Impact of increasing $Cs_3PMo_{12}O_{40}$ loading on vitrification properties of multicomponent borosilicate glass

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One option to deal with solid Mo(VI)- and Cs(I)-rich residual material remaining in tanks after vitrification process of high level liquid waste (HLLW) is the immobilisation in borosilicate glass for ultimate disposal. Due to its low solubility in borosilicate glass melts, Mo(VI) tends to form molybdate-rich phases during the vitrification process [1]. These phases may crystallize during melt cooling and are able to incorporate radionuclides within their crystal structure. If water-soluble alkali molybdates are formed, the release of radioactivity into the environment will be facilitated in case of water intrusion into a deep geological repository. The chemical composition of the formed phases depends strongly on the used borosilicate glass composition. Understanding factors favouring the formation of stable crystalline Mo(VI) phases in borosilicate glasses allows development of glass compositions capable of incorporating high Mo loadings.

In this project a multi-component borosilicate glass [2] was prepared with varying loadings of simulated nuclear waste residues (NWR), with $Cs_3PMo_{12}O_{40}$ and ZrO_2 as main components, and characterized by several techniques. Powder X-ray diffraction (XRD) and Raman spectroscopy studies confirm formation of crystalline $CaMoO_4$ and $BaMoO_4$ phases for total MoO_3-concentrations above 5.3 wt%. Linear combination least squares fit analyses of Ba L3 edge X-ray absorption near edge structure (Ba-L-XANES), performed at ANKA synchrotron facility Karlsruhe, and Raman spectra permit a quantitative estimation of the degree of crystallinity as a function of the MoO_3-concentration. Scanning electron microscopy (SEM) and energy-dispersive X-ray spectroscopy (EDX) show for 5.3 wt% MoO_3-loading formation of spheres with diameters of about 500 nm containing increased Mo, Ba and Ca content compared to the glassy matrix.

We have conducted micro X-ray fluorescence (μ-XRF), μ-Mo-K-XANES and μ-XRD experiments at the P06 beamline, PETRAIII, Hamburg. The size of the beam was about 500 x 500 nm and was generated by a 2 m undulator (U32-2) while the energy for XRF (XRD) measurements was calibrated to 20100 eV (20000 eV). For detection, a Si-drift Vortex detector (PILATUS 300k/1M detector, pixel size 172 x 172 μm) was used. Data evaluation was done by using the PyMCA (version 4.5.2) software. These studies give access to the elemental, Mo speciation and crystalline distribution in the glass products with 500 nm spatial resolution. For example, Mo rich (Figure 1, red) and Mo depleted regions (Figure 1, blue) are identified and correlated to X-ray diffraction patterns (Figure 2) in an aluminosilicate glass section. The combination of both techniques allows to characterize crystalline regions with high $CaMoO_4$ content. We are in a process of identifying the crystal phase with low Mo content. No evidence for formation of crystalline water soluble alkali molybdates is found, indicating that the chemical composition of the glass composite material used could be favourable for immobilization of Mo-rich nuclear waste with this specific chemical composition.

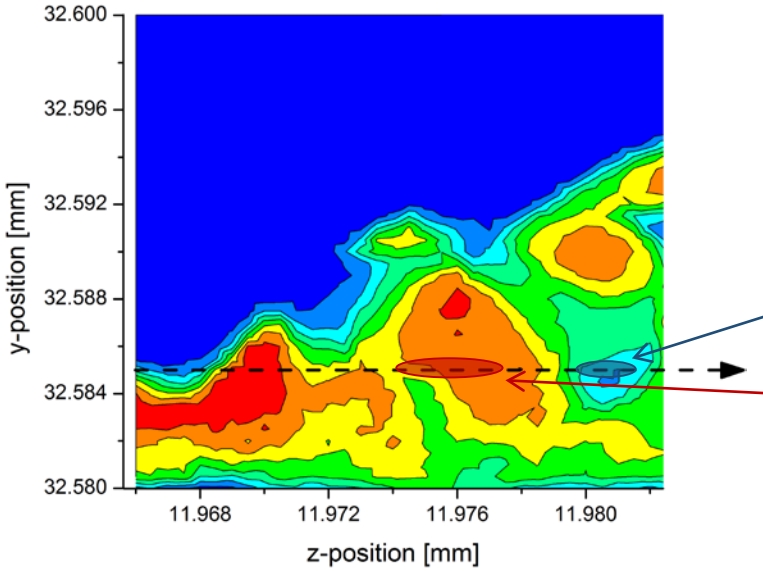

Figure 1: Mo Kα X-ray fluorescence map of an alumosilicate glass section showing the breaking edge of the glass sample. A XRD linescan was performed along the dashed line. The corresponding diffraction patterns are shown in Figure 2.

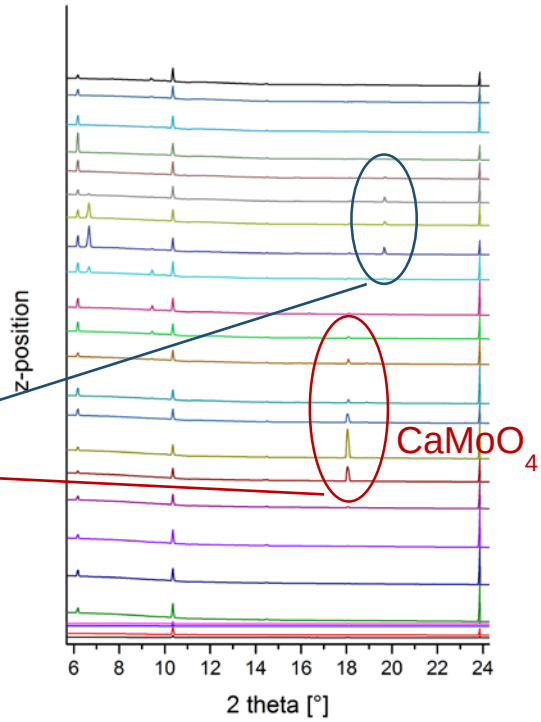

Figure 2: XRD patterns measured with 1 µm step size and 20 keV energy along the dashed line in Figure 1. The found two crystalline phases are marked with red and blue

References

[1] W. Lutze and R. Ewing (1988). Radioactive Waste Forms for the Future. Amsterdam: Elsevier Science Ltd.

[2] W. Grünewald, G. Roth, S. Hilpp, W. Tobie, A. Salimi, S. Weisenburger and B. Brendebach, Proceedings of Global 2009, Paris (2009).