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Manufacturing of (U,Pu)O_{2-x} mixed oxides with high plutonium contents (≥ 60 mol.% Pu)

DE LA RECHERCHE À L'INDUSTRIE



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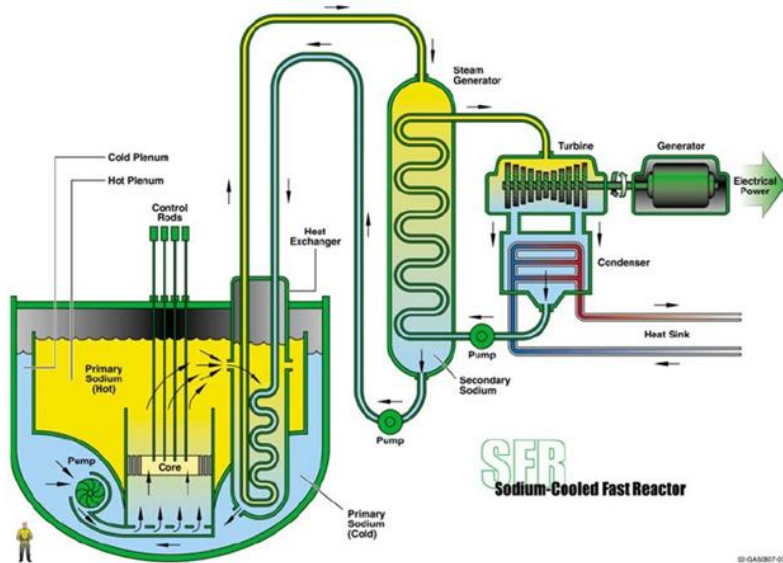
³ Université Paris-Saclay, CEA, SCCME, Gif-sur-Yvette, France

⁴ Univ. Montpellier, ICSM, CEA, CNRS, ENSCM, Marcoule, France

MOX



Currently studied as part of the fast reactors development.



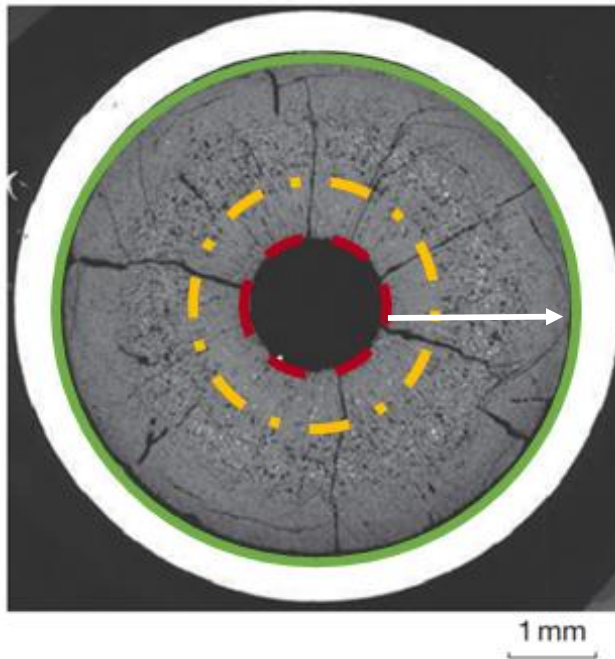
SFR (Sodium Fast Reactor) as ASTRID or Phenix reactor [1]

	MOX fuel for SFR
Pu content (y)	$0.15 < y < 0.35$
O/M	$1.94 < \text{O/M} \leq 1.99$
Porosity (%)	5%
Density	95 % TD
Microstructure heterogeneity	$\text{PuO}_2 < 100 \mu\text{m}$ $\text{UO}_2 < 200 \mu\text{m}$

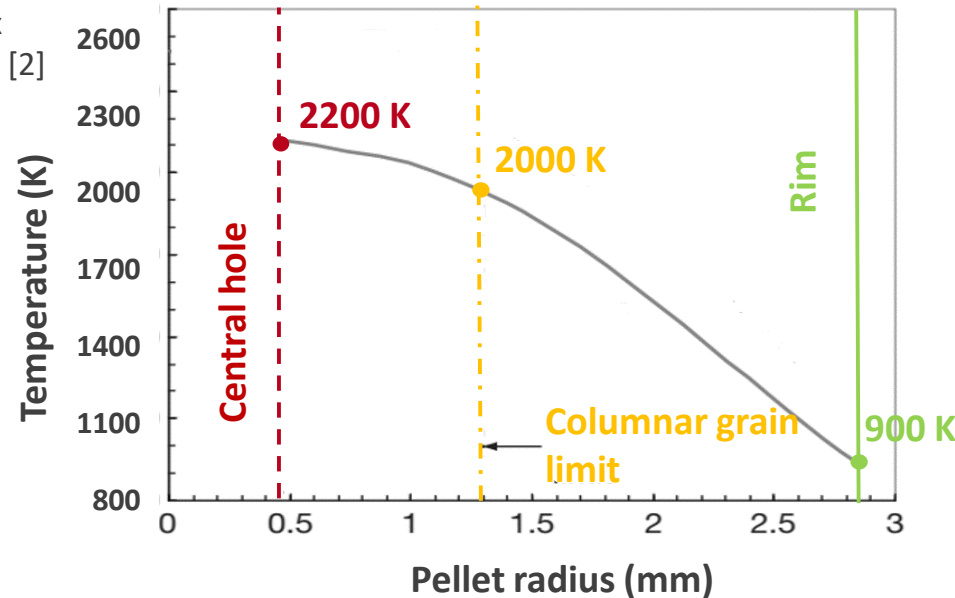
The main phenomena occurring at the beginning of life and high-temperature effects: fuel restructuring, radial redistribution of fuel constituents, and geometrical evolution.

[1] Direction de l'énergie nucléaire, le démonstrateur technologique ASTRID, 2012.

Under irradiation : Linear power $400\text{-}500 \text{ W.cm}^{-1}$
 Thermal Gradient from **900 K** to over **2200 K**



Micrograph of a Phenix pellet (Max flux plane) [2]
 Pu content : $\gamma = 0.20$
 $O/M^* = 1.978$
 Burnup: 13 at. %
Central hole
Columnar grain limit
Rim

