In situ local structure around yttrium in aluminosilicate melts at high temperature

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Knowledge on the local structure around rare earth elements (REE) in aluminosilicate melts is of great interest for the geochemistry of magmatic processes, particularly for understanding the partitioning of REE between melt and coexisting crystals in a more comprehensive way ([1],[2]). However, the high-temperature (HT) local structure around REE in melts is still not well constrained because in situ characterization at high temperature is a technically challenging task. Therefore, the local structure of REE in melts is usually studied in glasses, with the assumption that the local structure in glasses corresponds to the structure above the glass transition temperature (T_G) in the melt. Several authors reported that this is not invariably the case depending on the element of interest. The scope of this work is to investigate in situ the local structure of yttrium in silicate and aluminosilcate melts and thus to verify the results of [1] on the local structure of yttrium in aluminosilicate glasses, particularly the dependence of the local environment on melt composition.

The studied melt compositions ASI200 and ASI60 were taken from [2], synthesized from oxides and carbonates and doped with 2wt% Y. To collect high temperature EXAFS spectra the glass samples was fixed in the crunch of a resistance heater and heated stepwise to temperatures above T_G (max. 1200 K)[3]. The spectra at the Y K-edge (17038 eV) were collected at beamline C. A Si(111) fixed-exit two-crystal monochromator was used. The spectra were analyzed using the software Athena and Artemis [4]. Amplitudes and phase shift were calculated using Feff6 and checked on crystalline Y_2O_3. For Y_2O_3, HT-EXAFS spectra were collected to test the fitting model at HT and to verify backscattering phase shifts and amplitudes obtained by Feff. Due to large static disorder and non-Gaussian pair distributions in melts and glasses an asymmetric gamma-like distribution function was used to model the Y-O pair correlation of the first coordination shell in the glasses/melts.

The k^3-weighted EXAFS spectra of every temperature step of ASI200 and ASI260 are shown in Fig. 1 together with the resulting fit. The EXAFS amplitude decreases considerably from room temperature up to 1173 K for both compositions. ASI200 shows a stronger decrease of the amplitude with increasing temperature. The average bond length is plotted versus temperature in Fig. 2. The obtained average bond length shows a linear increase to 968 K for ASI200 and to 1024 K for ASI260, the change of the slope at this temperature indicates T_G. The analysis of the EXAFS data shows that there are no major changes in the local structure during the transition from glass to melt. The average bond length, the skewness and the asymmetry of the pair distribution function of Y-O increase according to the thermal expansion in the glassy state and to increase of disorder

above T_G. We were able to show that the local structure above T_G correspond well to the one of yttrium in quenched melts ([2]).

