

Cationic charge distribution in mixed actinide oxides at $An M_{4,5}$ edge by HR-XANES in mixed nanooxides

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Introduction and motivation

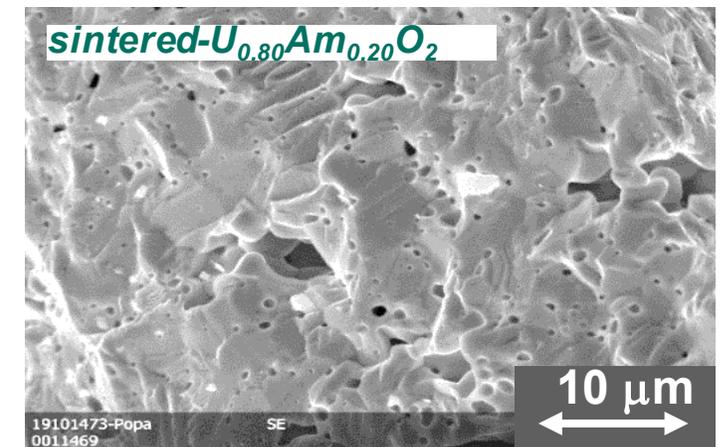
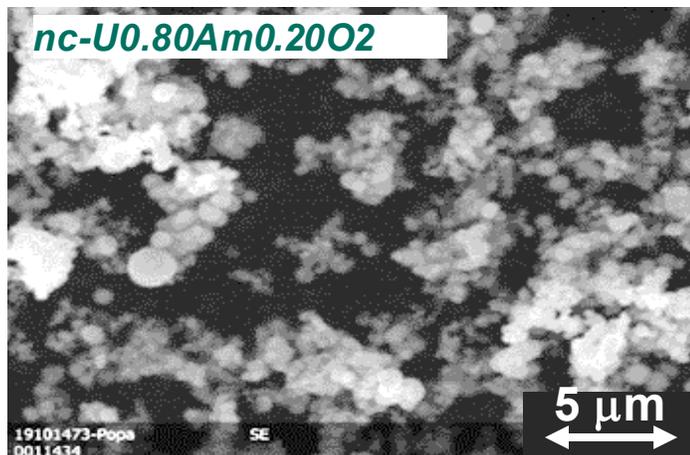
- Hydrothermal decomposition is an innovative approach for the safe and secure synthesis of actinide oxide nanocrystals.
- Mixed actinide oxides are of high interest for fundamental studies of structural properties in bulk and nanomaterials

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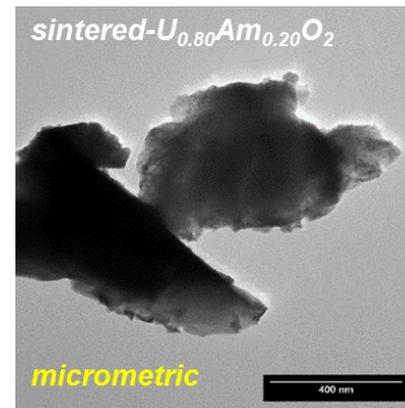
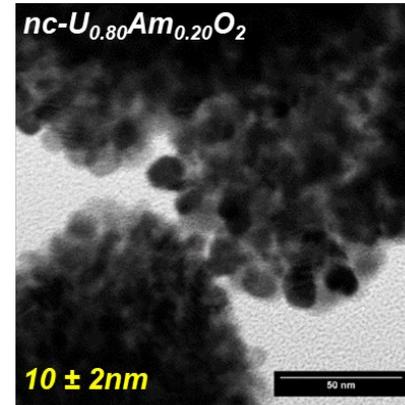
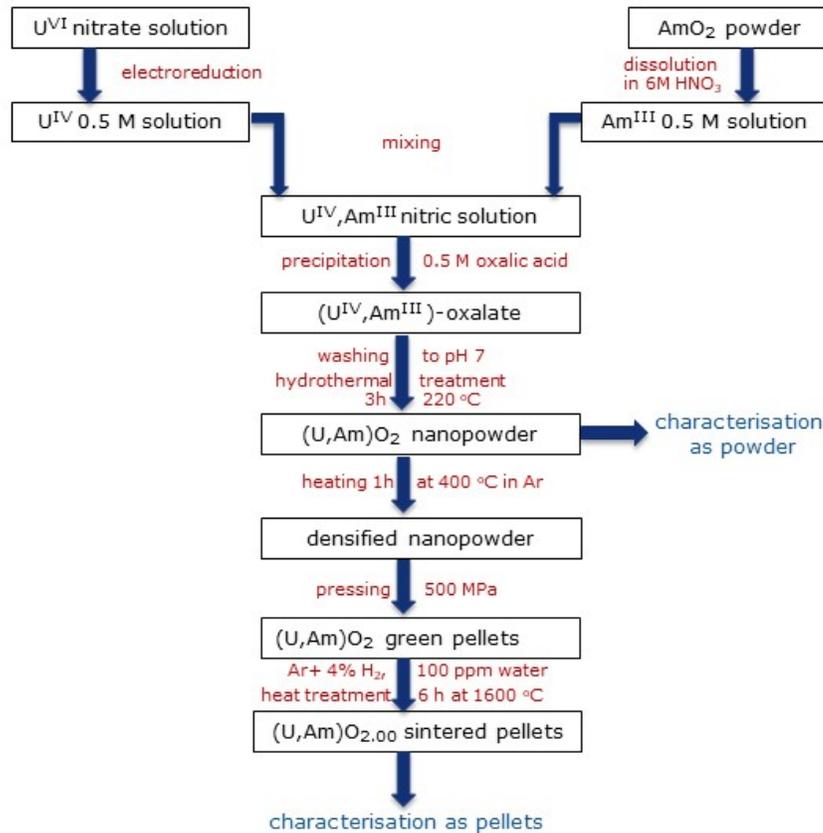
- Aimed for reuse of fissile isotopes from nuclear waste in the form of mixed oxide fuel.
- With perspective to improve sustainable usage of nuclear material resources.
- Optimisation of fuel production or reprocessing of spent fuel.

