Diploma thesis

Karlsruhe Institute of Technology

Institute for Nuclear Waste Disposal (INE)

Spectroscopic and microscopic investigations of vitrified simulated nuclear waste residue

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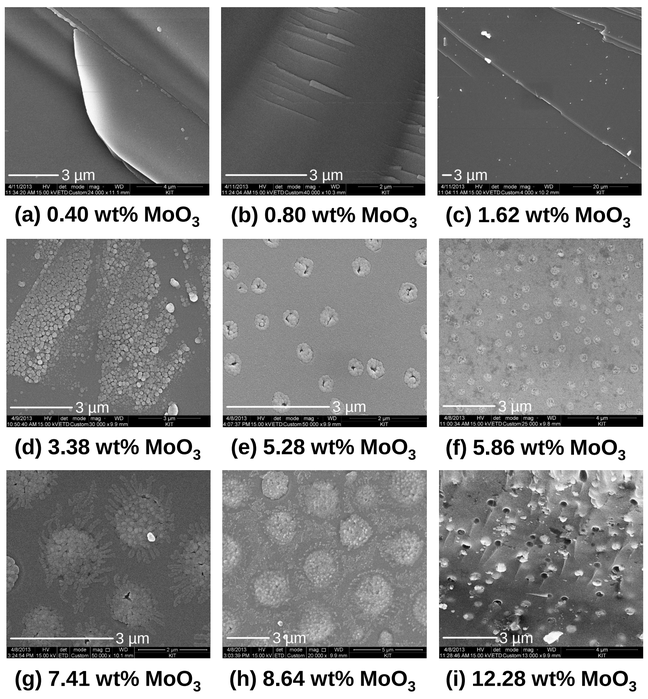
Introduction

Long term storage of Mo-rich liquid nuclear waste leads to formation of insoluble precipitate (main component: $Cs_3PMo_{12}O_{40}$) [1]. Immobilization by vitrification of this Mo-rich compound is a challenge due to phase separation during the vitrification process [2]. Mo-content limits waste loading of the glass and thereby causes large quantities of waste. Several borosilicate glass systems were used to vitrify a simulate of nuclear waste residue. The products have been investigated by several spectroscopic and microscopic techniques. The obtained results will reliably predict the formed products in case of water intrusion in a nuclear waste repository and thereby will help to verify thermodynamic models applied in risk assessment of a long term repository.

EDX-SEM and Raman/XRD



(a) 0.40 wt% MoO_3 (b) 0.80 wt% MoO_3 (c) 1.62 wt% MoO_3

(d) 3.38 wt% MoO_3 (e) 5.28 wt% MoO_3 (f) 5.86 wt% MoO_3

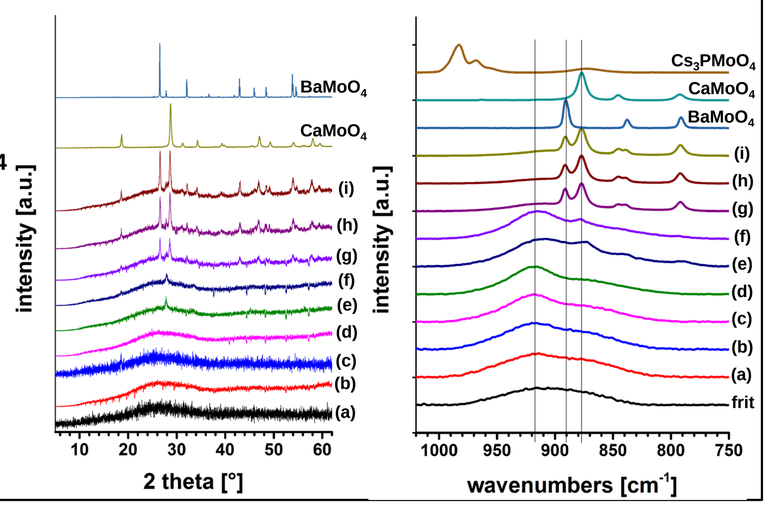
(g) 7.41 wt% MoO_3 (h) 8.64 wt% MoO_3 (i) 12.28 wt% MoO_3

(a) – (i): SEM images of vitrified simulated nuclear waste samples with increasing MoO_3-content:

