New insights on the structure of borosilicate glasses containing zirconium by combining Wide Angle X-ray Scattering and atomistic simulations

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Abstract

Borosilicate glasses containing zirconium are mostly encountered in the industrial field for high level nuclear waste immobilization. Zr low solubility, its nucleating role and influence on the glass chemical durability during alteration in aqueous conditions, were already tackled by means of XAS, NMR and Raman studies.
However, there are still open questions concerning the medium range order for Zr in relation with the nature and proportion of alkali and alkali-earth species in the glasses. It is therefore our purpose to investigate this issue, by combining Wide Angle X-ray Scattering (WAXS) and Empirical Potential Structure Refinement (EPSR) technique. Atomistic simulations were improved by using several constraints coming from previous 11B NMR experiments and Zr K-edge XANES ones.

Based on a series of five-oxide borosilicate glasses of nuclear interest (with Si, B, Zr, Na and Ca species), where zirconium concentration increases from 0 mol% to 8 mol% (0, 1, 2, 4, 6 and 8 mol%), we investigate Zr environment from the structural point of view. At first sight, the shape and location evolution of the main left peaks appearing in reciprocal space reflects changes in coordinate space for the medium range order. In particular, a right shift of the first peak is visible beyond a Zr concentration of 2 mol%, followed by a splitting of the third peak. An explanation of Zr environment evolution in relation with its second and third neighbours, and with Zr-O-X (X=Si, B, Zr) distribution angles is presented.
Moreover, this structural information is used to improve vibrational bands understanding in both polarized and unpolarized Raman spectra for the overall glasses.

Keywords: silicate glass, zirconium, atomistic modelling

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