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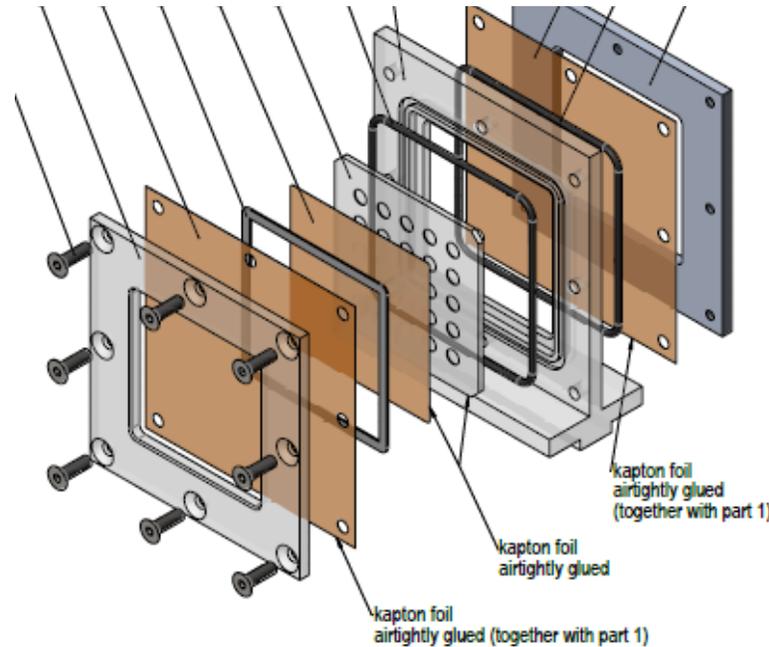
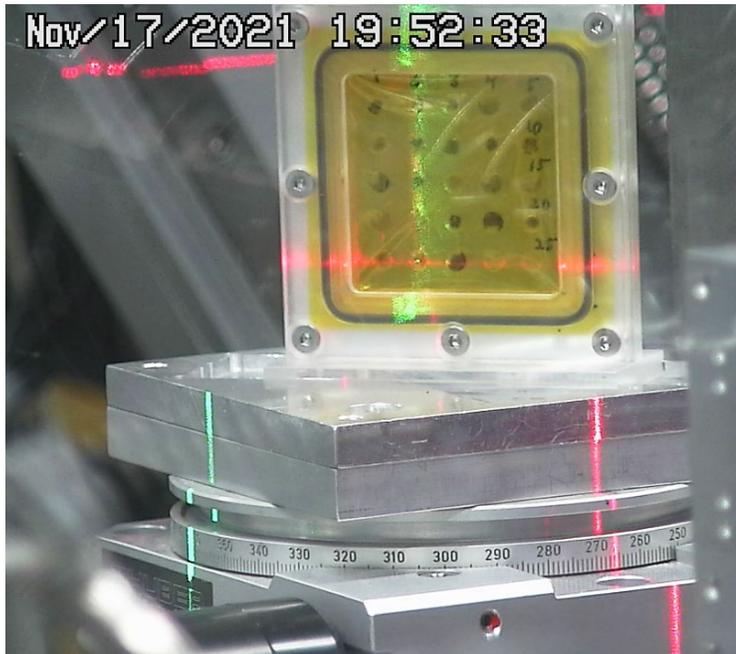
Synthesis



- $(U,Am)O_2$ solid solutions were synthesized by the hydrothermal decomposition of mixed oxalates.
- U^{IV} aq. solution was obtained by electroreduction of $UO_2(NO_3)_2$ solution in HNO_3 (4 mol/L) containing 0.5 mol/L of hydrazine.
- Am^{III} solution was obtained by dissolution of AmO_2 in HNO_3 (6 mol/L).
- The nitrate actinide solutions were mixed in the desired molar ratio.
- To ensure formation of high density materials heating 1h at 400 °C under Ar performed prior sintering 6 h at 1600 °C under an atmosphere of Ar/ H_2 (4%) and about 100 ppm of moisturizing water.

Flowcharts indicating the steps used for the production and conditioning of $(U,Am)O_2$ solid solutions (left) and SEM images of $nc-U_{0.80}Am_{0.20}O_2$ (ctr, top) and sintered $U_{0.80}Am_{0.20}O_2$ (ctr, bottom).

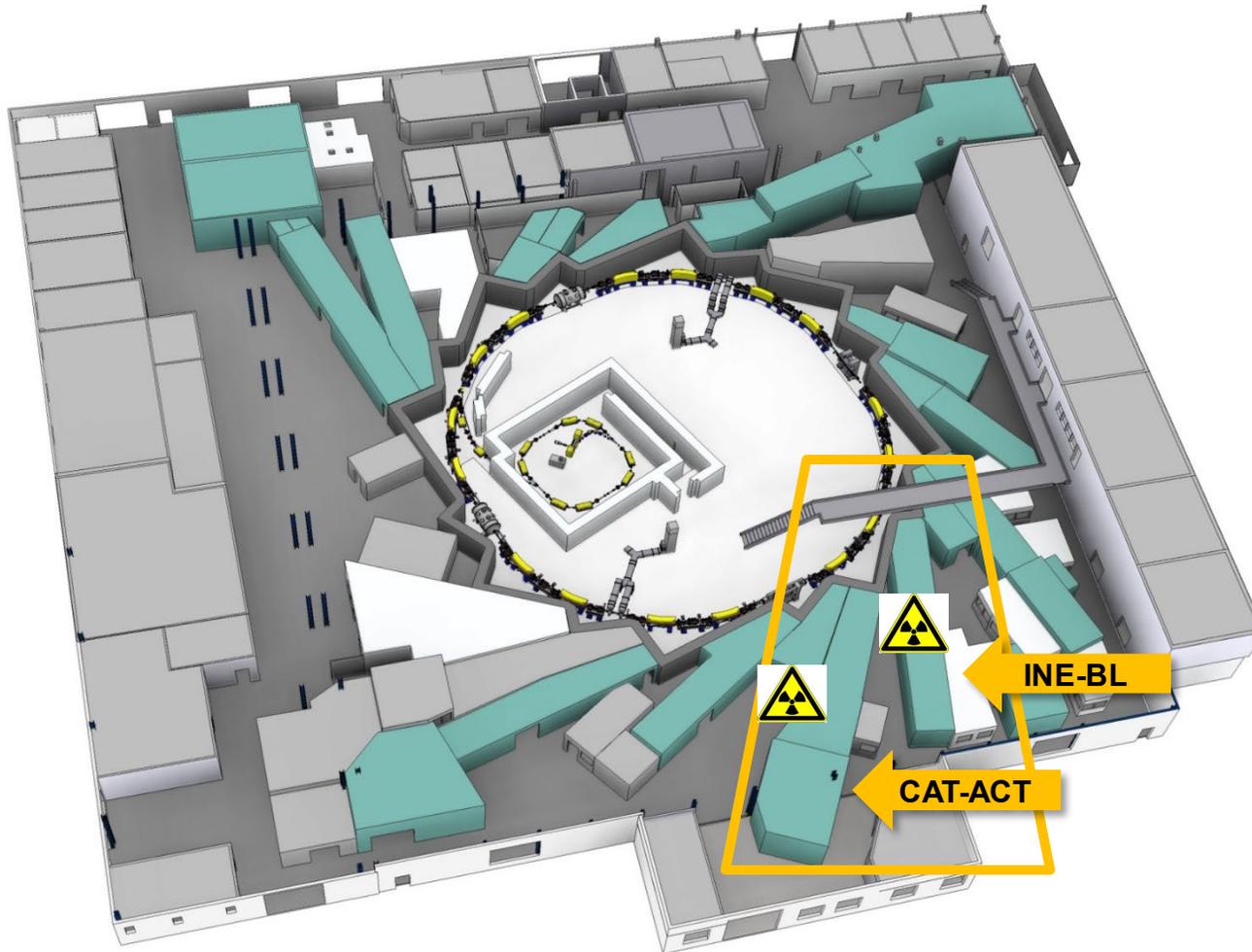
Sample preparation for SR-based investigation



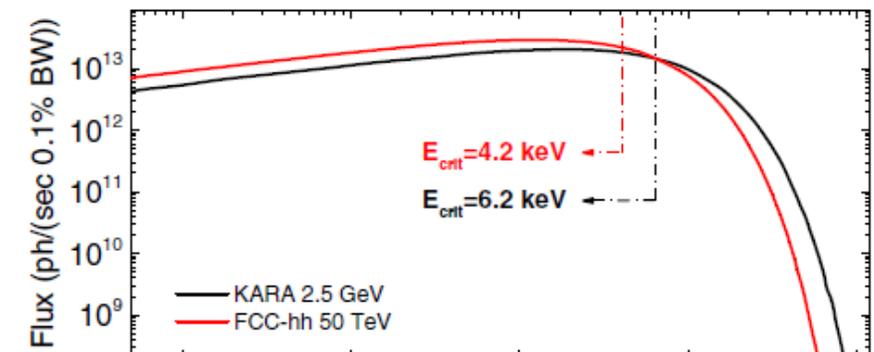
- Nanopowderes are encapsulated in epoxy.
- The Kapton foil of 8 μm and 13 μm are used for 1st and 2nd containment respectively.
- Plexiglass holder designed to fit sample positioning stage, allowing for 45° and 90° geometries.

