Spectroscopy analysis of mixed actinide oxides by an An M4,5 edge high energy resolution XANES (HR-XANES) in bulk- and nano-materials

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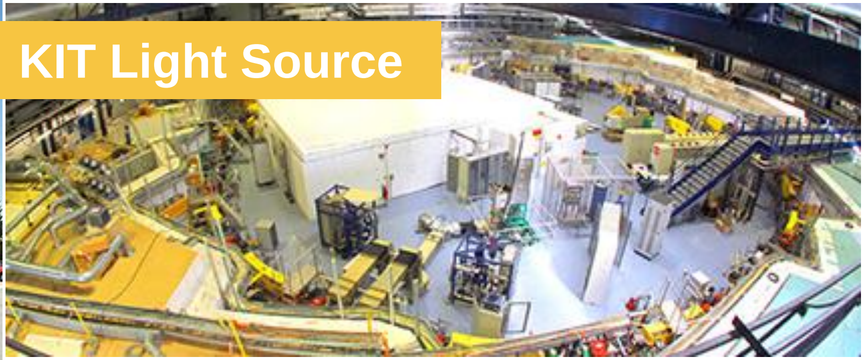
Institute for Nuclear Waste Disposal (INE)



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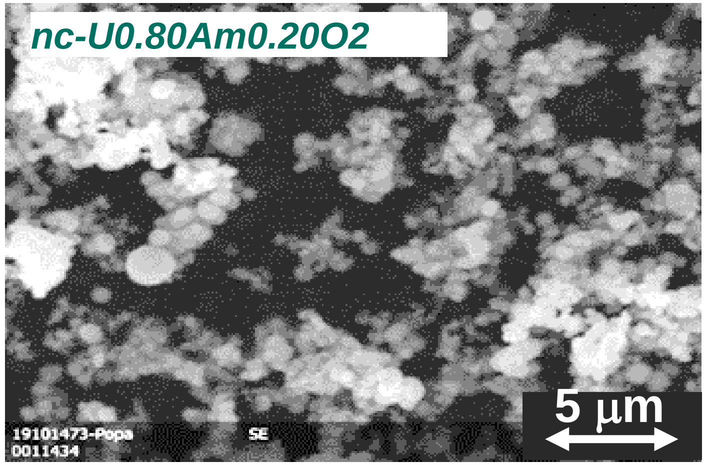
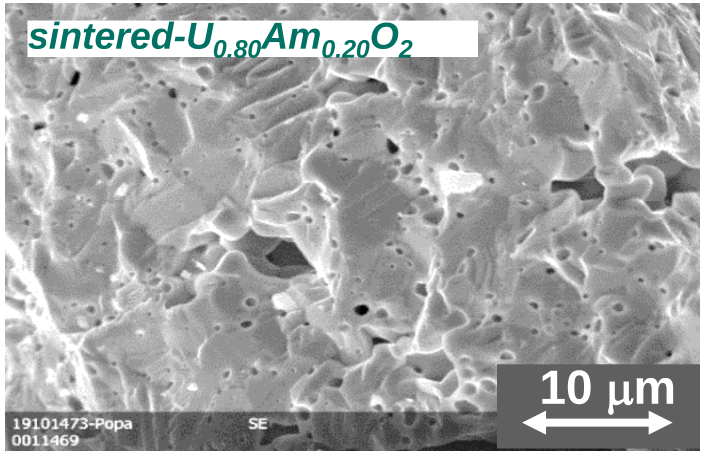
Introduction and motivation

- 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

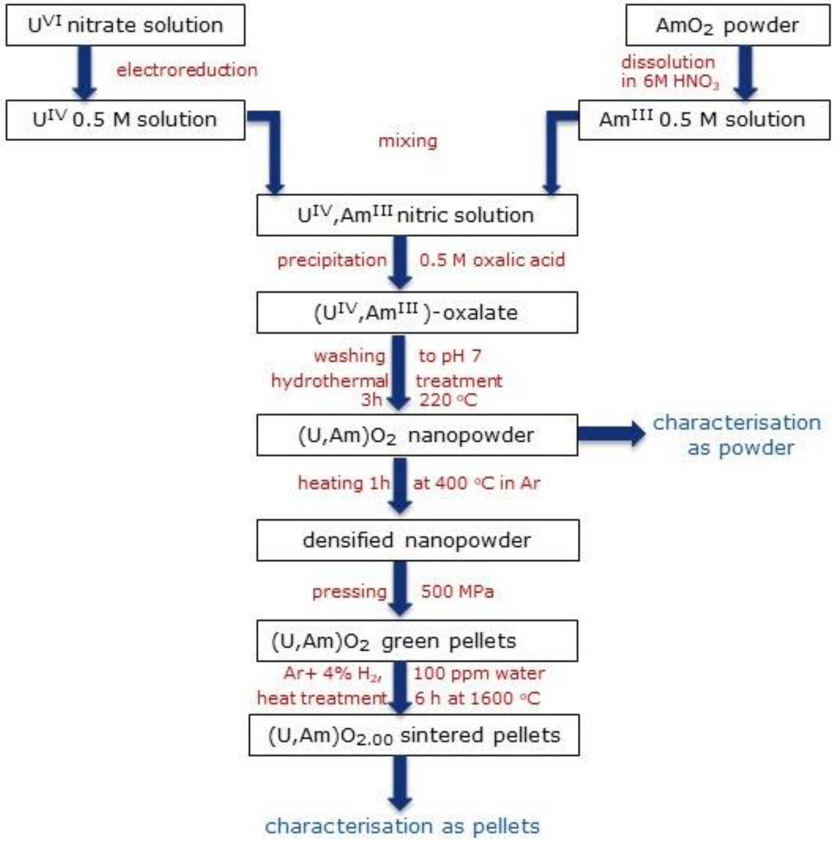
and

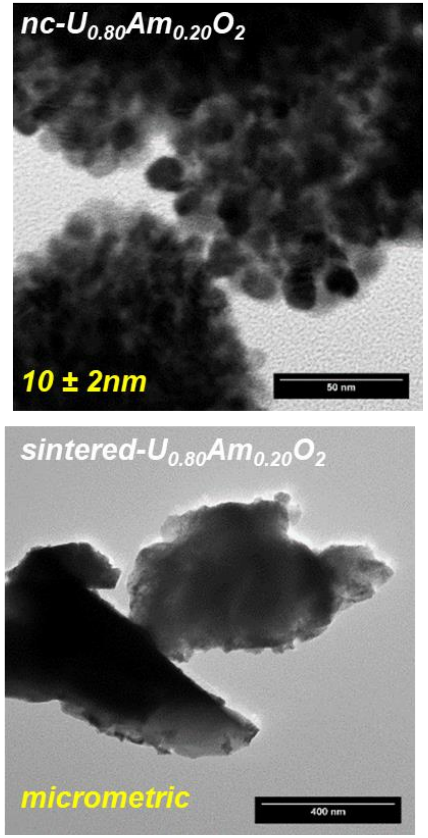
- Aimed for reuse of fissile isotopes from nuclear waste in the form of mixed oxide fuel.
- With perspective to improve sustainable usage of nuclear material resources.
- Optimisation of fuel production or reprocessing of spent fuel.





