

Coordination Environments of Highly Charged Cations (Ti, Cr, and Light REE's) in Borosilicate Glass/Melts to 1120°C

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Abstract. The local environments around Ti, Cr, and several light rare-earth elements (La, Ce, and Nd) were investigated by *in-situ* XANES spectroscopy in a number of complex borosilicate glasses and melts (to 1120 °C) that are used for nuclear waste storage. Examination of the high-resolution XANES spectra at the Ti K-edge shows that the average coordination of Ti changes from ~5 to ~4.5. Cr is dominantly trivalent in the melts studied. However, its average coordination is probably lower in the melt (tetrahedral ?) as revealed by the more intense Cr-K pre-edge feature. Ce also changes its average valence from dominantly +4 to +3.5 upon glass melting. These changes are reversible at T_g , the glass transition temperature (~500-550°C for these glasses). In contrast, the local environments of Nd, Pr, and La are unaffected by melting. Therefore, structural reorganization of these borosilicate glass/melts above T_g is variable, not only in terms of valence (as for Ce) but also speciation (Ti and Cr). Both the ability of B to adopt various coordination geometries (triangular and tetrahedral) and the chemical complexity of the glass/melts explain these changes.

Keywords: titanium, chromium, cerium, neodymium, lanthanum, borosilicate, glass, melt, T_g

PACS: 61.10.Ht, 64.70.Dv, 81.40.Gh, 61.43.Fs, 64.70.Pf, 21.65.+f

INTRODUCTION

Borosilicate glasses are wasteform glasses that are candidates for long-term storage of plutonium and other trivalent transuranic elements of high activity [1-3]. In these glasses, cerium is used as a surrogate for plutonium [4]. In addition, highly charged cations such as Ti, Cr, and REE's are thought to enhance nucleation (and form glass-ceramics). As a result, knowledge of the oxidation state and speciation of these elements is critical for assessing the durability of such wasteforms. The response of molten systems to quenching is difficult to predict because of the variable behavior of the different components present in the supercooled liquid. This is particularly significant above T_g (T_g is the glass transition temperature, ~500-550°C for the glasses studied), above which major structural changes can occur [5]. To study these effects, we have carried out *in-situ*, high-temperature X-ray Absorption Fine Structure (XAFS) spectroscopy at the Ti K-, Cr K-, La-L, Ce-L, and Nd L-edges in three selected borosilicate glass/melts to derive direct speciation information around these highly charged elements in silicate glass/melts.

EXPERIMENTAL

XAFS spectra were collected on beamline 4-3 at the Stanford Synchrotron Radiation Laboratory (Stanford, USA), as described in [6]. All XAFS data were collected under high-resolution conditions (SPEAR2 storage ring, 3 GeV, 20-100 mA, Si(220)). We used the XAFS data analysis software package ("xafs"; [7]) to normalize the XANES (x-ray absorption near edge structure) in absorbance. *In-situ*, high-temperature XANES spectra were collected using a heating loop furnace in the fluorescence-yield mode (see [8] for details). Ti and Cr XANES spectra were collected at the K-edge, whereas XANES for REE's were collected at the $L_{2,3}$ edges. Because of the chemical complexity of nuclear waste glasses [3] (and the resulting overlap between K and L edges), only XANES data were collected. Three borosilicate glass/melt systems were investigated. Two were synthesized at the Pacific Northwest National Laboratories ("Pu10B9IN1" and "Pu10Dy'CrSb") and are analogs of wasteform glasses that are candidates for the long-term storage of Pu and