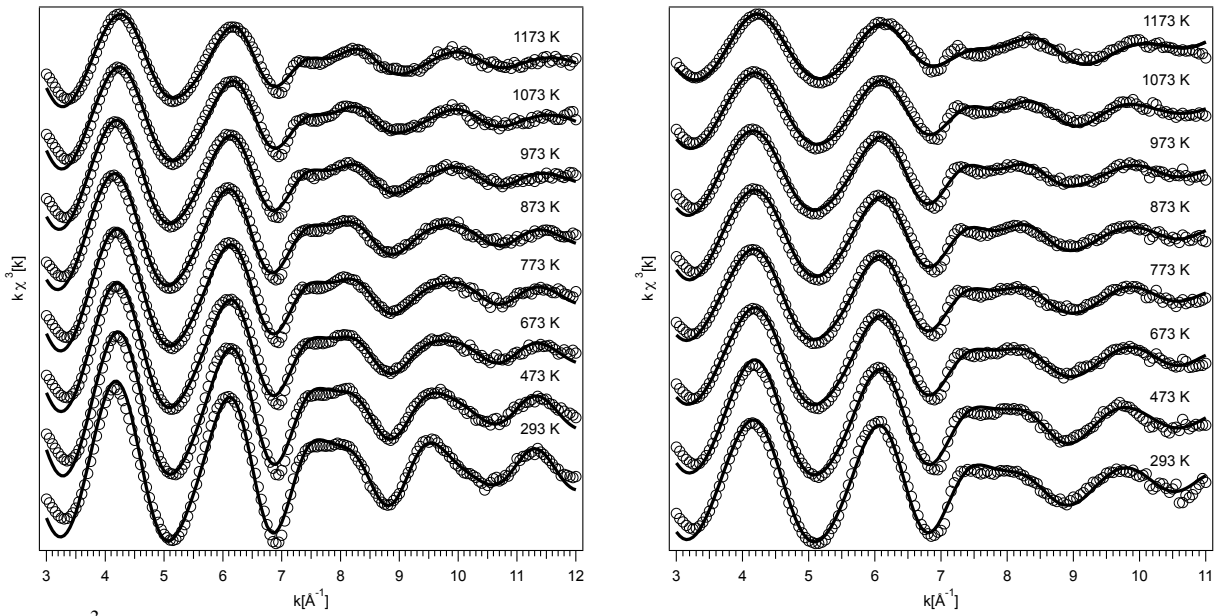

Fig. 1: k^3-weighted EXAFS for ASI200 (left) and ASI260 (right) of Y at the K-edge in aluminosilicate glasses/melts (2 wt% Y). Markers indicate data points and solid lines the fit.

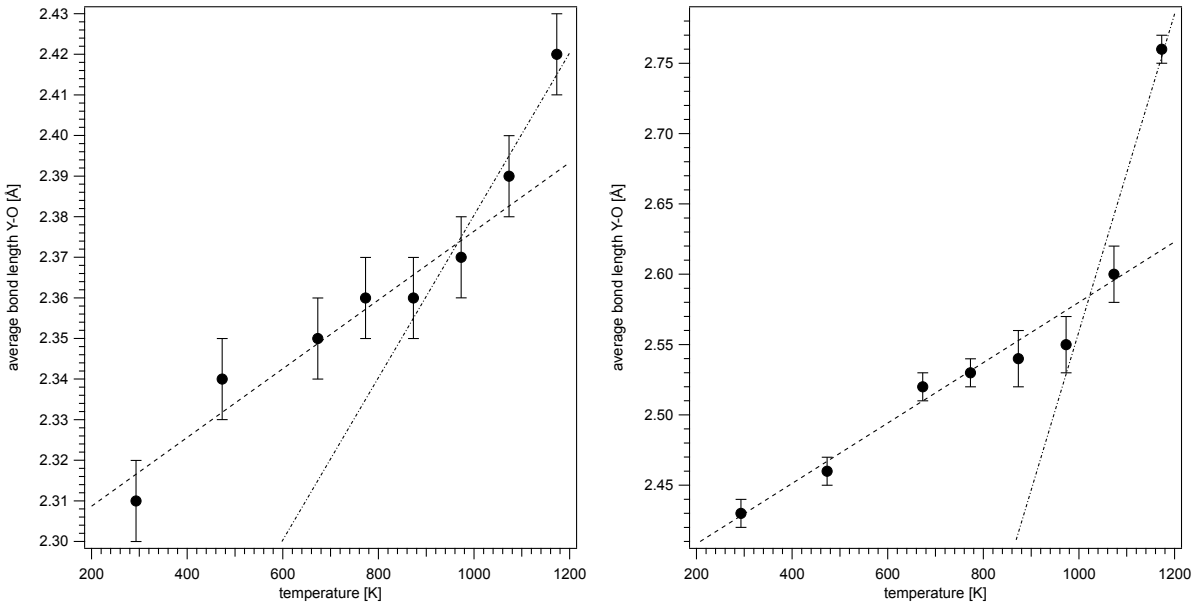

Fig. 2: Average Y-O bond length for ASI200 (left) and ASI260 (right) plotted against the temperature, the change of the slope indicates T_G.

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