The snapshot of sampleholder at the sample positioning stage (left) and schematics of multiposition sampleholder for solid samples (right).

KIT Synchrotron Light Source

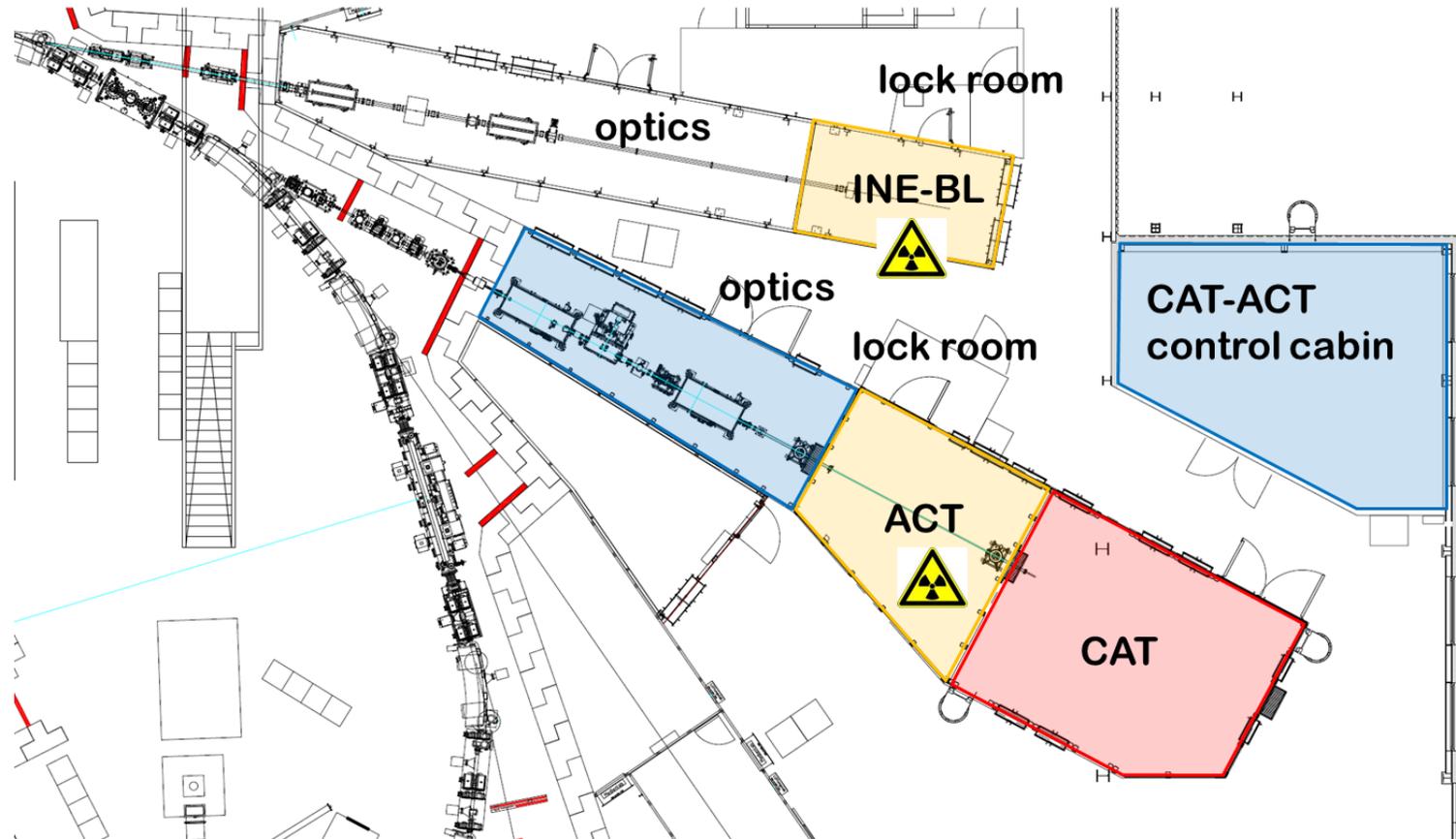


- 110-m **2.5-GeV** electron storage ring.
- Electron energy range: 0.5 – 2.5 GeV.
- Injector has a repetition rate of 1 Hz.
- Adjustable **electron bunch** lengths: 50 ps down to a few ps.
- **Single- and multi-bunch** operation modes.
- Insertion devices (ID): bending magnets (16), **wigglers** (2) and **superconducting undulator** (1).



<https://www.ine.kit.edu/english/1303.php>

INE-Beamline und CAT-ACT SR labs

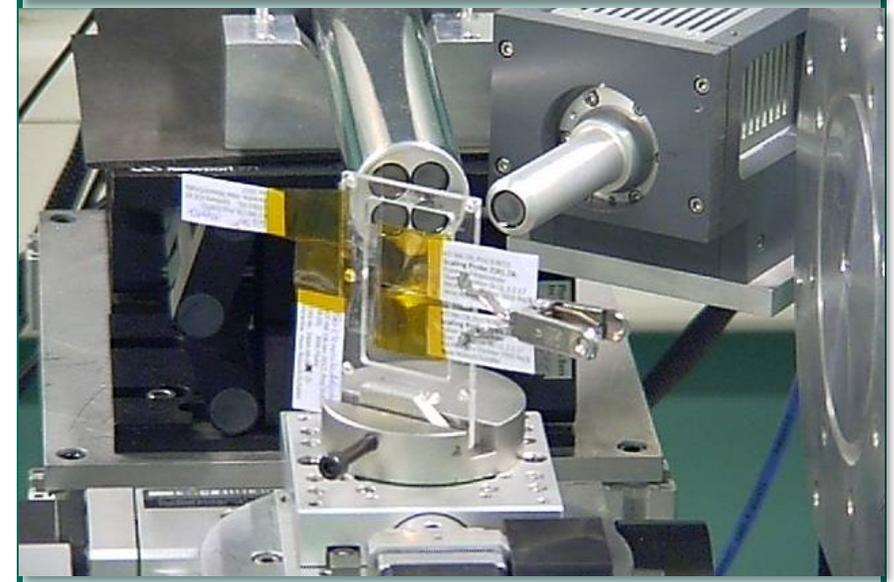
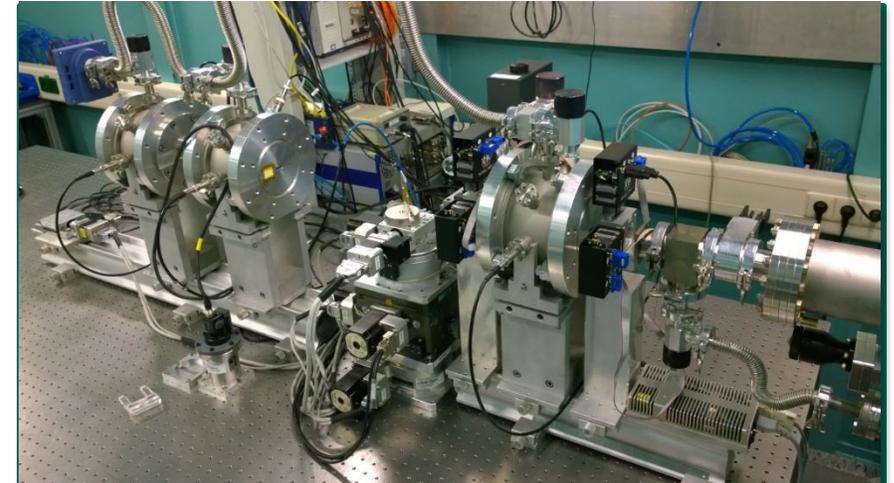


- INE-BL fully operational since October 2005 - 2nd dedicated SR beamline for radioactive materials in Europe
- CAT-ACT fully operational since fall 2016
- Energy range 2.1 – 55 keV, bending magnet (INE-BL) or superconducting wiggler source (CAT-ACT)
- XAS detection limits (A_n) $\sim 1 \cdot 10^{-6}$ mol/l, < 5 ppm

Both stations licensed for working with 10^6 times the exemption limit and up to 200 mg of fissile isotopes U-235 and Pu-239 within a double containment (sum rule applicable).