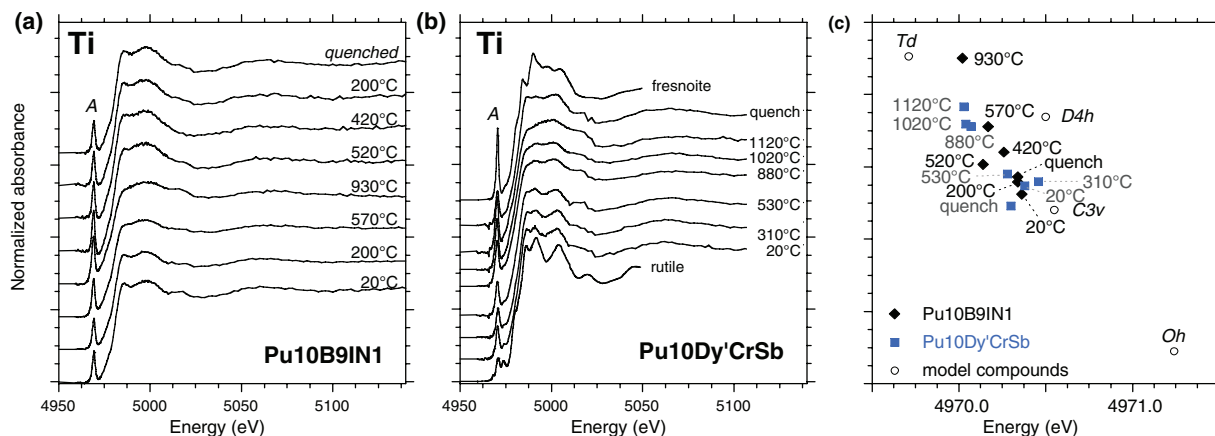


FIGURE 1. (a and b, left and middle) Ti K-edge XANES spectra for the two borosilicate glass/melts to 1120°C (T_g is about 500-550°C). The pre-edge feature is labeled A. (c, right) Refined pre-edge information for the spectra shown in Figures 1a and 1b, as compared to model compounds in which Ti is in various coordination geometries (T_d , D_{4h} , C_{3v} , and O_h).

other trivalent transuranic elements in the USA. The third one (SON68) is an analog of the R7T7 composition, free of artificial actinides (with 27 oxide components; see [3] for composition) used in France for nuclear waste storage. Less than 1 wt. % loss of Na and K were detected (as determined by electron microprobe analysis) after XAFS data collection at high temperature (a maximum of 2 hours was required to complete each XAFS experiment).

Titanium

Figures 1a and 1b show the high-resolution Ti K-edge XANES spectra collected for two borosilicate compositions (Pu10B9IN1 and Pu10Dy'CrSb, respectively) to 1120°C. In Pu10Dy'CrSb, the Ti K-edge XANES at 298K shows that some of the Ti atoms occur in rutile (TiO_2)-type environments (Fig. 1b). Figure 1c shows the refined pre-edge information using the method outlined in [6]). The borosilicate glasses show average pre-edges under ambient

conditions that are consistent with trigonal bipyramidal site symmetry (i.e., 5-coordinated). When the T exceeds T_g (~500-550°C), the pre-edge intensity and position indicate that some Ti occurs in tetrahedral geometry (T_d). This change in speciation above T_g is reversible, suggesting that the glass is not a structural analog of the melt. These results contrast sharply with earlier findings for B-free glass/melts [8], for which no Ti coordination change above T_g was detected.

Chromium

Figure 2 shows the normalized Cr K-edge XANES spectra collected for two borosilicate glass/melts (SON68 and Pu10B9IN1). The main Cr K-edge XANES for SON68 shows changes as a function of T similar to Ti: the main edge crest is broader due to thermal disorder and the pre-edge intensity (feature A in Fig. 2a) increases by a factor of three. Similar speciation changes are observed for Pu10B9IN1 glass/melt system.

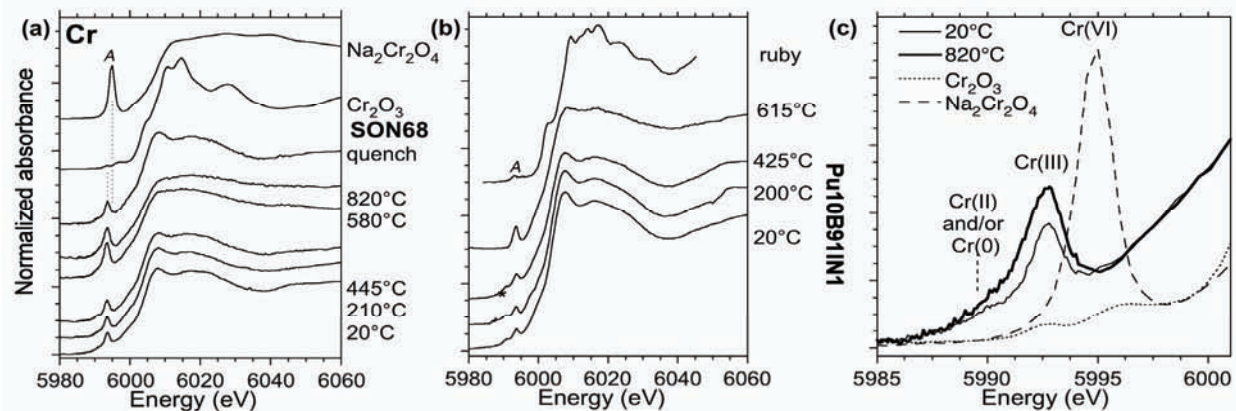


FIGURE 2. Cr K-edge XANES spectra for two borosilicate glass/melts to 820°C (T_g is 500-550°C). The pre-edge feature is labeled A. (c, right) The pre-edge region for the spectra shown in Figure 2a for SON68, compared with Cr-containing models.

