Names and affiliations of applicants (* indicates experimentalists):

Kristina Kvashnina[1,2*], Lucia Amidani[1,2*], Evgeny Gerber[1,2,]

[1] The Rossendorf Beamline at the ESRF (Grenoble, France)

[2] The Helmholtz-Zentrum Dresden-Rossendorf (HZDR), Institute of the Resource Ecology, Germany

Report:

We performed structural characterization of the PuO_2 nanoparticles, prepared by various synthetic methods. Prior the studies, we synthesized several types of PuO_2 NPs, using environmentally and waste storage relevant conditions, *i.e.* varying the pH (*e.g.* pH 8 and pH 12) and the precursor (Pu(III), Pu(IV), Pu(V) and Pu(VI)) – six samples in total, which were investigated by the High energyresolution fluorescnece detection (HERFD) method at BM20.

Fig.1 **. L$_3$ HERFD experimental data recorded** for six PuO_2 NPs samples and compared with a PuO_2 reference.

The Pu L$_3$ HERFD experiments were performed at the Rossendorf Beamline of ESRF. The energy of the X-ray beam was tuned by a double-crystal monochromator operating in channel-cut mode using a Si(111) crystal pair. Two rhodium-coated Si mirrors before and after the monochromator were used to collimate the beam and to reject higher harmonics. XANES spectra were simultaneously measured in total fluorescence yield (TFY) mode with a photodiode and in HERFD mode using an x-ray emission spectrometer.[1] The sample, each crystal analyzer and the silicon drift detector (Ketek) were positioned on their respective vertical Rowland circles of 0.5 m diameter. The Pu L$_3$ spectra were collected by recording the intensity of the Pu L$_{\alpha1}$ emission line (14,282.0 eV) as a function of the incident energy. The emission energy was selected using the [777] reflection of five spherically bent Si crystal analyzers (with 0.5 m bending radius) aligned at 75.7° Bragg angle. The intensity was normalised to the incident flux. A combined (incident convoluted with emitted) energy resolution of 2.8 eV was obtained as determined by measuring the full width at half maximum (FWHM) of the elastic peak.
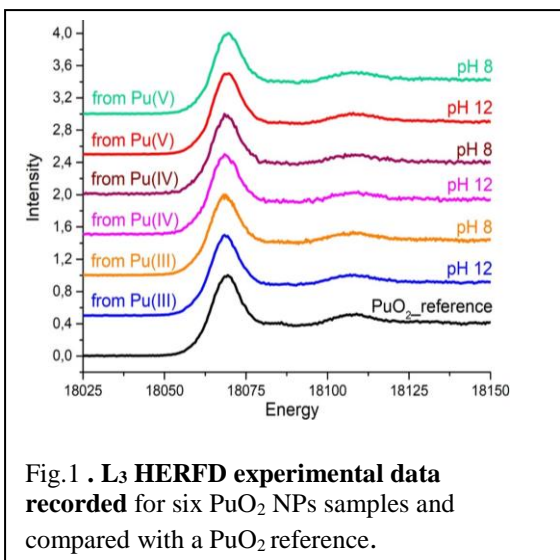
Information about Pu oxidation state has been obtained by the HERFD method at the Pu L_3 (Figure 1). Pu complexity and variety of colors is determined by its ground state electronic configuration [Xe] $5f^67s^2$. The 5f orbitals are close in energy to the 6d orbitals, which makes electrons from these orbitals more accessible for chemical bonding, leading to diversity of oxidation states and different Pu species. We analysed six colloidal Pu samples by the HERFD method, which is an element-selective technique as the energy of an absorption edge corresponds to the characteristic core-level energy. The information about the electronic structure, oxidation state and the local geometry of the absorbing atom can be obtained from the HERFD spectral shape – thanks to the possibility to record electronic transitions with high energy resolution with an X-ray emission spectrometer.[1]

