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**SPECTROSCOPIC APPROACH TO CHLORINE LOCAL ENVIRONMENT IN
ALUMINOBOROSILICATE GLASSES**

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ABSTRACT

Chlorine local environment has been investigated using spectroscopic approach (XAS and XPS) for Na- and Ca-bearing aluminoborosilicate glasses synthesised at 1.0 GPa. Based on Cl K-edge EXAFS results, Cl appears to show two local environments in glasses: one at long distance ~ 2.7 Å assigned to Cl^- species charge compensated by Na^+ and/or Ca^{2+} and one at short distance ~ 1.8 Å assigned to Cl-Cl and Si-Cl species. The Cl 2p XPS results cannot unambiguously confirm the presence of Si-Cl overlapped with $\text{Na}^+/\text{Ca}^{2+} \dots \text{Cl}^-$ species.

Keywords: chlorine incorporation mechanisms, nuclear waste glass, high-pressure

1. Introduction

Chlorine-36 is a troublesome radioisotopes produced by nuclear activity and found in high concentration in Tchernobyl soil^[1]. Vitrification process in Low Activity Waste (LAW) glass matrix is not an adequate solution for immobilising ^{36}Cl owing to the strong chlorine volatility. Recent study showed that Cl can be highly incorporated into aluminoborosilicate glass matrix if synthesised under high-pressure^[2]. Cl incorporation into the glass needs to be investigated for assessing the glass chemical durability.

Data on Cl incorporation mechanisms in glasses relies on Cl K-edge X-ray Absorption Spectroscopy (XAS)^[2-4]. Jolivet et al.^[2] and Thomas et al.^[4] stated that Cl incorporates as chloride species charge compensated by nearby alkaline or alkaline-earth cations (i.e. $\text{Na}^+/\text{Ca}^{2+} \dots \text{Cl}^-$). Surprisingly, Thomas et al.^[4] suggested that chlorine could also be present as Si-Cl units in silicon tetrahedral unit. On the contrary, Jolivet et al.^[2] excluded this possibility based on X-ray Photoelectron Spectroscopy (XPS). Previous NMR study did not exclude the presence of Si-Cl or Al-Cl, however, it would be in small proportion^[5]. The Si-Cl bond presence might influence the glass physical properties and it needs further confirmation for various range of glass compositions, especially aluminoborosilicate glass. We investigated the

Cl local environment in LAW glass compositions using combined XAS and XPS approach. Results are discussed in term of Cl incorporation mechanisms within the glass structure.

2. Materials and methods

Glasses were prepared under high-pressure conditions at 1250°C and 1 GPa following described protocol^[6]. The initial Cl-free glasses melted at 1200°C and ambient pressure were prepared from oxides and carbonates with added NaCl at <17 mol.% as chlorine source. High-pressure recovered glasses were characterized using Scanning Electron Microscope with Energy Dispersive Spectrometer for element concentrations and Laser Ablation Inductively Coupled Plasma Mass Spectrometer for B₂O₃ (Table 1). The investigated glass represents typical LAW compositions. The measured Cl ranges between 2.3 and 3.9 mol.%. We observed that the highest Cl content is measured for Ca-bearing glass composition in agreement with current knowledge on chlorine affinity for such glass compositions^[2].

Sample	Major element						Cl-Na			Cl-Ca			Cl-Cl			Cl-Si		
	SiO ₂	Al ₂ O ₃	B ₂ O ₃	CaO	Na ₂ O	Cl	r	CN	σ ²	r	CN	σ ²	r	CN	σ ²	r	CN	σ ²
<i>Na11Ca9</i>	66.0(1)	5.4(0)	13.3(0)	7.0(1)	8.2(1)	3.9(3)	2.77(1)	4.1(2)	0.035	2.68(1)	2.0(1)	0.019	1.88(0)	1.0(0)	0.011	1.72(0)	1.0(0)	0.010
<i>Na17Ca0</i>	66.0(4)	5.3(0)	13.4(0)		15.3(4)	2.3(1)	2.64(1)	4.0(4)	0.043				1.81(0)	1.0(0)	0.008	1.60(0)	0.9(0)	0.008
<i>Na21Ca0</i>	63.2(2)	5.9(0)	13.5(0)		17.3(1)	2.9(1)	2.69(1)	4.0(3)	0.026				1.92(1)	1.0(1)	0.014	1.75(1)	1.0(1)	0.011

Table 1. Glass composition in mol.% determined from SEM-EDS and LA-ICP-MS for B₂O₃.