Synthesis

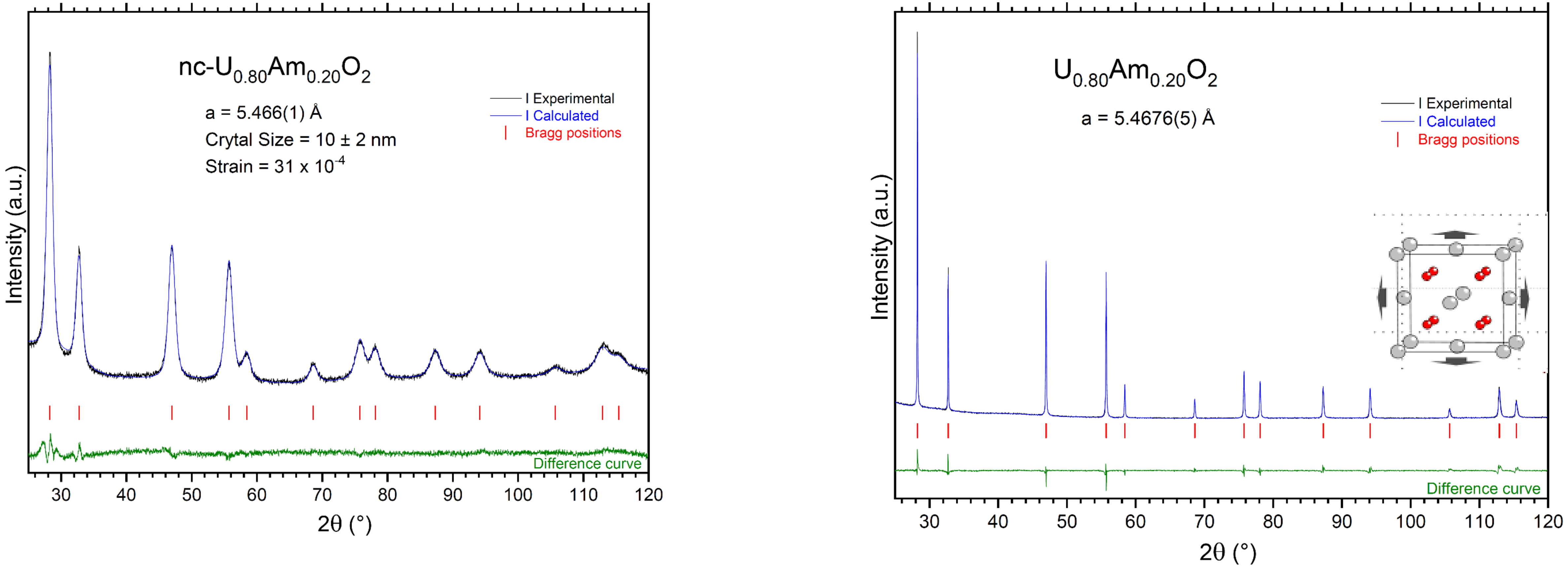

U^{VI} nitrate solution
electroreduction
U^{IV} 0.5 M solution
AmO_2 powder
dissolution in 6M HNO_3
Am^{III} 0.5 M solution
mixing
U^{IV},Am^{III} nitric solution
precipitation 0.5 M oxalic acid
(U^{IV},Am^{III})-oxalate
washing to pH 7
hydrothermal treatment 3h 220 °C
(U,Am)O_2 nanopowder
characterisation as powder
heating 1h at 400 °C in Ar
densified nanopowder
pressing 500 MPa
(U,Am)O_2 green pellets
Ar+ 4% H_2, 100 ppm water
heat treatment 6 h at 1600 °C
(U,Am)$O_{2.00}$ sintered pellets
characterisation as pellets



- (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 ºC under Ar performed prior sintering 6 h at 1600 ºC under an atmosphere of Ar/H2 (4%) and about 100 ppm of moisturizing water.

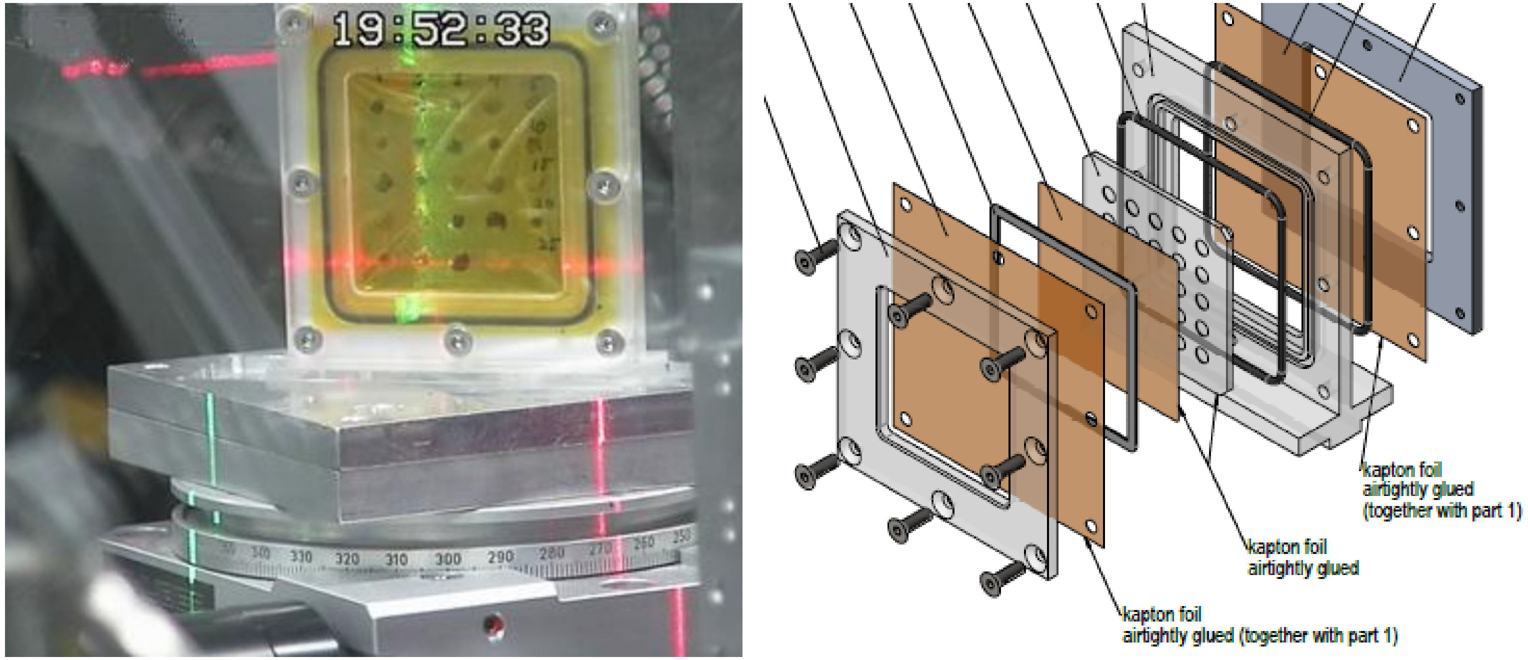
Flowcharts indicating the steps used for the production and conditioning of (U,Am)O_2 solid solutions (left) and SEM images of nc-$U_{0.80}Am_{0.20}O_2$ (ctr, top) and sintered $U_{0.80}Am_{0.20}O_2$ (ctr, bottom).

XRD characterisation: swelling of the fluorite structure



XRD patterns of the (left) nanocrystaline and (right) sintered (U,Am)O2 solid solutions obtained after synthesis/conditioning.

