup>, then Na<sup>+</sup>, then Ca<sup>2+</sup>. These experiments are based on thermodynamic calculations [1], thermodynamic measurements [2], molecular orbital calculation [3], and recently confirmed by viscosimetry measurements [4]. To our knowledge, there is no structural study which has confirmed this preferential charge balancing by alkali ions.

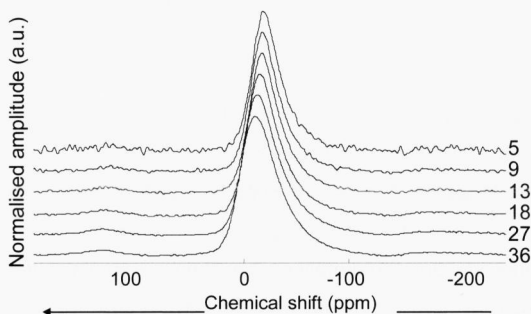
<sup>23</sup>Na nuclear magnetic resonance is an efficient tool for characterising Na<sup>+</sup> environments in crystals and glasses. <sup>23</sup>Na MAS-NMR is sensitive to Na coordination and second neighbours [5, 6]. Maekawa et al. [7] reported that <sup>23</sup>Na chemical shifts are correlated with Na-O distances ( $d_{\text{Na-O}} = -0.0119 \cdot \delta_{\text{iso}} + 2.5912$ ). Since <sup>23</sup>Na is a quadrupolar nucleus ( $I=3/2$ ), its NMR spectra are broadened by second order quadrupolar effects. However, the use of multiple quantum coherences enables to obtain two-dimensional spectra which separate chemical shift from quadrupolar induced shift. Further structural informations can then be obtained from these high-resolution MQ-MAS NMR spectra. Angeli et al. [8] have shown that an inversion of a MQ-MAS spectrum allows to distinguish two types of sodium sites, near the non bridging oxygen, or as aluminium charge compensator, and they confirm the

correlation to Na-O distance with molecular dynamics. Lee et al. [9] used  $^{23}\text{Na}$  MAS and MQ-MAS NMR to study the distribution of sodium ions in charge-balanced alumino-silicate glasses, and could differentiate Na sites in Si-O-T sites (T=Si, Al).

In this paper, we present a study of  $x\text{Na}_2\text{O}-(36-x)\text{CaO}-12\text{Al}_2\text{O}_3-52\text{SiO}_2$  ( $5 < x < 36$ ) glasses (mole %).  $^{23}\text{Na}$  chemical shift distributions were extracted from MQ-MAS NMR spectra, and they will be discussed using the empirical relationship with Na-O distances [7]. The aim is to obtain a structural argument for the preferential charge compensation of  $\text{AlO}_4$  tetrahedra by  $\text{Na}^+$  than by  $\text{Ca}^{2+}$  in peralkaline aluminosilicate glasses.

### Experimental procedures.

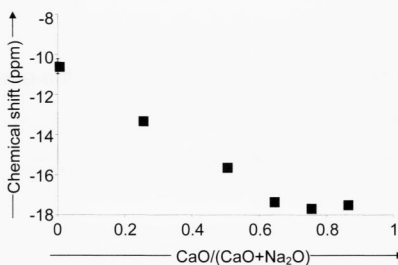
$x\text{Na}_2\text{O}-(36-x)\text{CaO}-12\text{Al}_2\text{O}_3-52\text{SiO}_2$  glasses ( $5 < x < 36$ ) were prepared by melting sodium and calcium carbonates, alumina and sand in a platinum crucible for 3 hours, at a temperature between 1300 and 1500°C depending on the sodium/calcium quantity. Mechanical stirring assured the homogeneity of the melts. The melts were then quenched on a steel plate, and annealed at a temperature close to the  $T_g$ .  $^{23}\text{Na}$  MAS NMR spectra were recorded at 9.4T, with a spinning rate of 12.5 kHz. 8  $\mu\text{s}$  pulses were used, with 2 s relaxation delay. Chemical shifts were referenced to 1M NaCl solution. The 3Q-MAS spectra were recorded with the z filter method. 4, 2 and 8  $\mu\text{s}$  pulses were successively used, with 2 s recycling delay. Rotor synchronized conditions were used (rotation frequency was 12.5 Hz), and 128  $t_1$  steps were recorded.



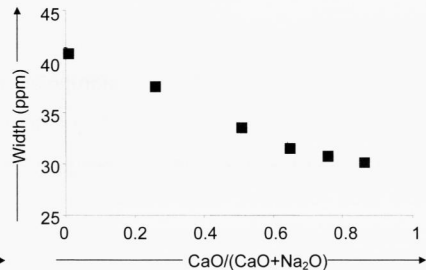
**Figure 1.**  $^{23}\text{Na}$  MAS-NMR spectra of  $x\text{Na}_2\text{O}-(36-x)\text{CaO}-12\text{Al}_2\text{O}_3-52\text{SiO}_2$  glasses.