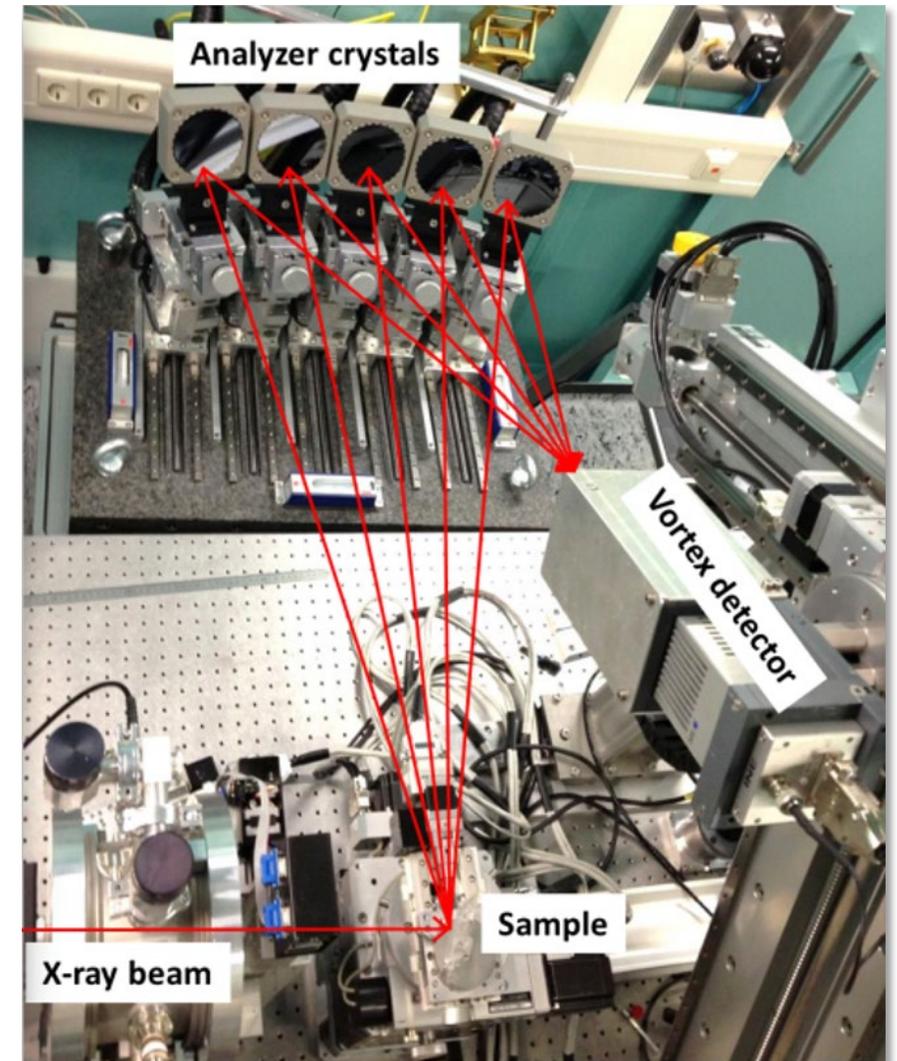
Experimental techniques: ACT & INE beamlines

- **Energy range** 2.1 keV - 25 keV (P to Pd K-edge, actinides up to Cf L₃ edge)
- **Source** 1.5 T Bending magnet (E_c=6keV)
- **Optics** water cooled DCM \ exchangeable crystal pairs Si(111), Si(220), Ge(422) \ collimating 1st & focuss. 2nd mirror \ Diagnostic modules
- **Beam size at sample** ~500μm × 500μm (standard beam size with mirror)
- **Flux at sample** position ~2×10¹⁰ photons/s at Zr K-/Pu L₃-edges using Ge(422)
- **Detectors** Vortex ME4 4 Element SDD & 1 EI. 60VX SDD
- **Samples** solid \ liquid (incl. in-situ)

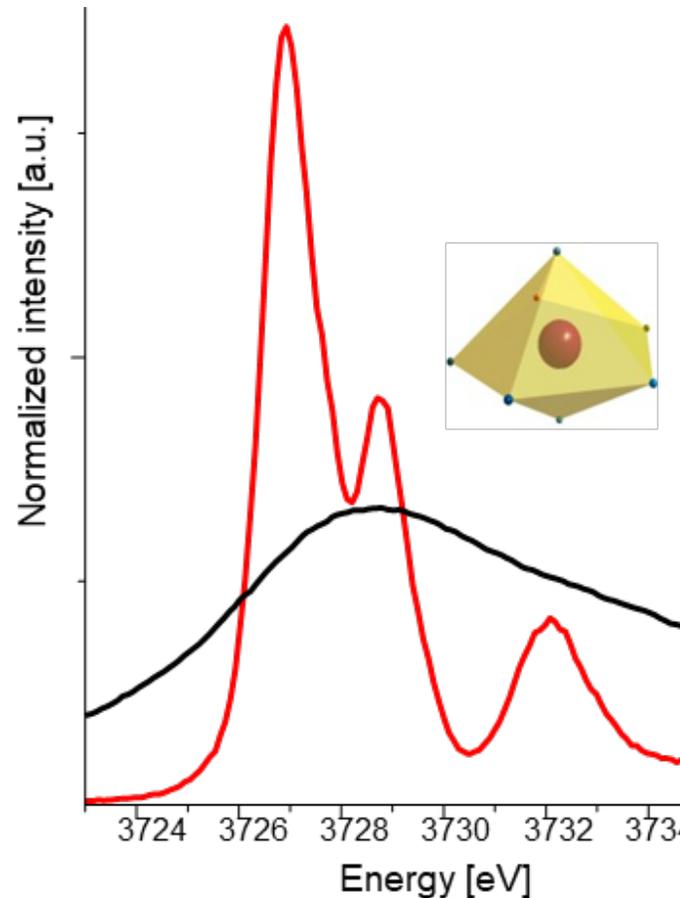
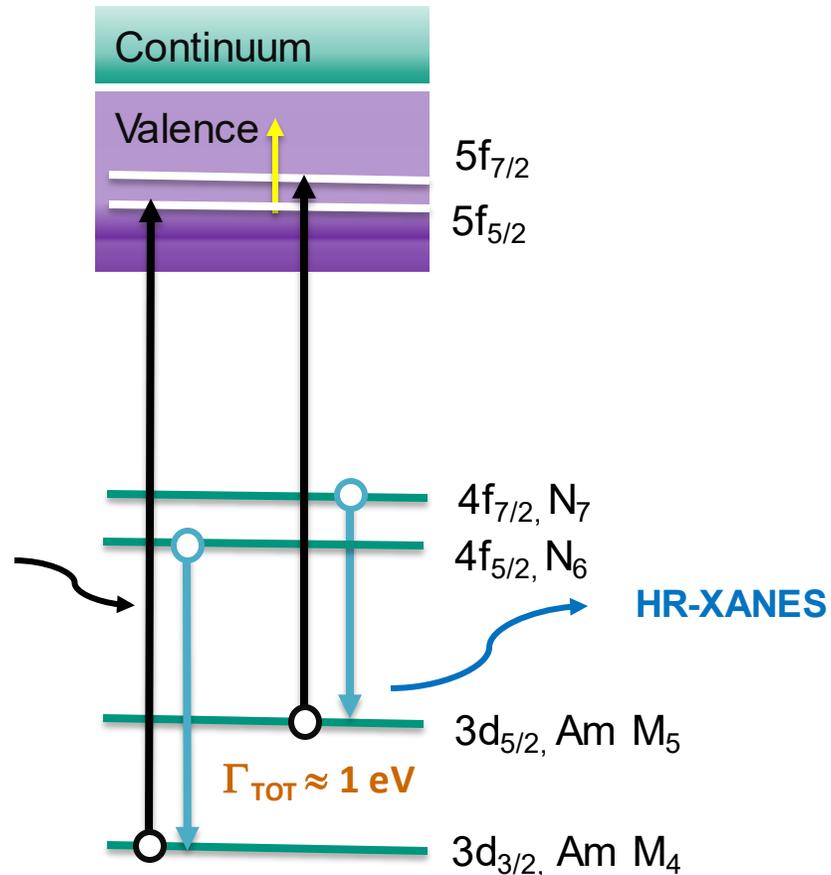