Cl EXAFS fitting results: r in Å, CN no dimension and σ² in Å².

Cl-bearing glasses were characterized using LUCIA beamline at SOLEIL synchrotron. Cl X-ray Absorption Near Edge Spectroscopy (XANES) and Extended X-ray Absorption Fine Structure (EXAFS) at K-edge between 2780 and 3780 eV. The Cl K-edge beamline calibration is achieved at the white line maximum of the spectrum using crystalline NaCl (2824 eV). The spectra are acquired in fluorescence mode. We tilted the sample holder by 2° to avoid self-absorption. We acquired at least two spectra per sample. We did not observe spectrum evolution under the X-ray beam suggesting that sample is not damaged.

Spectra were treated using Demeter software package^[7]. We used the crystalline NaCl spectrum to determine the energy line position ($\Delta E_0 = -2.31$ eV) and scattering amplitude ($S_0^2 = 0.82$). We used k-space range 2.7-8.0 \AA^{-1} and the radial distribution function ($R + \Delta R$) was fitted in the range 0.5-3.0 \AA . We used up to four different scattering paths taken from the Crystallographic Open Database^[8]: Si-Cl from SiCl_4 with $r_{\text{Si-Cl}} = 1.96$ \AA , Cl-Cl from Cl_2 with $r_{\text{Cl-Cl}} = 1.82$ \AA , Cl-Na from NaCl with $r_{\text{Na-Cl}} = 2.82$ \AA , Cl-Ca from CaCl_2 with $r_{\text{Ca-Cl}} = 2.74$ \AA used for Na11Ca9 glass. The parameter initialization is $\Delta r = 0$, $\sigma^2 = 0.003$ \AA^2 for the Debye-Waller attenuation factor; we set the CN at 1, 1, 4 and 2 for Si-Cl, Cl-Cl, Na...Cl and Ca...Cl, respectively.

We conducted XPS at the Cl 2p binding energy region (195 to 205 eV) using a Kratos Nova spectrometer operating at 1486.6 eV and under high-vacuum^[2]. Acquisitions were performed on glass chips obtained from the bulk experimental charge ($\sim 5 \times 5$ mm²). High-resolution spectra were collected with 0.1 eV step. Measurements were done with charge neutralization. The spectra were calibrated on the adventitious C 1s at 284.4 eV.

Spectra were treated using CasaXPS^[9]. Cl 2p peak was simulated with two doublet peaks ($2p_{3/2}$ and $2p_{1/2}$) corresponding to chloride and Si-Cl species and according to the literature data^[10,11]. To our knowledge, there is no information on the position of Cl_2 gas signal in the Cl 2p XPS region. We used Gaussian-Lorentzian peak line shape and a Tougaard baseline function. The $2p_{3/2}$ and $2p_{1/2}$ peaks have identical width, are separated by 1.6 eV and have an area ratio of $1/2$ for spin-orbit consideration.

3. Results and discussion

XANES spectra are shown in Fig. 1 for glasses and representative crystalline compounds (NaCl and CaCl_2). There is no visible pre-edge peak, which is consistent with Jolivet et al.^[2] that attributed the presence of the pre-edge to the incorporated Pd coming from

the PdCl₂ initial source. The spectrum line shape suggests that Cl is present within the glass as Cl⁻ local environments. The white line position (~2826 eV) is consistent with peak position observed for NaCl and CaCl₂ spectra. For Na₁₇Ca₀, there is a peak at 2837 eV that looks like the peak observed for NaCl in Fig. 1.

Cl⁻ species requires charge compensation by a surrounding cation. Previous studies^[2,12] showed that Cl has a higher affinity for Ca²⁺ than for Na⁺, however a combination of both such as Na⁺/Ca²⁺...Cl⁻ is most probable^[2]. Although, it has been inferred from previous works^[4], it is currently impossible from the sole use of XANES fingerprinting to confirm the presence of other Cl species.