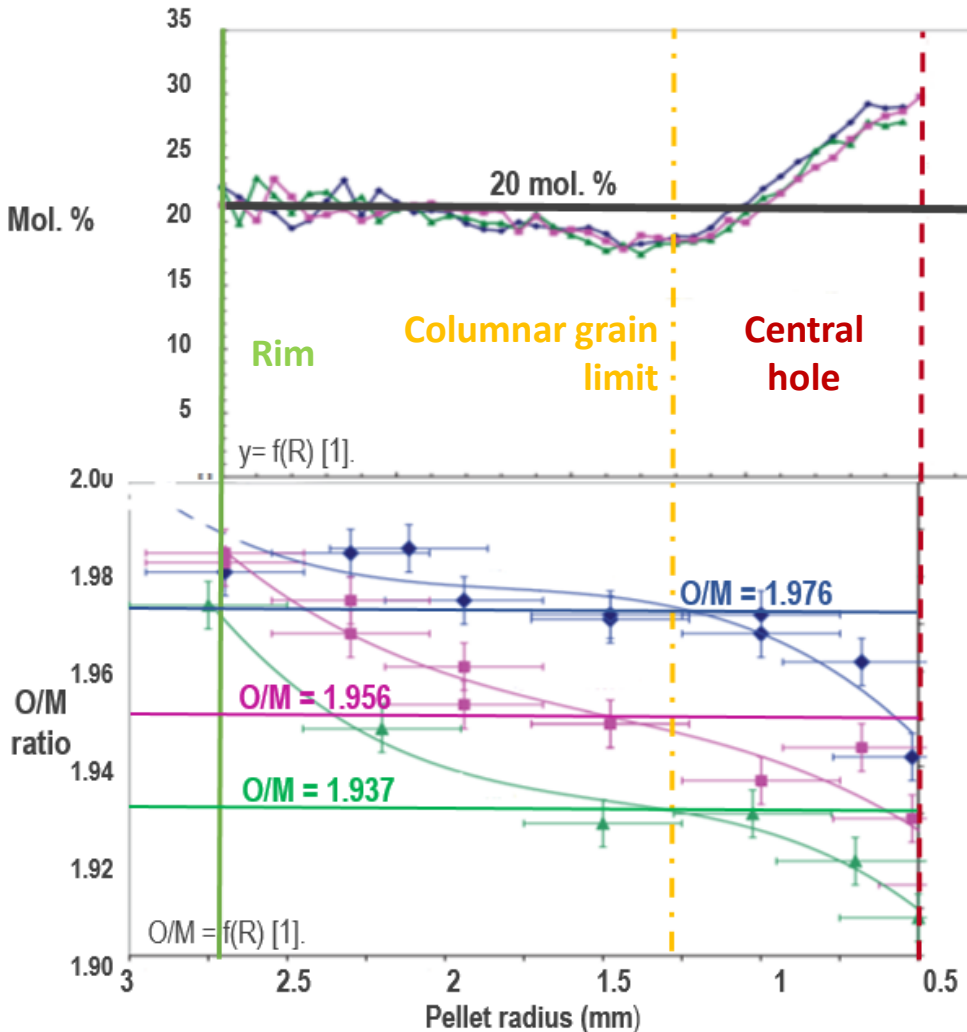


A 1300 K thermal gradient along the pellet radius is observed

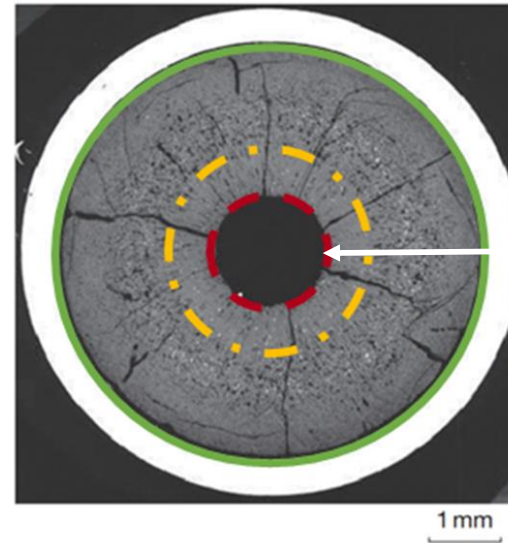
* with $M = U + Pu$

[2] Y. Guerin, C. Nucl. Mat., edited by Rudy J.M. Konings, (2012) 547-78.

Variation of the Pu content and the O/M ratio along the pellet radius for 3 different initial O/M ratios



Pu content (y)	$0.15 < y < 0.35$
O/M	$1.94 < O/M \leq 1.99$



Micrograph of a Phenix pellet (**Max flux plane**) [2]
 Pu content : $y = 0.20$
 O/M* = 1.978
 Burnup : 13 at. %
Central hole
Columnar grain limit
Rim

At max flux plane

	%Pu	O/M
Rim	==	↗
Columnar grain limit	→	==
Central hole	↗	↘

%Pu can locally reach up to 70 %

* with $M = U + Pu$

[2] Y. Guerin, C. Nucl. Mat., edited by Rudy J.M. Konings, (2012) 547-78.

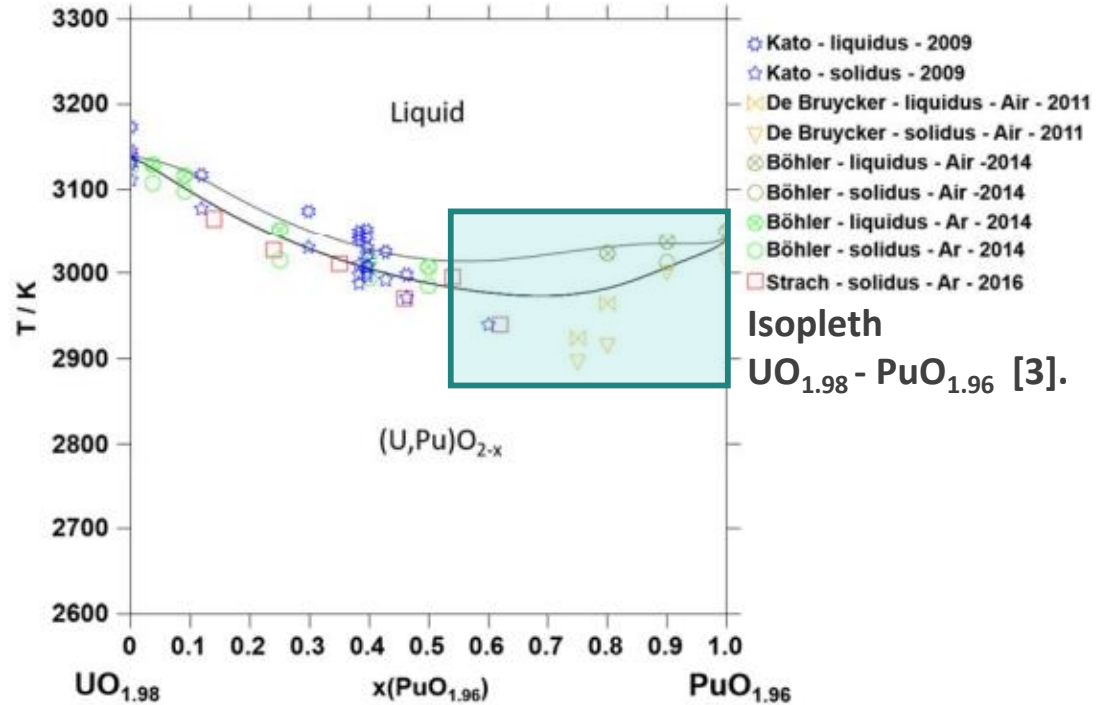
Impact on the structural, microstructural and thermodynamic properties

Example of the melting point

The local melting point depends upon both the O/M ratio and the Pu content



T_{melt} as Pu content (for $y < 0.75$)
 => diminution of the margin to fuel melting

**Goals**

Fill the lack of data (structural, microstructural, thermal and thermodynamic) for MOX with Pu content greater than 0.45 and more specifically for Pu > 0.60