Experimental techniques: ACT & INE beamlines

- **Energy range** operation with mirrors: 3.4 – 35 keV, mirror-less above (~55 keV)
- **Source** 2.5 T superconducting multipole wiggler ($E_c=10.2\text{keV}$, 15mm vacuum gap)
- **Optics** fixed-exit DCM with LN2 cooled crystals \ exchangeable crystal pairs Si(111) and Si(311) \ collimating 1st & focuss. 2nd mirror (FMB Oxford, GB)
- **Beam size at sample** ~1mm × 1mm (standard beam size with mirror) \ slits
- **Flux at sample** position ~ 10^{11} photons/s/100mA at 20keV, Si(111)
- **HR-XANES** 1 m Rowland circle Johann-type HRXES spectrometer (5 crystals: Si(111/ 311/ 220/ 331), Ge (111/ 220/ 311)) → (An M-edges)
- **Detectors** Mirion (Canberra) 8 element LEGe, KETEK + Vortex SDD
- **Samples** solid \ liquid (incl. in-situ)



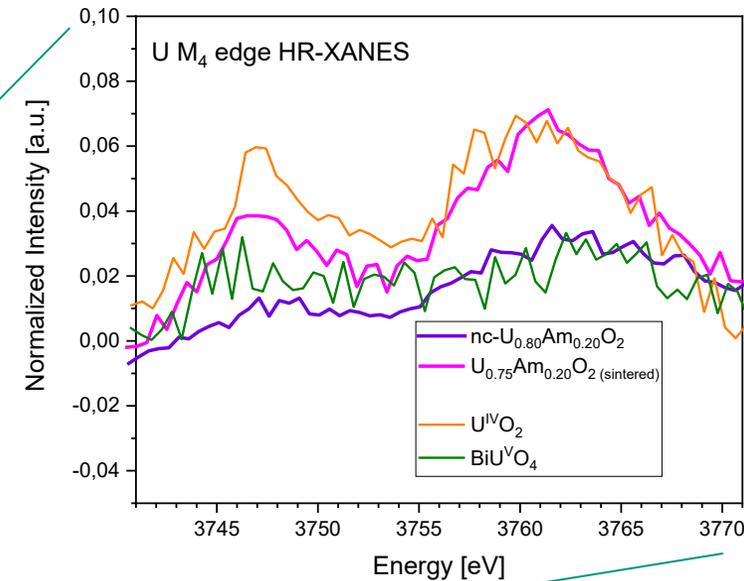
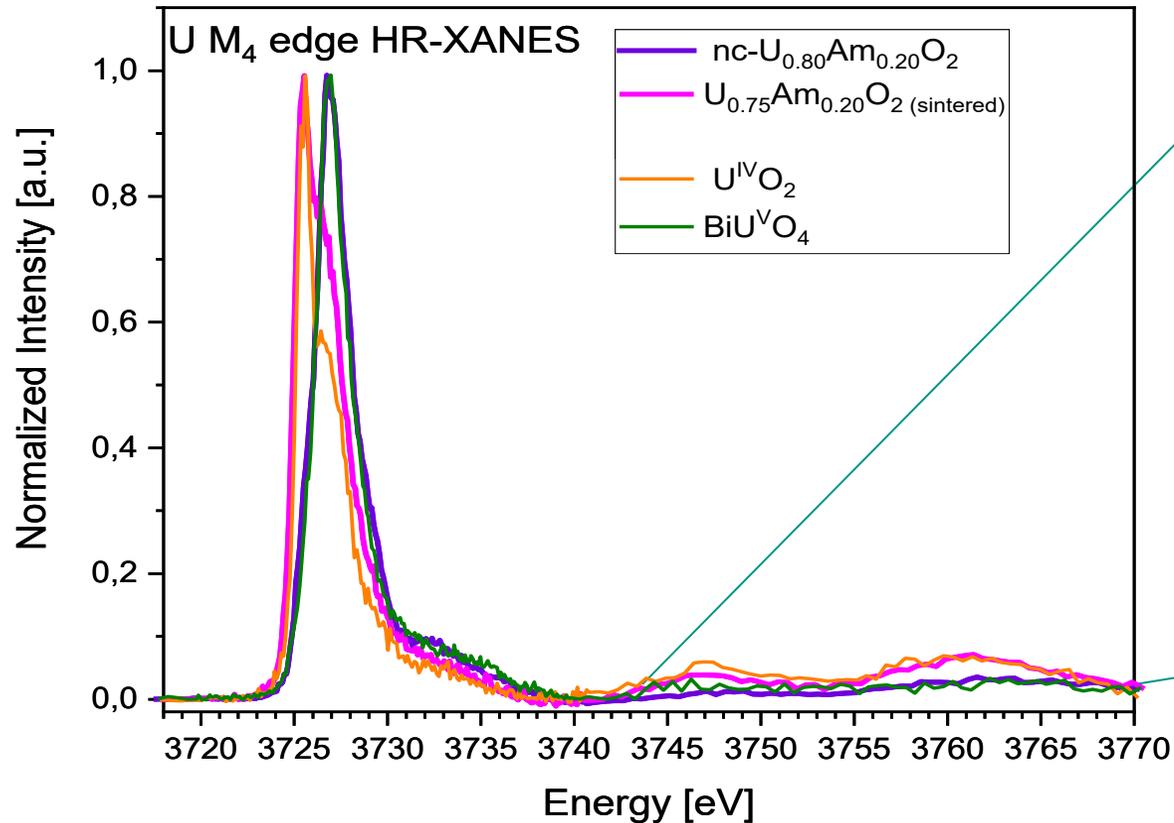
Mechanism of High-Energy Resolution XANES



- The X-ray photon is absorbed by exciting a core 3d electron to an empty 5f valence state.
- The 3d core-hole is filled with 4f electrons via M5N7 fluorescence emission.
- As function of the photon energy, sharp fine structures are observed in the HR-spectra.

Schematic electron excitations and emission transitions for An $M_{4,5}$ edges (left). U M_4 conventional (black) and HR-XANES (red) spectra of $UO_3 \cdot 1-2H_2O$ (meta-schoepite).