We show the glass Cl EXAFS spectra along with their fit in Fig. 2. Strikingly, we distinguish two major local environments for Cl: one at longer distance ~2.5 Å than the other ~1.5 Å. We assigned these two local environments to Na⁺/Ca²⁺...Cl⁻ and Si-Cl and/or Cl-Cl, respectively; in consistency with distances observed in model crystallographic structures. Whereas the presence of chloride species is consistent with the XANES spectra, the presence of other Cl species is less intuitive. It should be pointed out that the existence of short bond length chlorine species has been excluded in Jolivet et al.^[2] from EXAFS. Thomas et al.^[4] suggested the presence of Si-Cl with the replacement of O atoms from Si tetrahedral unit by Cl atoms based on XANES pre-edge peak analyses. McKeown et al.^[3] suggested that Cl-Cl units could be present with longer bond length (~2.45 Å). Here, we suggest that both long and short bond length chlorine species could coexist within the structure of aluminoborosilicate glasses synthesised under high-pressure conditions.

The results in Table 1 suggest that the chloride local environment in the investigated glasses has bond length of ~2.70 Å regardless of the charge compensating cation. The determined CN in the immediate surrounding of the Cl⁻ is either 4 or 2 for Na⁺ or Ca²⁺, respectively. It implies that more charge compensation is required to accommodate Cl⁻ units.

For Cl-Cl and Si-Cl, we determined a CN of 1 and bond length of ~ 1.85 and 1.70 Å, respectively. The presence of Cl₂ species could be due to the presence of μm bubbles filled with Cl₂ or an actual Cl₂ incorporation within the glass voids as suggested previously^[3].

The presented results are in agreement with Thomas et al.^[4] and in discrepancy with Jolivet et al.^[2]. Jolivet et al.^[2] used Cl 2p XPS to constrain the Cl incorporation and found that Cl 2p XPS spectra could be simulated with a single environment for Cl assigned to chloride. We have conducted XPS Cl 2p acquisitions shown in Fig. 3 and we considered a combination of two individual components corresponding to Cl 2p_{3/2} and 2p_{1/2} at ~ 198 and 200 eV for simulating the spectra. Literature data suggests that such peak position could be attributed to chloride species in agreement with our XANES data. Bello et al.^[11] showed that the signal corresponding to Si-Cl bonds is observed at energy of ~ 200 and 202 eV for Cl 2p_{3/2} and 2p_{1/2}, respectively; therefore overlapping with the predominant signal for chloride species. For Na₁₇CaO, which has the best signal-to-noise ratio, the latter proportion does not exceed 5% of the total Cl. The presence of Si-Cl implies the exchange between an oxygen by a chlorine atom in SiO₄ unit forming a SiO₃Cl structural unit. It is questioning considering that O²⁻ has a higher electronegativity than Cl⁻ and will be favoured in the iono-covalent Si network units; unless the high-pressure conditions promote this exchange.

4. Summary

We raise a substantial issue regarding the Cl incorporation mechanisms in aluminoborosilicate glasses. For three Cl-bearing glasses synthesised under high-pressure conditions, we determined the Cl local environment using combined XAS and XPS spectroscopic approach. It appears that two distinct Cl environments can be inferred: short distance ~ 1.5 Å assigned to Si-Cl bonds and long distance ~ 2.5 Å assigned to chloride species; suggesting that Cl potentially exchanges with O atoms within the glass structure.

Further work is required to unambiguously identify such species as it might have major impact on glass physico-chemical properties.

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Figure caption:

Fig. 1. Typical Cl XANES spectra acquired on glasses and crystalline compounds.

Fig. 2. EXAFS $R+\Delta R$ for Cl-bearing glasses. Magnitude and the Imaginary spectra are shown along with their fit.

Fig. 3. Cl 2p XPS spectra for glasses simulated with two doublet for chloride and Si-Cl species. The proportion of each species is also reported.

