Electronic structure of Gadolinium in quenched aluminosilicate melts - insight from 2p3d-RIXS

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Insights to the local structure of atoms in aluminosilicate melts is of great interest for geochemistry, petrology, ceramic and glass technology. In particular for understanding chemical fractionation in crystal-melt equilibria, the local structure of rare earth elements (REE) in dry and hydrous aluminosilicate melts may provide fundamental information and thus a more detailed view on the formation processes of igneous rocks on earth, moon and terrestrial planets. Previous investigations by Simon et. al. (2012) by EXAFS on the local structure around Y in aluminosilicate melt showed that the coordination of Y (representative for heavy REE) is a function of the melt composition and depends on melt polymerisation. They were able to show that the coordination number, the width of the Y-O pair distribution and the average bond length increases with increasing polymerisation [1].

Investigation of the electronic structure of REE in these melts may provide additional information on the local structure. A useful tool to probe the electronic structure of 4f-elements is resonant inelastic x-ray scattering (RIXS) [3]. In RIXS a core-electron is promoted to an excited state just as in XANES but also the energy dependent intensity of the scattered and emitted photons are measured, which gives additional information about the intermediate state, the final state, especially at energies of the pre-edge fine structure, which corresponds to 2p to 4f quadrupolar transitions in the case of lanthanides [3]. The scope of this study is to investigate the electronic structure of Gd in aluminosilicate glasses in order to gain insight into changes in the Gd coordination as a function of glass composition.

The studied ASI glass compositions were taken from [2] varying in the aluminium saturation index (ASI, molar ratio of $Al_2O_3/(Na_2O+K_2O+CaO)$) from 0.115 to 0.768, dry haplogranitic (HPG) compositions (ASI = 0.6 to 1.2) and hydrous HPG compositions (4 wt% H_2O). The glasses were synthesized from oxides and carbonates and doped with 2 wt% Gd. The hydrous HPG compositions were synthesized at 2 kbar in an internally heated pressure vessel (IHPV). 2p3d-RIXS and XANES have been collected for Gd_2O_3 and several Gd-doped aluminosilicate glasses at beamline W1 employing a Johann Spectrometer with a Rowland circle of 1 m and using a spherically bent Si(620) analyzer crystal.

The collected 2p3d RIXS of the pre-edges for ASI glasses (Fig. 1), the dry and hydrous HPG glasses (Fig. 2) show weak but distinct pre-edge features, which are probably related to quadrupolar transitions. The maximum of the pre-edge shows a slight shift to higher energy transfer (ET) with increase of the polymerisation for the ASI, the dry and the hydrous HPG glass compositions, respectively. In contrast, the maximum of the pre-edge for the hydrous HPG is shifted to lower ET compared to the dry HPG for a given composition. The preliminary results indicate that differences in the electronic structure are related to slight differences in intra-atomic multiplet splitting and thus to differences in chemical bonding and Gd site symmetry. The spectra extracted at constant excitation energy (over 2 eV) along the energy transfer axis for the different glass compositions (Fig. 3) show a more quantitative view of the pre-edge shift. The results obtained by a Gaussian fit of the pre-edge maximum show that the position of the maximum for ASI glasses shift by 0.3±0.03 eV from ASI 200 to ASI280, by 0.3±0.03 eV from the dry HPG06 to HPG12 and by 0.2±0.03 eV from the hydrous HPG06 to HPG12. Furthermore, the position shifts by 0.1±0.03 eV between dry HPG06 and hydrous HPG06, for hydrous HPG10 and HPG12 no difference was noticeable. The observed changes go along with structural differences obtained by EXAFS.

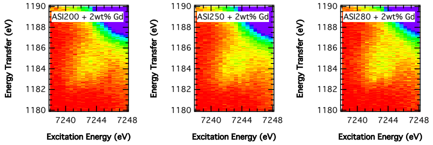

Figure 1: 2p3d RIXS for the ASI glasses collected around the pre-edge region of Gd L_3-edge.

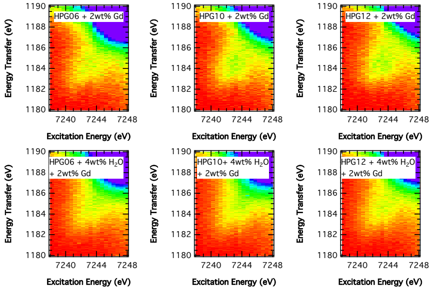

Figure 2: 2p3d RIXS for the dry and hyrous HPG glasses around the pre-edge of Gd L_3-edge.

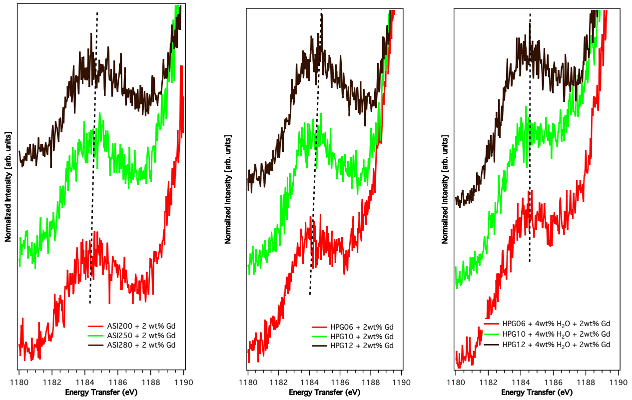

Figure 3: Cross sections of the 2p3d-RIXS at constant excitation energy integrated from 7242 eV to 7244 eV for ASI glasses (left), dry HPG (middle) and hydrous HPG (right).

References

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