**Results and discussion.**

Figure 1 shows the  $^{23}\text{Na}$  MAS-NMR spectra of the glasses. They are broad and asymmetric, with a tail on the high field side of the spectra. This shape is very common for  $^{23}\text{Na}$  NMR spectra in glasses, it is due to the distributions of chemical shift and quadrupolar constant [10]. The substitution of  $\text{Na}_2\text{O}$  by  $\text{CaO}$  in the glass compositions leads to a shift of the resonances to high field, and a decrease of the resonance width, as shown in Figures 2 and 3. This is attributed to a decrease of the distributions of chemical shift and quadrupolar constants, which means that the local order around sodium nuclei is less distributed. We notice that the increase of  $\text{CaO}$  in glasses produces a broadening of the spectra of  $^{27}\text{Al}$  and  $^{29}\text{Si}$  spectra (not shown here). Moreover, we observe on Figures 2 that the chemical shift do not change for  $\text{CaO}/(\text{CaO}+\text{Na}_2\text{O})$  ratios larger than 0.6 (i.e.  $\text{Na}_2\text{O}$  content larger than 13 %).

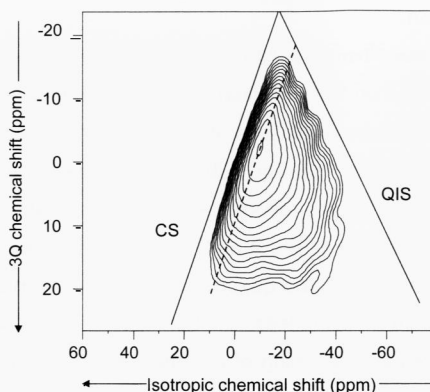


**Figure 2:**  $^{23}\text{Na}$  chemical shifts (measured on top of the spectra, uncorrected for quadrupolar induced shift) of  $x\text{Na}_2\text{O}-(36-x)\text{CaO}-12\text{Al}_2\text{O}_3-52\text{SiO}_2$  glasses



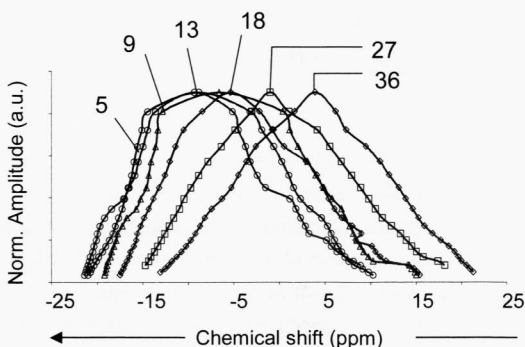
**Figure 3:** Width at half eighth of  $^{23}\text{Na}$  spectra of  $x\text{Na}_2\text{O}-(36-x)\text{CaO}-12\text{Al}_2\text{O}_3-52\text{SiO}_2$  glasses

It is difficult to extract informations on the local environment of sodium nuclei from one dimensional MAS-NMR spectra since the lineshape is broadened by the distributions of both chemical shift and quadrupolar constant, and it is not possible to know the relative amplitude of each distribution. MQ-MAS spectra enable to separate the chemical shift (CS) and quadrupolar induced shift (QIS), which are aligned along two axes with slope 1 and  $-10/17$ , respectively. Figure 4 shows a typical 3Q-MAS spectrum recorded on the  $x=36$  sample.



**Figure 4:**  $^{23}\text{Na}$  3Q-MAS NMR spectrum (sheared) of the  $36\text{Na}_2\text{O}-12\text{Al}_2\text{O}_3-52\text{SiO}_2$  glass. The CS and QIS axes are shown. The dotted line is the slice along CS axis at constant QIS.

It shows a broad resonance, spread along the two CS and QIS axes, which confirms that both chemical shift and quadrupolar constant distributions contribute to the one-dimensional MAS spectra. One can then measure the chemical shift distribution for a given quadrupolar constant by taking a slice of the 3Q-MAS spectrum parallel to the CS axis (constant QIS). Assuming that the quadrupolar constant distributions are similar for all glasses, we reported the chemical shift distributions for all the glasses in Figure 5.



**Figure 5:** Slices along CS axis on  $^{23}\text{Na}$  3Q-MAS NMR spectra of  $x\text{Na}_2\text{O}-(36-x)\text{CaO}-12\text{Al}_2\text{O}_3-52\text{SiO}_2$  glasses.