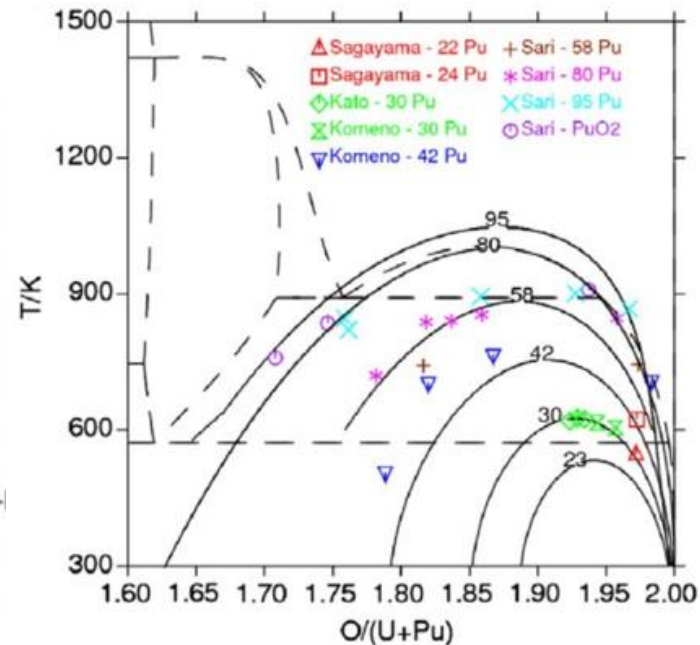
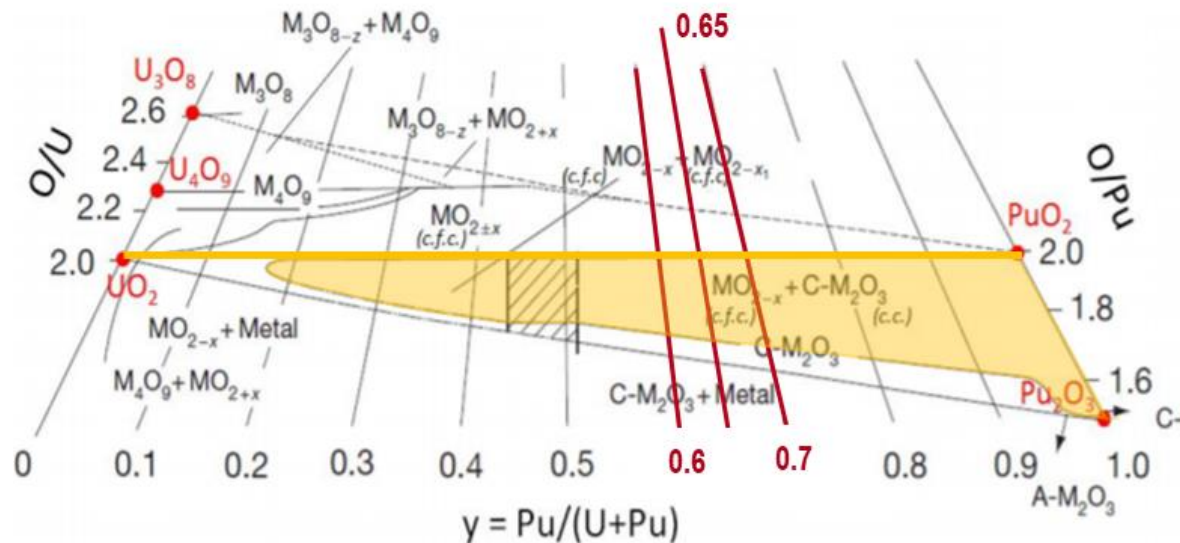


Feed the database for the fuel performance codes (GERMINAL) and enhance the modelling of the U-Pu-O phase diagram by the CALPHAD method.

[3] C. Guéneau *et al.*, CEA for Inspyre, www.eera-jpnm.eu/inspyre (2019).

Required properties for thermodynamic properties measurement

- Density after sintering > 94% TD
- Homogeneous chemical distribution of cations and oxygen (O/M ratio)
- Monophasic (solid solution) and stoichiometric (O/M = 2.00) material

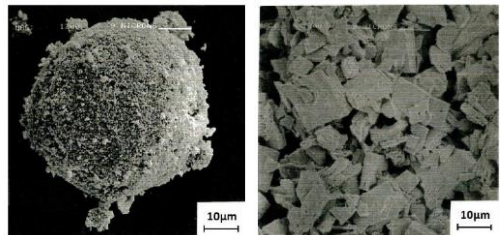


Ternary phase diagram U-Pu-O at **room temperature** for an O/M ratio between 1.5 and 2.7 [4]

[4] C. Guéneau *et al.*, *J. Nuc. Mat.* (2012) 21-59.

[5] C. Guéneau *et al.*, *J. Nuc. Mat.* 419 (2011) 145-167.

Phase separation temperature calculated as a function of the O/M ratio [5].



UO_2 PuO_2

Blending
30min

Milling
4h

Sieving
200 µm

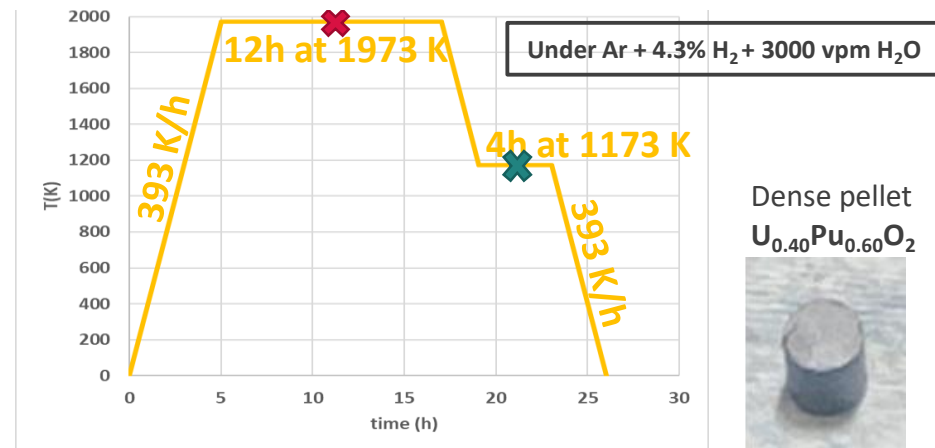
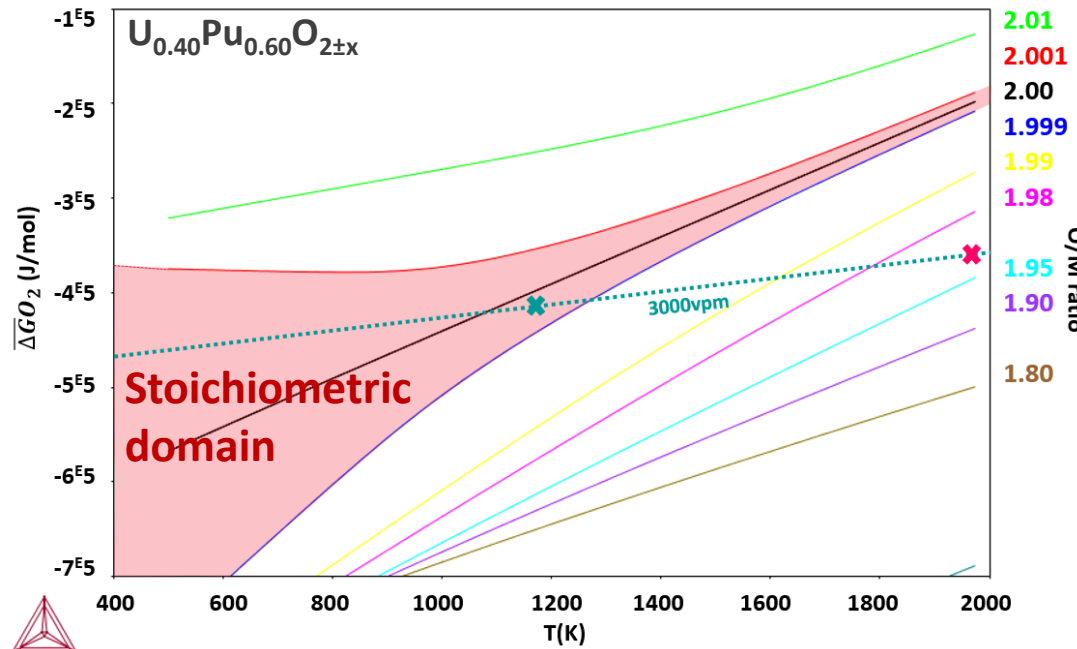
Pelletizing
450 MPa, ø 6 mm

