In situ HT-XRD study of the UO_2-PuO_2-Pu_2O_3 sub-system

R. Vauchy, Renaud Belin, Christine Gueneau, Thibaut Truphemus, Michal Strach, Alexis Joly, Jean-Christophe Richaud

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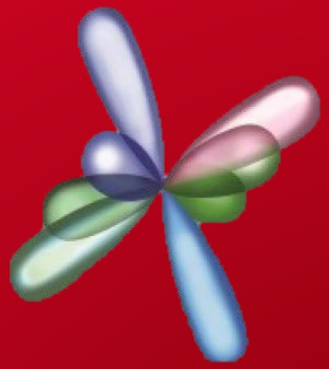

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In situ HT-XRD study of the UO_2-PuO_2-Pu_2O_3 sub-system

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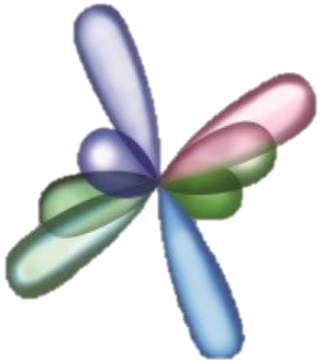
Presentation overview

- U-Pu-O : literature review
  - A phase diagram
  - UO_2-PuO_2-Pu_2O_3 at room temperature
  - UO_2-PuO_2-Pu_2O_3 at high temperature
- Studying UO_2-PuO_2-Pu_2O_3 *in situ* by HT-XRD
  - Our setup
  - Limitations of the setup
  - Selected samples and conditions
- Experimental results
  - Phase separation temperatures
  - How evaluating the O/M ratio
- Conclusions

U-Pu-O literature review



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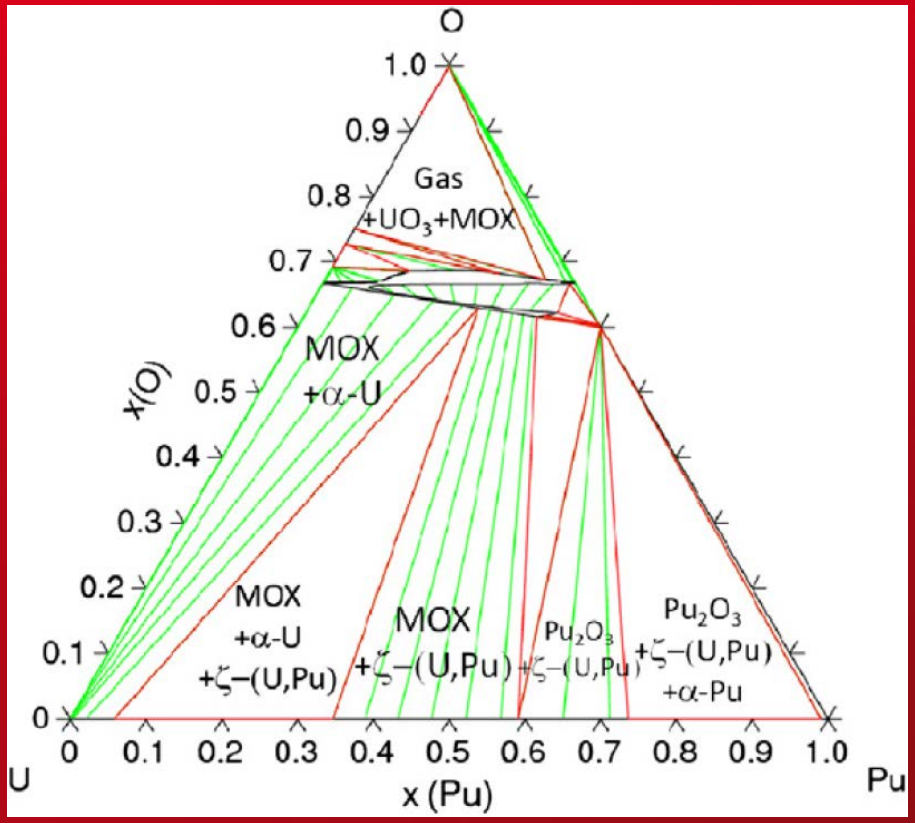
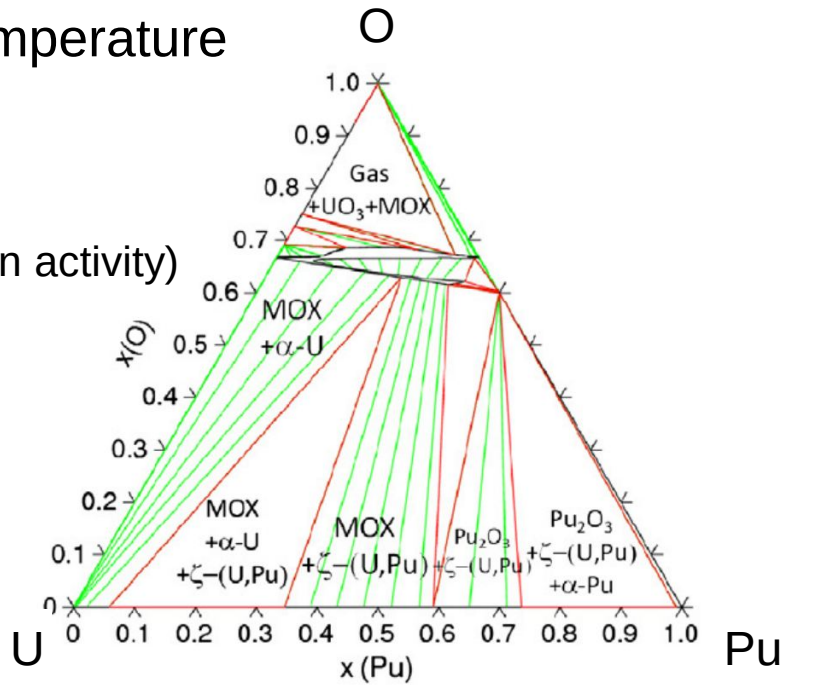


C. Guéneau *et al.*, *Journal of Nuclear Materials* 419 (2011) 145-167

A phase diagram

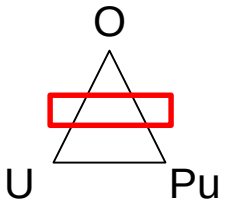
- Chart depicting phases **at equilibrium**
- Each point has composition and temperature coordinates
- HT-XRD ⟹ crystal structure and temperature
- In oxide samples, two variables :
  - Oxygen/Metal ratio (related to oxygen activity)
  - Temperature