Results: U M₄ HR-XANES*

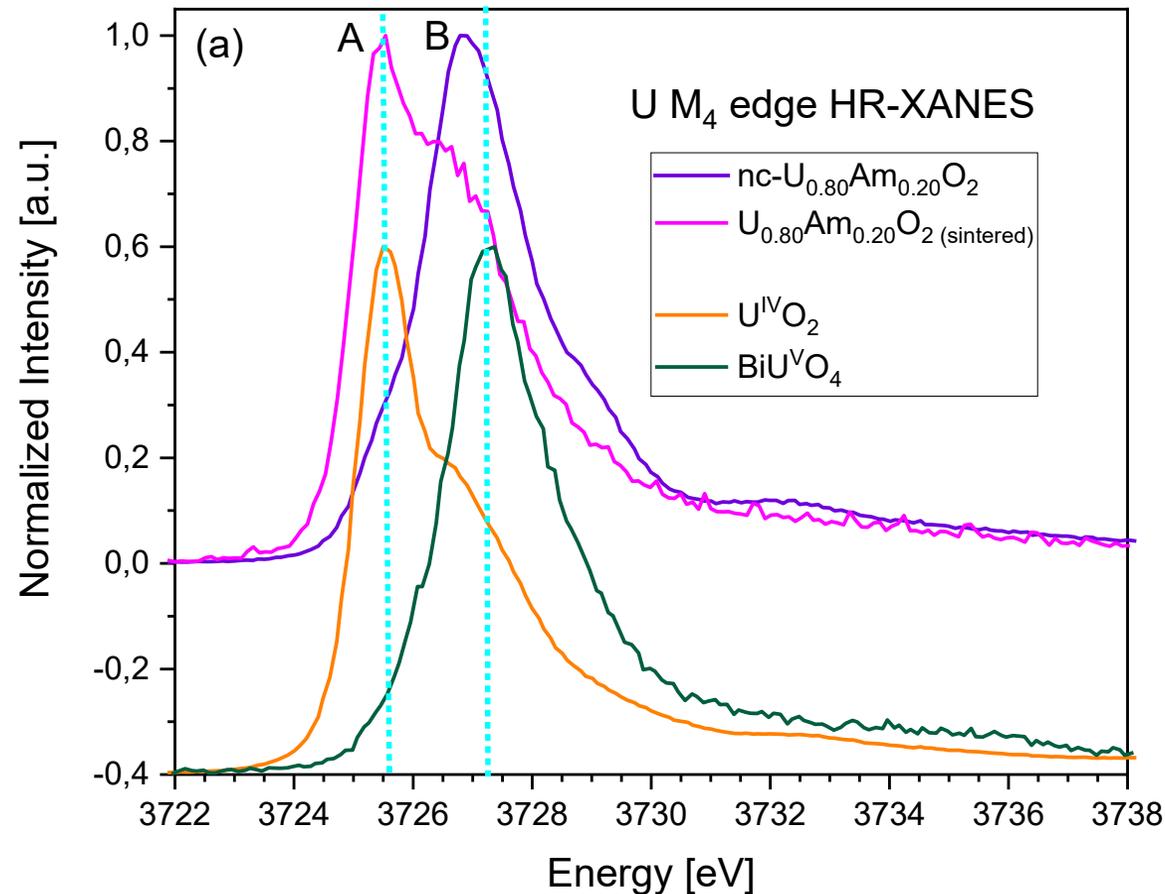


■ The post-edge region of the spectra exhibits two broad peaks typical for the FCC cubic structure, also confirmed by XRD measurements.

HR-XANES U M₄ edge for as-synthesised nanoparticles (lilac) and sintered (magenta) U_{0.80}Am_{0.20}O₂ samples (left). The post-edge range along with the U^{IV}O₂ (orange) and the BiU^VO₄ (green) references (right).

*CrystEngComm. *Synthesis and characterization of homogeneous (U,Am)O₂ and (U,Pu,Am)O₂ nanopowders J-F. Vigier et al. accepted

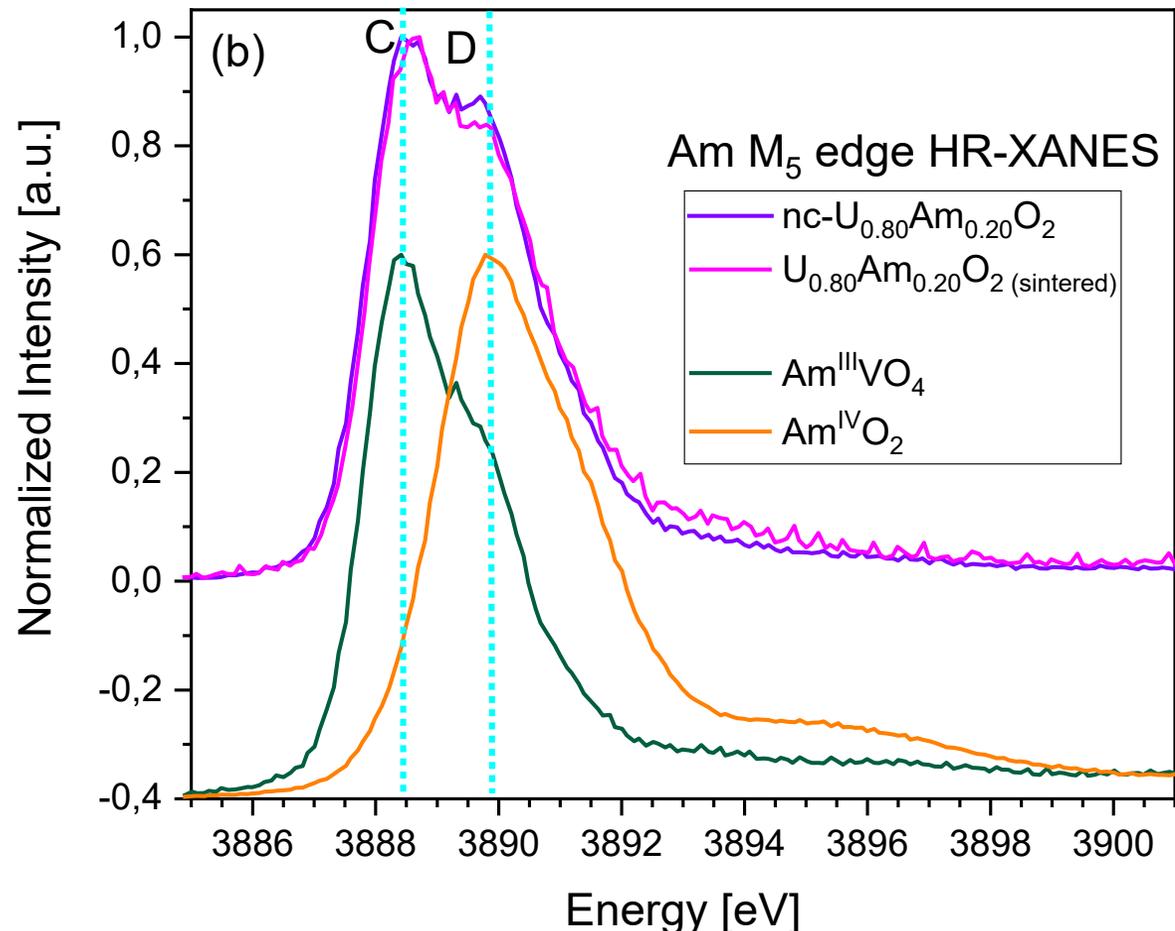
Results: U M₄ HR-XANES cont'd



- The U^V stabilizes on the surface of the nanocrystals (10-13 nm size) with cubic FCC structure and strongly reduces to U^{IV} upon sintering at 1600-1650 °C.
- The energy position of feature B in the BiU^VO₄ spectrum located at about 3727.3 eV is characteristic of the main absorption intensity of U^V.
- The energy position of feature A in the U^{IV}O₂ spectrum located at about 3725.5 eV is consistent with published data.
- This details can not be detected with conventional U L₃ edge XANES.
- Presence of an intermediate state for U is not ruled out for nanoparticles. (*Paola D'Angelo*)

U M₄ HR-XANES spectra for nc-U_{0.80}Am_{0.20}O₂ (lilac) and after sintering (magenta) along with U^{IV}O₂, BiU^VO₄, references.

