

**Experiment title:**

XAS study of uranium and plutonium local environment in (U,Pu)O<sub>2</sub> solid solution: influence of the Pu/(U+Pu) ratio and of the synthesis method

**Experiment number:**

MA-233

**Beamline:**

BM20

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12

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*Received at ESRF:*

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**Report:**

New synthesis methods were recently optimized in the CEA Atalante facility at Marcoule in order to obtain (U,Pu)O<sub>2</sub> solid solutions with a minimal content of synthesis impurities and a O/M ratio equal to 2.0. The impurities, mainly residual carbon, were probably responsible for the formerly detected disorder in the local environment of both actinides. The first method based on the oxalic co-precipitation of U(IV) and Pu(III) followed by the thermal conversion of the co-precipitate into oxide, produces solid solutions whose cell parameters deduced from X-Ray diffraction experiments obey the Vegard's law. The second one based on the internal gelation of a U(VI)-Pu(IV) solution (or a U(IV)+Pu(III) one) followed by a thermal treatment at around 1000°C, produces mixed oxide whose structure was more difficult to establish due to possible various oxidation states for plutonium in the oxide or obtainment of non-ideal solid solution.

The objective of this new experiment is to study the local uranium and plutonium environment of mixed U-Pu oxide depending on the molecular precursor i.e. either a crystallized mixed oxalate (oxalic co-precipitation) or a mixed hydrated oxide (internal gelation). Thus, the local environment around each cation will tell us if ideal solid solution is obtained or not with the two preparation methods.

**Results**

Five samples were prepared using both previously described methods:

- (U,Pu)O<sub>2</sub> with Pu/(U+Pu) equal to 15 at. % (internal gelation of U(IV) and Pu(III))
- (U,Pu)O<sub>2</sub> with Pu/(U+Pu) equal to 28 at. % (oxalic co-conversion)
- (U,Pu)O<sub>2</sub> with Pu/(U+Pu) equal to 45 at. % (oxalic co-conversion)
- (U,Pu)O<sub>2</sub> with Pu/(U+Pu) equal to 55 at. % (oxalic co-conversion)
- (U,Pu)O<sub>2</sub> with Pu/(U+Pu) equal to 50 at. % (internal gelation of U(VI) and Pu(IV))

Measurements were performed at 15K using an helium cryostat and for each sample U L<sub>3</sub> edge (Fig. 1 and 2) and Pu L<sub>2</sub> edge (Fig. 3 and 4) XANES and EXAFS spectra were collected.

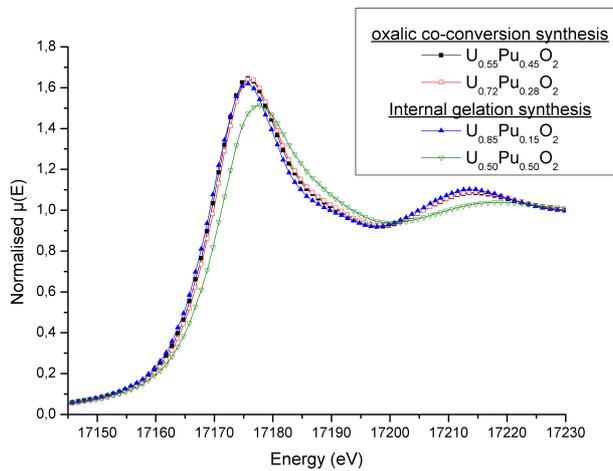


Fig 1: Uranium L<sub>3</sub> edge XANES spectra.

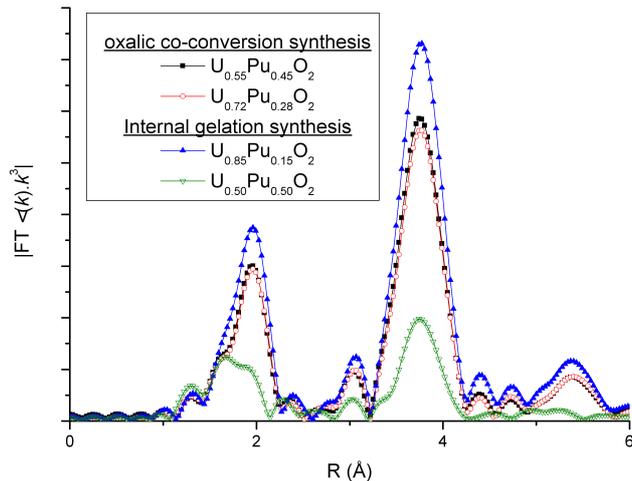


Fig 2: Fourier transforms U L<sub>3</sub> edge ( $2.4 < k(\text{Å}^{-1}) < 14.4$ ).

