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Determination of Cr Environments in Borosilicate Glass Formulations used for Radioactive Waste Storage

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Introduction: A variety of first row transition elements typically found in radioactive waste sludges are being incorporated in borosilicate glasses to simulate vitrification processes for long-term radioactive waste storage. A problem frequently observed during vitrification is unwanted crystallization of Fe, Mn, and Cr spinel phases. Different vitrification processes are being devised to control the valence-state of these transition elements in waste glass formulations in order to produce a crystal-free homogeneous glass phase while maximizing waste loading. As a follow-up to an earlier borosilicate glass Cr valence study using XANES, Cr EXAFS data were gathered on the same glasses to more quantitatively determine the Cr coordination environments.

Methods and Materials: The glasses contain approximately 2 wt.% Cr_2O_3 and were synthesized under different redox conditions, where CO gas was bubbled through the corresponding melt at various time intervals. EXAFS data were also gathered for the octahedral Cr crystalline standards: eskolaite (Cr_2O_3) and uvarovite ($Ca_3Cr_2Si_3O_{12}$), as well as for the tetrahedral crystalline standard: crocoite ($PbCrO_4$).

Results: EXAFS fitting results indicate that most of the glasses investigated have average Cr-O distances near 2.00 Å and coordination numbers near 6.0, typical of octahedral Cr. Two of the more oxidized glasses have partial radial distribution functions (RDFs), where the first shell peak is damped compared with that in the RDFs for the more reduced glasses (Fig. 1). The first shell amplitude reduction for the more oxidized glasses can be explained by a two site model. EXAFS fitting results for one of the oxidized glasses indicates a Cr population that has 27% tetrahedral Cr^{+6}, where the average Cr-O distance is 1.62 Å, and 73 % octahedral Cr^{+3}, where the average Cr-O distance is 2.00 Å.

Conclusions: XANES and EXAFS indicate that these borosilicate glasses contain predominantly octahedral Cr^{+3}. Minority populations of tetrahedral Cr^{+6} can be observed in the more reduced glasses.

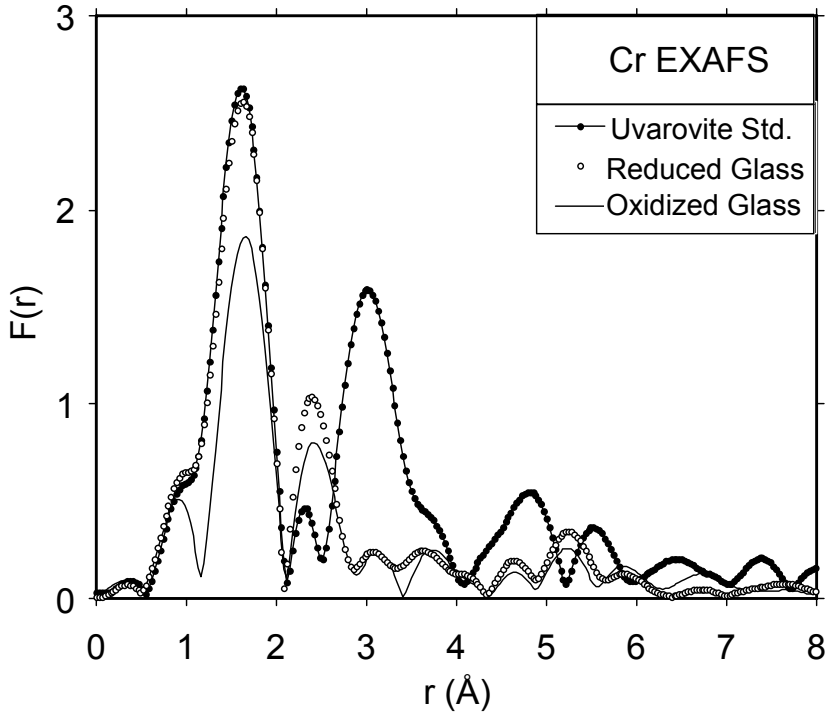

Figure 1. Cr EXAFS data for the octahedral Cr standard Uvarovite (points and line) and for two borosilicate glasses: oxidized (points) and reduced (line).