Results: Am M₅ HR-XANES



- Am^{III} dominates in both samples (feature C @ 3888.8 eV).
- The shoulder (D) is at the energy position of the main spectral maximum of Am^{IV}O₂ also present in the in Am^{III}VO₄.
- After sintering the intensity of the shoulder decreases and this suggests reduction of Am^{IV} to Am^{III}.
- The presence of Am^{IV} (feature D @ 3890 eV) is a new finding since americium is found to be in its trivalent oxidation state in the U_xAm_yO_{2+δ} (y=0 to 0.5) bulk system in previous studies*, even after calcination under air.
- Am is likely to be partially oxidized on the surface of the nanoparticles.

* Epifano et al. *J. Nucl. Mater.*, 2020, 531, 151986 & 151991

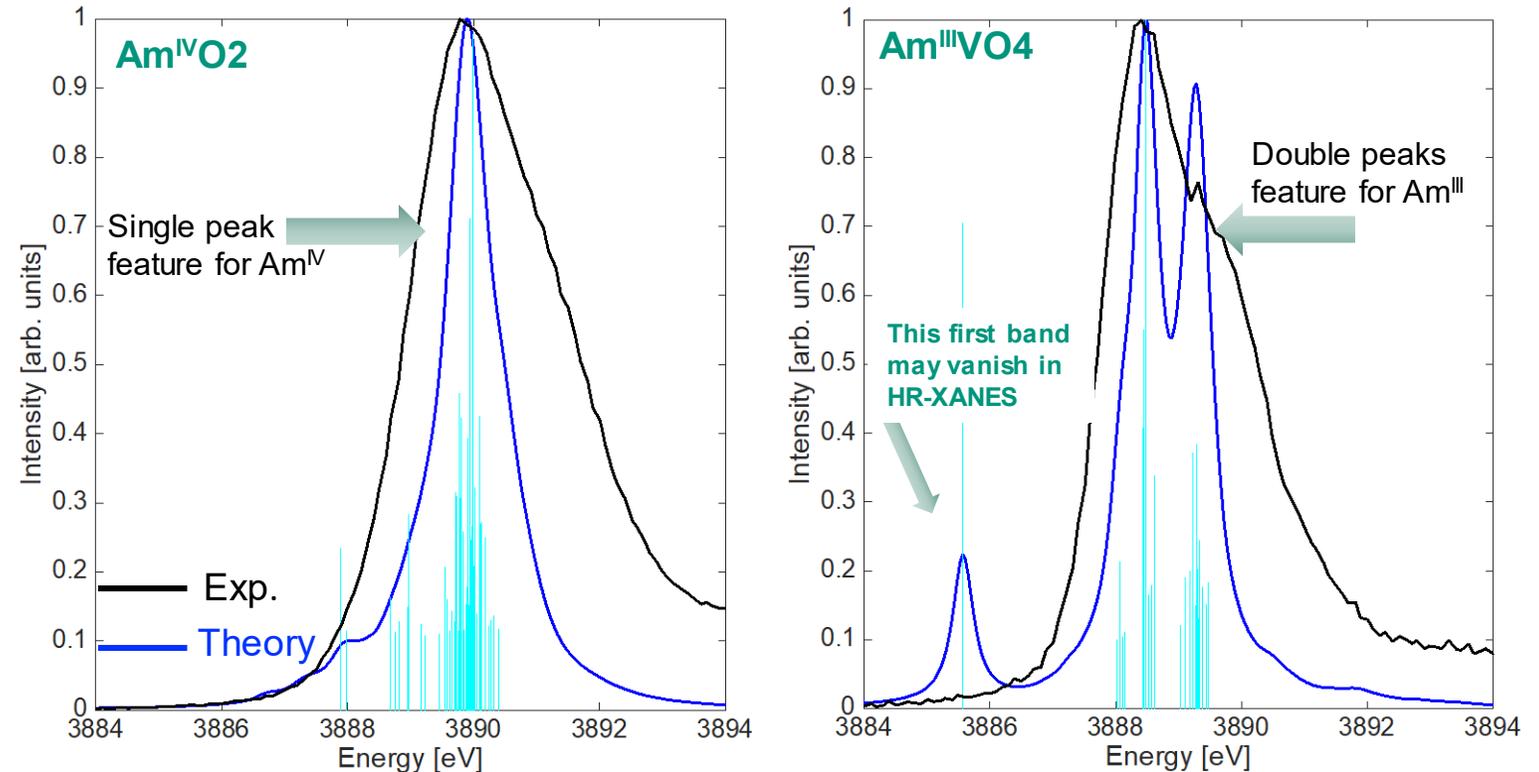
Am M₅ HR-XANES spectra for nc-U_{0.80}Am_{0.20}O₂ (lilac) and after sintering (magenta) along with Am^{III}VO₄, Am^{IV}O₂ references.

Results: DFT Am M₅ XANES calculations w/o consideration of the final state

Computational Details

- DFT method (ADF program package). Open-shell electronic structures that correspond to the initial, intermediate and final states.
- Molecular cluster approach, i.e. Am^{IV}O₂ is modelled with the molecular (AmO₈)¹²⁻ cluster. Point charges are added to mimic the long range interaction of the crystal host.
- Based on the DFT output, multiplet energies are calculated by using the LFDFT module in the ADF program package.