Sintering
Ar/4.3% H₂ + α vpm H₂O

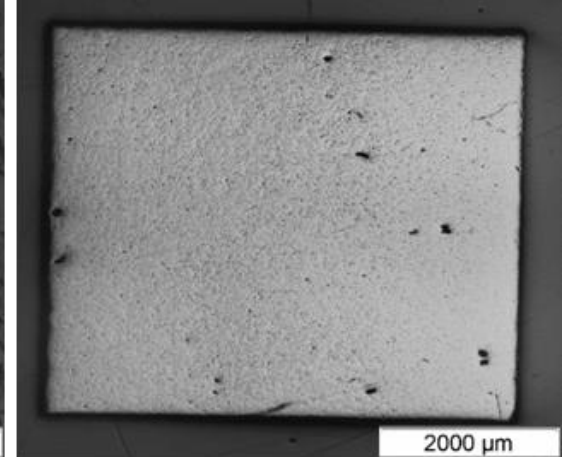
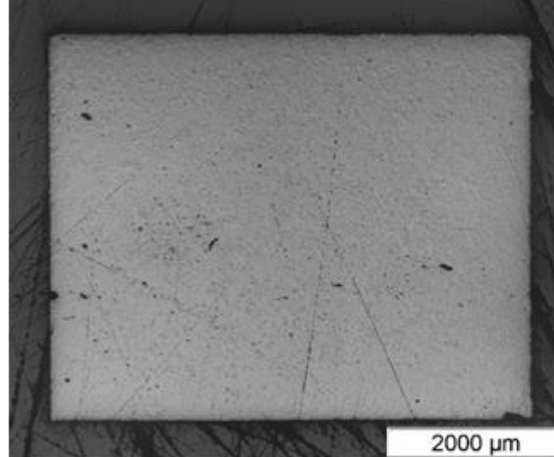
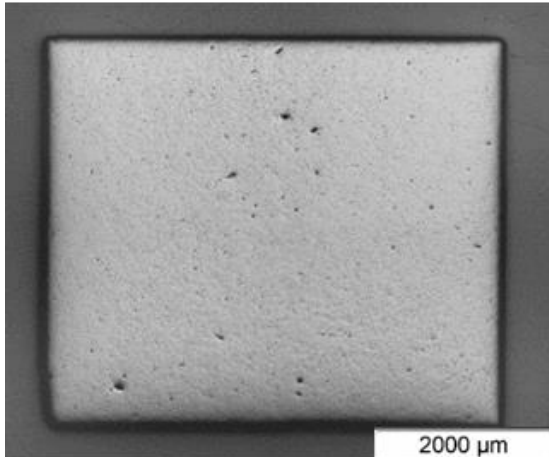
Homogenize

Remove agglomerates

Densify
Form solid solution
Fix O/M ratio



- [6] T. Truphemus, Thèse de doctorat (2013), University of Aix-Marseille.
[7] R. Vauchy *et al.*, Ceramics international 40 (2014), 109991-109999.



γ	0.60	0.65	0.70
Density ¹	97.0 ± 0.1 % TD	96.0 ± 0.1 % TD	95.8 ± 0.1 % TD
Density (Image analysis)	96.6 ± 1.1 %	96.5 ± 1.0 %	95.1 ± 1.4 %
Chemical analysis γ (TIMS ²)	0.59 ± 0.02	0.63 ± 0.02	0.69 ± 0.02
Optical microscopy	OK	OK	OK

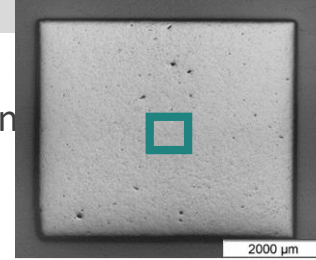
Dense pellets with the microstructure and Pu content targeted

¹ Hydrostatic density by immersion

² Thermal Ionization Mass Spectroscopy

Setting: Map of 1024x1024 pixels = 1 μm^2 / - 20kV electron accelerating voltage - 20 ms. pixel⁻¹

MIMAS ($\text{U}_{0.90}\text{Pu}_{0.10}\text{O}_{2.00}$) [8]: Dosage, first blending, dosage, blending-dilution, pelletizing, sintering, grinding, inspection.

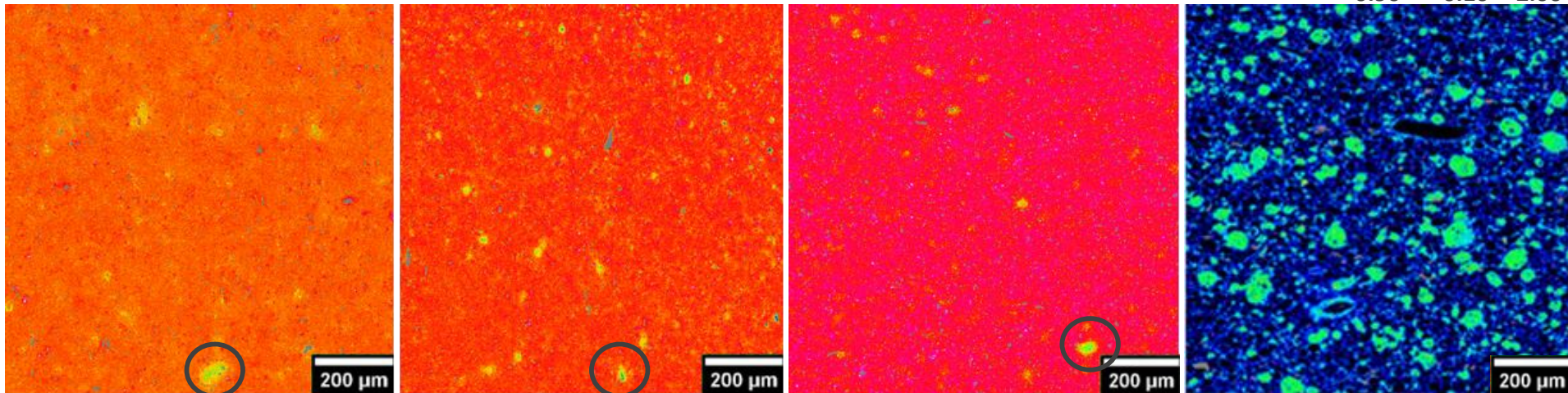


$\text{U}_{0.40}\text{Pu}_{0.60}\text{O}_2$

$\text{U}_{0.35}\text{Pu}_{0.65}\text{O}_2$

$\text{U}_{0.30}\text{Pu}_{0.70}\text{O}_2$

MIMAS $\text{U}_{0.90}\text{Pu}_{0.10}\text{O}_{2.00}$



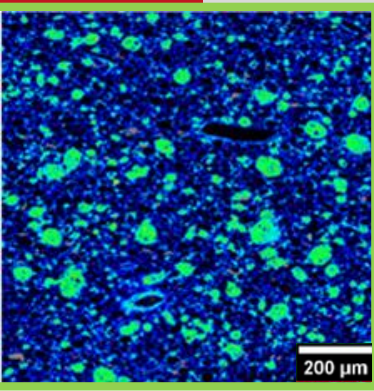
0 11 23 34 45 57 68 79 91 Pu/(U+Pu) (%mas)