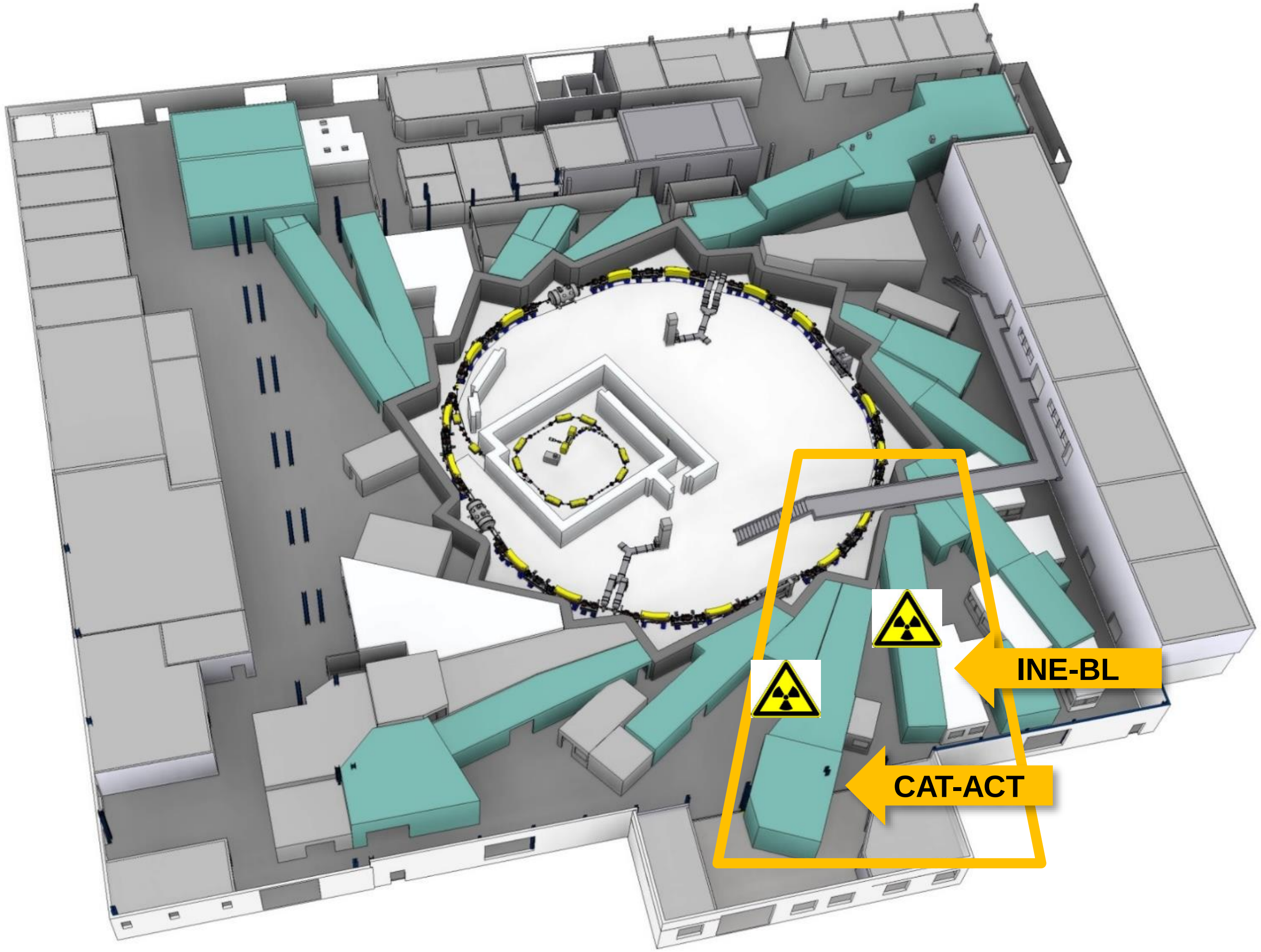
Sample preparation for SR-based investigation



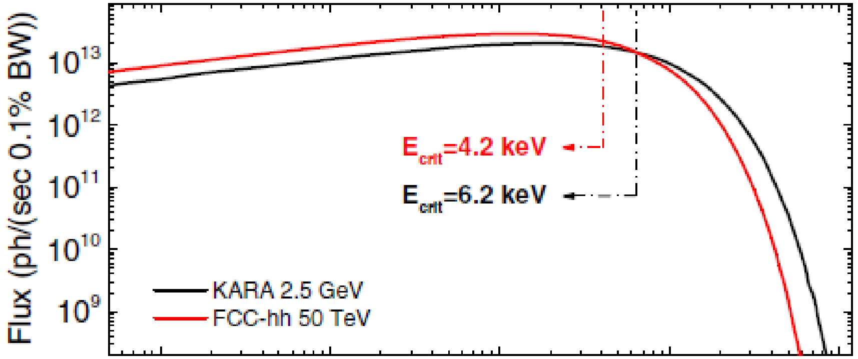
- Nanopowderes are encapsulated in epoxy.
- The Kapton foil of 8 μm and 13 μm are used for 1st and 2nd containment respectively.
- Plexiglass holder designed to fit sample positioning stage, allowing for 45° and 90° geometries.

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

KIT Synchrotron Light Source

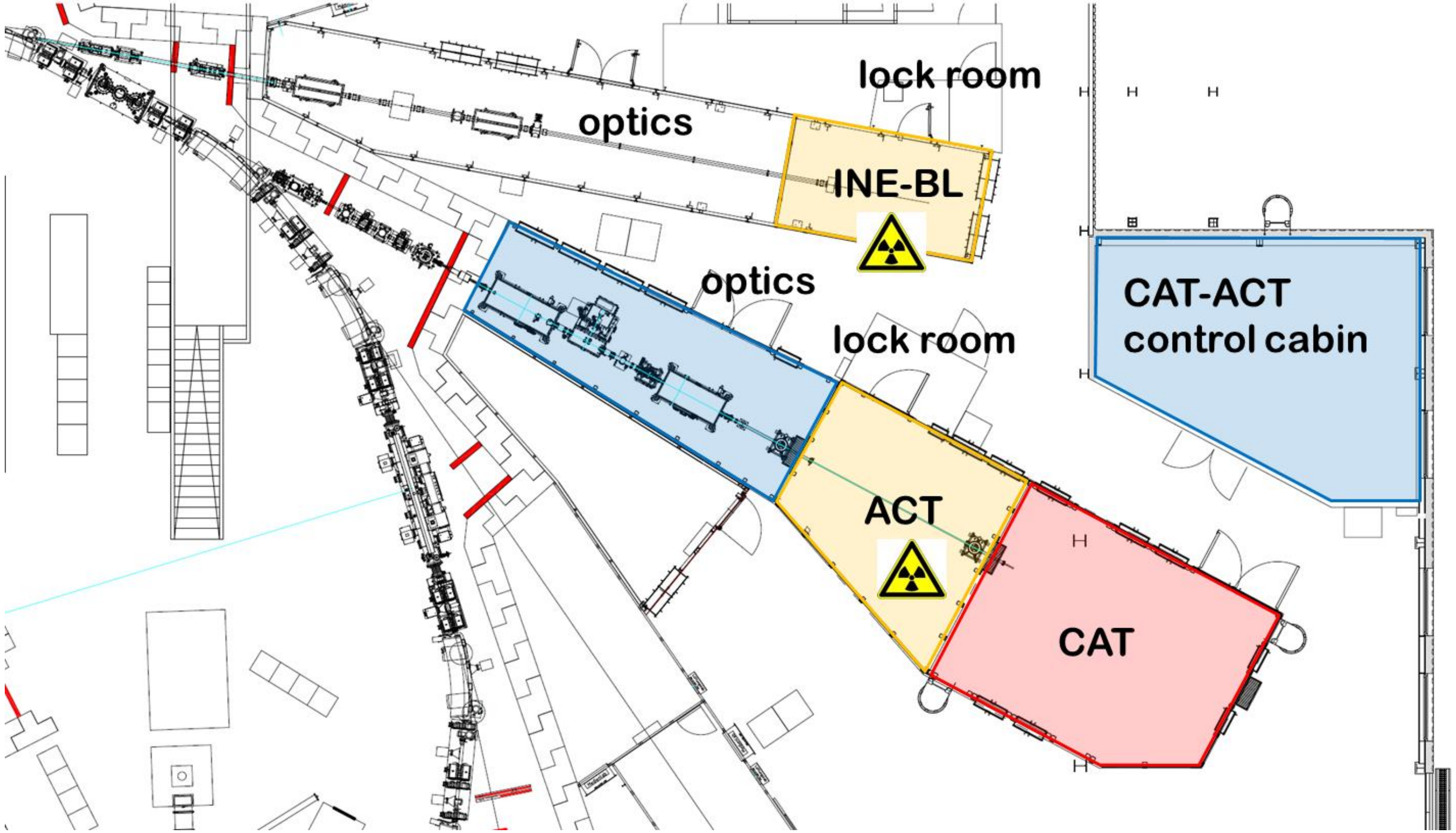


- 110-m **2.5-GeV** electron storage ring.
- Electron energy range: 0.5 – 2.5 GeV.
- Injector has a repetition rate of 1 Hz.
- Adjustable electron bunch lengths: 50 ps down to a few ps.
- Single- and multi-bunch operation modes.
- Insertion devices (ID): bending magnets (16), wigglers (2) and superconducting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