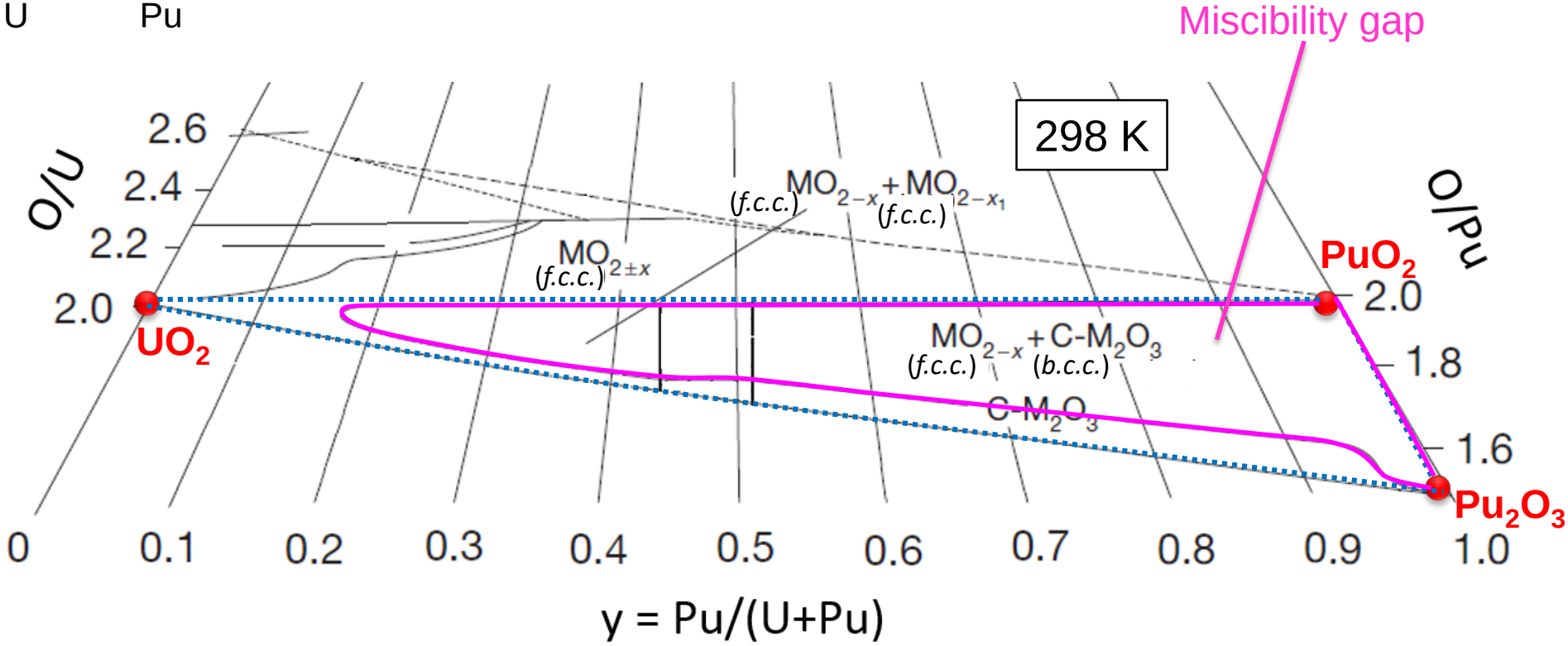


Calculated U-Pu-O phase diagram at RT

Guéneau *et al.*, *Journal of Nuclear Materials* 419 (2011) 145-167

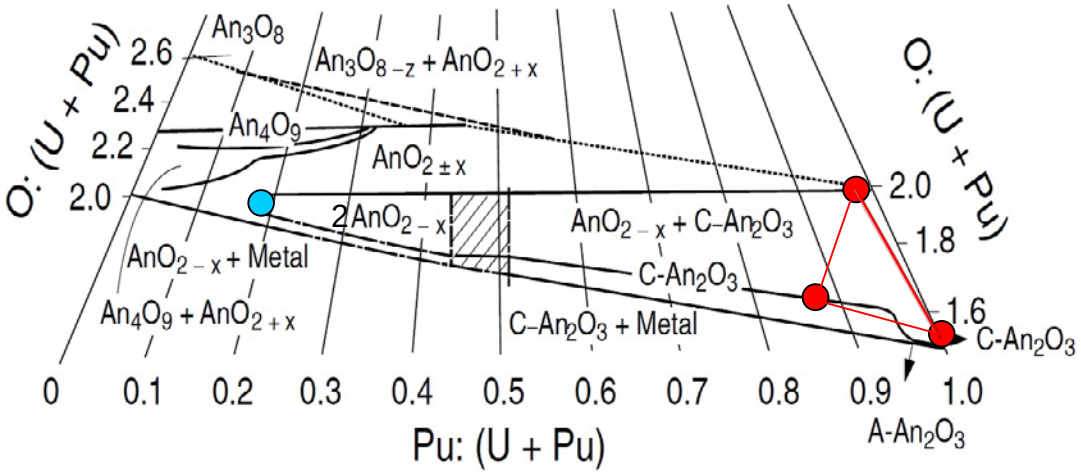
UO_2-PuO_2-Pu_2O_3 at room temperature





Sari *et al.*, *Journal of Nuclear Materials* 35 (1970) 267-77

Experiment vs. Modeling



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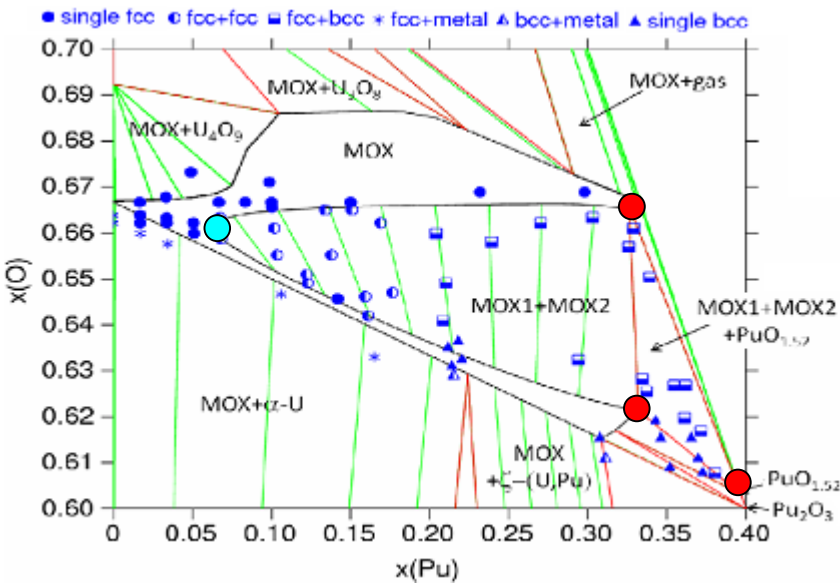
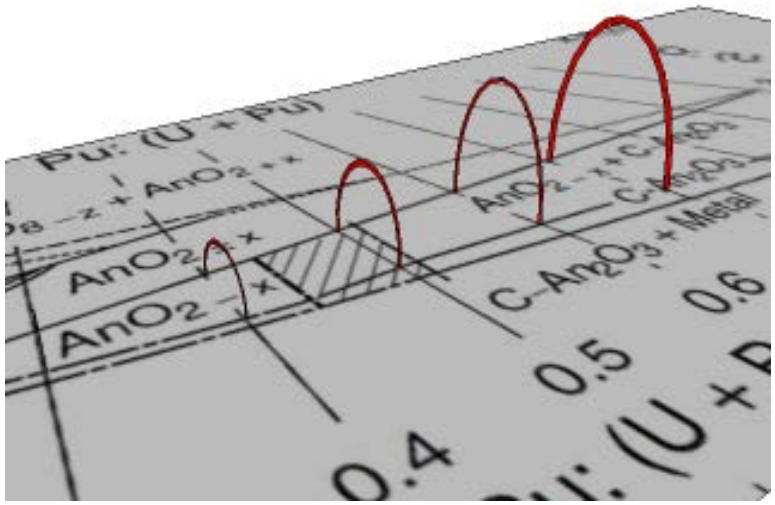
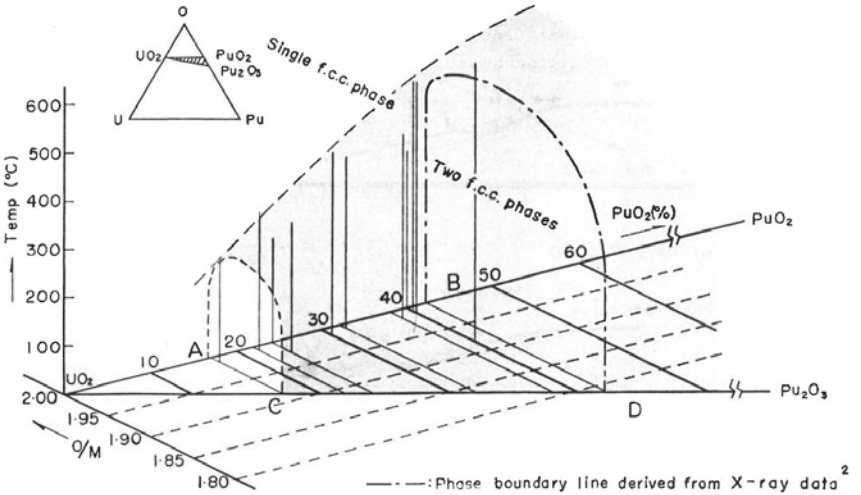


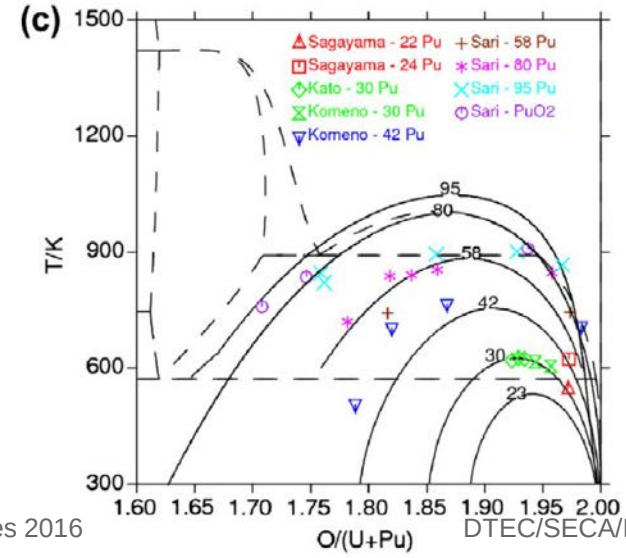
Guéneau *et al.*, *Journal of Nuclear Materials* 419 (2011) 145-167

- Experiment and modeling in good agreement
- Same low Pu content limit for the miscibility gap (~17% Pu)
- Biphasic domain MO_{2-x} + M_2O_3 not modeled
- Existence of a triphasic domain $2MO_{2-x}$ + M_2O_3
- Calculated composition range far from the hatched area of Sari

UO_2-PuO_2-Pu_2O_3 at HT

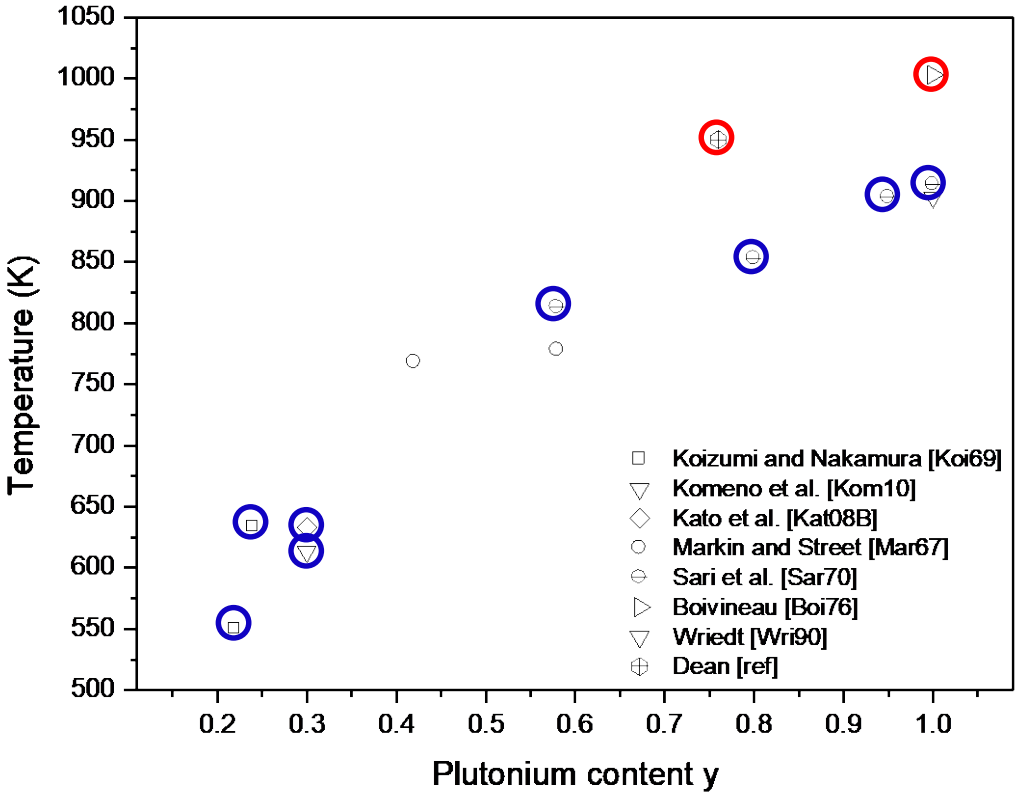






UO_2-PuO_2-Pu_2O_3 at HT

Experimental values for the critical temperature of phase separation found in the literature using DTA and HT-XRD



The critical T progressively increases with Pu content

At low Pu content, only DTA results
Scattering confirms the difficulties in measuring at low Pu content