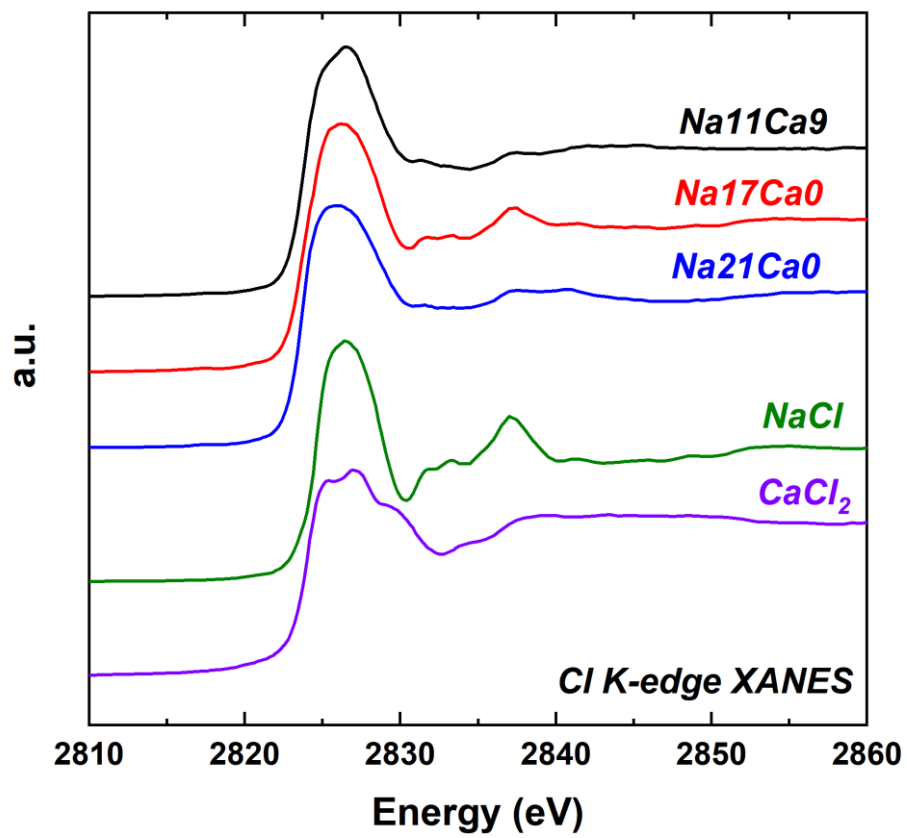


Figure 1

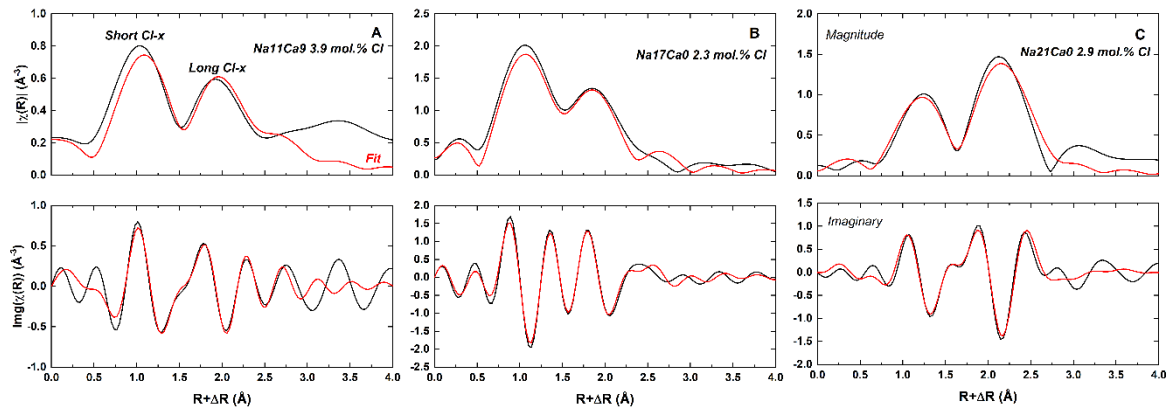


Figure 2

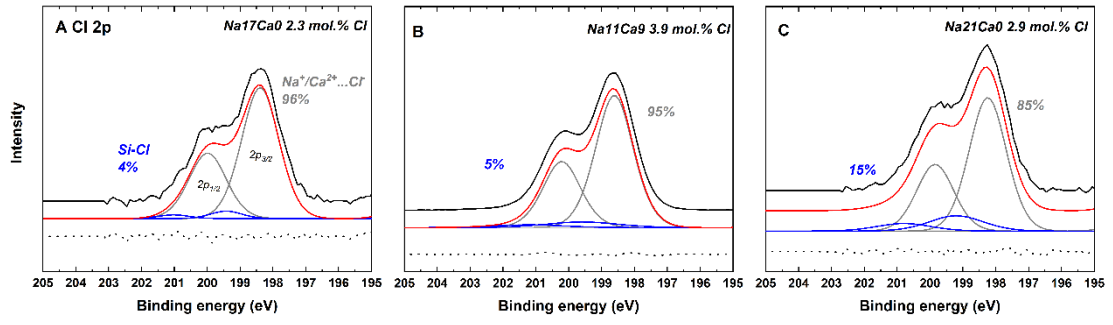


Figure 3