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

INE-Beamline und CAT-ACT SR labs

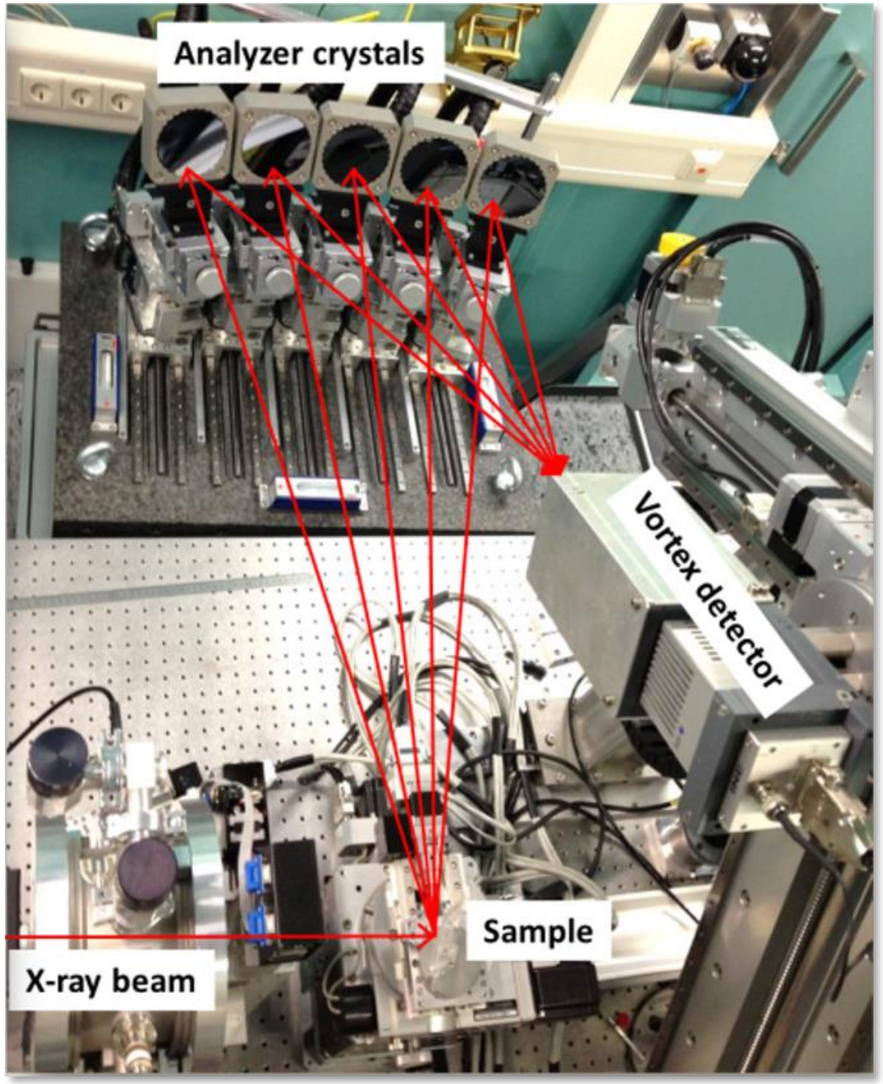


- INE-BL fully operational since October 2005 - 2nd dedicated SR beamline for radioactive materials in Europe
- CAT-**ACT** fully operational since fall 2016
- Energy range 2.1 – 55 keV, bending magnet (INE-BL) or superconducting wiggler source (CAT-ACT)
- XAS detection limits (*An*) ~ $1 \cdot 10^{-6}$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

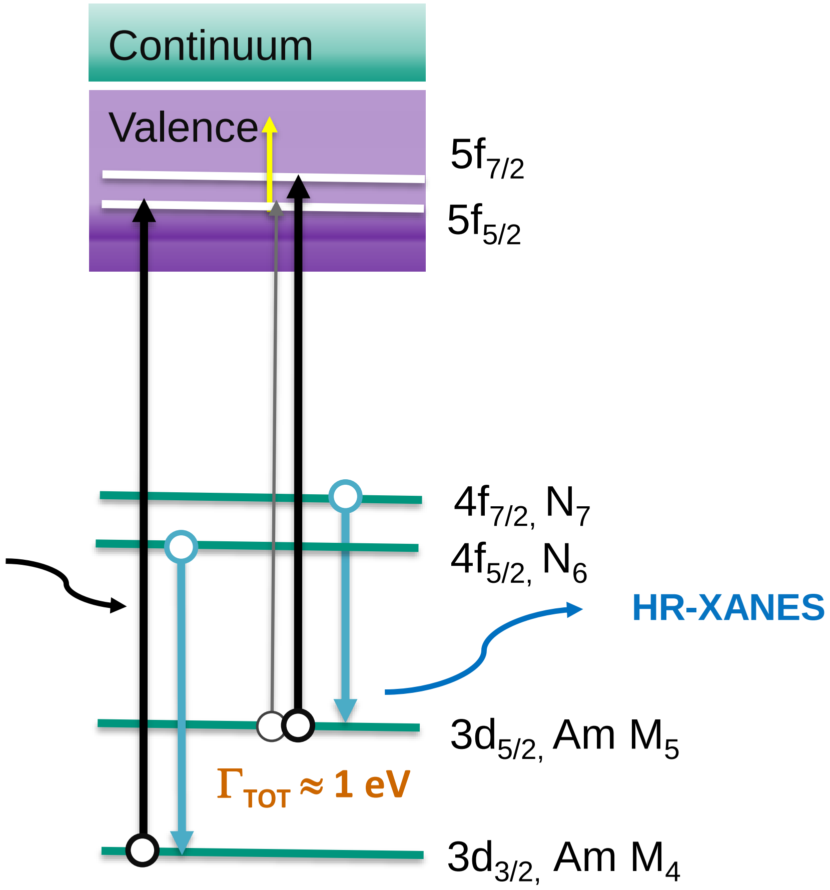
Both stations licensed for working with 10^6 times the exemption limit and up to 200 mg of fissile isotopes U-235 and Pu-239 within a double containment (sum rule applicable).

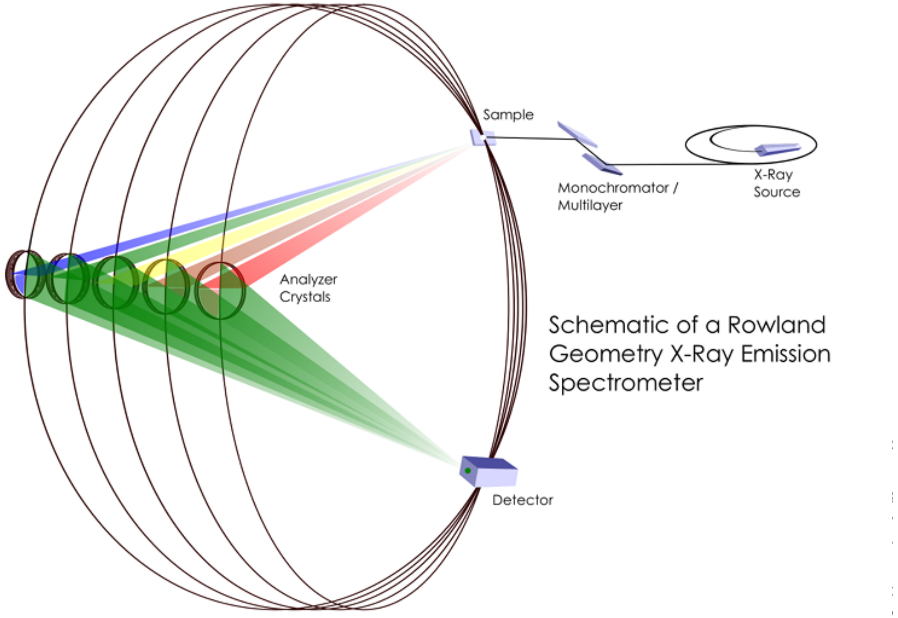
Experimental techniques: ACT beamline

- **Energy range** operation with mirrors: 3.4 – 35 keV, mirror-less above (~55 keV)
- **Source** 2.5 T superconducting multipole wiggler (Ec=10.2keV, 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 at *An* $M_{4,5}$ edges

