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Structural characterization of uranium and lanthanide loaded borosilicate glass matrix

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Introduction

Spent nuclear fuel remains highly radioactive after reprocessing due to actinides and fission products, which requires a safe containment within a durable, long-lived inert medium over extended timescales. Borosilicate glass is a potential candidate for this purpose, thus understanding the effects caused by the combined presence of uranium and actinides within these matrices is of great importance.

Methodology

- ✓ neutron diffraction (ND) experiments: PSD diffractometer/BNC (λ_0=1.068 Å, Q≤9.8 Å^{-1}) & 7C2 diffractometer/LLB (λ_0=0.726 Å, Q≤15.3 Å^{-1}), with Reverse Monte Carlo (RMC) simulations
- ✓ X-ray absorption fine structure (XAFS) spectroscopy
- ✓ leaching tests (ASTM C1285-21) were performed with porewater in corporation with thermal analysis techniques

Description of the research problem

The focus of this study is on the structural changes that occur in the borosilicate glass when loaded with mixture of lanthanides and uranium – a novel combination that has not been explored yet. The simulated waste form incorporates Ce(IV) oxide, Nd(III) oxide, Eu(III) oxide, and U(VI) oxide, allowing a comprehensive analysis of the combined effects of these elements, thus providing a more realistic model for nuclear waste encapsulation. Four distinct glass samples were synthetized and investigated to gain deeper insight into the structural evolution of this complex system.The following samples were synthetized and investigated:

70wt.%[Matrix]+20wt.%UO_3+10wt.%CeO_2, denoted as MUCe

70wt.%[Matrix]+20wt.%UO_3+10wt.%Nd_2O_3, MUNd

70wt.%[Matrix]+20wt.%UO_3+10wt.%Eu_2O_3, MUEu

60wt.%[Matrix]+10wt.%UO_3+10wt.%CeO_2+10wt.%Nd_2O_3+10wt.%Eu_2O_3, MUCNE

Matrix: 55SiO_2·10B_2O_3·25Na_2O·5BaO·5ZrO_2 (mol%), REF

Results - atomic structure from ND data via Reverse Monte Carlo simulation - the samples were fully amorphous

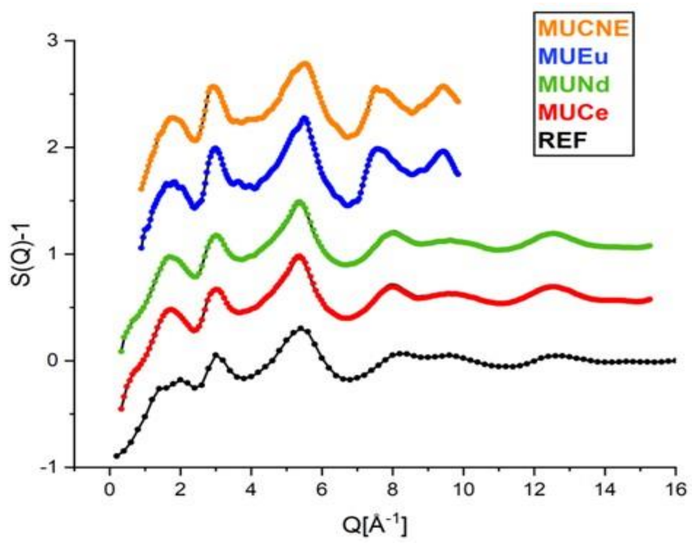


Fig 1. Total S(Q) derived from ND on REF (7C2), MUCe (7C2), MUNd (7C2), MUEu (PSD) and MUCNE (PSD), each data set is accompanied with the respective RMC fit curves (black solid lines).