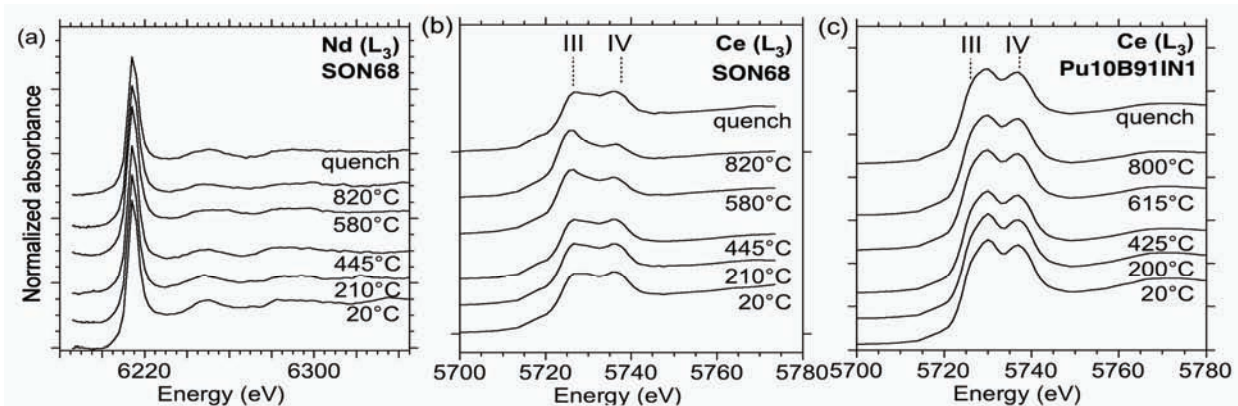


FIGURE 3. Nd and Ce- L_3 edges in SON68 and Pu10B91IN1 glass/melts to 820°C (T_g is 500-550°C). Only SON68 shows structural changes above T_g around Ce; a reversible increase from Ce(III) to Ce(IV) was observed.

Figure 2c also shows the pre-edge feature for SON68 compared to various Cr-containing model compounds. No evidence of oxidation states lower than Cr(III) was found. The pre-edge feature consists of a component arising from Cr(III), but with a less centrosymmetric site (probably C_{3v} , D_{4h} or T_d or some combination of these sites) than that in Cr_2O_3 or in ruby (O_h). Higher valences of Cr were not detected. The pre-edge intensity increases at a constant energy position above T_g , indicating that less centrosymmetric Cr sites are observed in the melt. Such changes are related to an increase in the amounts of Cr(III) with T_d symmetry. As was found for Ti, these structural changes are reversible, suggesting that the Cr local environment is not preserved below T_g .

Light Rare Earths Elements

Figure 3 shows the normalized Nd and Ce L_{III} -edge XANES spectra collected for two borosilicate glass/melts (SON68 and Pu10B91IN1). No detectable changes were observed for Nd (Fig. 3a) or for Pr and La in these systems (data not shown). Only SON68 shows an increase in the relative concentration of Ce(III) relative to Ce(IV) (average valence of 3.5 in the melt). In contrast, the oxidation state of Ce in Pu10B91IN1 remains dominantly tetravalent. The presence of other valence couples in SON68 and their absence in Pu10B91IN1 helps explain the variations in the oxidation state of Ce in these two glasses/melts.

CONCLUSIONS

In the three compositions, major structural reorganizations were observed on quenching around Ti, Cr, and Ce but none around La, Pr, Nd, Pr, and Ce in chemically simpler borosilicate glass/melts, such as Pu10B91IN1. These results contrast with those for B-free melts, in which no changes in Ti speciation were

observed [8]. The possibility that B adopts both triangular and tetrahedral geometries is the most likely reason for these structural changes above T_g . However, the chemical complexity of the glass/melt systems probed also appears to enhance structural reorganization in the glass/melts, as observed at the Ce- L_3 edge in SON68 (but not in Pu10B91IN1 under similar conditions). Quenching has a significant effect on the speciation of these transition elements in borosilicate melts. Thus, their presence in borosilicate melts may induce a structural instability in the glass involving potential nucleation around these elements, especially if radioactive decay locally heats up these systems near T_g (500-550°C).

ACKNOWLEDGMENTS

This study was supported by NSF Grant CHE-0431425 (Stanford Environmental Molecular Science Institute). We wish to thank K. Keefer (PNNL) and P. Trocellier (CEA) for providing the glass samples.

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