Title: Deciphering Bridging and Non-Bridging Oxygen proportions in aluminoborosilicate glasses using XPS.

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Description:

Nuclear waste glasses represent the adopted solution for the immobilization of radioactive waste produced in modern industrial countries. If the range of used glass compositions is relatively large, the most popular glass formulation has a common ground: aluminoborosilicate with SiO_2-B_2O_3-Al_2O_3 as network formers and additional network modifiers such as CaO and Na_2O. The incorporation of the nuclear waste radioisotopes is widely studied and it is currently assumed in the literature that the oxygen speciation (Bridging Oxygen BO and Non-Bridging Oxygen NBO) is a major control to their incorporation. Although crucial as it represents the glass degree of polymerization, the quantification of BO and NBO is often a complicated task. Recently, we have demonstrated that it is possible to determine each proportion using O 1s X-ray Photoelectron Spectroscopy, however, the systematic of O 1s XPS spectra on a large database of glass compositions remains to be addressed.

In the frame of the ADAM&EVE project (https://miti.cnrs.fr/prime/adameve/), we propose to investigate the change in the O 1s XPS spectra for compositions ranging from simple silicate to more complex aluminoborosilicate glasses with CaO and/or Na_2O as network modifying cations within the structure. In the present work, we will perform high-temperature syntheses using box furnace or vertical tube furnace at temperature close to the melting temperature. We also intend to investigate the change in the redox condition syntheses in a gas mixing furnace to see if such conditions influence the distribution of BO and NBO at ambient pressure. Different quenching rate will be experienced as it is a recognized parameter influencing the degree of glass polymerization.

The glass will be characterized using Magic Angle Spinning Nuclear Magnetic Resonance (MAS NMR) for determining the network unit distribution (B and Al speciation) to extract the BO and NBO proportions. The obtained O 1s XPS spectra will be treated using standard deconvolution methods and will be compared to the NMR results and theoretical calculations. The entire set of results will be implemented into a database for determining the systematic beyond the acquisition of the O 1s XPS spectra. Model for oxygen speciation in glass will be constructed from the subsequent data analyses using advanced coding.

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Platform: at LPG, high-temperature furnaces, Raman; at IMN, SEM EDS, Solid-State NMR, XPS.

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