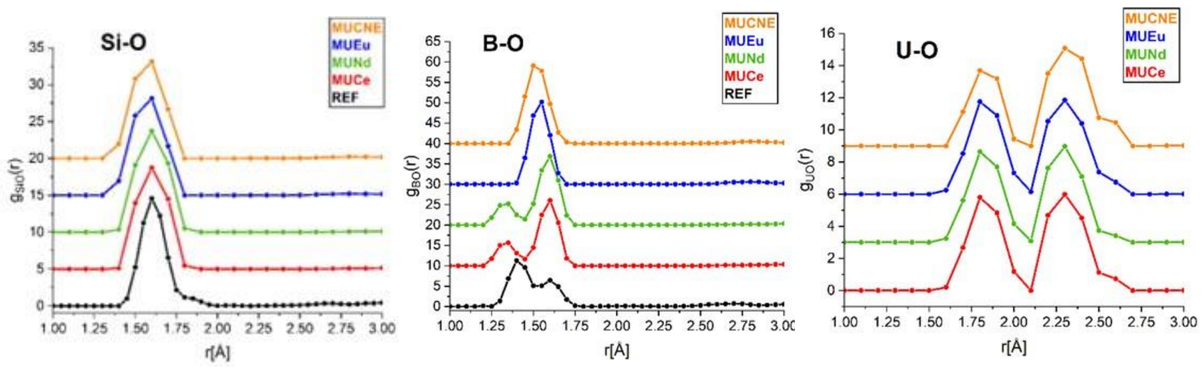
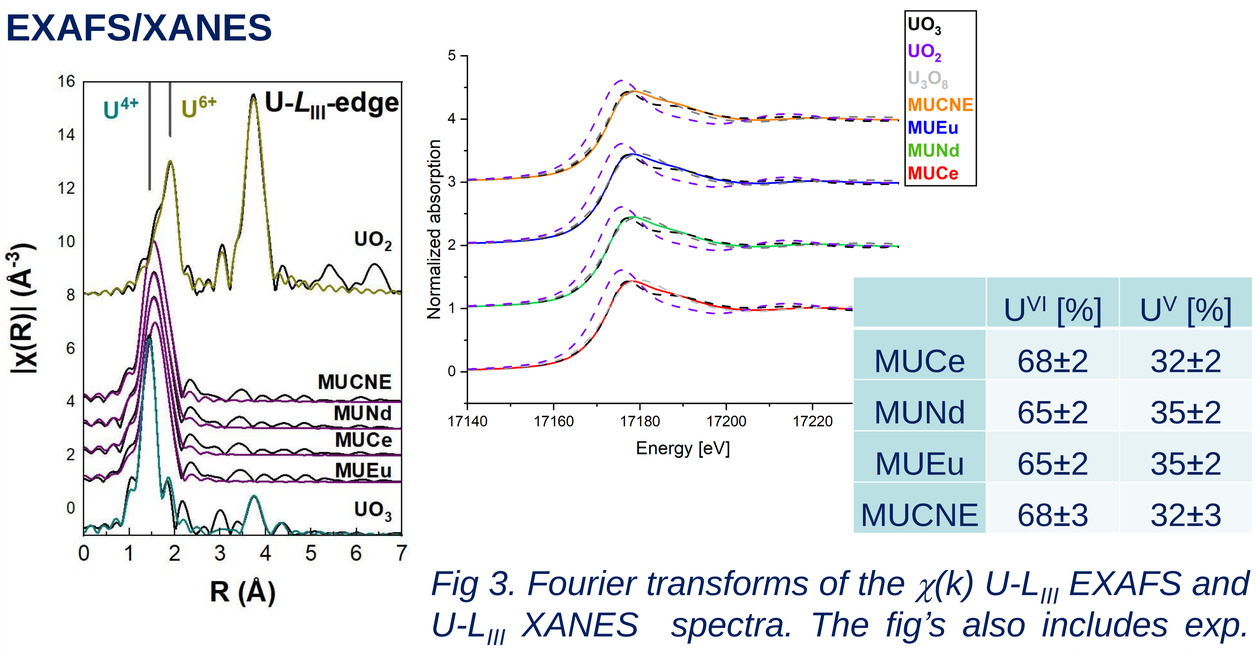


Fig 2. Partial atomic pair correlation functions for Si-O, B-O and U-O.

	Coordination number, CN_{ij}		
	Si-O (r_1:1.30-r_2:1.90)	B-O (r_1:1.20-r_2:1.75)	U-O (r_1:1.60-r_2:2.70)
REF	3.70±0.02	3.05±0.02	-
MUCe	3.87±0.03	3.40±0.03	6.60±0.05
MUNd	3.86±0.03	3.51±0.03	6.19±0.05
MUEu	3.63±0.05	3.25±0.02	6.60±0.05
MUCNE	3.84±0.03	3.47±0.03	6.54±0.05

Table 1 Average coordination numbers, determined from RMC simulations for Si-O, B-O and U-O atomic pairs.

