Combustion synthesis of (U,Pu)O_2 solid solution: from parametric study to sintered pellet

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Supplementary information

Stoichiometric conditions according to Jain [36]**:**

$$Pu(NO_3)_4 + \frac{20}{18}C_6H_8O_7 \rightarrow PuO_2 + \frac{40}{6}CO_2 + \frac{40}{9}H_2O + 2N_2$$

$$UO_2(NO_3)_2 + \frac{10}{18}C_6H_8O_7 \rightarrow UO_2 + \frac{10}{3}CO_2 + \frac{20}{9}H_2O + N_2 + \frac{1}{2}O_2$$

Theoretical calculation of stoichiometric conditions for a two oxidant-system:

When mixing two metals (M_1 and M_2) with different oxidant valences, several definitions enter in conflict. Monnier [32] and Peter Soldani [41] proposed to calculated the optimal richness, considering the optimal richness of each mixtures (Fuel/Metal 1 and Fuel/Metal 2):

$$\phi = \phi_{M_1}\frac{M_1}{M_1 + M_2} + \phi_{M_2}\frac{M_2}{M_1 + M_2}$$

Deganello and Tyagi proposed to consider a valences for the mixture according to the valences of the two metals and the M_1/M_2 ratio [53]:

$$V_{M_1+M_2} = V_1\frac{M_1}{M_1 + M_2} + V_{M_2}\frac{M_2}{M_1 + M_2}$$

References for HERFD-XANES deconvolution

The HERFD-XANES spectra were deconvoluted with a reference dataset, on Microsoft Excel solver. A linear combination of references was use to generate a model. Each reference corresponds to a specific oxidation state of actinide.

- **Pu M_4 edge :**
    - Pu(III): $Pu^{III}PO_4$

$PuPO_4$ was obtained by hydrothermal treatment of Pu(III) aqueous solution in hydrochloric media with H_3PO_4 (24 hours at 140°C). The powder obtained was then calcinated 1 hour at 1100°C under reductive atmosphere (Ar 95.7% ; H_2 4,3%) to obtain monazite type $PuPO_4$. The sample was characterized by PXRD measurement to confirm the formation of monazite type $PuPO_4$.

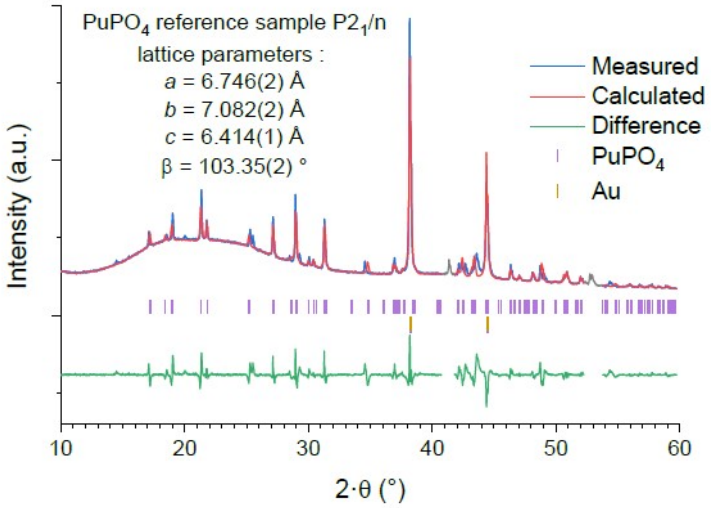

Figure S 1: PXRD-pattern of $PuPO_4$ powder used for Pu(+III) reference

- Pu(IV): $Pu^{IV}O_2$*

PuO_2 was obtained by oxalic precipitation of Pu(+IV), the sample was then calcinated 1 hour at 1100°C under air atmosphere. The stoichiometry of the oxide (O/M = 2.00) was checked by PXRD measurement (Figure S 2).

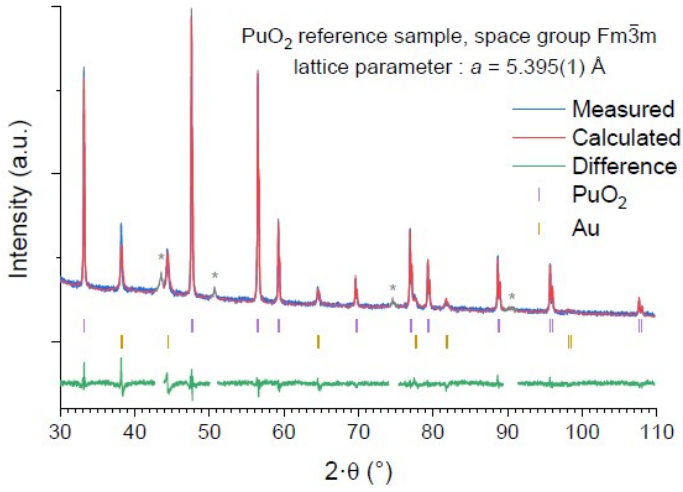

Figure S 2 : PXRD-pattern of PuO_2 powder used for spectrometer alignment and Pu(+IV) reference

- Pu(V): $Na_3(Pu^{V}O_2)(CO_3)_2$

$Na_3(Pu^{V}O_2)(CO_3)_2$ was obtained according to the protocol reported by Madic *et al.* [61] by electroreduction of a Pu(+VI) stock solution in sodium carbonate media. The structure was checked by Raman spectroscopy (Figure S 3). Additionally the HERFD-XANES spectra was compared to the $K(Pu^{V}O_2)CO_3$ reported by Pidchenko *et al.* and exhibit similar behavior [62].