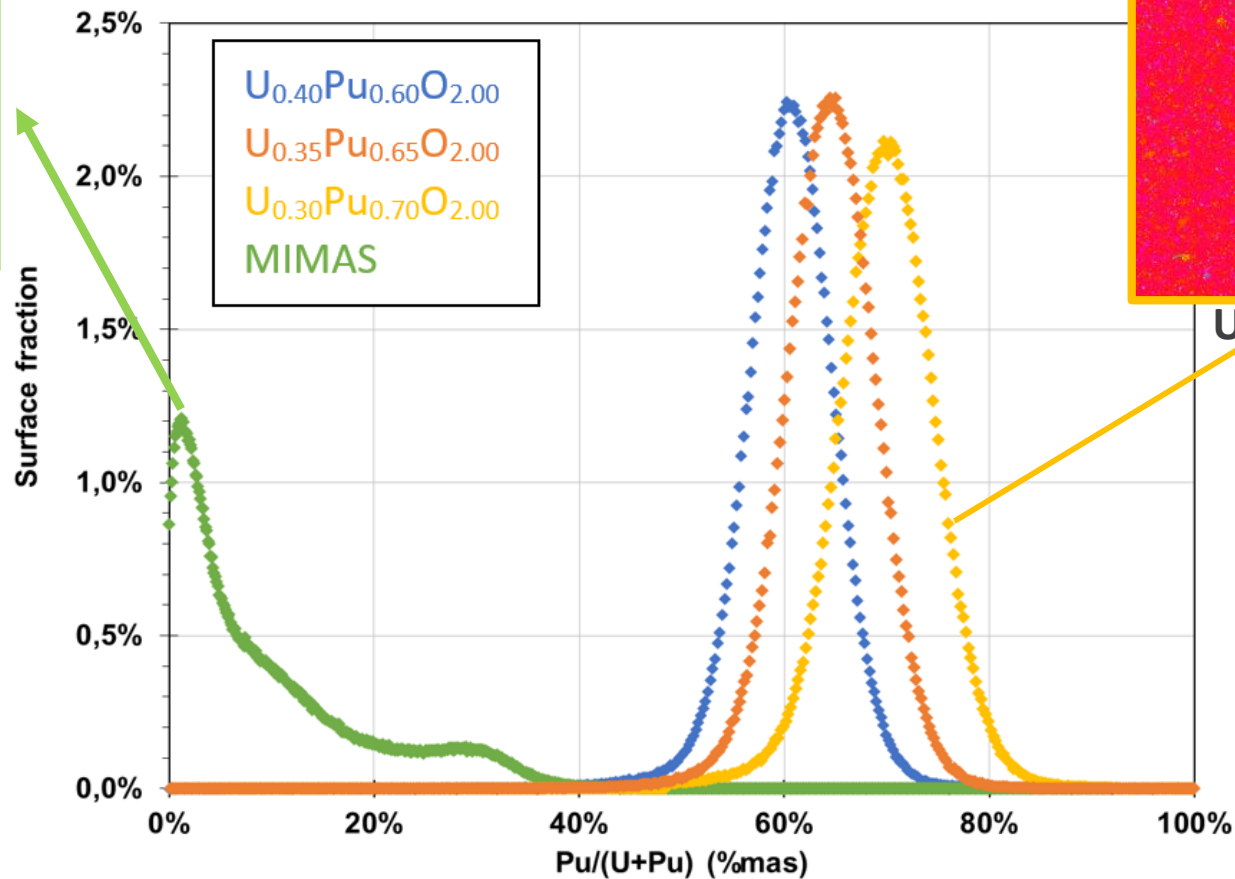
0 10 20 30 40 50 60 70 80 Teneur Pu (%mas)

y	0.60	0.65	0.70
Electron Probe Micro-Analysis (EPMA)	$y = 0.595 \pm 0.048$ Homogeneous distribution of cations	$y = 0.629 \pm 0.039$ Homogeneous distribution of cations	$y = 0.704 \pm 0.056$ Homogeneous distribution of cations

[8] O. Kahraman *et al.*, *J. App. Phys.* 132 (2022) 115106.

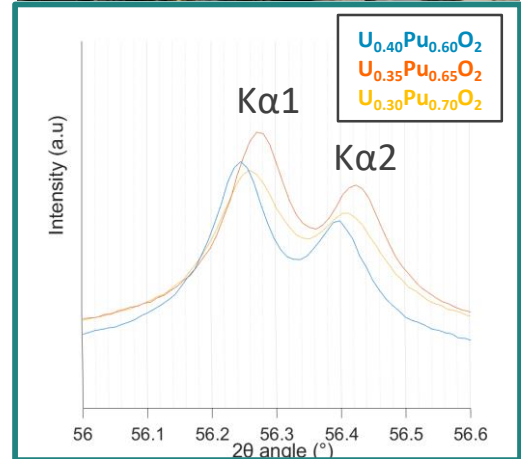
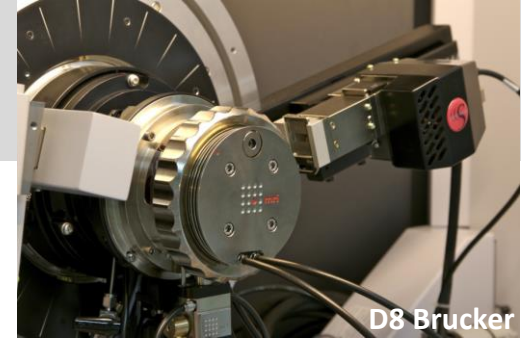
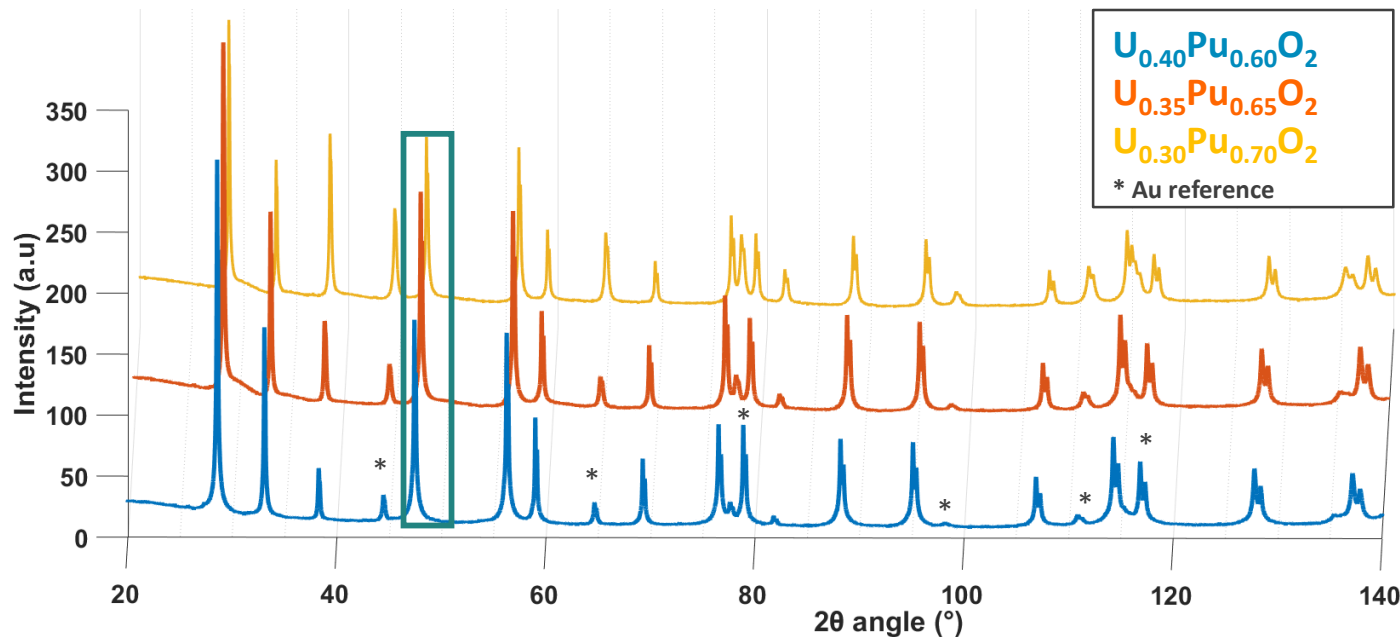


