

X-ray Absorption Studies of Manganese Valence and Local Environment in Borosilicate Waste Glasses

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Beamline: X23A2

Introduction: XANES and EXAFS data were collected and analyzed to characterize the manganese environments in borosilicate glass formulations to be used for immobilization of nuclear wastes. Mn can become a major constituent in some radioactive wastes, due to the use of Mn-compounds in waste pretreatment processes.

Methods and Materials: X-ray absorption fluorescence data, that included the Mn K-absorption edge near 6539 eV, were collected for five powdered crystalline Mn-silicate and Mn-oxide standards, as well as for 16 powdered borosilicate glasses. The glass samples were synthesized in crucible and joule-heated melter environments, where melt REDOX conditions were varied by adding sugar reductant. MnO concentrations for the glasses range from approximately 0.4 to 14 wt.% as determined from quantitative X-ray fluorescence techniques.

Results: Mn XANES data are statistically identical for all glasses investigated, and indicate that most, if not all manganese is divalent in these borosilicate glasses. EXAFS analysis for the glasses indicate average Mn-O distances near 2.07Å, coordination numbers between 5 and 6, and first shell Debye-Waller factors that are larger than those found for the standards. Mn first shell bond distances and coordination numbers for the glasses plot in a range between average r and n distributions found for crystalline silicates with divalent Mn (Fig. 1).

Conclusions: XANES and EXAFS findings indicate Mn⁺⁺ in glass that is most likely in a distribution of environments which may include 4-, 5-, and 6-coordinated sites. EXAFS fitting results show that the average manganese environments in these glasses are statistically invariant with respect to composition, to different melt environments, as well as to various REDOX conditions.

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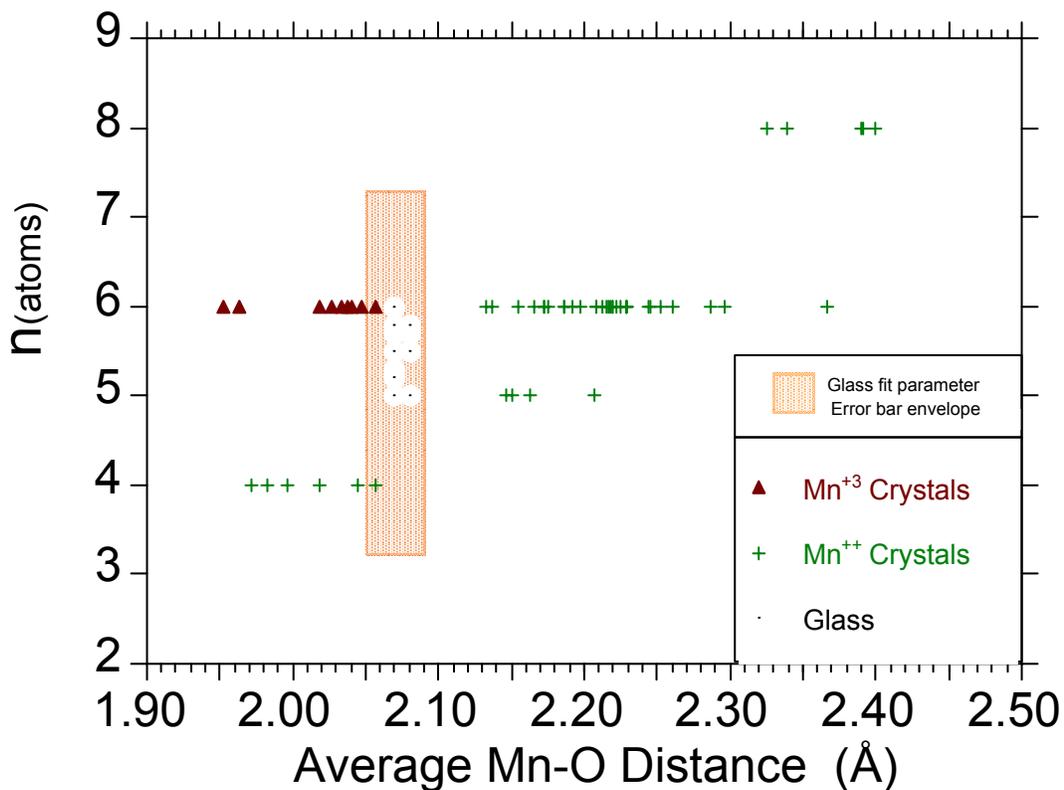


Fig. 1. Average Mn-O first shell distances and coordination numbers of crystalline Mn-silicates and EXAFS fitting results for the glasses investigated.