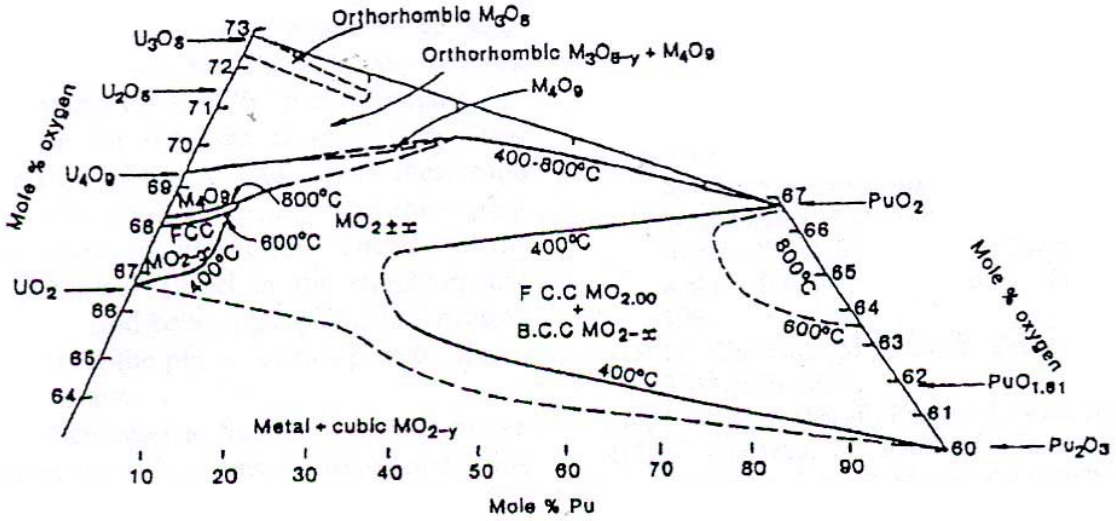
At higher Pu content, T of phase separation obtained with DTA are lower than those obtained with HT-XRD

At y=1 (PuO_2), HT-XRD value (1000 K) in agreement with the description of the Pu-O phase diagram

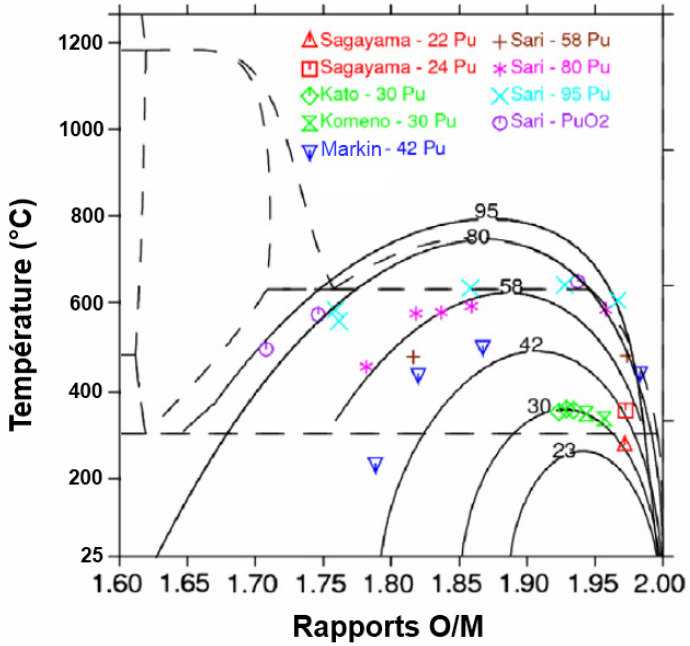
DTA data underestimate the T

HT-XRD provides a large amount of experimental data that lead to reliable T

Experiment vs. Modeling



Markin & Street, *Journal of Inorganical Nuclear Chemistry* 29 (1967) 2265-2280.

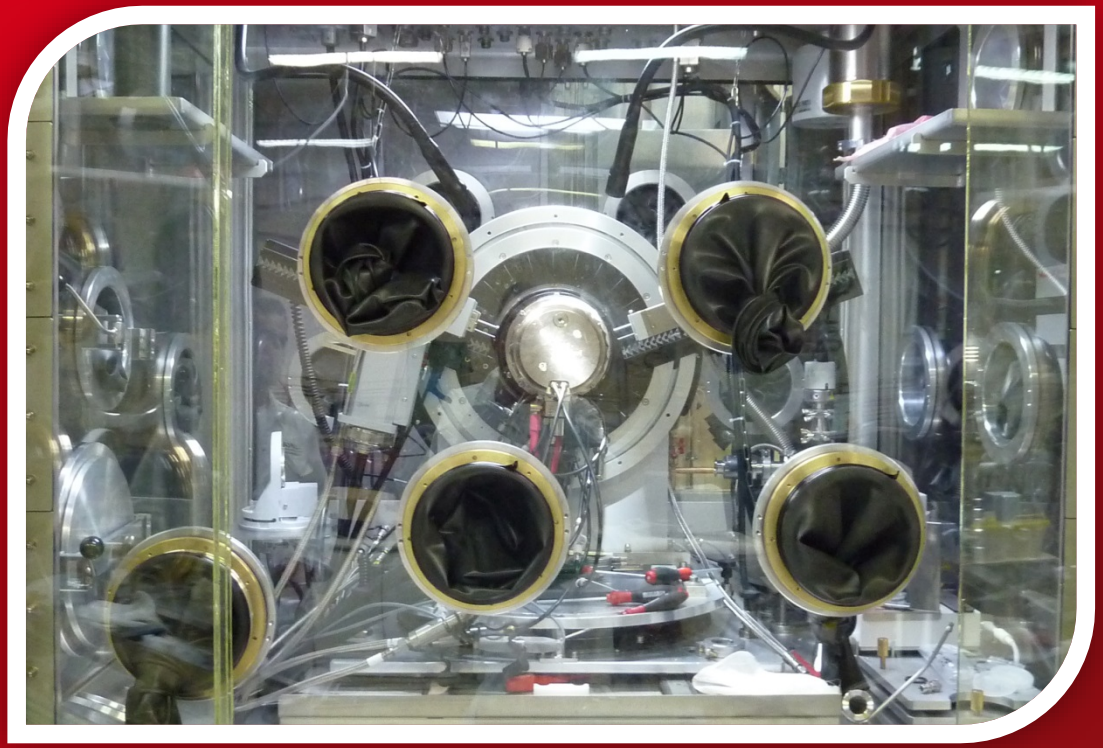


Guéneau *et al*, *Journal of Nuclear Materials* 419 (2011) 145-167

- Good agreement between experimental and modeling for y ≤ 0.40
- Difference for y > 0.40 : calculations overestimate $T_{separation}$

New HT studies are required to better describe the phase separation phenomenon

Studying UO_2-PuO_2-Pu_2O_3 *in situ* by HT-XRD



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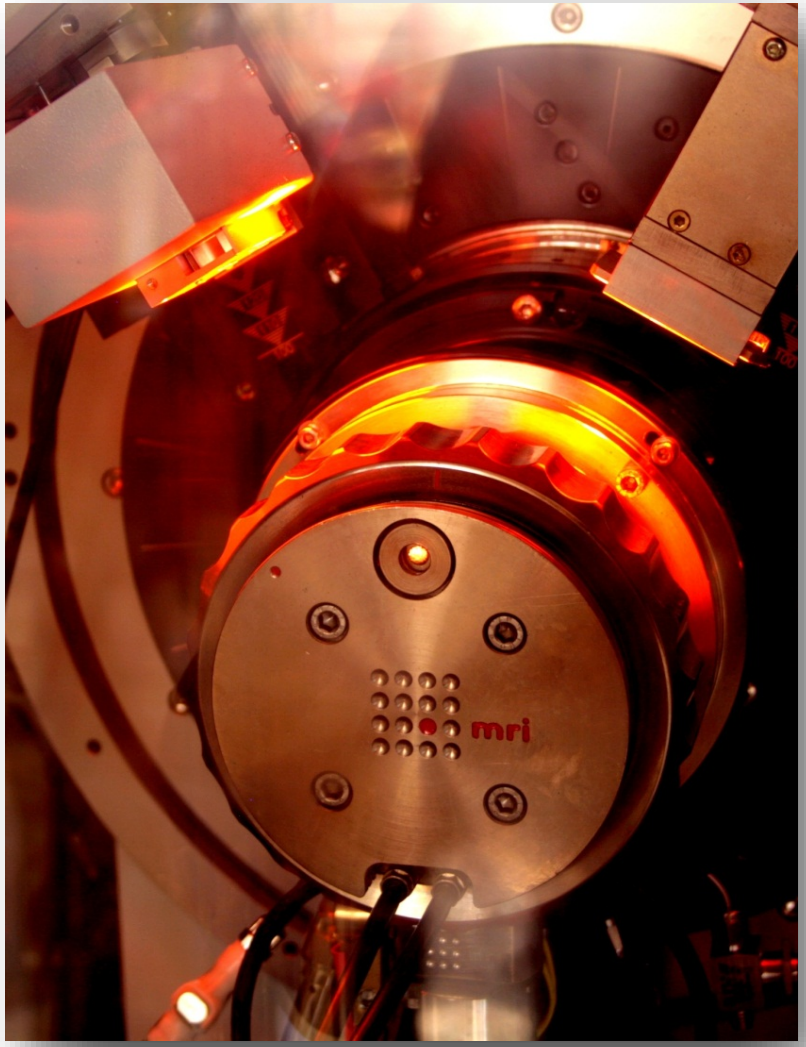
The High-Temperature X-Ray Diffraction setup



X-ray diffraction technical details

Goniometer in dedicated a **shielded glove-box**

XRD type : Bragg-Brentano θ-θ

Brand : BRUKER® D8 Advance XRD

Source : copper radiation ($K\alpha_1$+ $K\alpha_2$ radiation : λ = 1.5406 and 1.5444 Å) at 40 kV and 40 mA