Fig. 1 shows HERFD data recorded for six PuO_2 NP samples at the Pu L_3 edge compared to both the spectrum of the PuO_2 reference [2]. Electrons at the Pu L_3 absorption edge are excited from the core 2p level to the empty Pu 6d electronic levels. All spectral features of PuO_2 NPs are very similar, corresponding to those of the PuO_2 reference and are well reproduced by calculations based on the bulk PuO_2 crystal structure[2]. Therefore, HERFD results at the Pu L_3 edge confirm that the local environment of all PuO_2 NPs samples is similar to bulk PuO_2, in agreement with the previous HRTEM, XRD and HEXS results. This is also supported by a comparison of the area under the white line (WL) and its FWHM [2]. Moreover, the HERFD data confirms the presence of the Pu(IV) oxidation state as the dominant valence of PuO_2 NPs, as seen from the positions of the Pu white line.
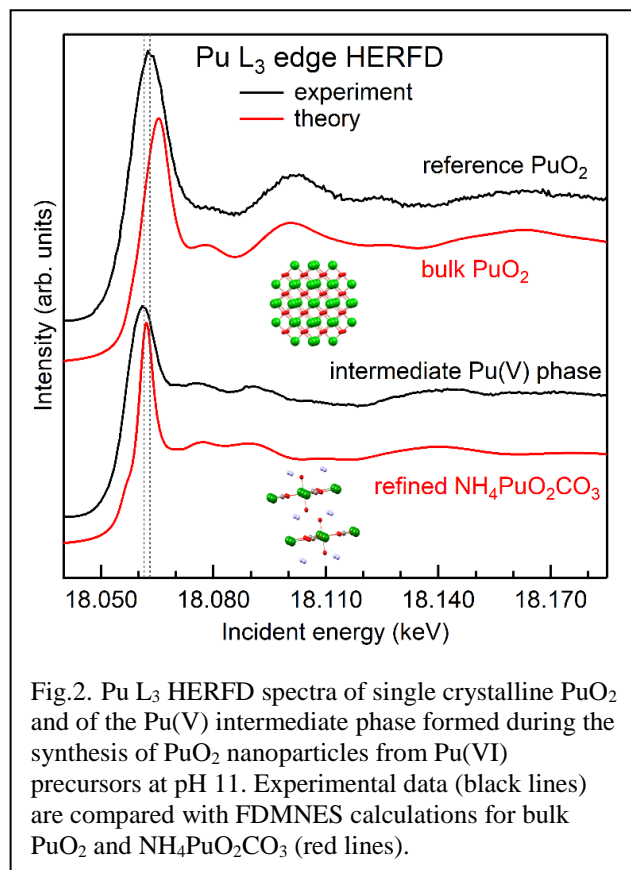

Fig.2. Pu L_3 HERFD spectra of single crystalline PuO_2 and of the Pu(V) intermediate phase formed during the synthesis of PuO_2 nanoparticles from Pu(VI) precursors at pH 11. Experimental data (black lines) are compared with FDMNES calculations for bulk PuO_2 and $NH_4PuO_2CO_3$ (red lines).

The case of the PuO_2 NPs formation from Pu(VI) precursor under pH 11 was very different. We found that transformation to the PuO_2 NPs phase from Pu(VI) solution proceeds through two step-proces: during the first minutes of synthesis we observed the formation of an intermediate Pu phase consisting of yellow sludge. Later, the intermediate phase was completely dissolved within ~10 hours and then, as a result of longer redox reactions the PuO_2 NPs were formed. HERFD experiments at the Pu L_3 edge gave us the opportunity to identify the intermediate phase forming in the course of the PuO_2 NPs growth. Fig.2 shows the comparison of the Pu HERFD L_3 edge data recorded for PuO_2 and the intermediate Pu phase during the PuO_2 NPs formation. The L_3 spectrum of Pu(V) compounds always shows a very characteristic energy shift towards low energies and a decrease of the L_3 white line intensity compared to Pu(IV) and Pu(VI) systems. The chemical shift of the intermediate Pu phase is clearly resolved in the HERFD data reported in Fig.2 and indicates the presence of the Pu(V) oxidation state. Moreover, HERFD at the L_3 edge is, extremely sensitive to the local structure around the absorber, which results in specific post-edge features. Ab-initio calculations on different structures were used to identify the intermediate Pu phase during the synthesis of PuO_2 NPs. We simulated the HERFD spectra of several compounds containing Pu in order to determine the Pu speciation of the intermediate Pu phase structure. The best agreement is found for $NH_4PuO_2CO_3$, in which Pu is indeed present in the pentavalent state. Results are published in Angewandte Chemie [3].

References:
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