MIMAS [8]
 $U_{0.90}Pu_{0.10}O_{2.00}$



Homogeneous cations distribution in the matrix with U-rich agglomerates surface fraction < 5 % and the Pu content targeted

Setting: 0.1 g of powder - angle step 0.1 ° each 5s – 2θ angle 20-140°



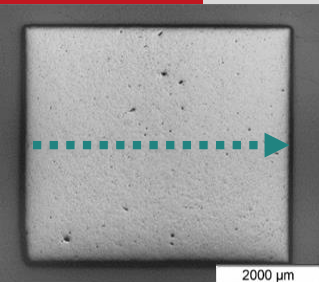
Evolution of the (311) pic of the fcc structure function of the Pu content.

Determination of the lattice parameter
 => Estimation of the matrix O/M ratio

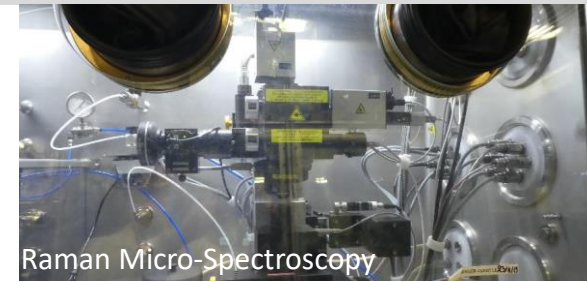
Duriez *et al.* law [4]
 $a(U_{1-y}Pu_yO_{2-x}) \text{ \AA} = 5.470 - 0.074y + 0.34x$

y	0.595	0.629	0.700
X-Ray diffraction	$a = 5.426 \pm 0.001 \text{ \AA}$ $O/M = 2.000 \pm 0.004$	$a = 5.424 \pm 0.001 \text{ \AA}$ $O/M = 1.998 \pm 0.004$	$a = 5.420 \pm 0.001 \text{ \AA}$ $O/M = 1.998 \pm 0.004$

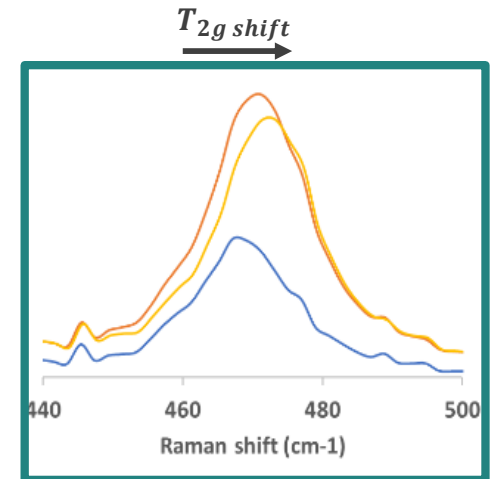
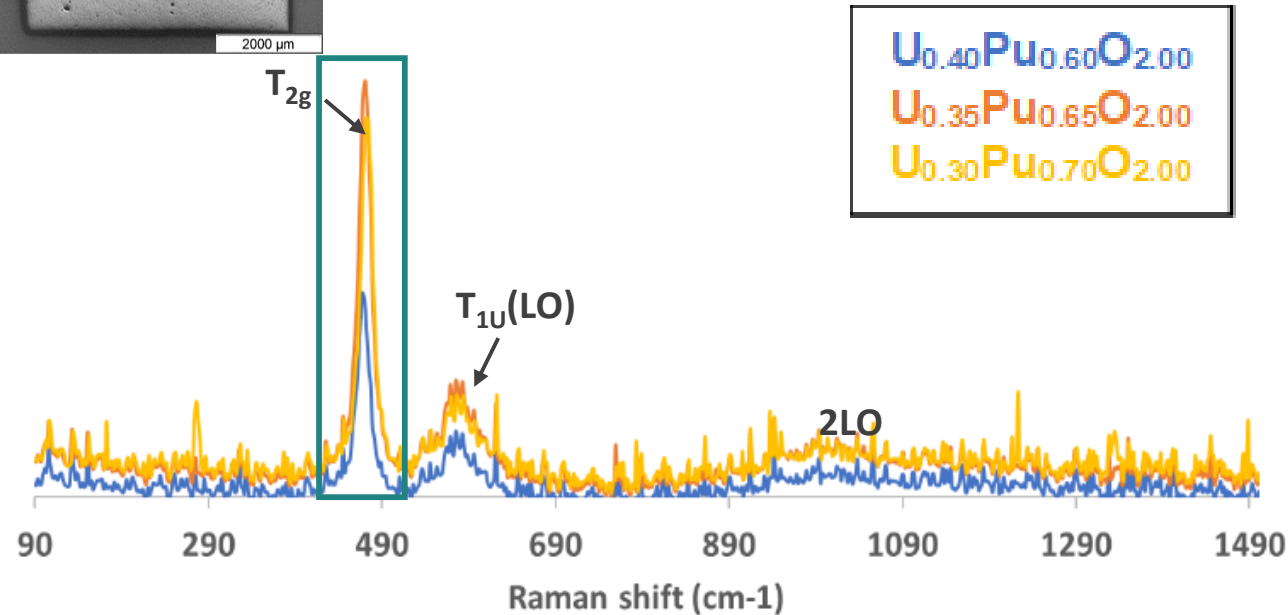
Monophasic and stoichiometric mixed oxides