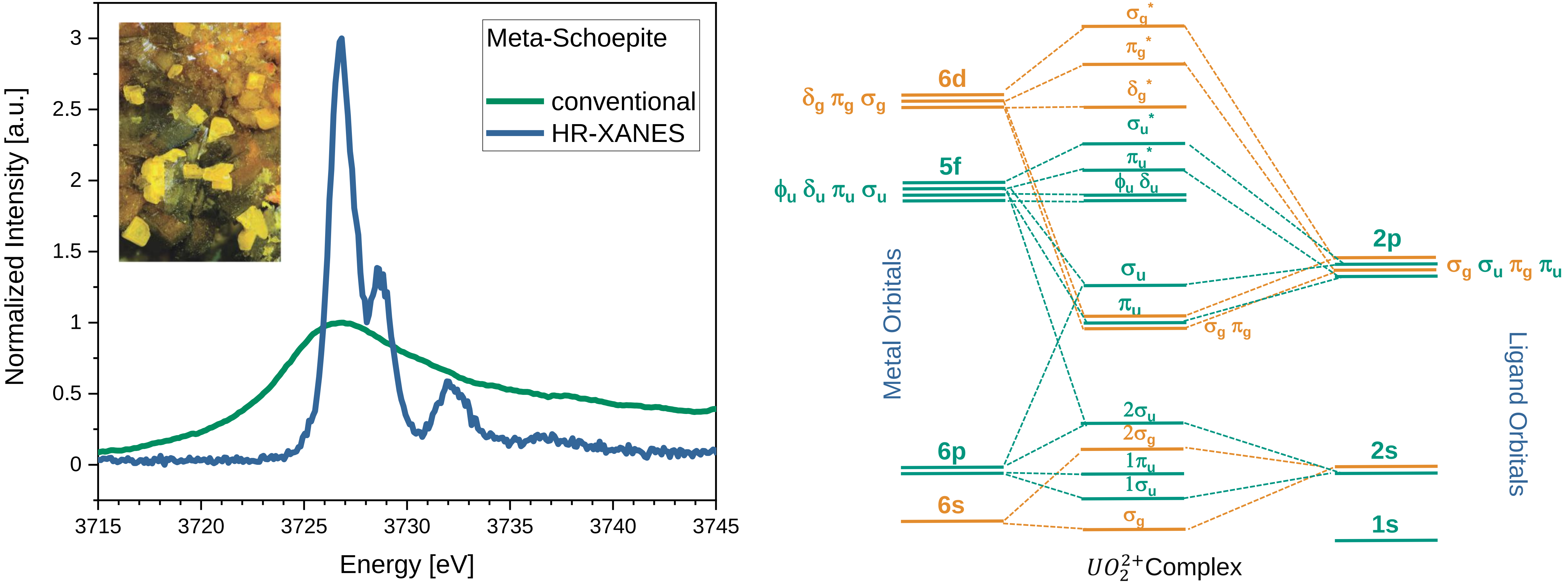




- Broadening effects:
  - Core-hole lifetime: high energy absorptions edge have short core-hole lifetimes.
  - Experimental: spectrometer improves exp. broadening
    - FLUO mode: the final state core-hole lifetime has bigger influence.

Schematics of electron excitations and emission transitions for An $M_{4,5}$ *edges (left) and of a Rowland geometry X-ray spectrometer (right).*

Mechanism of High-Energy Resolution XANES at *An* $M_{4,5}$ edges

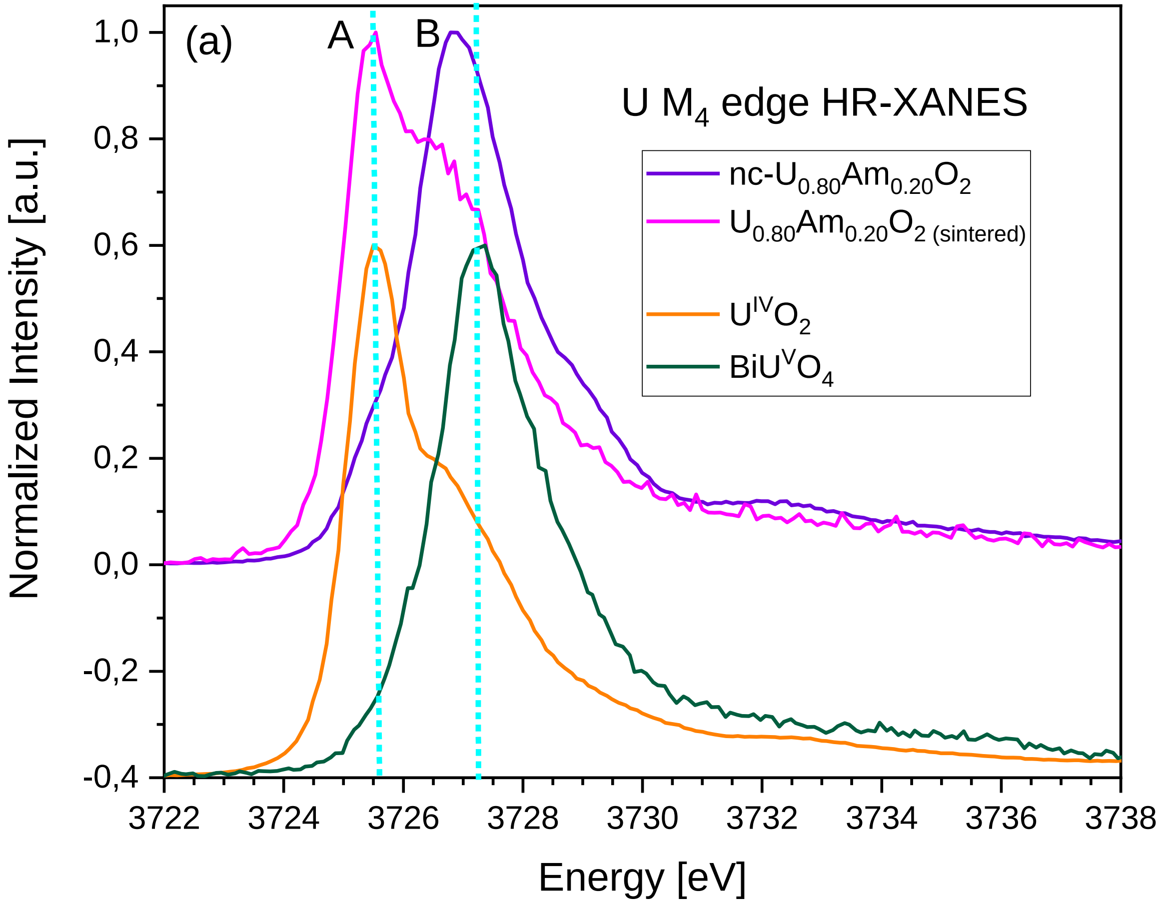


*U M_4 conventional (green) and HR-XANES (rblue) spectra of $UO_3\cdot 1\text{-}2H_2O$ (meta-schoepite, left) and a bonding scheme for actinyl (right, after**).*

***Journal of Physics: Conference Series**. *Actinide and lanthanide speciation with high-energy resolution X-ray techniques T. Vitova et.al. **2013**, 430, 012117*

