

Speciation of La³⁺ and Eu³⁺ in the altered layer of a borosilicate glass used as a model of glass nuclear wasteforms

E. Molières, O. Majérus¹, P. Jollivet and F. Angéli

DTCD/SECM-LDLC, CEA Marcoule, 30207 Bagnols-sur-Cèze, France

¹LCMCP-ENSCP, UMR CNRS 7574, Chimie Paristech, 75231 Paris, France

Rare Earths (RE) are a significant part of nuclear fission products that are incorporated, together with highly radiotoxic minor actinides (Np, Am, Cm), in aluminoborosilicate glass nuclear wasteforms. The long-term chemical durability of these glass wasteforms relies on the formation of a protective layer, that slows down the diffusion of water towards the pristine glass [1]. This layer is part of the total altered layer of the glass and is supposed to be composed of a dense silicate phase and of embedded insoluble phases, depending on the compositions of the glass and of the altering solution. As insoluble metals, rare earths are retained in the altered layer and modify the glass dissolution kinetics [2]. The aim of this study is to characterize their environment in pristine and altered glasses of simple compositions (soda lime borosilicates). L₃-edge EXAFS is used as a chemically selective technique able to provide information on the speciation of RE in the altered layer : connection to the hydrated silicate network, clusterization level, possible precipitation of hydroxydes or oxydes. In addition, this study may provide insight into the position of actinides in the altered layer, since RE are good chemical analogues of Am³⁺ and Cm³⁺ ions.

A series of 5 glasses with increasing La₂O₃ content (molar compositions (60-x) SiO₂ – 18 B₂O₃ – 18 Na₂O – 4 CaO – x La₂O₃ – 0.15 Eu₂O₃ with x = 0; 2; 4; 8; 12), a glass with 4 mol% Eu₂O₃ (similar as the La-glass with x =4), and a glass with 4 mol% La₂O₃ and no calcium oxide were studied in this work. All glasses were 100% altered in buffered water (pH 7 and pH 9.5) at 90°C in static conditions at S/V = 15 cm⁻¹. In these conditions, the Si concentration is rapidly close to the saturation value with respect to a-SiO₂ and the altered layer can form and densify by Si-O condensation. XAFS spectroscopy was performed at the La L₃-edge (5483 eV) and at the Eu L₃-edge (6977 eV) at ~90 K using a N₂ cryostat, on the E4 beamline at HASYLAB. References were crystalline RE oxyapatites with Ca₂RE₈(SiO₄)₆O₂ composition, La(OH)₃:Eu, La₂(CO₃)₃ and La- or Eu-bearing sodium silicate glasses. All samples were crushed in powder and an appropriate amount was pelletized with cellulose for transmission mode measurements.

The EXAFS oscillations were extracted using the Athena-Artemis softwares. A linear pre-edge and a polynomial post-edge line were used to simulate the atomic absorption and normalize the edge. For the La L₃-edge, the background was simulated with a spline on the 0.2 to 10.2 Å⁻¹ range, using a low r cut-off of 1.0 Å and a k-weight = 3. For the Eu L₃-edge, the range could be extended to 12.2 Å⁻¹. The La L₃-edge spectra present a multielectronic excitation at 5609 eV, that was removed by interpolating the data on the 5600-5630 eV range with a 3d order polynomial function. The first shell of the k³chi(k) Fourier transform was fitted with a single scattering RE-O contribution, on the 1.4 – 2.5 Å range. Diffusion phase and amplitude functions were calculated using FEFF6 and their adequacy was checked by fitting the crystalline references. When possible, a second neighbour shell was also fitted using a single scattering RE-Si contribution.

EXAFS k³chi(k) functions and their Fourier transforms (calculated using a Hanning apodisation window on the 2.5-9.5 Å range) are shown in Figure 1 for the 4La glass, pristine and altered at pH 7 and 9.5. The spectrum of La(OH)₃ is added for comparison. Structural parameters resulting from the best fits are given in Table 1.

The La environment is similar in all glasses with increasing La₂O₃ content from 2 to 12 mol%, with an expected increase of the La-O mean distance from 2.48 to 2.52 Å. The mean coordination sphere has about 6 oxygens.