The same high field shift as in one dimensional MAS spectra (Figure 1) is observed when Na<sub>2</sub>O is substituted by CaO. Since no quadrupolar effect is expected, we can correlate this high field shift to an increase in sodium-oxygen distance, as was established by Maekawa et al. [7]:  $d_{\text{Na-O}} = -0.0119\delta_{\text{iso}} + 2.5912$ . Longer Na-O distance is expected when sodium acts as a charge compensating ion for AlO<sub>4</sub> tetrahedra than when it is located on non bridging oxygens (Si-O...Na) [8]. Figure 5 thus reflects that the relative population of Na<sup>+</sup> ions in charge compensating sites (more negative chemical shift, longer Na-O distance) increases when the quantity of CaO increases in the glasses. Furthermore, the shift of the distributions is much smaller for glasses containing 13 % and less Na<sub>2</sub>O (Figure 5). This explains the change in slope observed for CaO/(CaO+Na<sub>2</sub>O) ratios smaller than ca. 0.6 (Figures 2 and 3). Since the glasses contain 12 mol.% Al<sub>2</sub>O<sub>3</sub>, the absence of shift of 3Q slices below 13% Na<sub>2</sub>O (Figure 5) means that when the quantity of Na<sup>+</sup> decreases below the Al<sub>2</sub>O<sub>3</sub> content, all the Na<sup>+</sup> are located in charge compensating sites. We conclude then the charge compensation of AlO<sub>4</sub> sites is preferentially assumed by Na<sup>+</sup> ions, otherwise a statistical site occupation would have been observed.

### **Conclusion.**

MQ-MAS spectra enable to extract the <sup>23</sup>Na chemical shift distributions. Sodium ions in charge compensation sites of AlO<sub>4</sub> tetrahedra have larger Na-O distances than sodium on non-bridging oxygens. When substituting Na<sub>2</sub>O by CaO in the glasses, the Na<sup>+</sup> ions are distributed non-uniformly when their quantity is lower than the quantity of Al<sub>2</sub>O<sub>3</sub> in the glasses. Sodium in charge compensating sites are preferentially observed. This is a structural evidence of the preferential charge compensation of AlO<sub>4</sub> tetrahedra by alkali ions which was shown previously only indirectly by the evolution of properties (e.g; viscosity).

### **Acknowledgements.**

E. Antoni thanks Saint-Gobain for her PhD grant. B. Revel (centre commun de mesures RMN) is acknowledged for his technical assistance for NMR measurements.

**References.**

- [1] Roy B.N., Navrotsky A.: Thermochemistry of charge-coupled substitutions in silicate glasses: the system  $(M^{n+}_{1/n})AlO_2-SiO_2$  ( $M = Li, Na, K, Rb, Mg, Ca, Sr, Ba, Pb$ ). *J. Am. Ceram. Soc.*, **67** (1984) p. 606.
- [2] Bouhifd M.A., Courtial P., Richet P.: Configurational heat capacities : alkali vs. alkaline-earth aluminosilicate liquids. *J. of Non-Cryst. Solids*, **231** (1998) p. 169.
- [3] Navrotsky A., Geisinger K.L., McMillan P., Gibbs G.V.: The tetrahedral framework in glasses and melts- inferences from molecular orbital calculations and implications for structure, thermodynamics, and physical properties. *Phys. Chem. Minerals*, **11** (1985) p. 284.
- [4] Korsgaard M., Pind M., Moller Sorensen P., Sie Woldum H.: Derivation of the temperature dependant constants for  $KAlO_2$  and  $NaAlO_2$  in a viscosity predictive model for high aluminosilicate melts. *Glass Sci. Technol.* **76** (2003) n°6 p. 270.
- [5] Xu X., Stebbins J.F.:  $^{23}Na$  NMR chemical shifts and local Na coordination environments in silicate crystals, melts and glasses. *Phys. Chem. Minerals*, **20** (1993) p. 297.
- [6] Kohn S.C., Smith M.E., Dirken P.J., Van Eck E.R.H. et al.: Sodium environments in dry and hydrous albite glasses: Improved  $^{23}Na$  solid state NMR data and their implication for water dissolution mechanism. *Geochim. Cosmochim. Acta*, **62** (1998) n°1 p. 79.
- [7] Maekawa H., Nakao T., Shimokawa S., Yookawa T.: Coordination of sodium ions in  $NaAlO_2-SiO_2$  melts: a high temperature  $^{23}Na$  NMR study. *Phys. Chem. Minerals.*, **24** (1997) p. 53.
- [8] Angeli F., Delaye J. M., Charpentier T.: Influence of glass composition on the Na-O bond distance: a  $^{23}Na$  3Q-MAS NMR and molecular dynamics study. *J. of Non-Cryst. Solids*, **276** (2000) p. 132.
- [9] Lee S.K., Stebbins J.F.: The distribution of sodium ions in aluminosilicate glasses: a high-field Na-23 MAS and 3Q MAS NMR study. *Geochim. Cosmochim. Acta*, **67** (2003) n°9 p. 1699.
- [10] Mackenzie K.J.D., Smith M.E.: Multinuclerar solid state NMR of inorganic materials. Pergamon (2002) p.68.