** R. G. Denning et al., *J. Phys. Chem. A* **2007,** *111*, 4125-4143

Results: U M_4 HR-XANES cont‘d

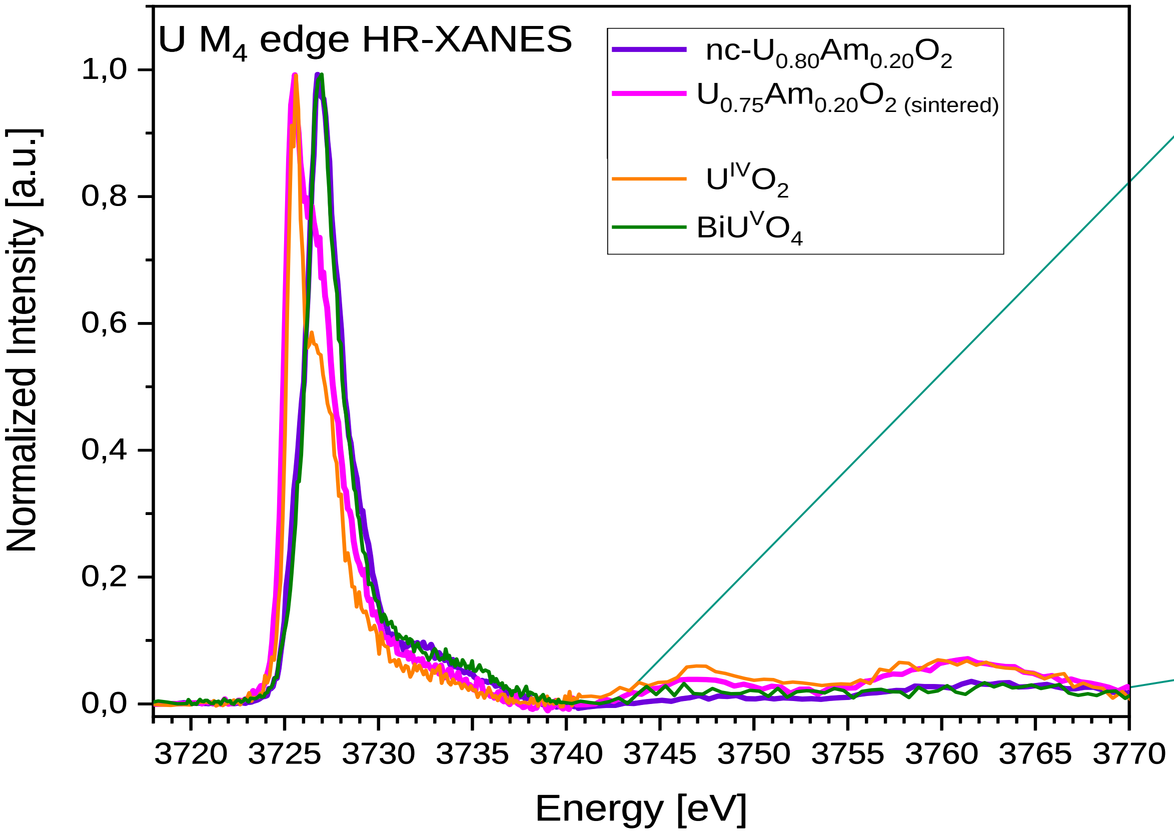


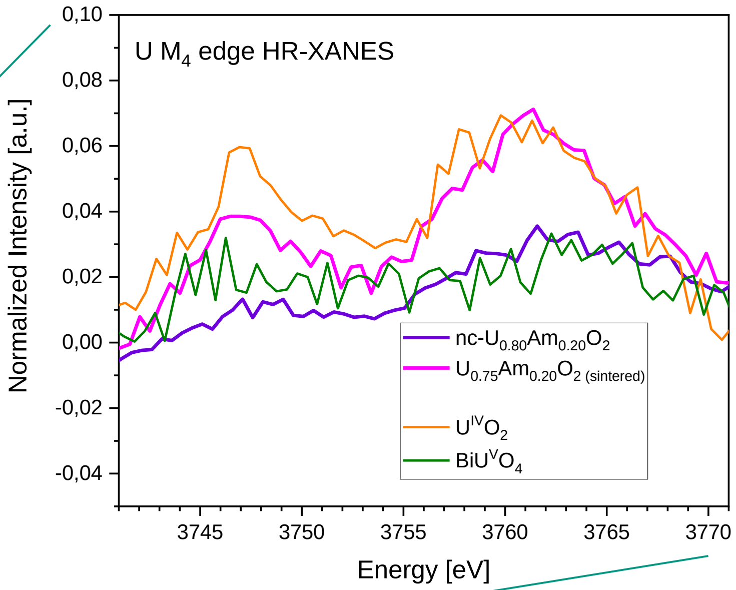
- The U^V stabilizes on the surface of the nanocrystals (10-13 nm size) with cubic FCC structure and strongly reduces to U^{IV} upon sintering at 1600-1650 °C.
- The energy position of feature B in the BiU^VO_4 spectrum located at about 3727.3 eV is characteristic of the main absorption intensity of U^V.
- The energy position of feature A in the $U^{IV}O_2$ spectrum located at about 3725.5 eV is consistent with published data.
- This details can not be detected with conventional U L_3 edge XANES.
- Nanoparticles can be described as a core-shell structure, with surface U^V and majority of U^{IV} in core.

U M_4 HR-XANES spectra for nc-$U_{0.80}Am_{0.20}O_2$ (lilac) and after sintering (magenta) along with $U^{IV}O_2$, BiU^VO_4, references.

***CrystEngComm**. *Synthesis and characterization of homogeneous (U,Am)O_2 and (U,Pu,Am)O_2 nanopowders J-F. Vigier et.al. **2022**, 24, 6338*

Results: U M_4 HR-XANES*



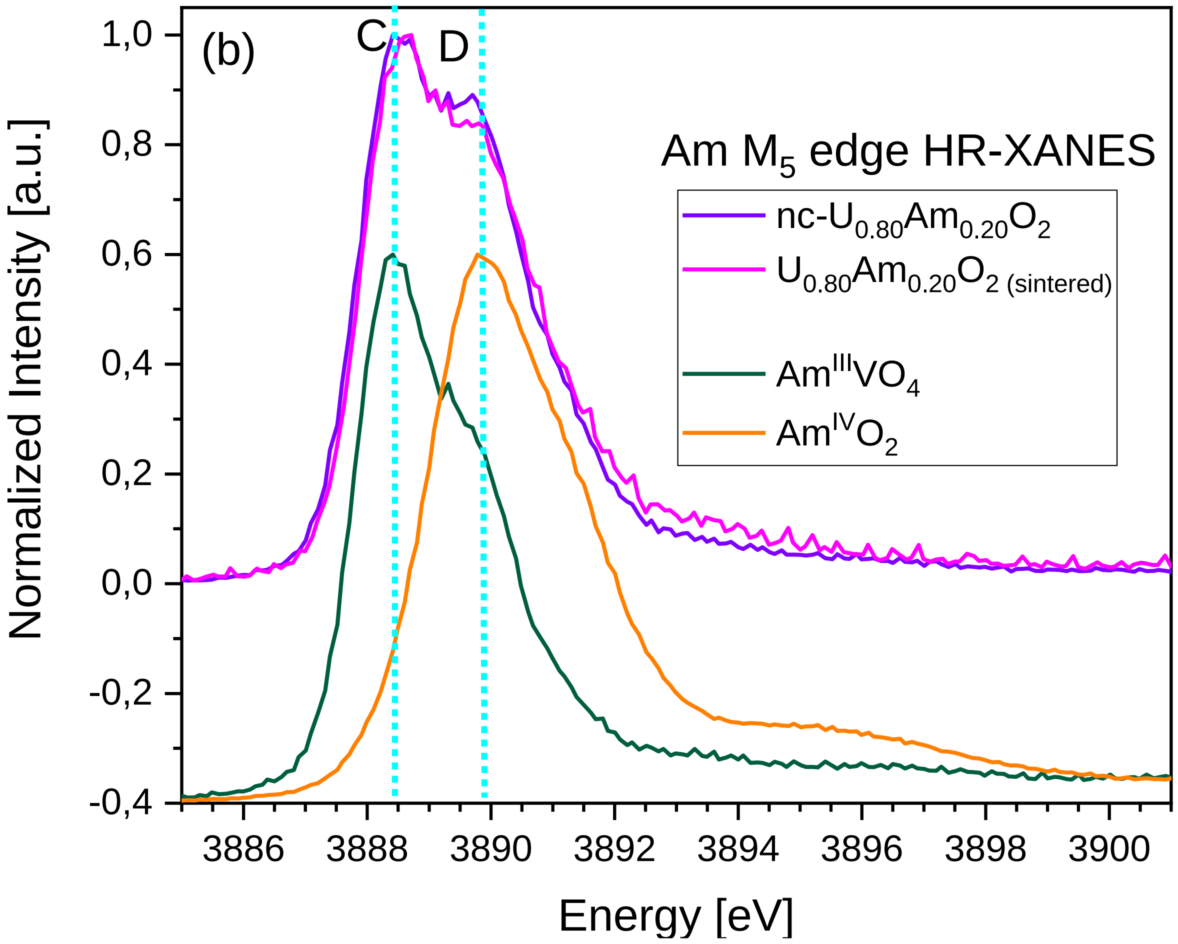


- The post-edge region of the spectra exhibits two broad peaks typical for the FCC cubic structure, also confirmed by XRD measurements.