Line (3000 μm): 2x30 s/point each 1.5 μm
Average of 2000 spectrums



Raman Micro-Spectroscopy

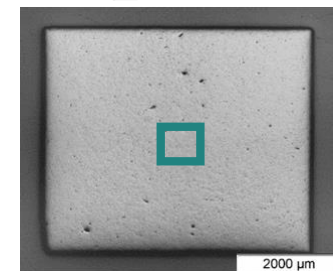
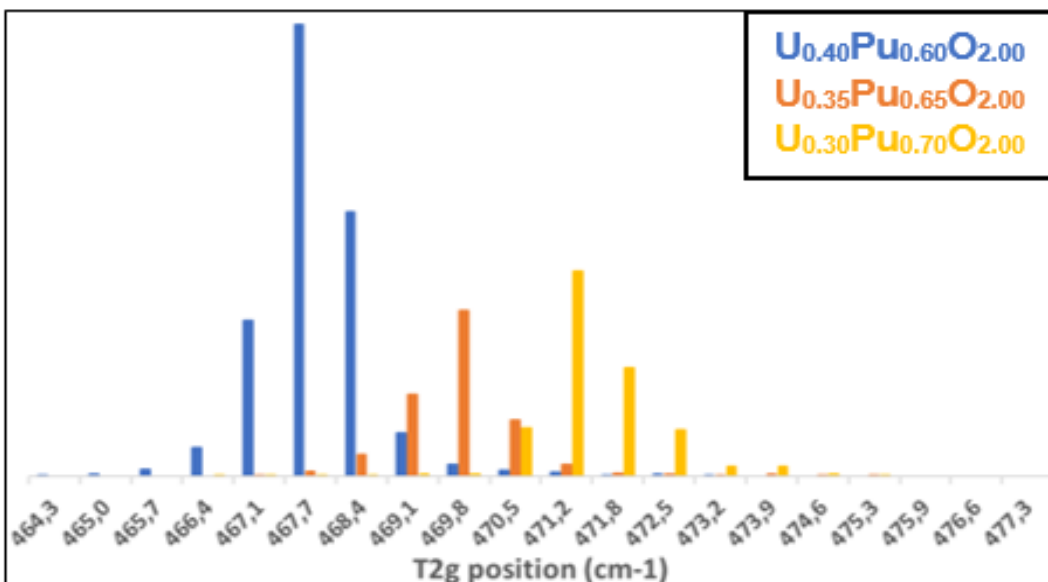
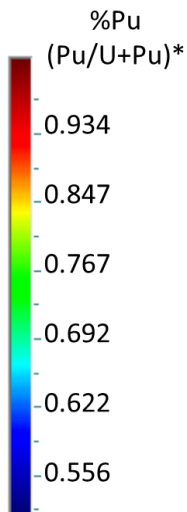
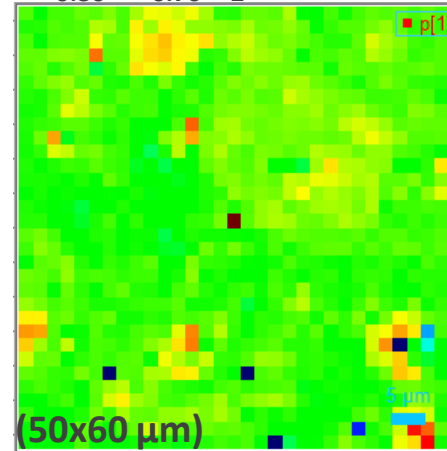
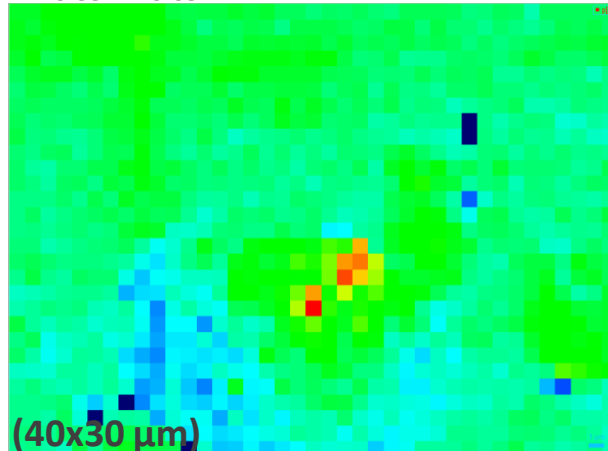
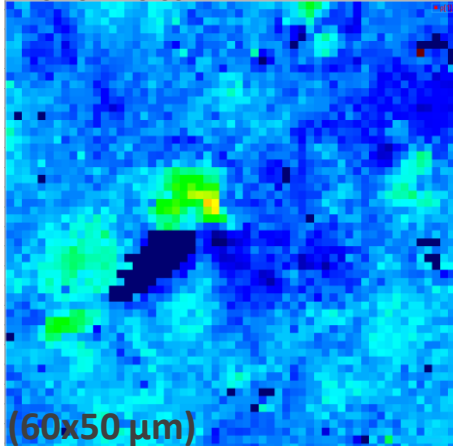


y	0.60	0.65	0.70
Raman μ -spectroscopy	$T_{2g} = 467.5 \text{ cm}^{-1}$ $\rightarrow y = 0.605 \pm 0.003^*$	$T_{2g} = 469.4 \text{ cm}^{-1}$ $\rightarrow y = 0.670 \pm 0.003^*$	$T_{2g} = 471 \text{ cm}^{-1}$ $\rightarrow y = 0.729 \pm 0.003^*$
O/M (XRD)	2.000 ± 0.004	1.998 ± 0.004	1.998 ± 0.004

* %Pu: Pu/(U+Pu) ratio calculated for O/M = 2.00

[10] L. Medyk *et al.*, *J. Nuc. Mat.*, 541 (2020) 152439.

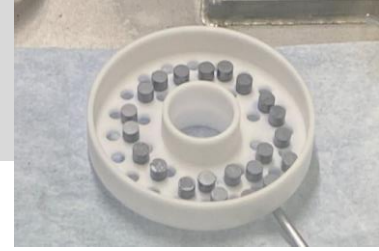
Maps: 2x30 s/point each 1.5 μm



Monophasic solid solution
with a local homogeneous
cations distribution with
surface fraction agglomerates
< 5% and the Pu content
targeted

*%Pu: Pu/(U+Pu) content calculated for O/M = 2.00

[10] L. Medyk *et al.*, *J. Nuc. Mat.*,541 (2020) 152439.

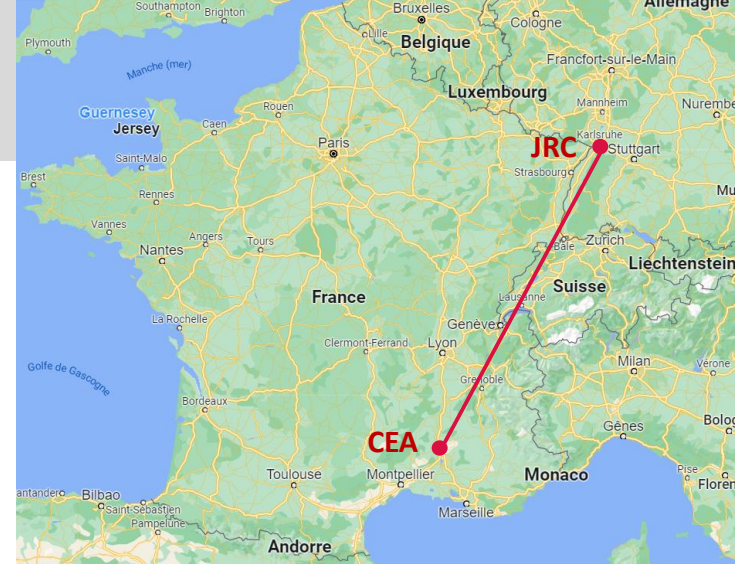


Conclusions:

Optimization of the manufacturing process

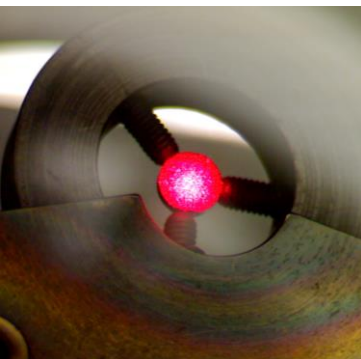
- High density (> 94% TD)
- Microstructure with the required properties
- Homogeneous cationic distribution
- Monophasic and stoichiometric mixed oxides

