ESRF	**Experiment title:** Characterization of Mo species in Mo-rich nuclear waste glass simulates by high energy resolution X-ray absorption spectroscopy	**Experiment number:** EC-1081
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Shifts: 18	**Local contact(s):** Kristina Kvashnina	

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Report:

Highly radioactive liquid waste (HLW) from nuclear fuel reprocessing is commonly immobilized in borosilicate glass matrices to generate a disposable waste form. Homogeneous incorporation into borosilicate glass matrices of molybdenum present in high concentration in reprocessing waste is challenging [1]. Mo(VI) shows a very low solubility in borosilicate glasses and tends to separate into molybdate-rich phases during the vitrification process. These phases may crystallize during the cooling period of the glass melt and can incorporate significant amounts of radioactive isotopes within their crystal structure. However, the chemical composition of the formed phases is strongly dependent on the composition of the borosilicate glass used, as well as the applied conditions within the vitrification process. If water soluble phases such as alkali molybdates are formed, the release of radioactivity into the environment will be facilitated in case of water intrusion into a deep geological repository. Understanding of the formation behavior of Mo(VI) phases in borosilicate glasses allows the development of glass compositions capable to incorporate high Mo loadings, yet avoiding the formation of water soluble phases. Mo K-edge high-energy resolution fluorescence detected X-ray absorption near edge structure (HERFD-XANES) investigations have been performed to characterize the local coordination environment of Mo(VI) in nuclear waste simulates with varying MoO_3 concentrations vitrified in a multi-component borosilicate (‘VPC’) glass.

Experimental details:

Mo K-edge (20 keV) HERFD-XANES measurements of 23 powdered glass samples with various MoO_3 (0.5, 1, 2, 3, 4, 4.5, 5, 5.5, 6, 7, 8 and 12 wt%) and Nd_2O_3 (0 and 8.4 wt%) contents and ten different crystalline (MoO_2, MoO_3, $CaMoO_4$, $BaMoO_4$, Na_2MoO_4, $MgMoO_4$, Li_2MoO_4) and amorphous (Ba-, Na- and Ca-borosilicate glasses containing 1 wt% MoO_3) reference compounds pressed as pellets were performed applying a five analyzer crystals spectrometer at the ID26 undulator beamline at ESRF. For the experiments the primary

X-ray beam was monochromatized by a Si(311) double crystal monochromator. The emitted Mo Kα fluorescence was diffracted by five bent Ge(999) crystals at 77.74° Bragg angle and focused on a Ketek SD detector.

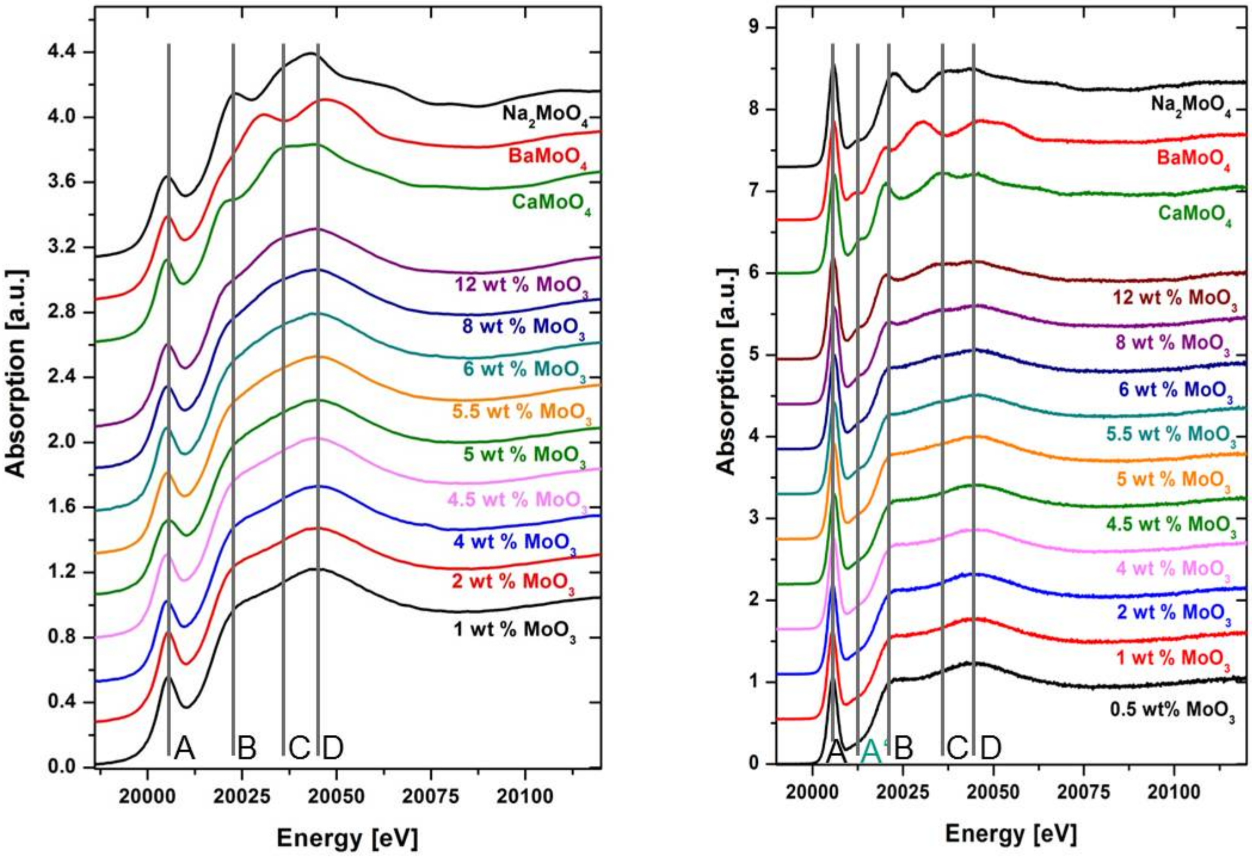

Fig. 1: standard Mo K-edge XANES (left) and HERFD-XANES (right) spectra of glasses with varying MoO_3 concentrations and crystalline molybdates;