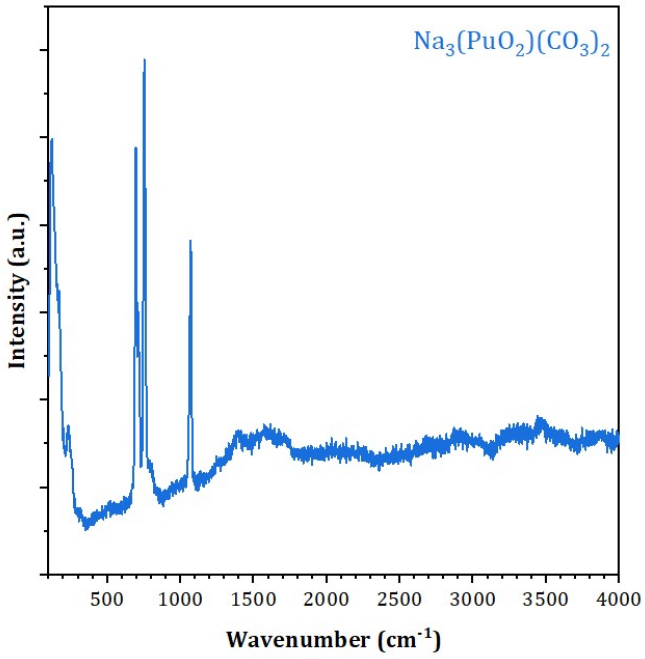

Figure S 3 : Raman spectrum of $Na_3(Pu^{V}O_2)(CO_3)_2$ used as Pu(+V) reference

- Pu(VI): $(Pu^{VI}O_2)(CO_3)_3^{4-}$

$(Pu^{VI}O_2)(CO_3)_3^{4-}$ in aqueous media was obtained by electrooxidation of a Pu(IV) stock solution in nitric media. This solution was then added dropwise to a 2 mol·L^{-1} sodium carbonate solution, leading to the formation of Pu(VI) carbonate complexes. The solution was filtrated in order to avoid the presence of colloids. The obtention of the $(Pu^{VI}O_2)(CO_3)_3^{4-}$ complex was checked by UV-vis spectroscopy (Figure S 3).

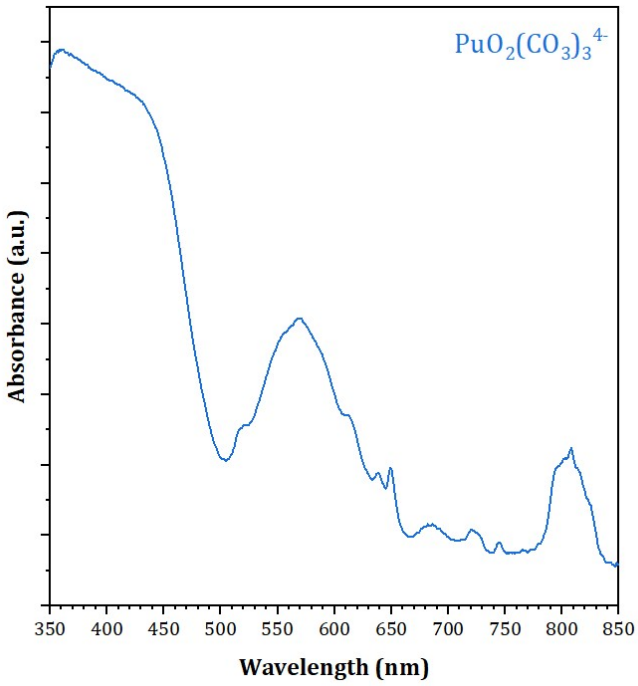

Figure S 4: UV-vis spectrum of $(Pu^{VI}O_2)(CO_3)_3^{4-}$ complex used as Pu(+VI) reference

