Title: Local structure around cations in glasses: how worth increasing the EXAFS k-range?

Myrtille O.J.Y. Hunault (1), Georges Calas (2), Laurence Galoisy (2), Gérald Lelong (2), Laurent Cormier (2)
(1) *Synchrotron SOLEIL, L'Orme des Merisiers, Saint-Aubin, BP 48, 91192 Gif-sur-Yvette Cedex, France*
(2) Institut de minéralogie, de physique des matériaux et de cosmochimie (IMPMC) – MNHN, UPMC - Paris 6, IRD, CNRS, 4 place Jussieu 75252 PARIS Cedex 05, France

myrtille.hunault@synchrotron-soleil.fr

EXAFS and XANES have provided unique information on the structural organization around cations in glasses, demonstrating the existence of well-defined polyhedral units. Cations may occur as modifiers, playing either a depolymerizing role for the polymeric framework, or as charge compensators for other cations. Some cations may occur in a network-forming site, with well-defined topological relationships relative to the polymeric network. [1] Beyond the coordination shell, more precise structural information in glasses is needed to get a coherent model on the structural properties of all glass components. Fitting EXAFS data in glasses at high k values, provided a high signal/noise ratio, is expected to improve the structural knowledge of the glass structure, allowing for instance to detect the presence of minor species or providing more constraints on the polyhedral units. In amorphous structures, the EXAFS signal is damped at high k, which implies a nonlinear and drastic increase of the data acquisition time. Hence comes an optimization issue for any synchrotron user: is it worth acquiring longer k-range spectra?

We will present an analysis of EXAFS data on uranium-bearing borate glasses. During centuries, uranium has been used as an efficient coloring agent in glasses. Nowadays it is an interesting surrogate of transuranic elements in glasses. In glasses and ceramics, U is mainly present in the forms of U(VI) and U(IV), with minor amounts of U(V). Silicate glasses show uranyl sites U(VI) with an original geometry, based on shorter distances between U and equatorial oxygens than in most uranyl complexes found in crystals and aqueous solutions. This intermediate speciation of U(VI) in glasses is also illustrated by their color, which may vary from green to brown, depending on the glass chemical composition.

Here we investigate the significance of increasing the EXAFS k-range beyond $k=20Å^{-1}$ in the case of uranium(VI) in binary borate glasses. Uranium L_3 edge EXAFS data were collected at room temperature in transmission mode on the XAS endstation of the MARS beamline at the SOLEIL synchrotron. The EXAFS reveals the change from uranyl towards uranate speciation of U(VI) upon increasing the alkali content in alkali borate glasses. Detailed structural information are necessary to determine the evolution of the uranyl bond distances and understand the glass color change from pale green to dark yellow with the glass composition. This case will be compared to the case of zirconium in borosilicate glasses, where the increased EXAFS energy range provided an enhanced resolution in the real space, especially concerning minor contributions in the medium range organization around Zr(IV) cations in a networking position.[2]

References :

[1] Calas, G. et al. 2014. *Procedia Materials Science*, 2nd International Summer School on Nuclear Glass Wasteform: Structure, Properties and Long-Term Behavior, SumGLASS 2013, 7 (January): 23–31. https://doi.org/10.1016/j.mspro.2014.10.005.

[2] Jollivet, P., et al. 2013. *Journal of Non-Crystalline Solids* 381 (December): 40–47. https://doi.org/10.1016/j.jnoncrysol.2013.09.013.

Please include the grant or other support information for your research on a separate line at the bottom of your abstract. If yes, then the support acknowledgment also should be included on your poster.]