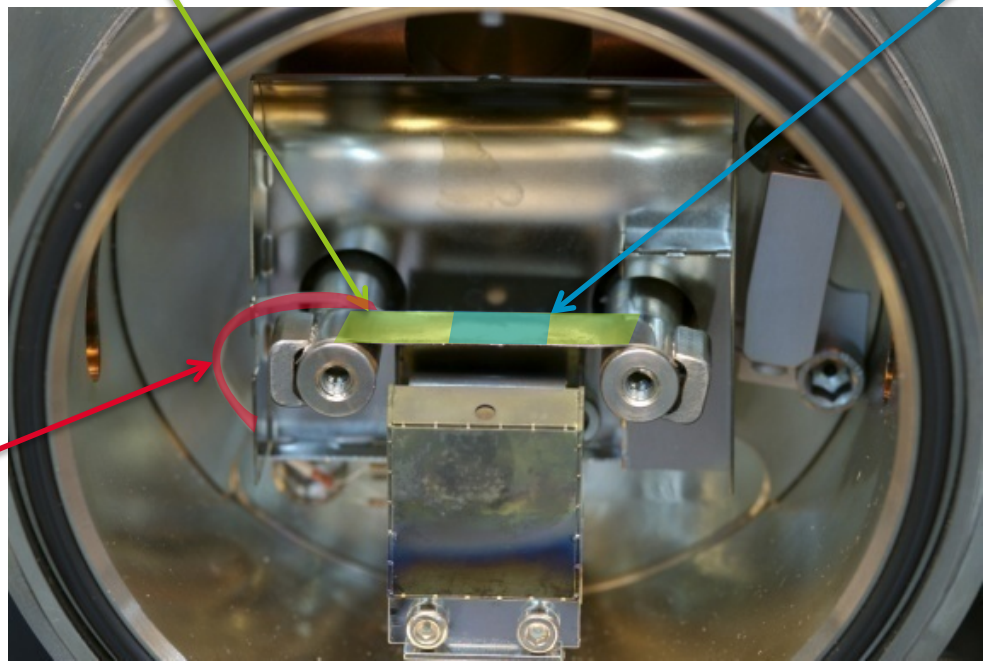
Detector : LynX'Eye PSD **fast-counting detector**

Heating stage : MRI®, Mo or W strip and Ta radiant heater **up to 2273 K** on **powders** and **1273 K** on bulk samples

Control of oxygen activity and temperature required

R. Vauchy *et al. Appl. Mater. Today 3, 2016, 87-95*

Controlling the temperature



Calibration : W powder (ALDRICH® 99.999%)

→ **±20 K between RT and 1973 K**

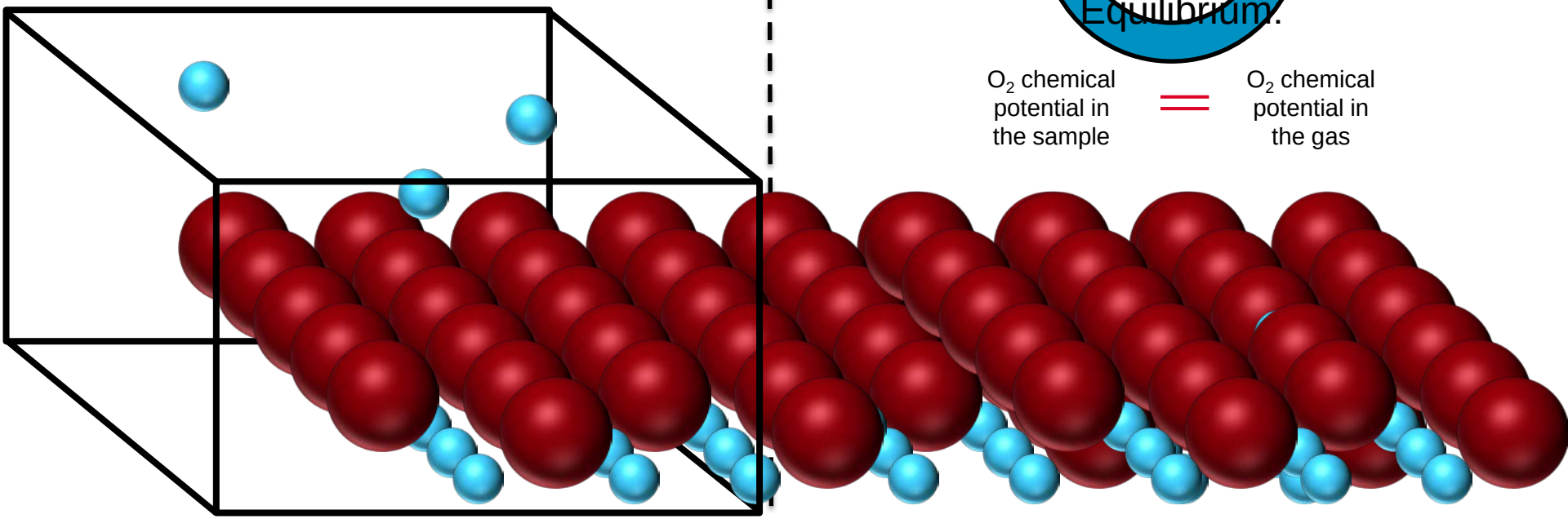
Prompt cooling/heating rates + fast counting detector

→ **Suited for kinetics studies**

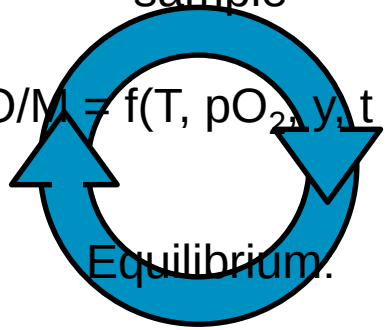
Controlling the oxygen activity : 2 approaches

Sample in a closed container (crucible)

Fixed oxygen activity (constant O/M)