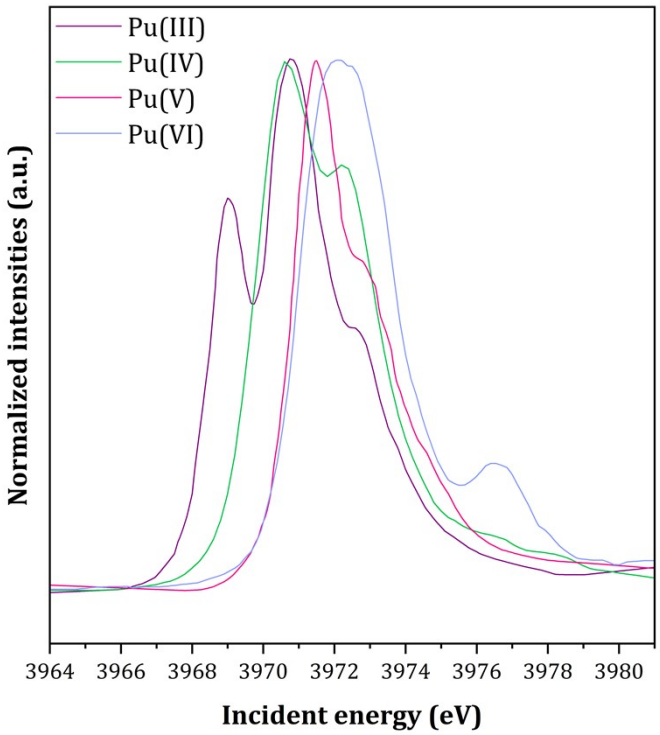

Figure S 5 : HERFD-XANES spectra of plutonium references recorded at plutonium M_4 edge: Pu(+III) is $Pu^{III}PO_4$, Pu(+IV) is PuO_2, Pu (+V) is $Na_5(Pu^{V}O_2)(CO_3)_3$ and Pu(+VI) is $(Pu^{VI}O_2)(CO_3)_3^{4-}$

- **U M4 edge :**
    - U(IV) : UO_2

UO_2 was obtained by U(+VI) precipitation with hydrogen peroxide, the sample was then calcinated 6 hours at 1000°C under reductive atmosphere (Ar 95.7% ; H_2 4,3%). The stoichiometry of the oxide (O/M = 2.00) was checked by PXRD measurement.

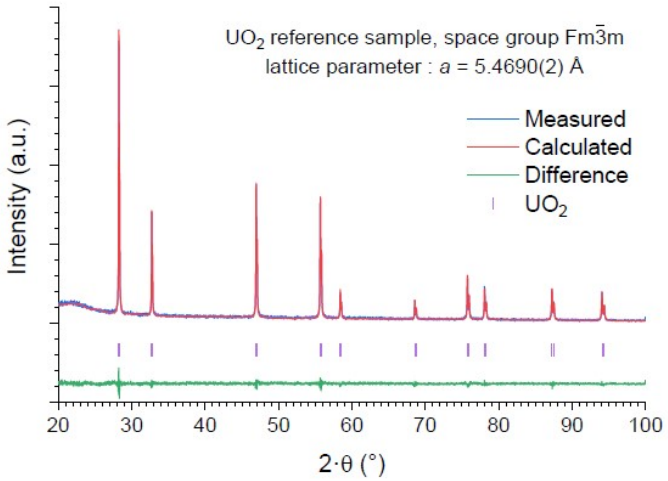

Figure S 6: PXRD-pattern of UO_2 powder used for spectrometer alignment and U(+IV) reference

    - U(+V)

KUO_3 spectra at uranium M_4 edge was taken from Leinders *et al.* work in reference [63].

- U(+VI)

β-UO_3 spectra at uranium M_4 edge was taken from Leinders *et al.* work in reference [63].

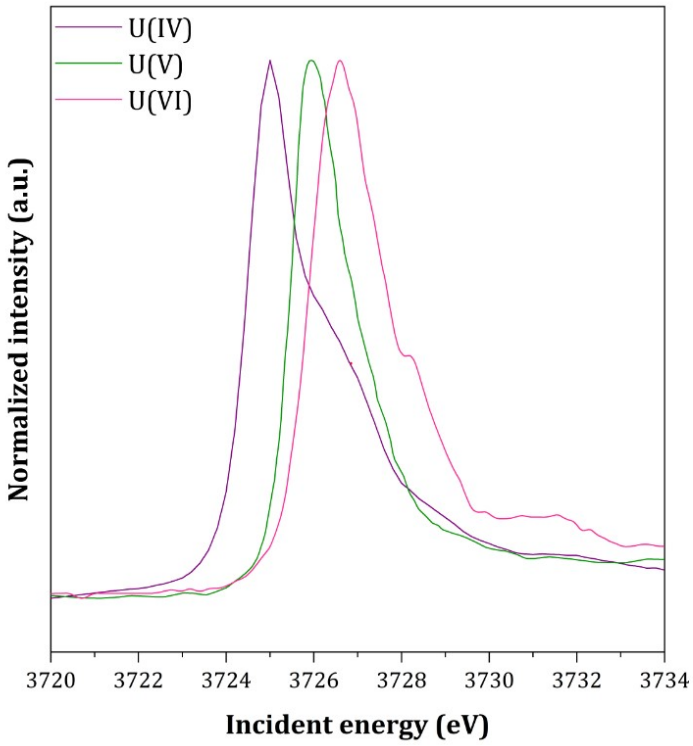

Figure S 7 : HERFD-XANES spectra of uranium references recorded at uranium M_4 edge: U(+IV) is UO_2, U(+V) and U(+VI) are taken from [63]

References

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[61] C. Madic, D. E. Hobart, and G. M. Begun, "Raman spectrometric studies of Actinide(V) and -(VI) complexes in aqueous sodium carbonate solution and of solid sodium Actinide(V) carbonate compounds," *Inorg. Chem.*, vol. 22, pp. 1494–1503, 1983.

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