

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

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Studying trace elements (TE) partitioning data provides useful information about the formation processes of igneous rocks on earth, moon and terrestrial planets, and thus knowledge on their partitioning behaviour during melt crystallisation is essential. Temperature, pressure, crystal chemistry and melt compositions are well known parameters that control the partitioning of TE between coexisting phases (e.g. [1]). In particular, the trace element partition coefficients of Provatke and Klemme's [2] between melt and titanite suggest a strong control of the melt composition, because they vary over several orders of magnitude at constant crystal composition. Only little is known about structural changes in the local environment of these trace element that accompany these huge variations, especially for rare earth elements (REE). EXAFS data on Y ([3], [4]) and preliminary EXAFS of Gd and Yb in a suite of melt compositions similar to those of [2] show a considerable change in the structural environment of these elements. Investigation of the electronic structure of the REE in these melts provides additional information for understanding the influence of the melt composition on the local structure of these elements. A useful tool to probe the electronic structure of 4f-elements is resonant inelastic x-ray scattering (RIXS) [4]. 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, and the pre-edge fine structure. The pre-edge corresponds to 2p to 4f quadrupolar transitions in the case of lanthanides [4]. The scope of this study is to investigate the electronic structure of Yb in aluminosilicate glasses in order to gain insight into changes in the Yb coordination as a function of glass composition.

The studied melt compositions were taken from [2] varying in the aluminium saturation index (ASI, molar ratio of $\text{Al}_2\text{O}_3/(\text{Na}_2\text{O}+\text{K}_2\text{O}+\text{CaO})$) from 0.115 to 0.755. The glasses were synthesised from oxides and carbonates and doped with 2wt% Yb. 2p3d-RIXS and XANES have been collected for Yb_2O_3 , $\text{Yb}_3\text{Al}_5\text{O}_{12}$ and several Yb-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 RIXS of the pre-edges for the model compounds (Fig. 1) and glasses (Fig. 2) show weak but different pre-edge features, which are probably related to quadrupolar transitions. 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 Yb site symmetry. Similar to the RIXS, The extracted high-resolution XANES spectra for the model compounds (Fig. 3) reflect the difference in the structural environment of Yb, which is regular ^[6]Yb for Yb_2O_3 and regular ^[8]Yb for $\text{Yb}_3\text{Al}_5\text{O}_{12}$. For the glasses (Fig. 4) the pre-edge shifts to slightly higher energies and increases slightly in intensity with increasing ASI. These changes may be assigned to an increase of the Yb-O distance as indicated by the shift of the maximum at 8980-8990 eV together with a potential change in coordination. For Y, an element chemically quite similar to Yb, an increase in the distance to the nearest oxygen neighbours and a change of the coordination from 6 to 8 was found for the same suite of glass compositions [3], [4]. We were able to show that the electronic structure of Yb changes with melt composition. To quantify the results calculation of spectra is needed to interpret the data.

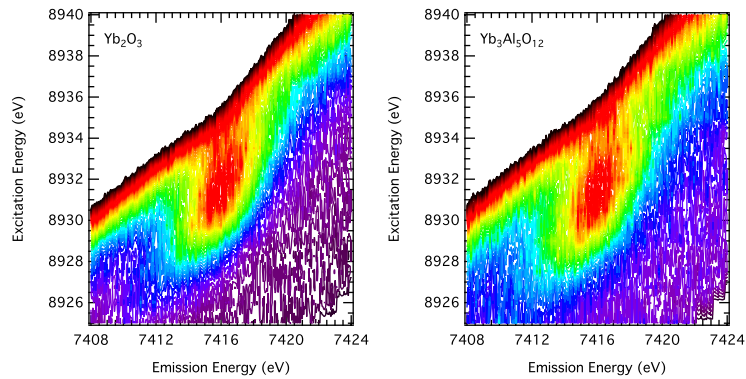


Figure 1: 2p3d RIXS for the model compounds collected in the pre-edge region of the Yb L₃-edge.