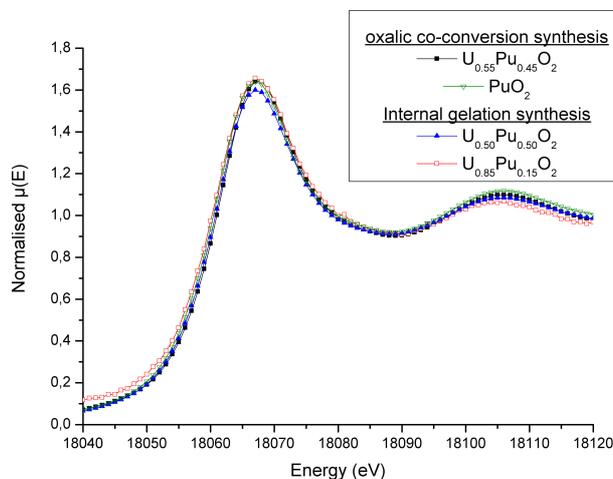


Fig 3: Plutonium L<sub>3</sub> edge XANES spectra.

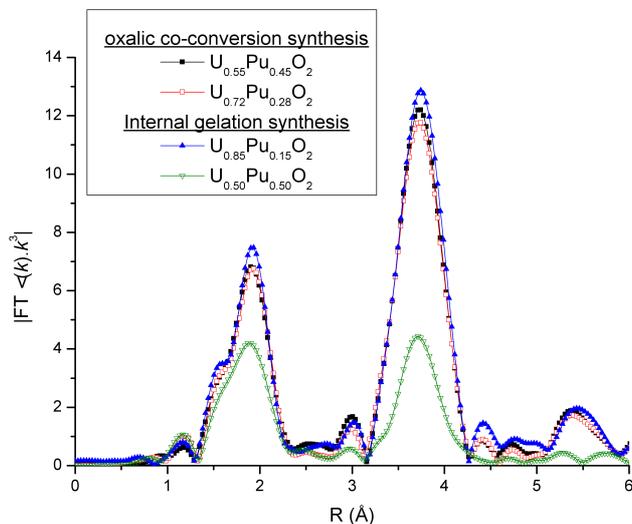


Fig 4: Fourier transforms Pu L<sub>2</sub> edge ( $2.4 < k(\text{Å}^{-1}) < 14.0$ )

Concerning all the samples synthesised by oxalic co-conversion and the  $\text{U}_{0.85}\text{Pu}_{0.15}\text{O}_2$  sample obtained by inter gelation of a U(IV)-Pu(III) solution, the same conclusions are obtained:

- XANES interpretation shows that uranium and plutonium ions oxidation degree is +IV.
- EXAFS fits demonstrate that both uranium and plutonium local environments are the same and corresponds to the face centred cubic structure expected. Moreover a shortening of bond lengths is observed as the plutonium content increases.

**These new XAS characterization clearly demonstrated the formation of an ideal (U,Pu)O<sub>2</sub> solid solution with oxalic co-conversion synthesis method. Same conclusion can be made for the sample based on the internal gelation of a U(IV)-Pu(III) solution ( $\text{U}_{0.85}\text{Pu}_{0.15}\text{O}_2$ ).**

This is not the case for the sample obtained by internal gelation of a U(VI)-Pu(IV) solution ( $\text{U}_{0.5}\text{Pu}_{0.5}\text{O}_2$ ). Compared to the other samples, a shift of the white line and a shoulder at +20 eV can be observed on the uranium XANES spectrum collected on this sample. Those features clearly indicate that a significant part of uranium is oxidized to  $\text{U}^{+VI}$ . Moreover, Fourier transforms confirms this observation as two U-O distances are evidenced in the first coordination shell: the first and short U-O distance is attributed uranyl-type bond and the second corresponds to U-O distance expected for a fluorite type solid-solution. Concerning the plutonium environment, the same behaviour observed in our previous study [1] is obtained:  $\text{Pu}^{+IV}$  ions in a disordered (U,Pu)O<sub>2</sub> solid solution. The sample obtained by internal gelation seems thus to be of mixing of two phases: a  $\text{U}^{+VI}$  phase without a long range order and a disordered (U,Pu)O<sub>2</sub> solid solution. Clearly, the thermal treatment of the last sample was not efficient to reduce all U(VI) into U(IV).

[1] P. Martin et al, J. Alloys & Compounds 444-445(2007)410-414.