HR-XANES U M_4 edge for as-synthesised nanoparticles (lilac) and sintered (magenta) $U_{0.80}Am_{0.20}O_2$ samples (left). The post-edge range along with the $U^{IV}O_2$ (orange) and the $BiU^{V}O_4$ (green) references (right).

***CrystEngComm**. *Synthesis and characterization of homogeneous (U,Am)O_2 and (U,Pu,Am)O_2 nanopowders J-F. Vigier et.al. **2022**, 24, 6338*

Results: Am M_5 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 $Am^{IV}O_2$ also present in the in $Am^{III}VO_4$.
- 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 $U_xAm_yO_{2+\delta}$ (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 M_5 HR-XANES spectra for nc-$U_{0.80}Am_{0.20}O_2$ (lilac) and after sintering (magenta) along with $Am^{III}VO_4$, $Am^{IV}O_2$ references.

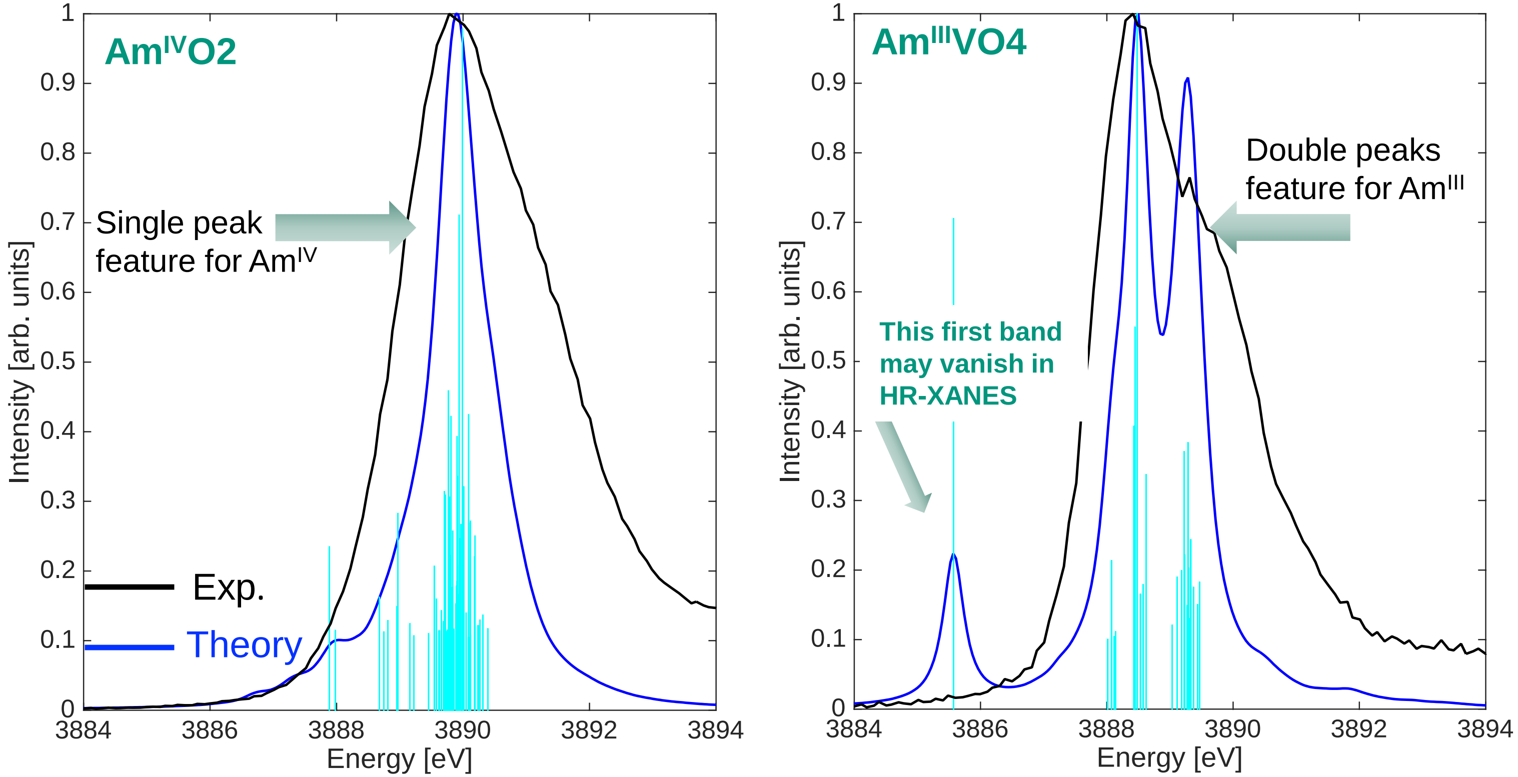
***CrystEngComm**. *Synthesis and characterization of homogeneous (U,Am)O_2 and (U,Pu,Am)O_2 nanopowders J-F. Vigier et.al. **2022**, 24, 6338*

Results: DFT Am M_5 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. $Am^{IV}O_2$ is modelled with the molecular $(AmO_8)^{12-}$ 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



Single peak feature for Am^{IV}

Double peaks feature for Am^{III}

This first band may vanish in HR-XANES

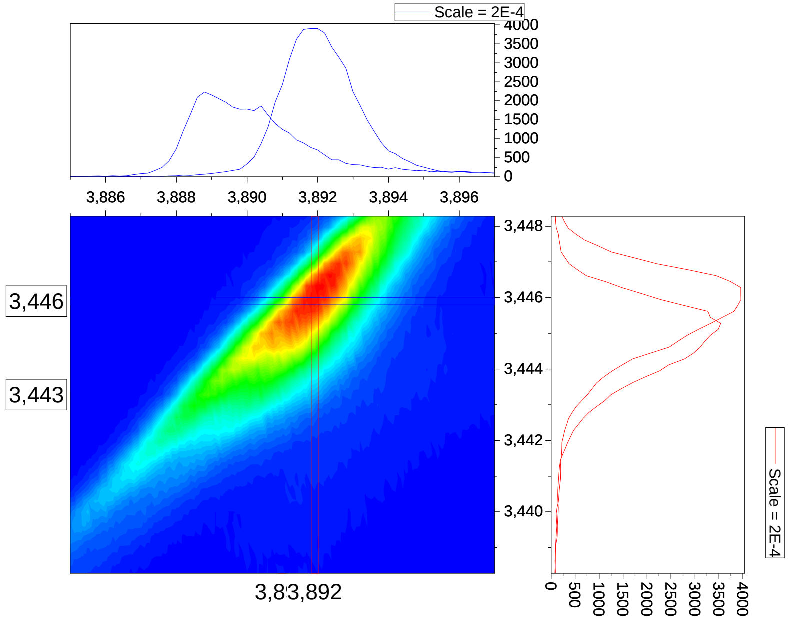
The cyan bars are the calculated oscillator strengths of the $5f^n \rightarrow 3d^9\ 5f^{n+1}$ transitions, which are convoluted with a Lorentizan function giving rise to the blue curves.

