ESRF	**Incorporation of rare earth elements in quenched silicate melts at trace element level**	**Experiment number**: EC 827
Beamline: ID24	**Date of experiment**: from: 8.6.11 to: 14.6.11	**Date of report**: 24.8.12 *Received at ESRF:*
Shifts: 18	**Local contact(s)**: Kristina Kvashnina	

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Report:

The scope of this study is the local structure around Rare Earth Elements (REE) in quenched alumino-silicate melts. XANES, EXAFS and RIXS measurements at room temperature were performed at the La, and Gd L_3 edge for model compounds ($^{[6]}La_2O_3$, $^{[9]}LaN_3O_9*6H_2O$, $^{[6]}LaCl_3$, $^{[6]}Gd_2O3$, $^{[9]}GdN_3O_9*6H2O$, $^{[6]}GdCl3$) and a set of glass compositions taken from Prowatke and Klemme (2005). The studied melt compositions vary in the aluminium saturation index (ASI, molar ratio of $Al_2O_3/(Na_2O+K_2O+CaO)$) from 0.115 to 0.755.

The spectra were collected at the ID 26 using a Si(111) monochromator crystals for high flux. XANES and EXAFS spectra on model compounds were recorded in transmission mode. RIXS, XANES and EXAFS spectra on the glasses were recorded using the high-resolution wave-length dispersive spectrometer with one spherically bent Si(440) analyzer crystal for La and four spherically bended Ge (422) analyzer crystals for Gd.

Here only the Gd data are shown. RIXS spectra for both, model compounds (Fig.1) and glasses (Fig.2) show slightly different pre-edge features, which are probably related to quadrupolar transitions. The preliminary results indicate that differences in the pre-edge are related to slight differences in intra-atomic multiplet splitting and thus to differences in chemical bonding and Gd site symmetry.

Furthermore, the extracted high resolution XANES (Fig. 3) for the model compounds, show significant differences in the main edge structure reflecting the different coordination of the nearest neighbors, which is also present in differences of the EXAFS.

For the quenched glasses, high resolution XANES (Fig. 3, right) show that the maximum of the pre-edge shifts to lower energies and increases slightly in intensity with increasing ASI. These changes might be related to an increase of the Gd-O distance as indicated by the shift of the maximum at 7285-7295 eV in the XANES to lower energies (Fig. 3, right) and a slight shift of first maximum of the EXAFS Fourier-transform (Fig. 4).

Overall all spectra indicate that the Gd coordination changes with melt composition.

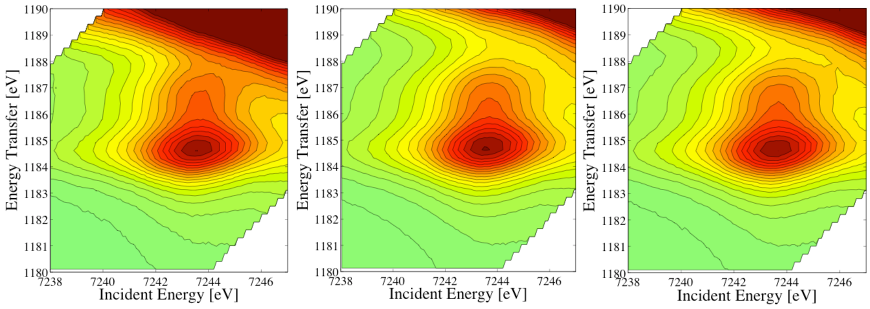

Figure 1: 2p3d RIXS collected around Gd L_3 pre-edge for Gd_2O_3 (left), GdN_3O_9*6 H_2O (middle) and $GdCl_3$ (right). Minor differences in position and shape are related to slight differences in site-symmetry of Gd.