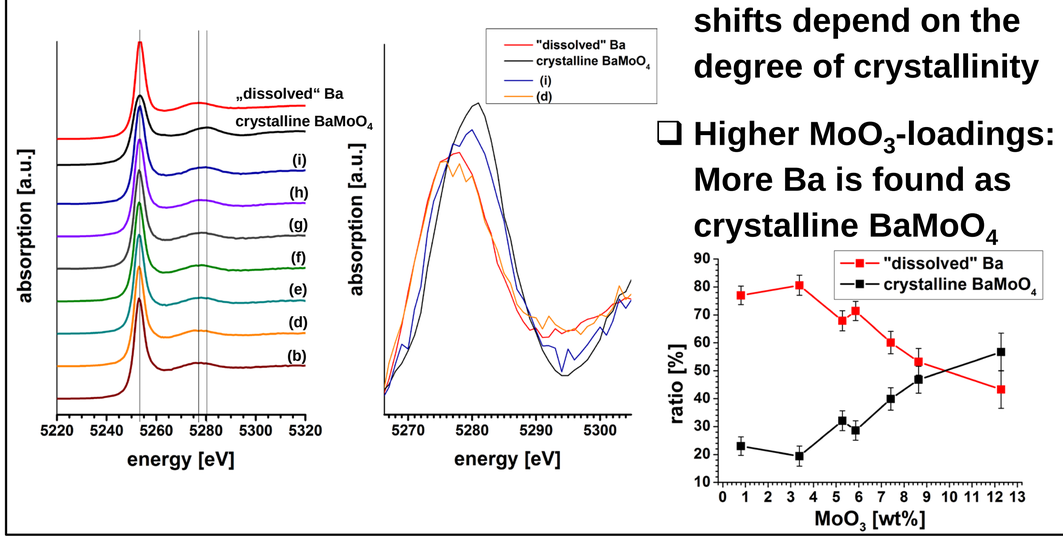
- ❑ **Formation of spherical crystalline phases with high Mo, Ba and Ca content**
- ❑ **Diameter varies from 80 nm – 2.45 µm depending on the cooling rate**

XRD and Raman:

- ❑ **Formation of crystalline $CaMoO_4$ and $BaMoO_4$ for 5.28 wt% MoO_3-loading**
- ❑ **No evidence for formation of water soluble $NaMoO_4$**