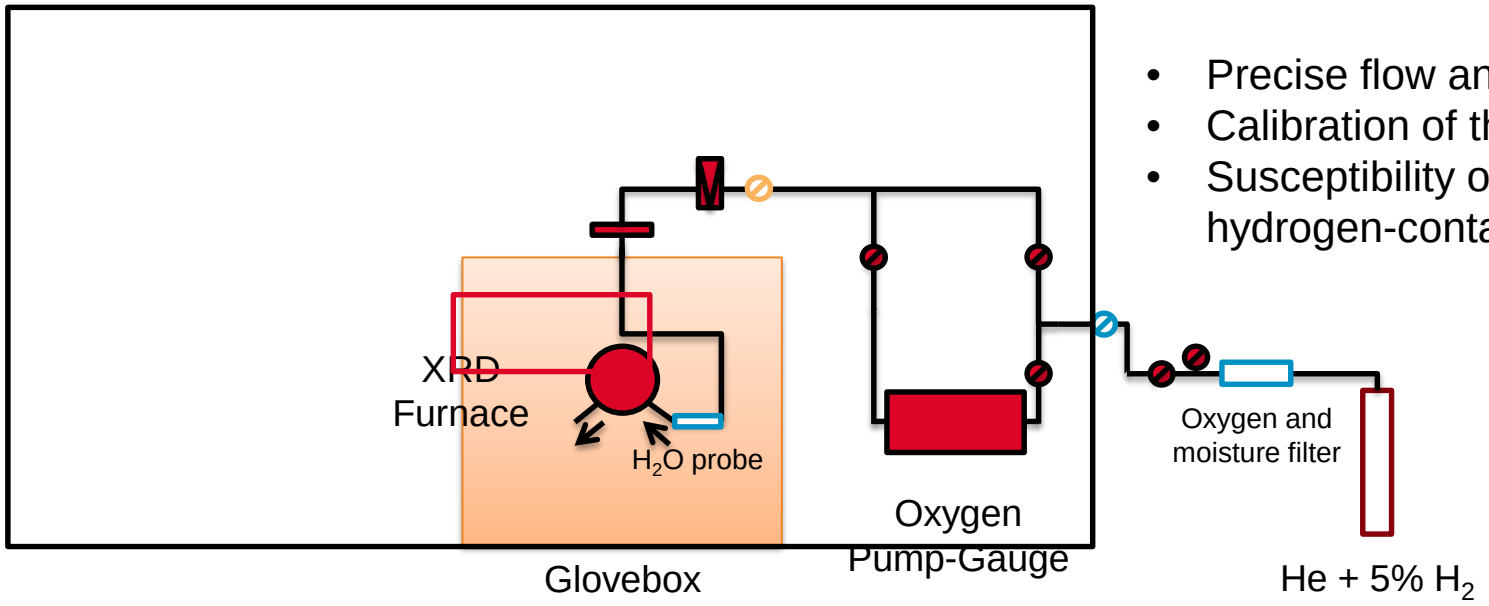


Free exchange allowed between gas and sample



O_2 chemical potential in the sample = O_2 chemical potential in the gas

Controlling the oxygen activity



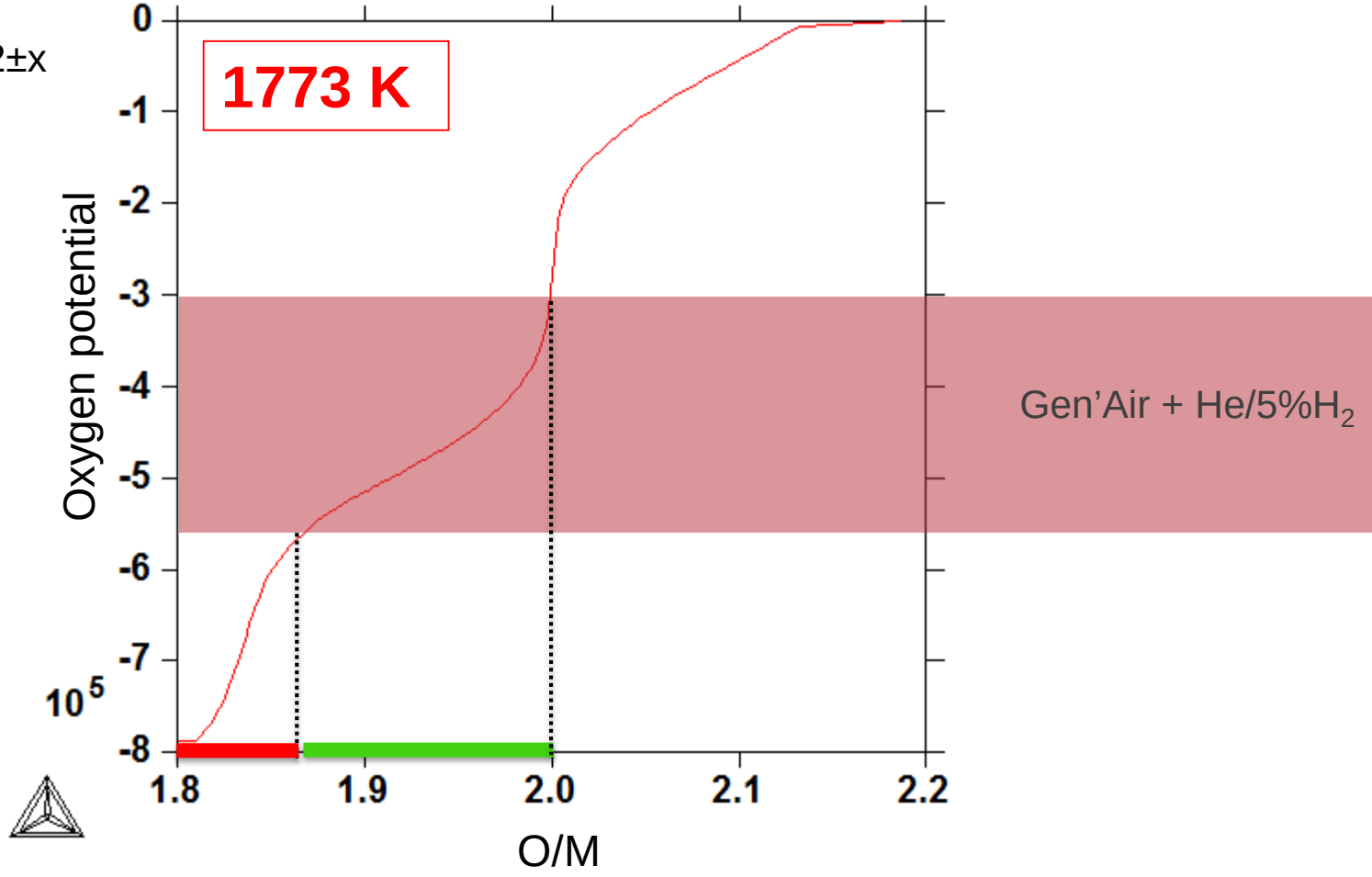
- Precise flow and pressure control
- Calibration of the probe
- Susceptibility of the probe to hydrogen-containing gas mixtures

- Certain species in the used gas might react with the studied sample
- H_2 rises security issues
- Direct measurement of pO_2 in the vicinity of the sample is (usually) impossible
- The pipeline needs particular attention

Control of oxygen activity is challenging

Controlling the oxygen activity

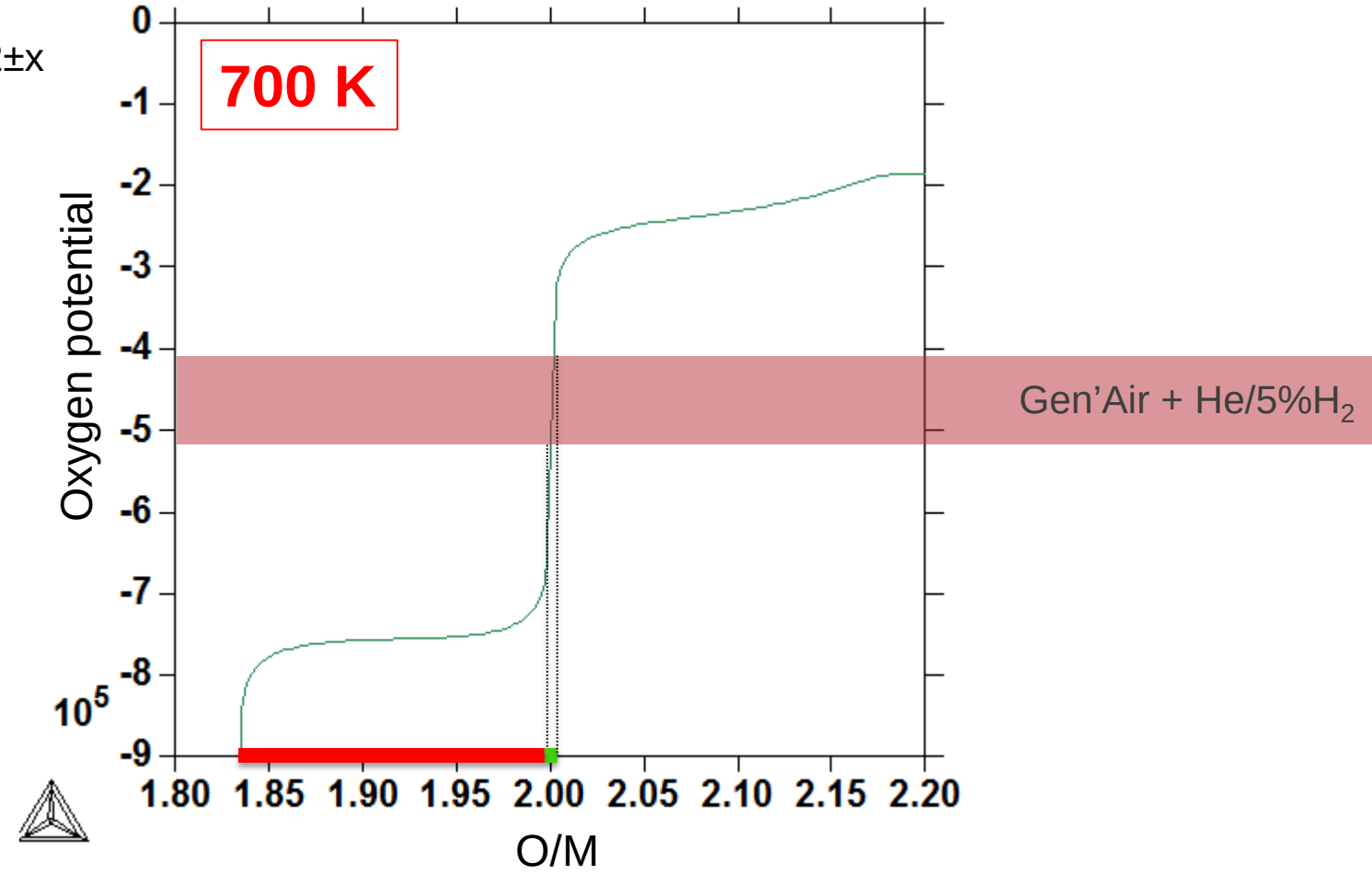
$U_{0.65}Pu_{0.35}O_{2\pm x}$



- Relatively wide range of **achievable O/M ratios**
- Sample can reach low O/M ratios at equilibrium with the gas mixture