Results - local environments of uranium and lanthanides with EXAFS/XANES



	U^{VI} [%]	U^{V} [%]
MUCe	68±2	32±2
MUNd	65±2	35±2
MUEu	65±2	35±2
MUCNE	68±3	32±3

Fig 3. Fourier transforms of the χ(k) U-L_{III} EXAFS and U-L_{III} XANES spectra. The fig's also includes exp. data and fitting curve of reference UO_3-UO_2 and U_3O_8

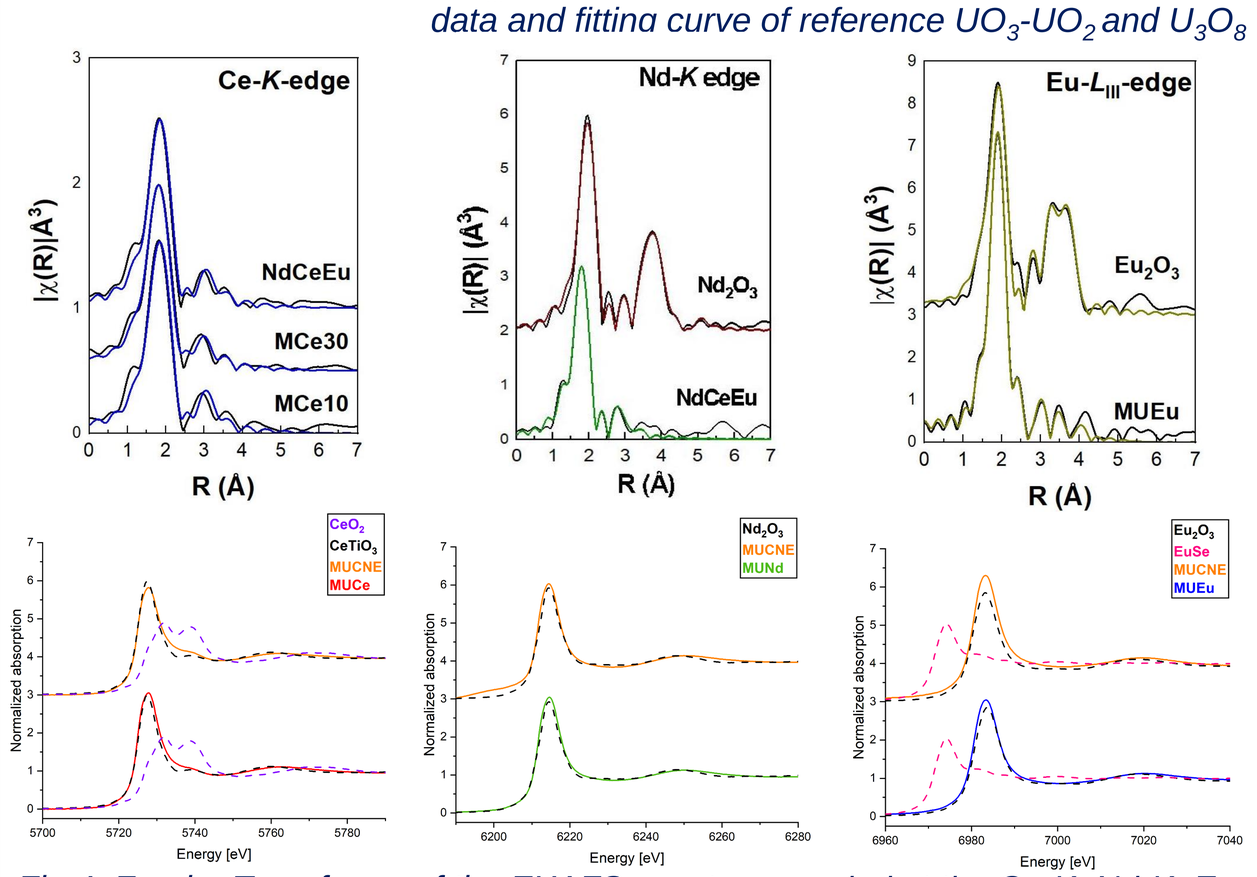


Fig 4. Fourier Transforms of the EXAFS spectra recorded at the Ce-K, Nd-K, Eu-L_{III} edge and Ce-L_{III}, Nd-L_{III}, Eu-L_{III} XANES spectra compared to the reference compounds.

Conclusions

The glass matrix was simultaneously loaded with UO_3 and lanthanide oxides (CeO_2, Nd_2O_3, and Eu_2O_3) as chemical surrogates for actinides.

ND with RMC simulation confirmed that the basic glass structure is comprised of SiO_4 and BO_3/BO_4 units. X-ray absorption spectroscopy indicated the presence of Ce mainly as Ce^{III} and the co-existence of U^{V} and U^{VI}. U acts as an intermediate oxide and reduces the number of four-coordinated B, lanthanide ions serve as modifiers, with their increasing concentration shifting the B-O coordination from 3 to 4. No redox sensitivity was observed, the Nd existing purely in the Nd^{III} oxidation state. MUEu and MUCNE samples containing only Eu^{III} ions. LCF analysis of the U L_{III}-edge indicated no U^{IV} presence.

Leaching tests showed increased dissolution of Si, B, and Na, compared to the glass matrix; MUCNE sample exhibited the most stable structure.

Acknowledgments

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