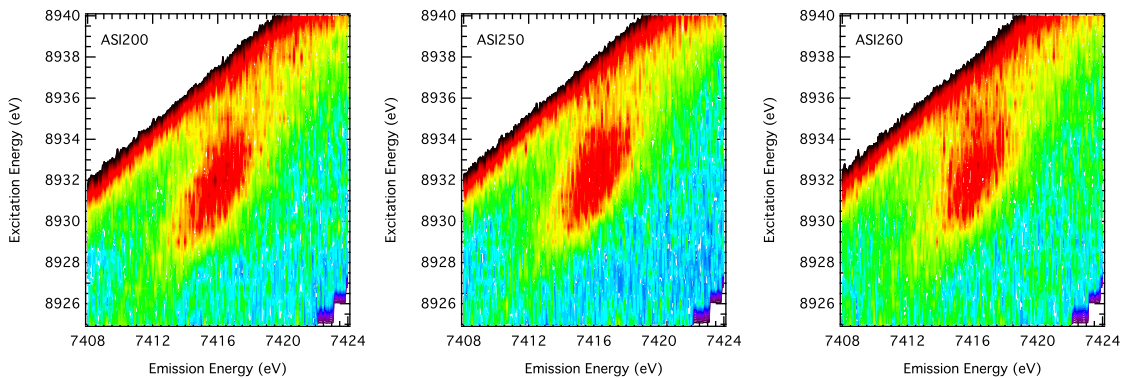


Figure 2: 2p3d RIXS for the glasses at the pre-edge of the Yb L₃-edge.

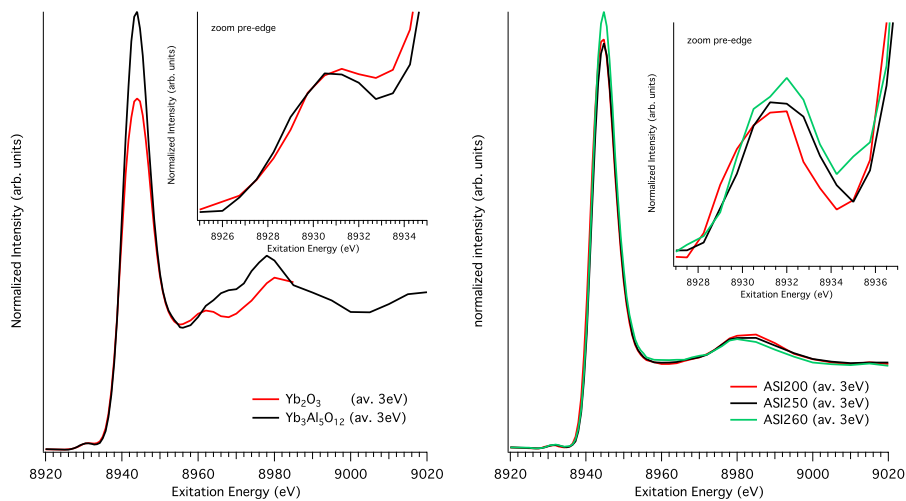


Figure 3: High resolution XANES (averaged over 3eV of the emission spectrum) for the model compounds (left) show differences in the pre-edge and near edge structure which is due to the different coordination; for the glasses (right) the pre-edge and the near edge structure indicate change in bond length and site symmetry.

References

- [1] J. Blundy, B. Wood, Earth Planet. Sci. Lett. 210, 383–397 (2003).
- [2] S. Provatke, S. Klemme, Geochim. Cosmochim. Acta 69, 695-709 (2005).
- [3] S. Simon, M. Wilke, S. Klemme, R. Chernikov, HASYLAB Annual Report (2011).
- [4] S. Simon, M. Wilke, S. Klemme, R. Chernikov, Chem. Geol. (submitted)
- [5] Kvashnina, K. O., Butorin, S. M. and Glatzel, P. (2011) J. Anal. At. Spectrom. 26,1265-1272.