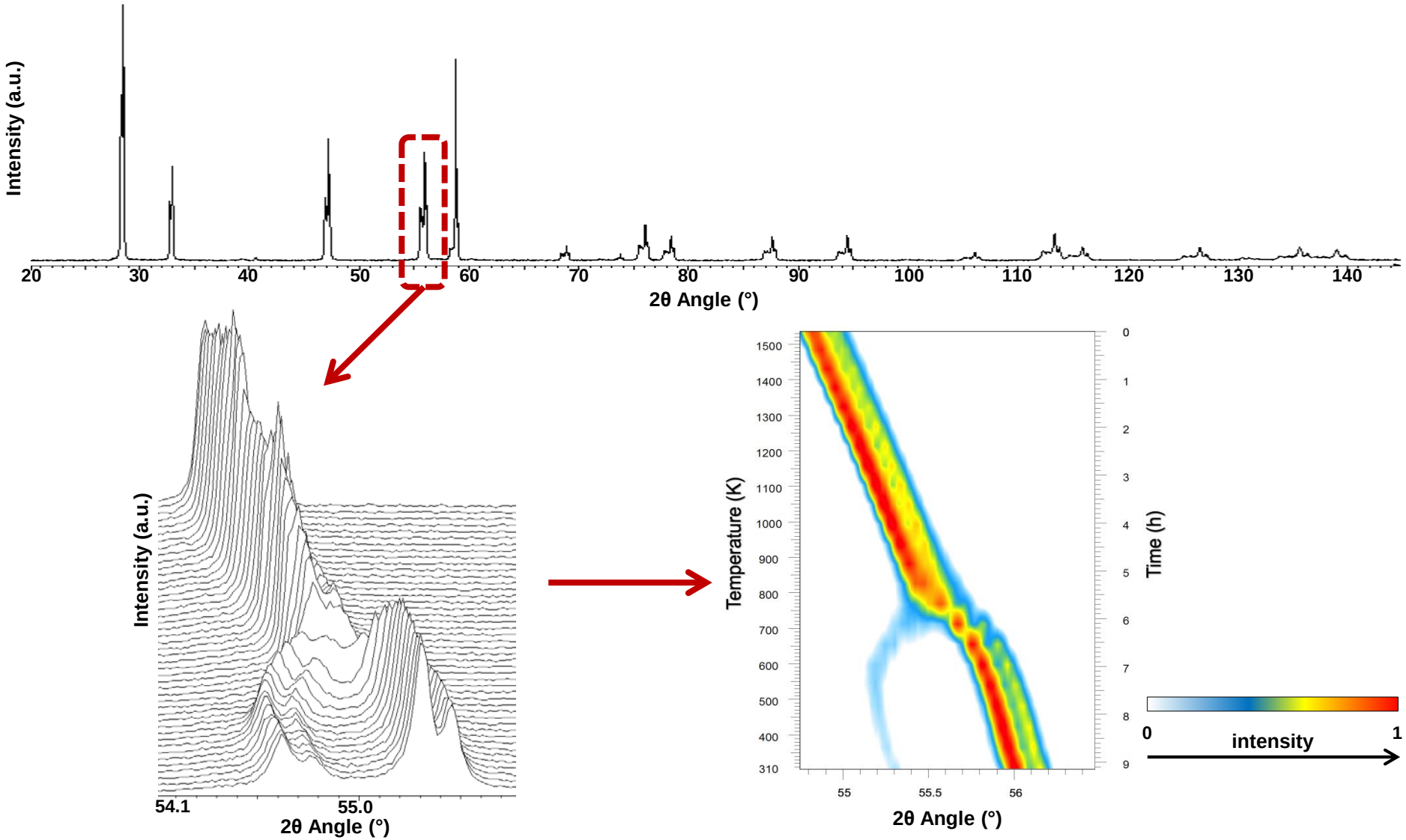
Controlling the oxygen activity

$U_{0.65}Pu_{0.35}O_{2\pm x}$

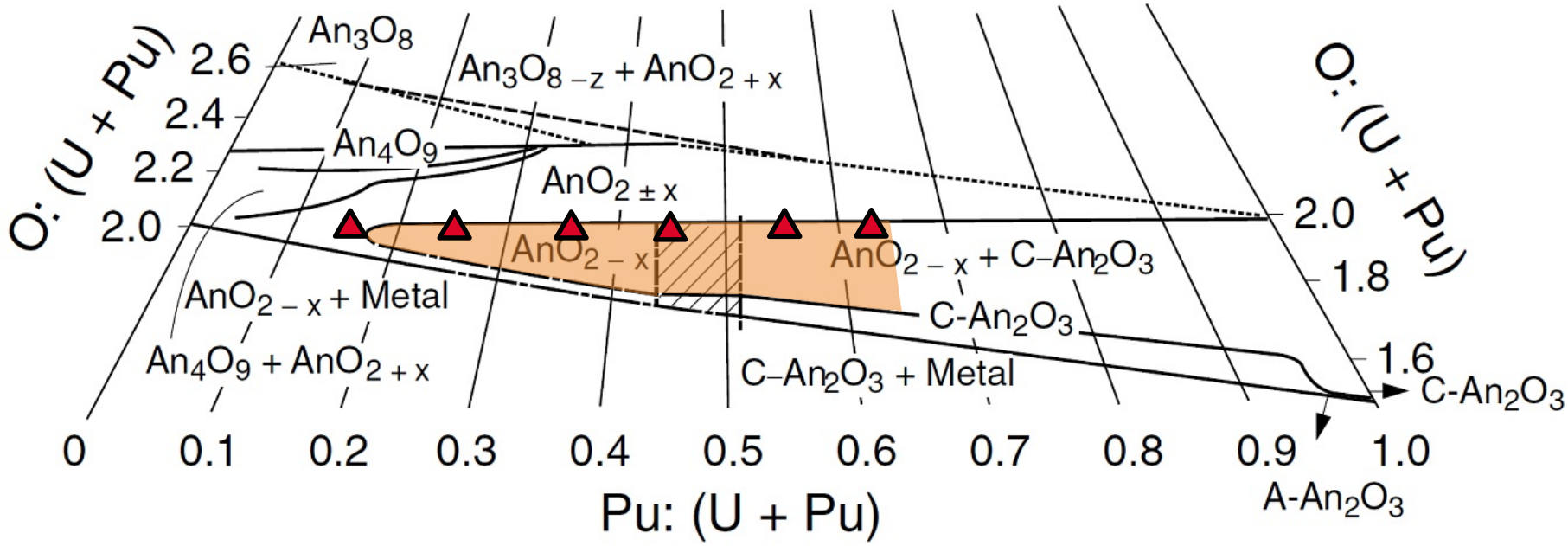


- **Very restricted** achievable O/M ratios
- Sample can not reach low O/M ratios at equilibrium with the gas mixture

How to read the data : iso-intensity map

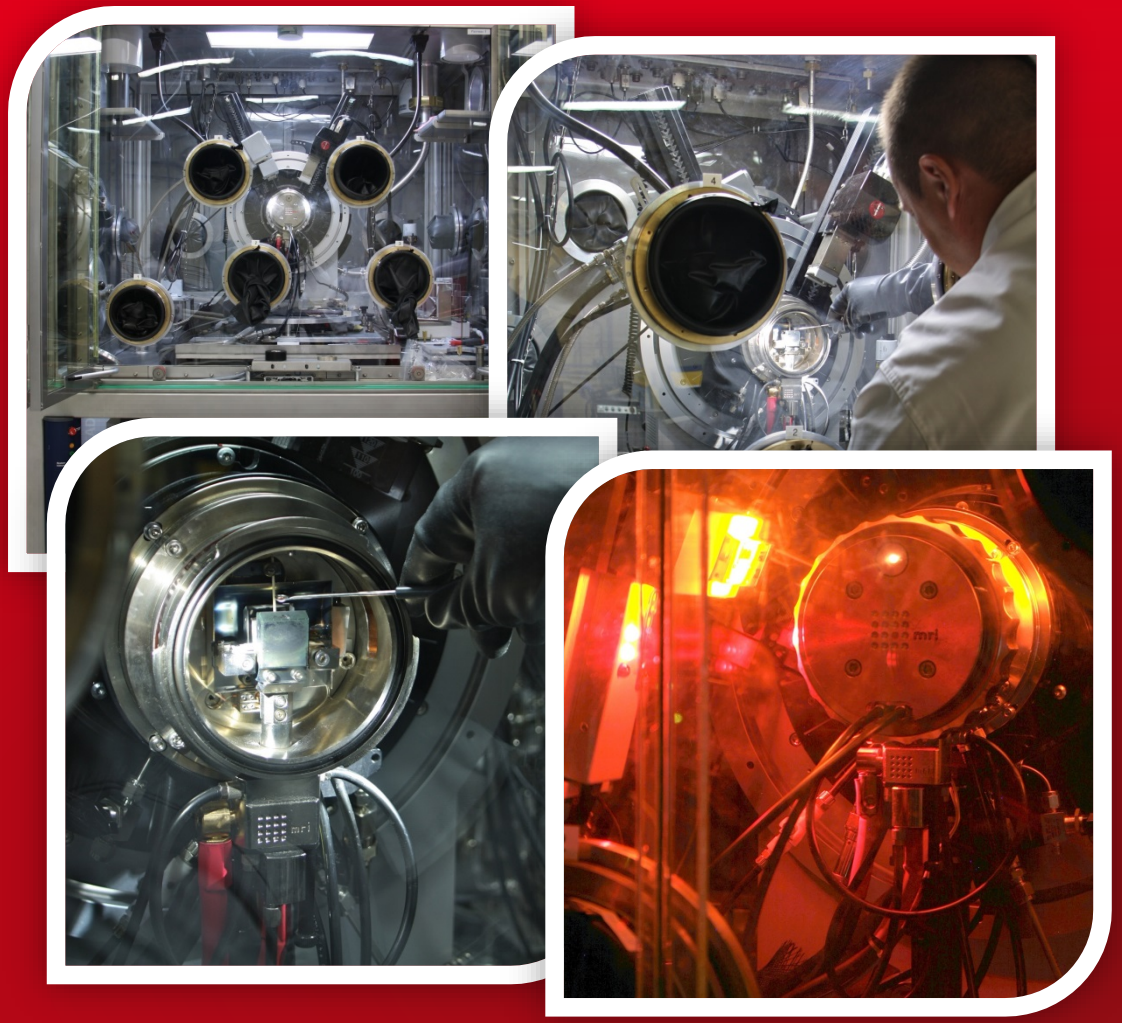


Samples and conditions



Reduction experiments under He + 5% H_2

Experimental results



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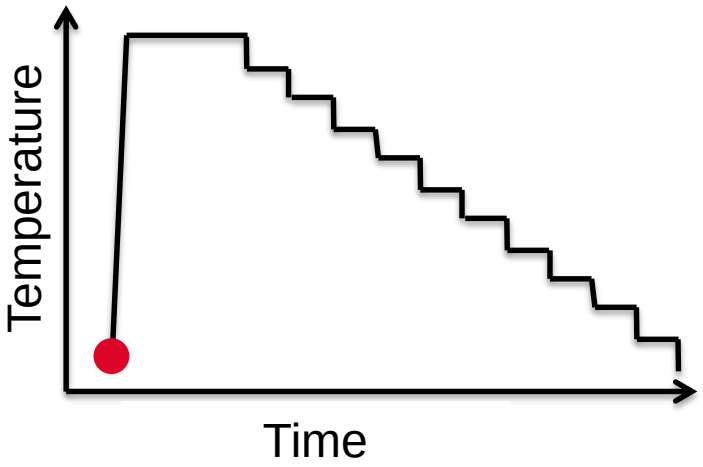
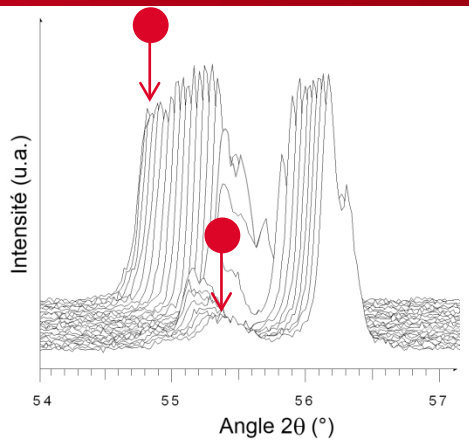
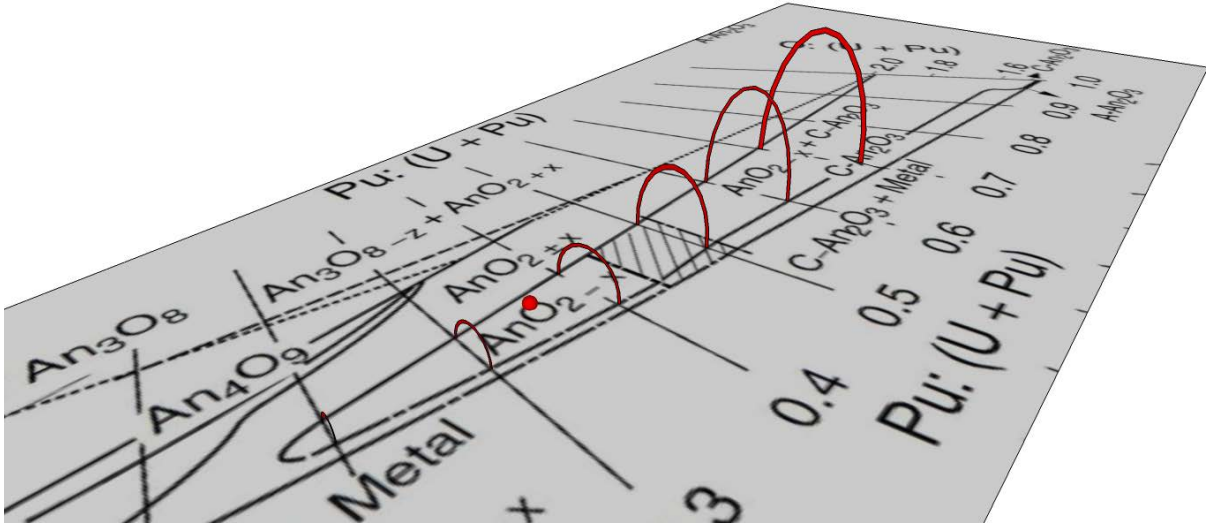
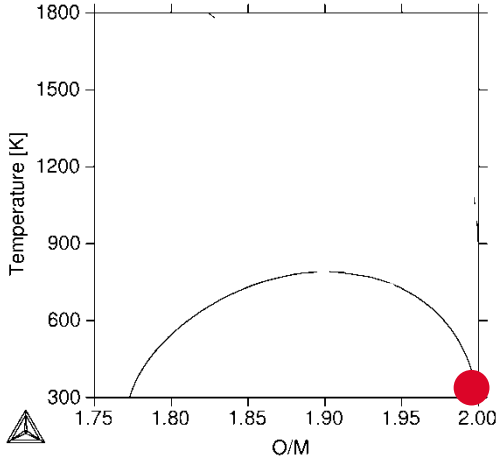
In situ observation of phase separation