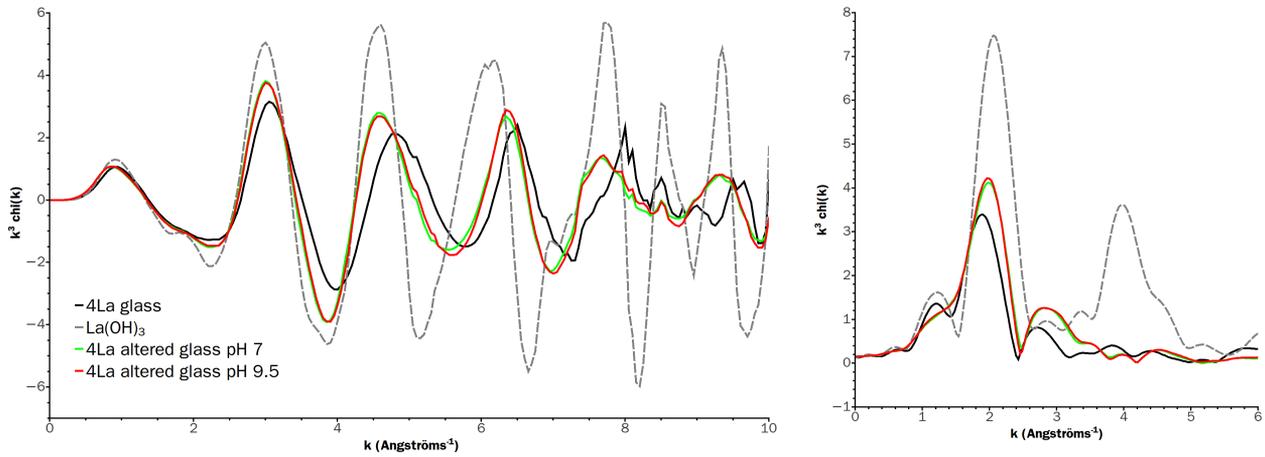


Figure 1: La L_3 -edge EXAFS $k^3 \chi(k)$ functions (left) and magnitudes of Fourier transforms (right) of 4La pristine glass and of 4La 100% altered glasses at pH 7 and pH 9.5. The spectrum of $\text{La}(\text{OH})_3$ is given for comparison.

	R_{fit}	$d(\text{RE-O})$ (Å)	Sigma (Å ²)	Cum3 (Å ³)	Cum4 (Å ⁴)	$N \cdot S_0^2$ (amp)	ΔE_0 (eV)
2La glass	0.0086	2.48	0.0162	0.0015	0.000110	6.1	3.13
4La glass	0.0116	2.50	0.0169	0.0019	0.000095	6.1	3.13
8La glass	0.0119	2.52	0.0157	0.0021	0.000000	6.1	3.13
12La glass	0.0100	2.52	0.0176	0.0017	0.000104	6.1	3.13
2La gel pH 7	0.0035	2.56	0.0191	0.0014	0.000087	9.5	3.13
8La gel pH 7	0.0044	2.56	0.0208	0.0014	0.000200	9.5	3.13
0Ca gel pH 7	0.0037	2.56	0.0194	0.0012	0.000133	9.5	3.13
4Eu glass	0.0084	2.40	0.0123	0.0013	0.000380	6.0	7.00
4Eu gel pH 7	0.0107	2.45	0.0116	0.0009	0.000030	8.0	7.00

Table 1: Structural parameters obtained from the fit of the EXAFS first shell using a single-scattering RE-O contribution. The other glasses and gels of the study yield very similar parameters.

The RE environments in the 100% altered glasses are remarkably similar whatever the pH (7 or 9.5) and whatever the presence/absence of Ca^{2+} ions. La^{3+} ions are coordinated to about 9 oxygens at a mean distance of 2.56 Å. The disorder of the coordination sphere in the gel is close to that in the pristine glass. Concerning Eu^{3+} ions, they have an average 6-fold coordination sphere, with 2.40 Å mean distance in the glass, that transforms into a 8-fold coordination sphere, with 2.45 Å mean distance, in the alteration gels. Thus, the RE environment has been re-constructed during the alteration, presumably by complete Si-O-La bond hydrolysis and recondensation in the resulting gel. The most noticeable result is that the RE environment is clearly different from that of La hydroxyde (Figure 1), with shorter La-O distances (2.56 instead of 2.59 Å in $\text{La}(\text{OH})_3$) and no appearance of La-La second neighbours. Instead, the second shell that is observed in the gels could be successfully assigned to Si neighbours at about 3 Å by fitting. These findings are consistent with complementary spectroscopic results, that indicate that RE keep strong connections to the silicate network, inducing depolymerization (Raman, ²⁹Si and ¹⁷O NMR).

References

- [1] P. Frugier, S. Gin, Y. Minet, T. Chave, B. Bonin, N. Godon, et al., *J. of Nucl. Mat.*, **380**, 8 (2008). *Phys. Rev. B* **50**, 1234 (2000). [2] E. Molières, PhD thesis of University Paris 6, 2012.