	$U_{0.40}Pu_{0.60}O_2$	$U_{0.35}Pu_{0.65}O_2$	$U_{0.30}Pu_{0.70}O_2$
Chemical analysis	0.591 ± 0.019	0.631 ± 0.020	0.689 ± 0.021
EPMA	0.595 ± 0.048	0.629 ± 0.039	0.704 ± 0.056
Raman μ -spectroscopy	0.605 ± 0.003	0.670 ± 0.003	0.729 ± 0.003
O/M (XRD)	2.000 ± 0.004	1.998 ± 0.004	1.998 ± 0.004

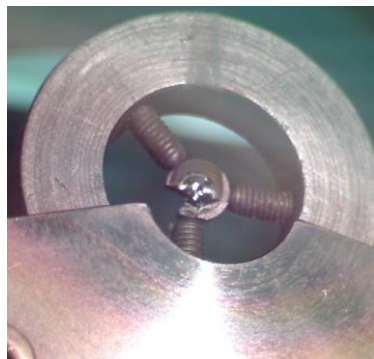


Next steps:

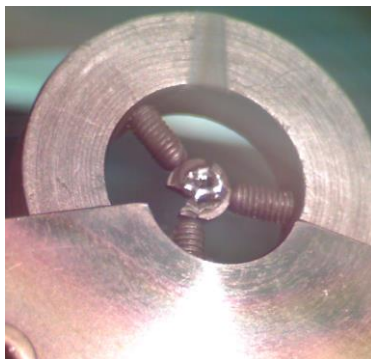
- Thermodynamic properties measurements at JRC-Karlsruhe (melting temperature, enthalpy, heat capacity, conductivity, ...) and at Marcoule (thermal expansion and oxygen potential).



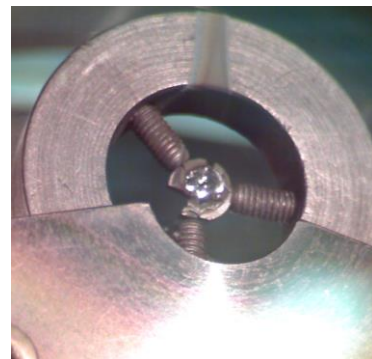
Before



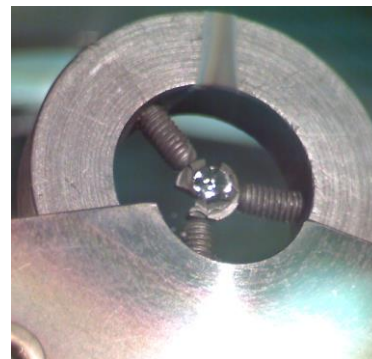
Shot 1



Shot 2



Shot 3



Shot 4

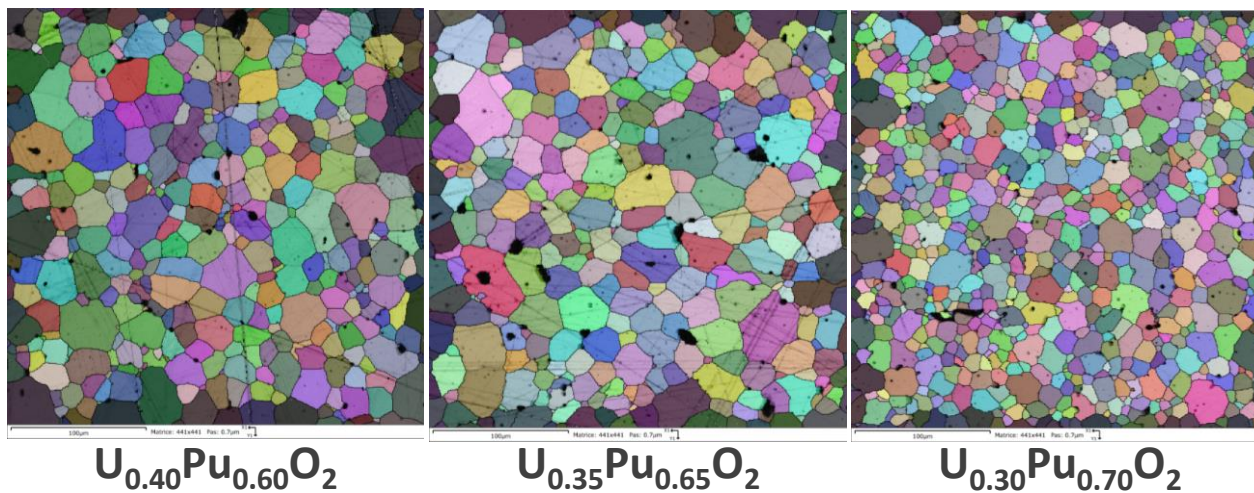


Thank you for you attention

Acknowledgments

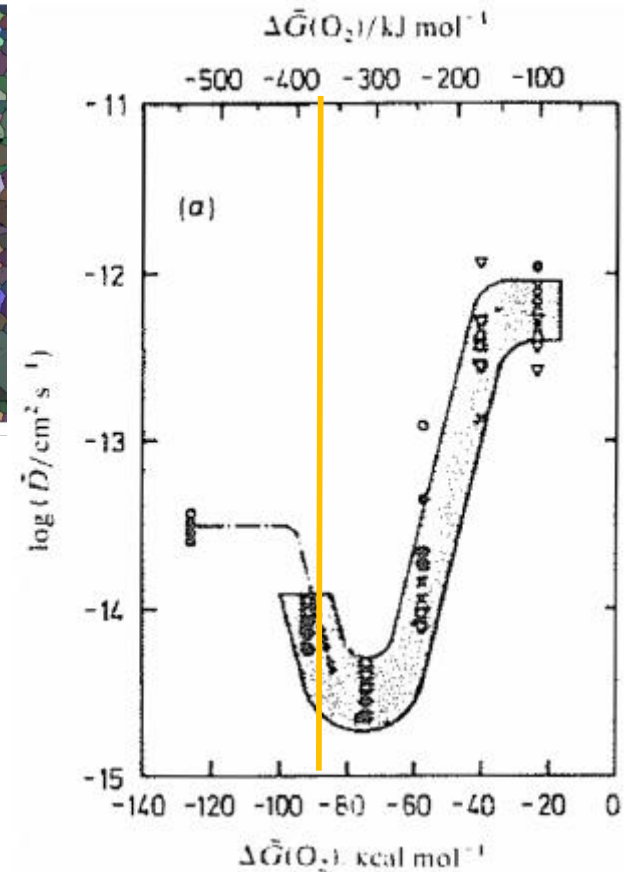
F. Lebreton¹, M. Alibert¹, C-M. Aloin¹, M. Pons¹, L. Barnouin¹, G. Gabriel¹, P. Signoret¹, J. Lorino¹, L. Picard¹, O. Miollan¹, O. Kahraman¹.

1 CEA, DES, ISEC, DMRC, Université Montpellier, Marcoule, France



	$U_{0.40}Pu_{0.60}O_2$	$U_{0.35}Pu_{0.65}O_2$	$U_{0.30}Pu_{0.70}O_2$
SEM/EBSD	$12.3 \pm 1 \mu m$	$15.8 \pm 1 \mu m$	$12.1 \pm 1 \mu m$

Homogenous distribution of the grain size along the pellet.



U-Pu interdiffusion coefficient according to the oxygen potential at 1873 K; circle: $0.175 \leq y \leq 0.177$, black circle: $0.150 \leq y \leq 0.174$, cross: $0.110 \leq y \leq 0.140$, triangle down: $0.06 \leq y \leq 0.09$ and triangle up: $0.003 \leq y \leq 0.05$ [6]

[6] S. Mendez, 1995, Etude de l'interdiffusion U-Pu appliquée au combustible MOX, thèse, université d'Aix Marseille III