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Institute for Nuclear Waste Disposal (INE)

# Impact of increasing $MoO_3$ loading on the composition of multicomponent borosilicate glass

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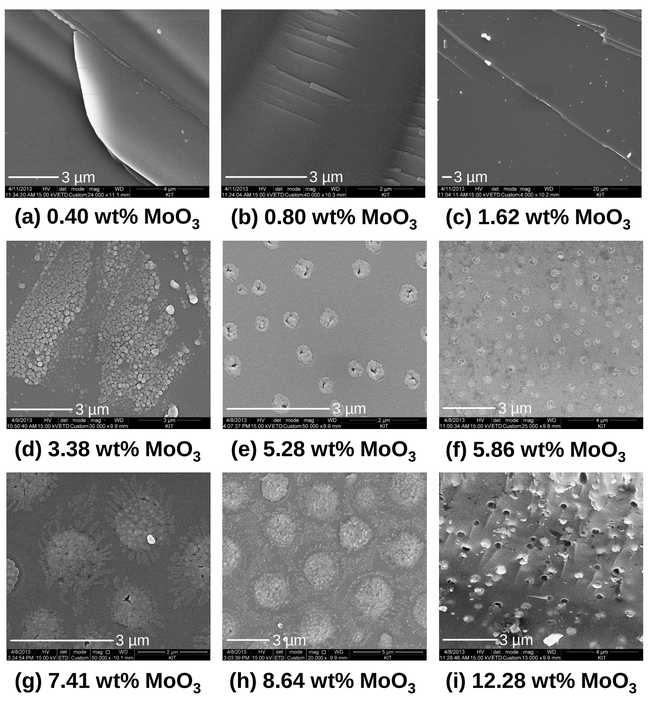
## Introduction

Long term storage of Mo-rich liquid nuclear waste leads to formation of insoluble precipitates (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. VPC* borosilicate glass was used to vitrify simulate of a $MoO_3$ rich nuclear waste residue with varying $MoO_3$ loading. The products have been investigated by several spectroscopic and microscopic techniques. The obtained results will help to predict the possible formation of soluble species, which might be mobilized in case of water intrusion into a nuclear waste repository, thereby supporting long time risk assessment. *(VPC = Vitrification Project China)

## EDX-SEM and Raman/XRD/TEM



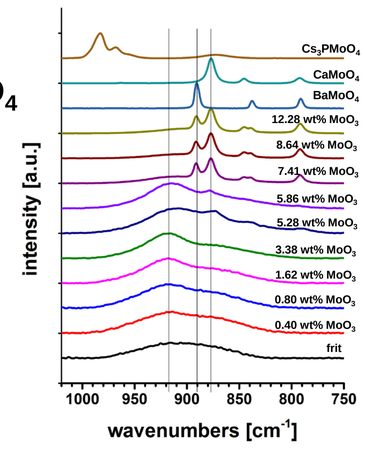

(a) 0.40 wt% $MoO_3$ (b) 0.80 wt% $MoO_3$ (c) 1.62 wt% $MoO_3$
(d) 3.38 wt% $MoO_3$ (e) 5.28 wt% $MoO_3$ (f) 5.86 wt% $MoO_3$
(g) 7.41 wt% $MoO_3$ (h) 8.64 wt% $MoO_3$ (i) 12.28 wt% $MoO_3$

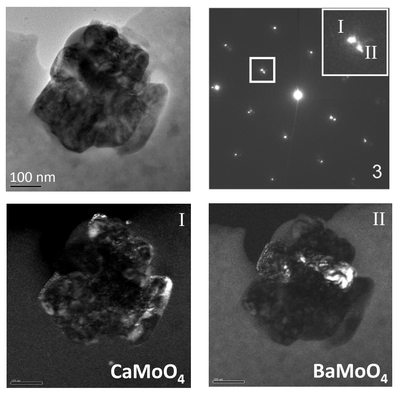
**(a) – (i): SEM images of vitrified simulated nuclear waste samples with increasing $MoO_3$-content:**

- ❑ **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**

### Raman and TEM:

- ❑ **Formation of crystalline $CaMoO_4$ and $BaMoO_4$ for $MoO_3$-loading:**
  - ❑ **5.28 wt% (Raman, XRD)**
  - ❑ **3.4 wt% (TEM)**
- ❑ **Isolated lattices**