Conclusions and future work

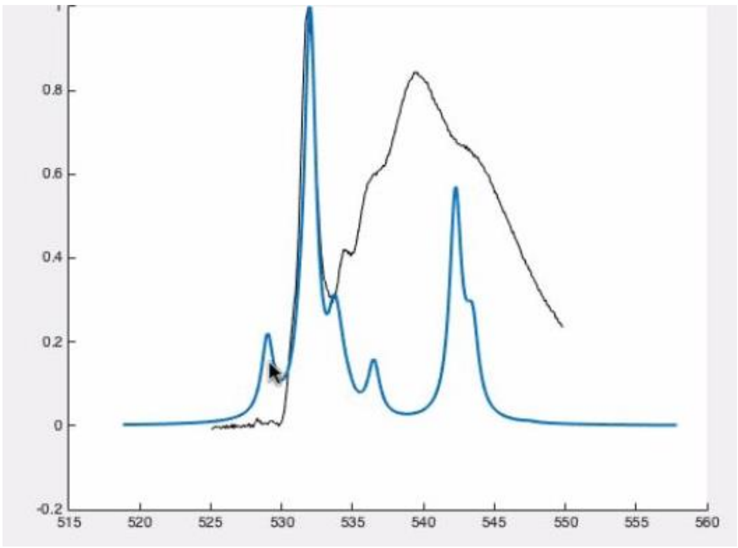
- An $M_{4,5}$ edge HR-XANES is a powerful tool for electronic structure and oxidation states studies. Here nc- $U_{0.80}Am_{0.20}O_2$ and bulk $(U, Am)O_2$ had been studied by U M_4 and Am M_5 HR-XANES.
- Typical oxidation states detected are the majority of U^{V} and Am^{III} with minor amount of Am^{IV} stabilized in the as prepared nc-$U_{0.80}Am_{0.20}O_2$ crystals.
- Minor contribution of Am^{IV} is present in the nanocrystals likely as a result of surface oxidation of the predominant Am^{III} core-shell structure.
- 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 effect of significant U reduction in $(U, Am)O_2$ upon sintering also observed for Am doping as low as 1% (5% - 10%).

Conclusions and future work

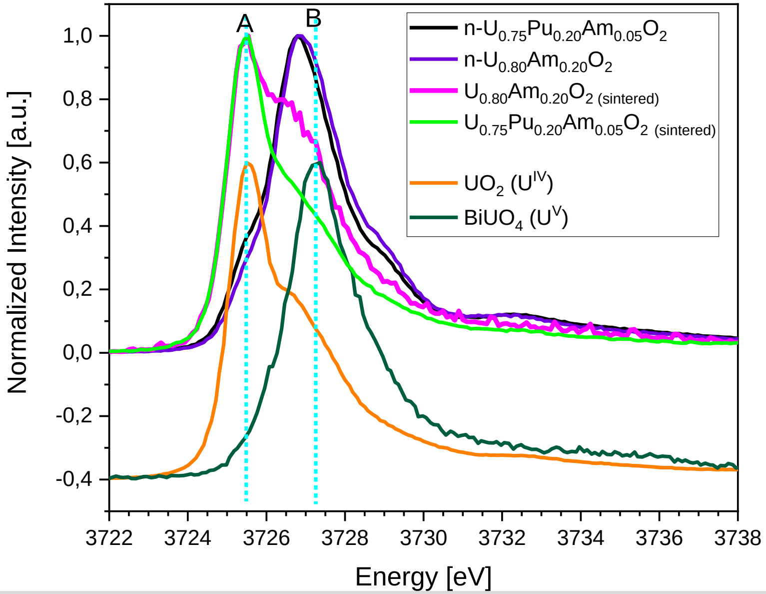
- **RIXS** analysis for the quantitative evaluation of the multiple oxidation states for uranium and americium (LCF)..
- **Soft X-ray** O K-edge XANES at the XSPEC beamline.
- **DFT** calculations of CC-RIXS.
- **Sample complexity** investigation of tri-metallic system (U, Am\Pu)$O_{2.}$



O K-edge



U M4 edge



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THE ACTINIDE BOND

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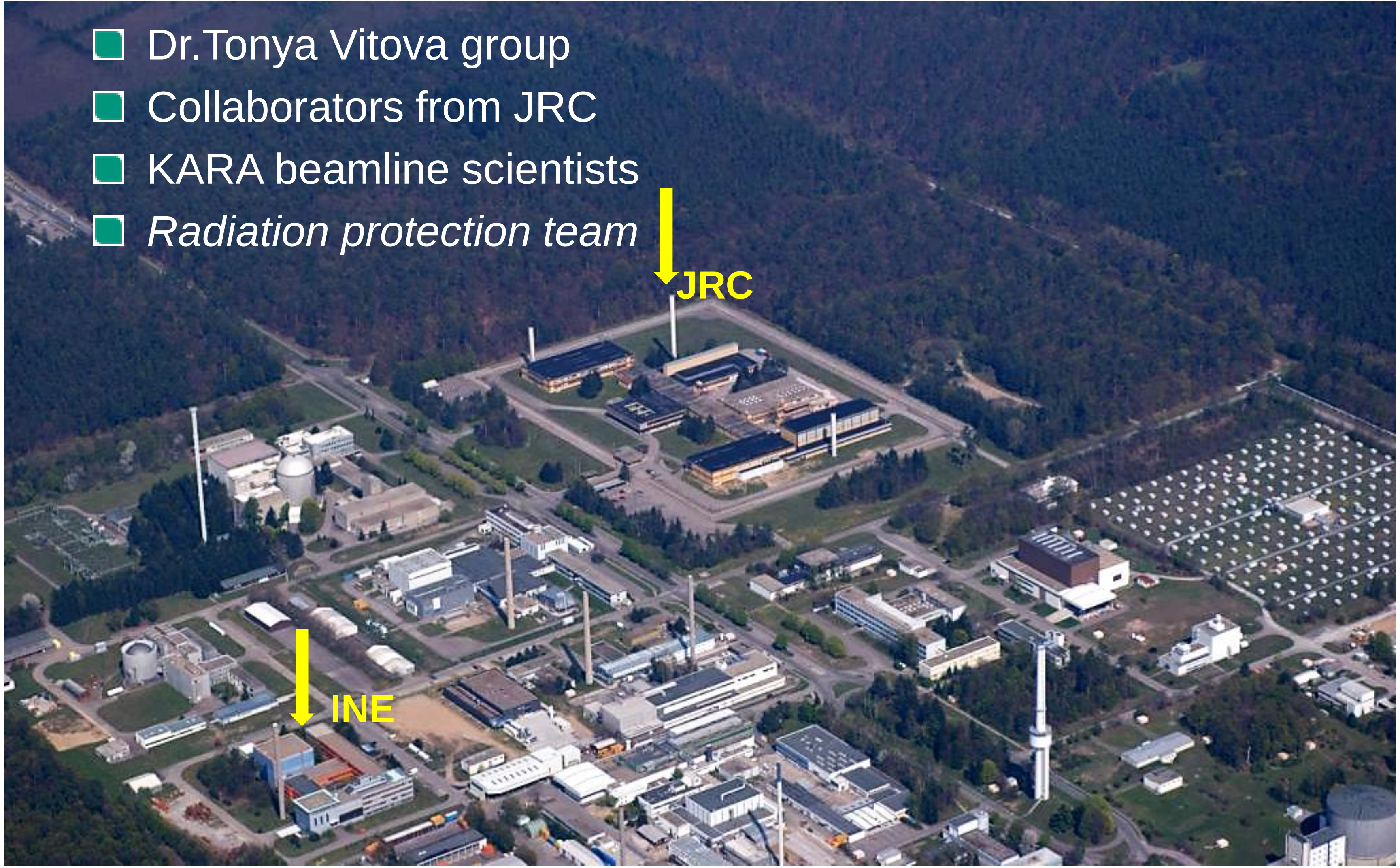
- KARA beamline scientists
- *Radiation protection team*



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