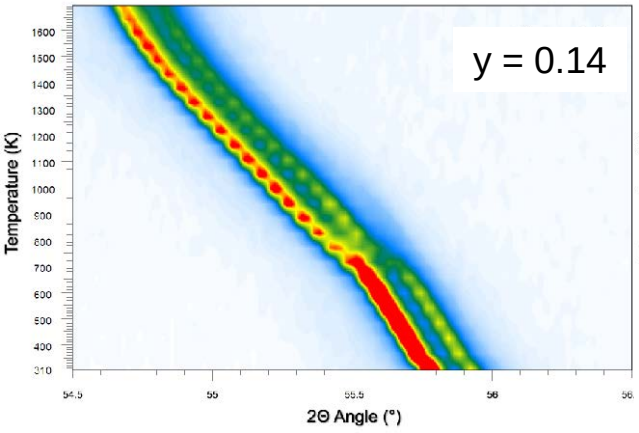


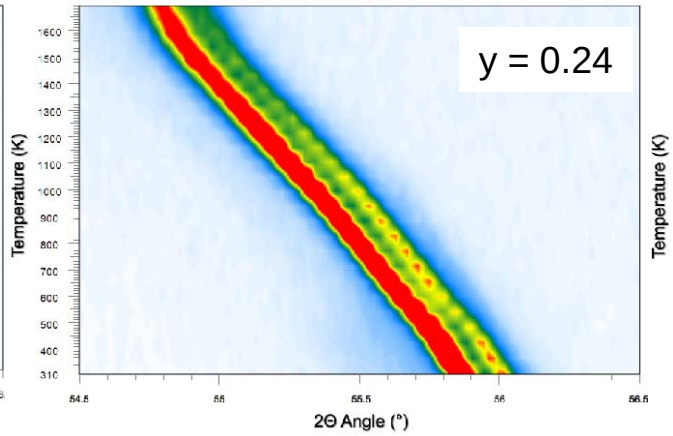


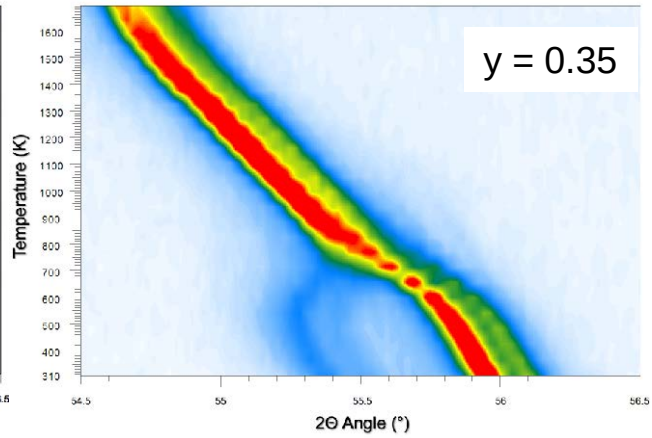


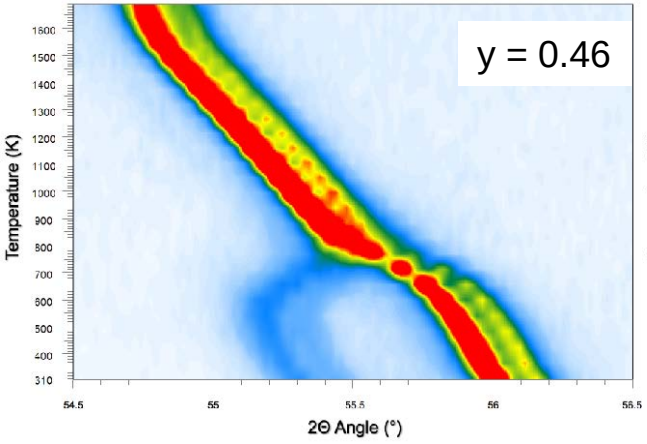


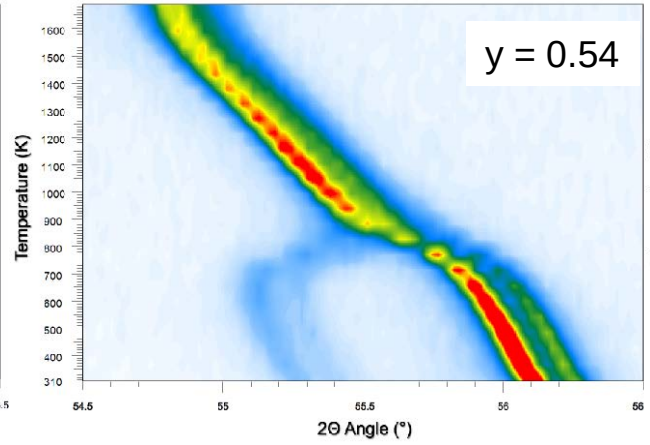
XRD iso-density maps

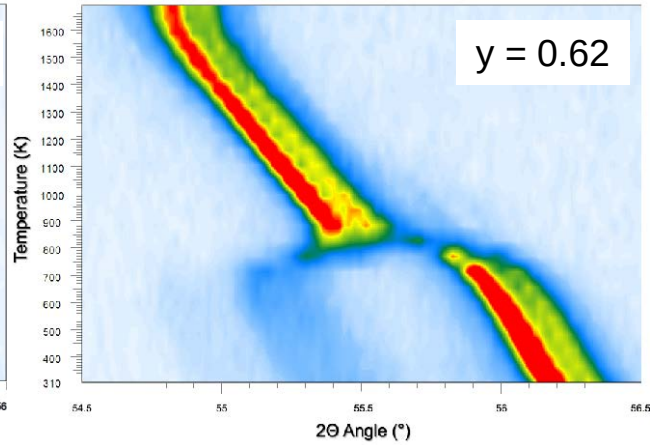




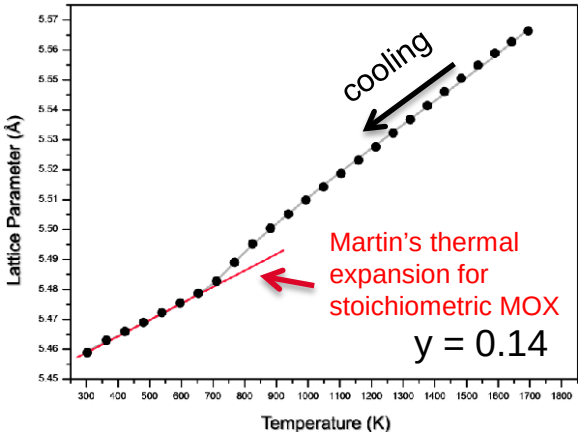


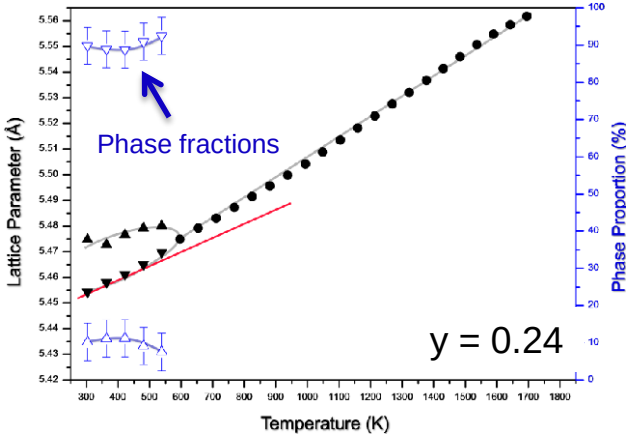


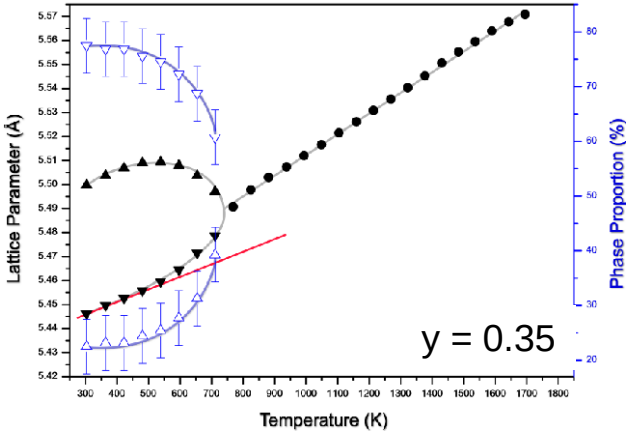


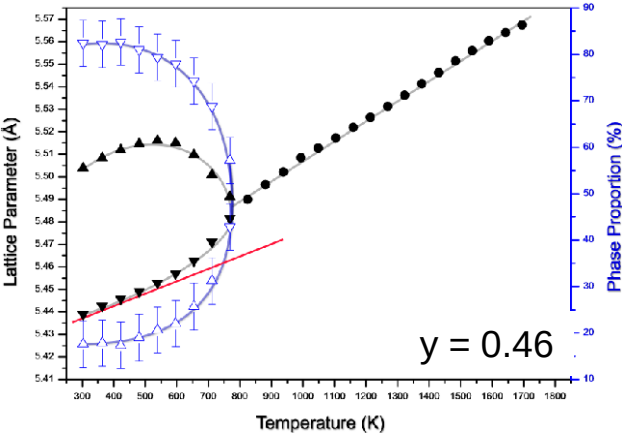