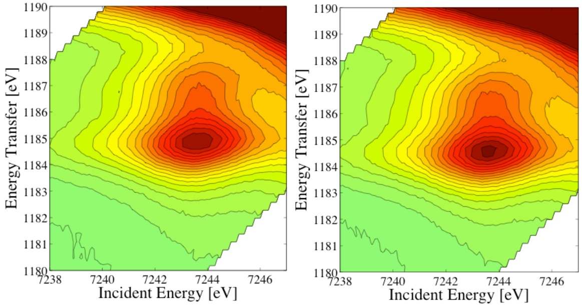

Figure 2: 2p3d RIXS collected around Gd L_3 pre-edge on quenched glasses (left) ASI200 (right) ASI260.

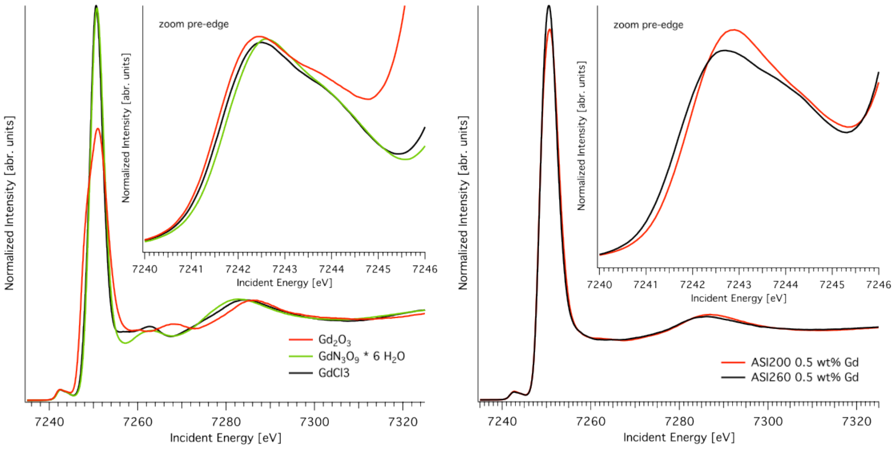

Figure 3: High resolution XANES of model compounds (left) show slight differences in the pre-edge and significant differences in the main edge structure due to different crystal structure and chemistry; for the glasses (right) the pre-edge and the main edge structure indicate change in bond length and symmetry.

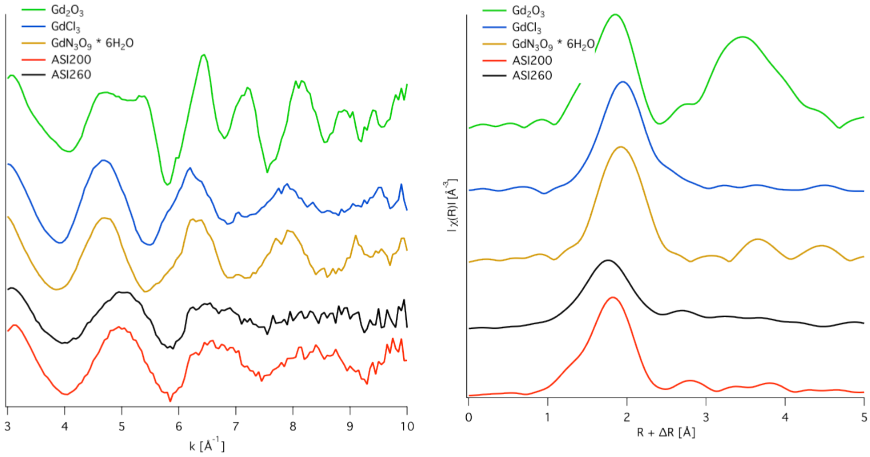

Figure 4: k^3-weighted EXAFS (left) and Fourier-transform (right) of Gd at the L_3-edge for model compounds and glasses. (Fourier-transform uncorrected for phase-shifts).

References: Prowatke & Klemme (2005) Geochim. Cosmochim. Acta 69, 695-709.

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