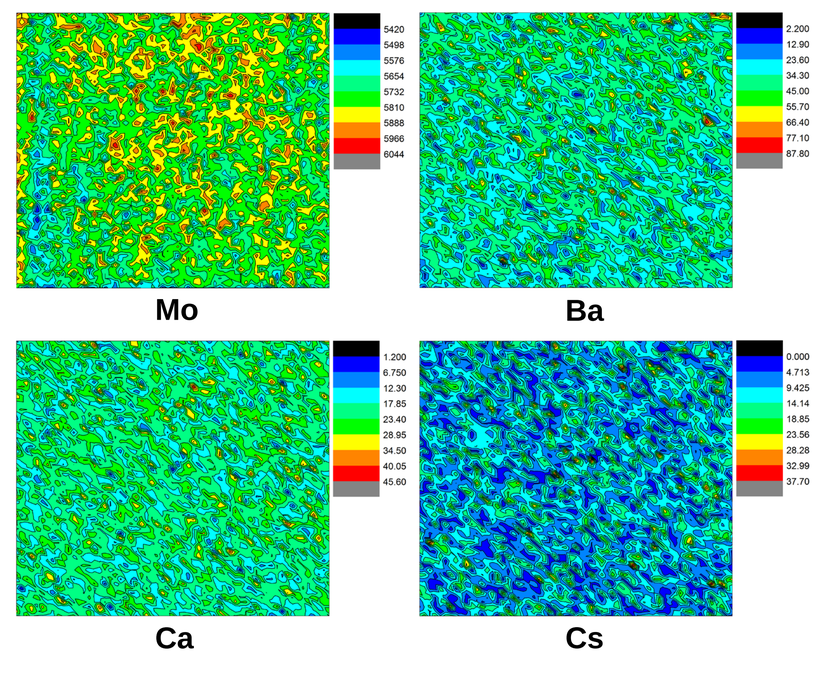


Ba L_3-edge XANES



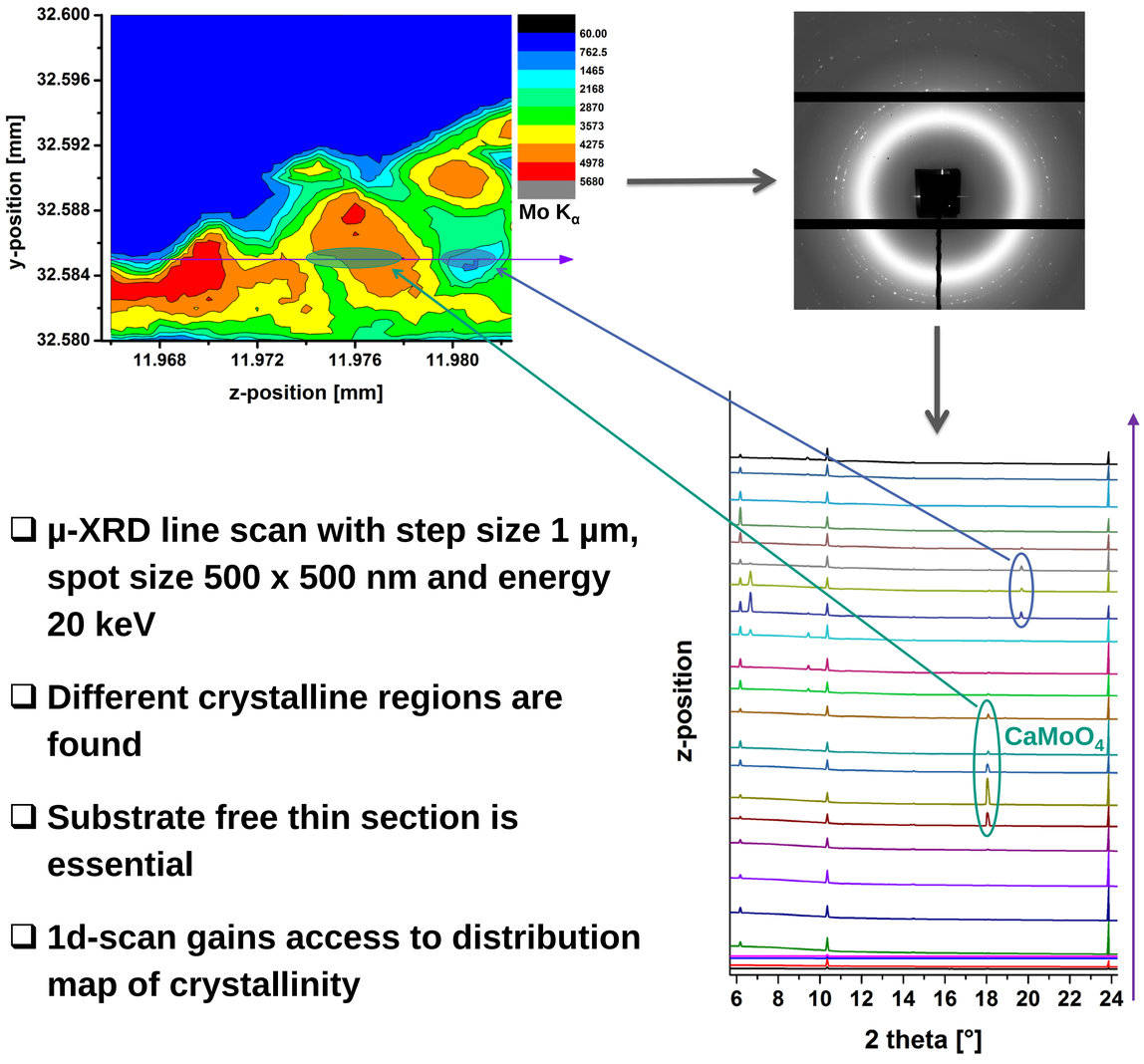
- ❑ **The post–edge resonance shifts depend on the degree of crystallinity**
- ❑ **Higher MoO_3-loadings: More Ba is found as crystalline $BaMoO_4$**

µ-XAS and µ-XRD



15 µm x 15 µm elemental distribution maps of a ~70 µm thin section, 5.86 wt% MoO_3:

- ❑ **No clear correlations found**
- ❑ **Experiments performed with 500 nm spatial resolution at P06, PETRAIII**



- ❑ **µ-XRD line scan with step size 1 µm, spot size 500 x 500 nm and energy 20 keV**
- ❑ **Different crystalline regions are found**
- ❑ **Substrate free thin section is essential**
- ❑ **1d-scan gains access to distribution map of crystallinity**

Conclusion

- Waste loadings above 5.3 wt% MoO_3 lead to formation of spherical crystalline phases of water-insoluble $CaMoO_4$ and $BaMoO_4$, the size depends on cooling rate (80 nm – 2.45 µm). Barium is found dispersed and crystalline in equal amounts in the 12 wt% MoO_3 sample.
- $Cs_3PMo_{12}O_{40}$ Keggin structure is decomposed by vitrification at 700 – 1300 °C, nevertheless the waste products are suitable for final disposal in a deep geological repository.
- Advanced synchroton based techniques provide insight into the elemental and crystalline distribution on a sub-microscale.

References

[1] I. V. Khonina, A. A. Lumpov, A. Y. Shadrin, B. Y. Zilberman, N. G. Kravchenko, *Radiochemistry* **2010**, *52*, 175-179.
[2] W. Lutze, R. C. Ewing, *Radioactive Wasteforms for the Future*, Amsterdam, **1988**.

Acknowledgement

We gratefully acknowledge KIT and Helmholtz Association of German Research Centers for the financial support (VH-NG-734). We thank HASYLAB and ANKA for the granted beamtime.