Comparison with experimental data



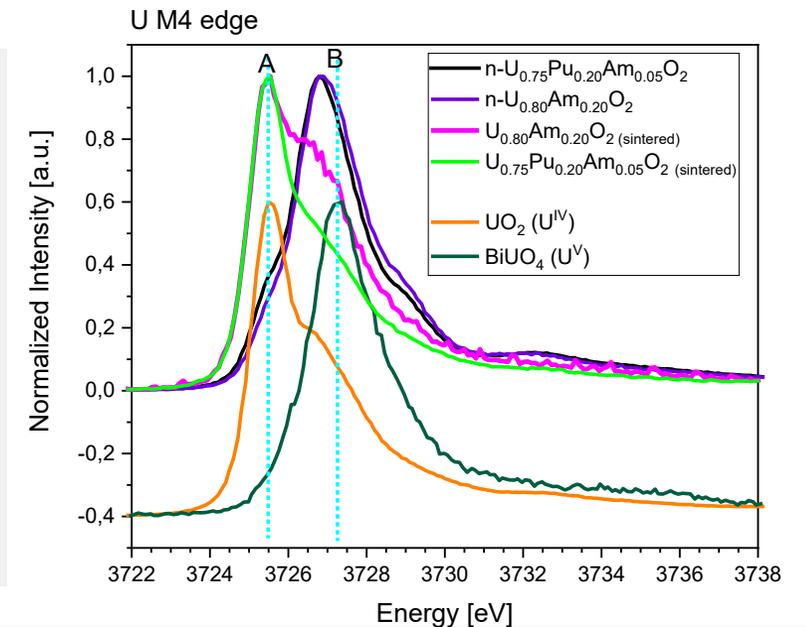
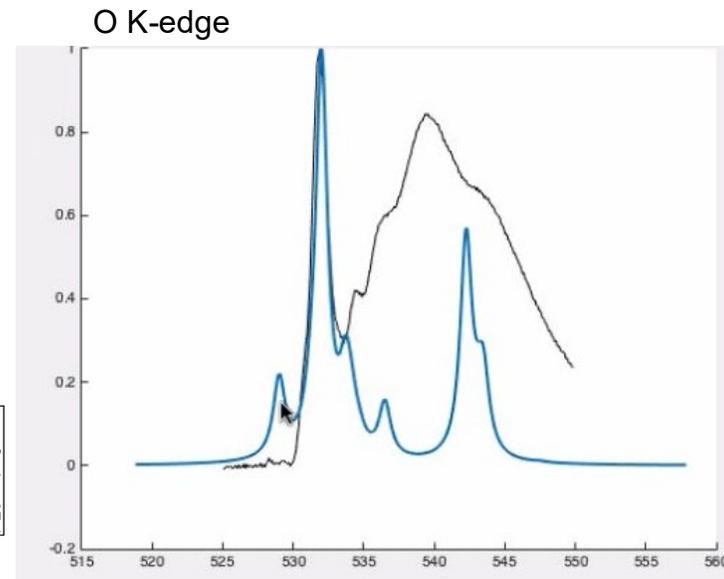
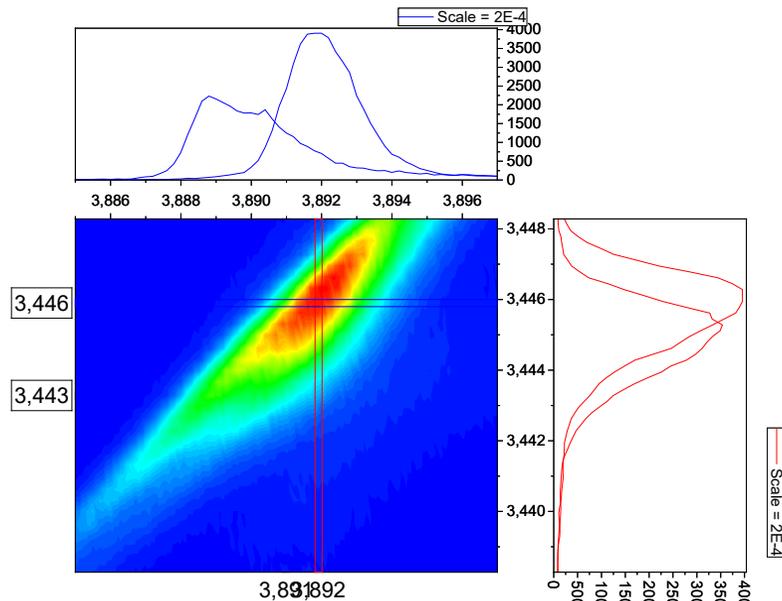
The cyan bars are the calculated oscillator strengths of the $5f^n \rightarrow 3d^9 5f^{n+1}$ transitions, which are convoluted with a Lorentzian function giving rise to the blue curves.

Conclusions and future work

- Oxidation state of advanced solid solution synthesis of nc- $U_{0.80}Am_{0.20}O_2$ and bulk $(U, Am)O_2$ had been studied by U M_4 and Am M_5 HR-XANES.
- Typical oxidation states detected are the majority of U^V and Am^{III} with minor amount of Am^{IV} stabilized in the as prepared nc- $U_{0.80}Am_{0.20}O_2$ crystals.
- The U^V stabilizes on the surface of the nanocrystals (10-13 nm size) with cubic FCC structure and strongly reduces to U^{IV} upon sintering at 1600-1650 °C.
- Minor contribution of Am^{IV} is present in the nanocrystals for Am content down to 5%, likely as a result of surface oxidation of the predominant Am^{III} .
- The effect of significant U reduction in $(U, Am)O_2$ upon sintering also observed for Am doping as low as 1% (5% - 10%).
- Optimization of sample preparation. Epoxy resin has probably a protective effect against oxidation.

Conclusions and future work

- **RIXS** analysis for the quantitative evaluation of the multiple oxidation states for uranium and americium (LCF).
- **Soft X-ray** O K-edge XANES at the XSPEC beamline.
- **DFT** To develop a method that calculates atomic multiplet energies corresponding to the initial, intermediate and final states of the HR-XANES mechanism.
- **Sample complexity** investigation of tri-metallic system (U, Am\Pu)O₂.



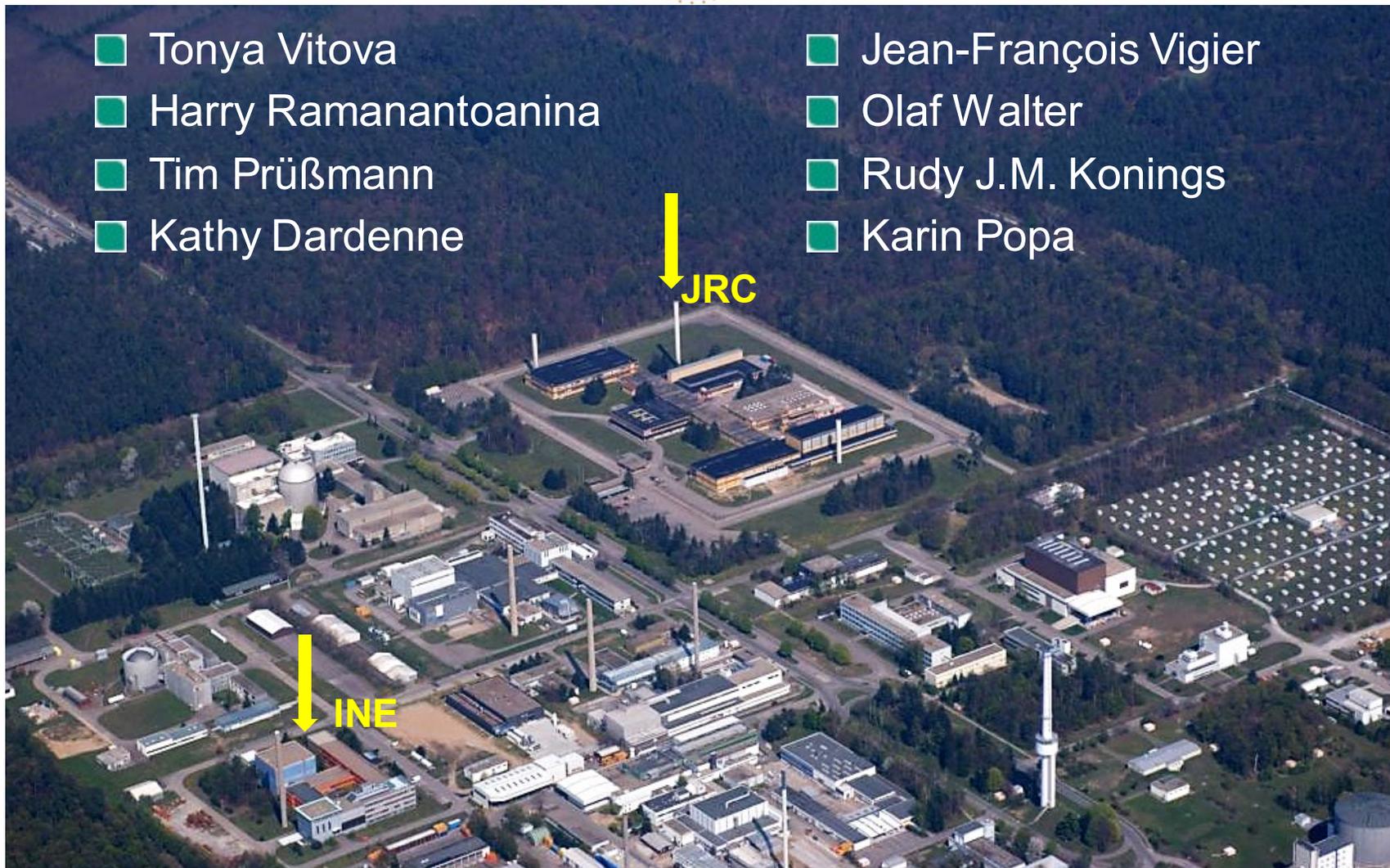
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- Karin Popa



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