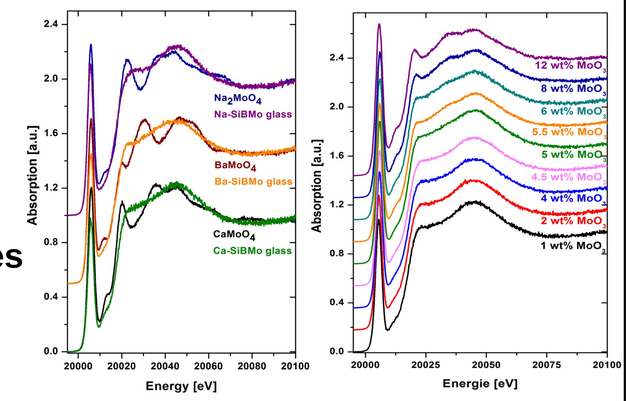


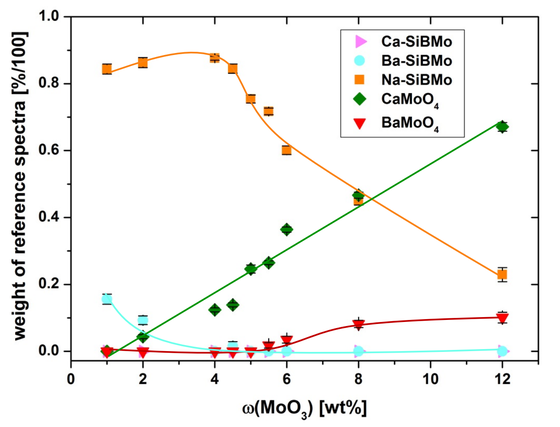




## Mo K-edge HR-XANES†

**Linear Combination Least Squares (LCLS) fits:**

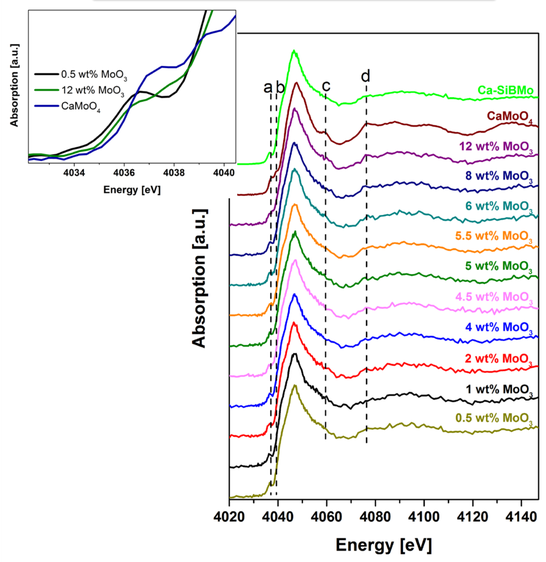
- ❑ **Quantitative speciation of Mo-phases in heterogeneous samples**
- ❑ **Dissolved $[MoO_4]^{2-}$ preferentially compensates charge by $Na^+$**
- ❑ **From 2 wt% $MoO_3$: crystalline $CaMoO_4$**
- ❑ **From 5.5 wt% $MoO_3$: crystalline $BaMoO_4$**




†high energy resolution XANES (HR-XANES)

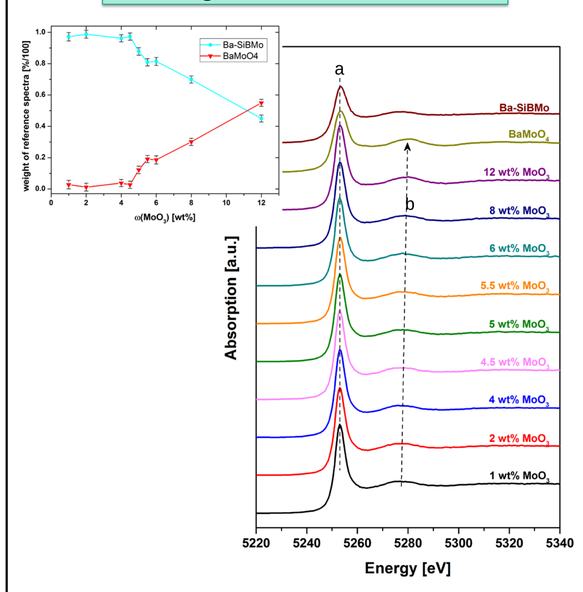
## Ca $L_3$-edge XANES




**Weak spectral trend towards high $MoO_3$ concentrations:**

- ❑ **Double pre-edge (a, b) in 12 wt% $MoO_3$ indicates formation of $CaMoO_4$**
- ❑ **Small size of crystallites influences the spectrum?**

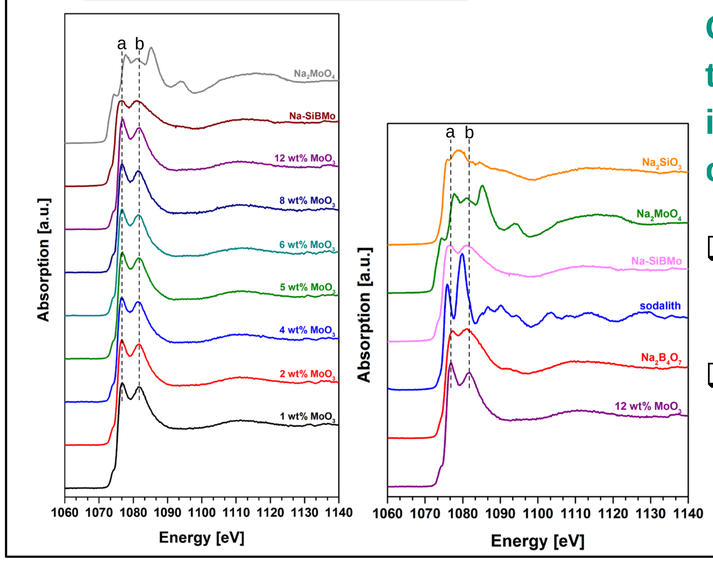
## Ba $L_3$-edge XANES




**Post-edge feature shifts to higher energies:**

- ❑ **Increasing contribution of crystalline $BaMoO_4$ towards high $MoO_3$ concentrations (LCLS fit analyses)**

## Na K-edge XANES







**Glass spectra resemble the Na-SiBMo spectrum independent of the $MoO_3$ concentration:**

- ❑ **No formation of $Na_2MoO_4$**
- ❑ **Confirms Mo K-edge HR-XANES results**

## Conclusion

- Waste loadings above 5.3 wt% $MoO_3$ lead to formation of spherical crystalline phases of water-insoluble $CaMoO_4$ and $BaMoO_4$. For low $MoO_3$ concentrations (0.5 wt%), Mo prefers $Na^+$ as charge balancing cation.
- $Cs_3PMo_{12}O_{40}$ 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 synchrotron based HR-XANES technique allows quantitative speciation of amorphous and crystalline $MoO_3$ rich glass phases.

### 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**.

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