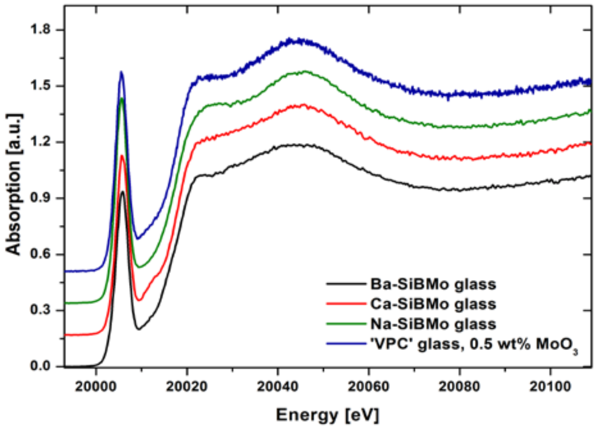

Fig. 2: Mo K-edge HERFD-XANES spectra of 0.5 wt% MoO_3 in 'VPC' glass or 1 wt% MoO_3 in simplified borosilicate glass with Ca/Ba/Na charge compensating cation.

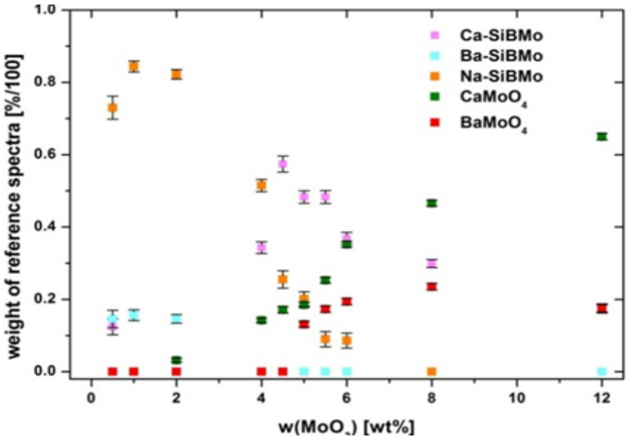

Fig. 3: Weight of reference spectra describing the glass spectra as a function of increasing MoO_3 loadings in the glass.

Results and discussion:

The Mo K-edge HERFD-XANES provides more detailed spectra in comparison to the standard XANES technique by overcoming experimental and core-hole lifetime broadening effects. [2,3] The Mo K-edge HERFD-XANES and standard XANES spectra measured in transmission mode at the INE-Beamline, ANKA, Karlsruhe ([4]), Germany, of multi-component borosilicate glasses ('VPC glasses') containing varying MoO_3 loadings are shown in Fig. 1 together with the spectra of crystalline $CaMoO_4$, $BaMoO_4$ and Na_2MoO_4 as reference compounds. The spectral features of the HERFD-XANES (Fig. 1 right) are more pronounced compared to the standard measurements (Fig.1 left). For example, the pre-edge feature A is more intense and feature A' is observable only in the HERFD-XANES spectra. The Mo K-edge HERFD-XANES spectra of borosilicate glasses containing 1 wt% MoO_3 and one type of network modifier (Ca^{2+}, Ba^{2+} or Na^{+} designated as Ca-SiBMo, Na-SiBMo and Ba-SiBMo, respectively) and a 'VPC' glass containing 0.5 wt% MoO_3 (see Fig. 2) exhibit different spectral features indicating increased sensitivity to minor changes of coordination environment around dissolved molybdate groups.

The shape of the spectral features of the glass spectra change systematically as a function of the MoO_3 concentration (see Fig.1 right). Visual inspection shows that the spectrum of the glass with the highest MoO_3 loading (12 wt%) resembles that of crystalline $CaMoO_4$. By modeling the HERFD-XANES spectra of the glasses by linear combination least squares fit analyses, the evolution of the Mo(VI) coordination structure with increasing MoO_3 content was quantified. The $CaMoO_4$, $BaMoO_4$, Ca-SiBMo, Na-SiBMo and Ba-SiBMo reference HERFD -XANES were used in modeling the data. This choice of reference compounds for the fits was based on results obtained from SEM-EDX, powder X-ray diffraction (XRD) and Raman spectroscopic analyses. XRD and Raman studies confirmed formation of crystalline $CaMoO_4$ and $BaMoO_4$ phases for MoO_3 concentrations above 4 wt%. These phases are associated with spherically shaped regions on the glass surface, which increase in size with increasing MoO_3 content, and shown in SEM-EDX to be rich in Ca, Ba, Mo and O.

The results of the HERFD-XANES fits are depicted in Fig. 3. For low MoO_3 concentrations an amorphous environment dominates and Na^{+} cations preferably compensate molybdate charge over Ba^{2+} and Ca^{2+}. With increasing MoO_3 concentration, the favored Mo atomic environment shifts from amorphous to crystalline and $CaMoO_4$ and $BaMoO_4$ phases form. At the highest MoO_3 concentration crystalline $CaMoO_4$ dominates, as expected from visual inspection of spectra. We find no evidence for the formation of water soluble crystalline alkali molybdates, indicating that the chemical composition of the glass used is favorable for immobilization of Mo-rich nuclear waste with this specific chemical composition.

References:

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