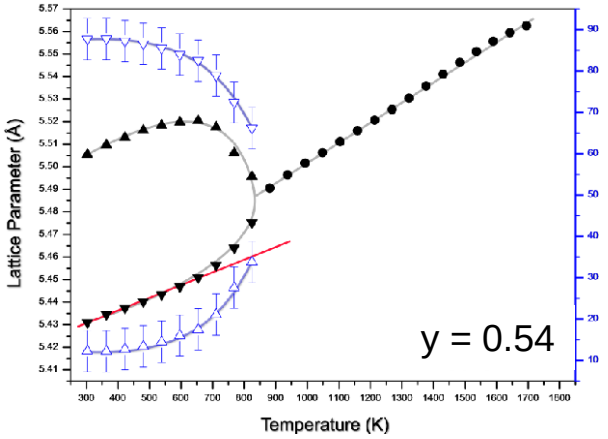
Lattice parameters and phase fractions

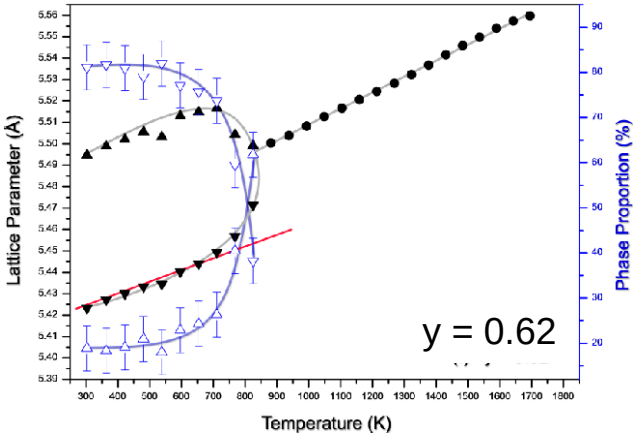




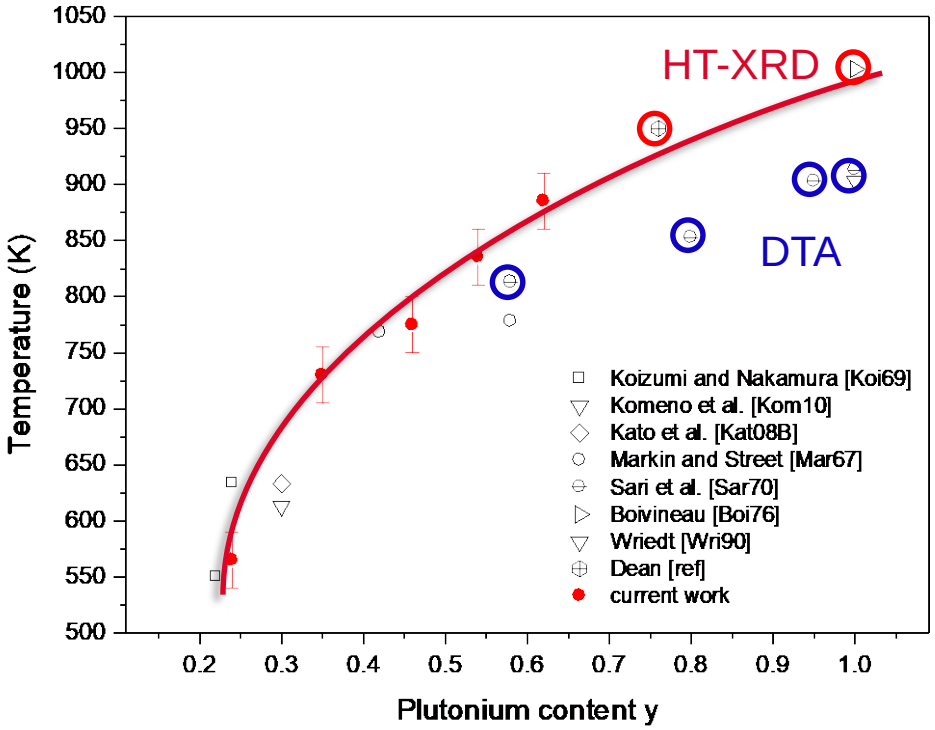


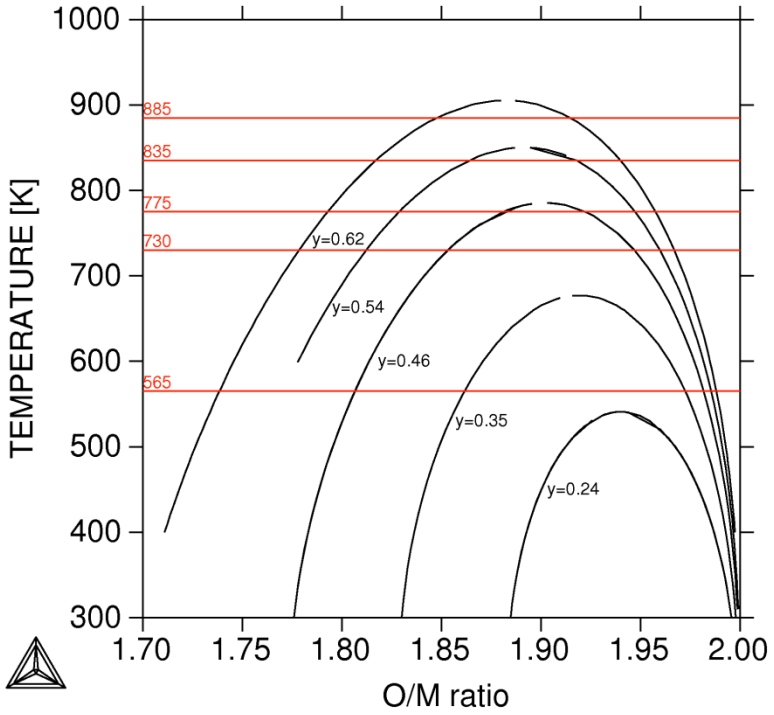






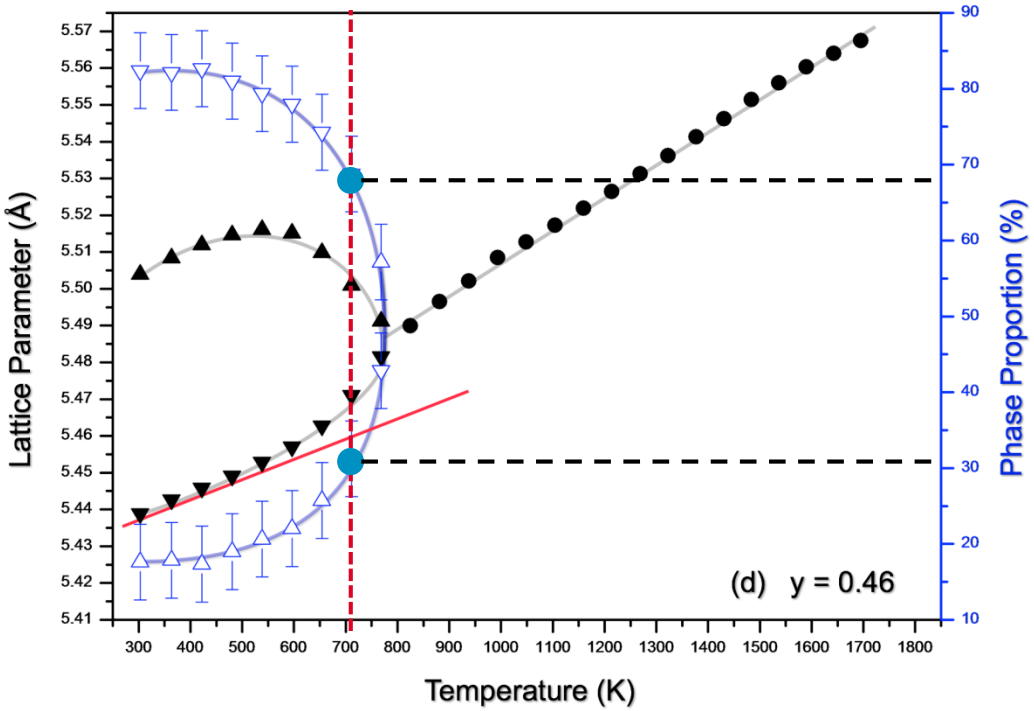
Temperature of phase separation

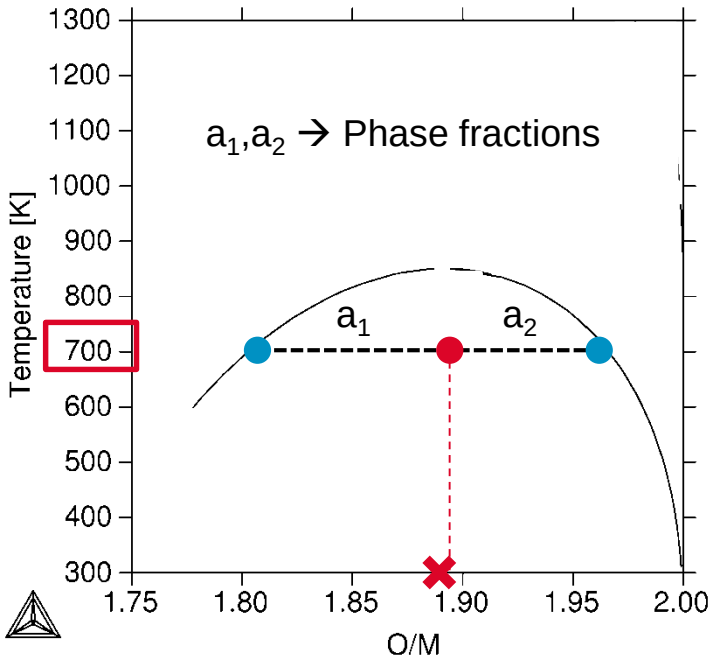




Evaluation of the O/M ratio ?

O/M determination : Calculations to overcome limitations





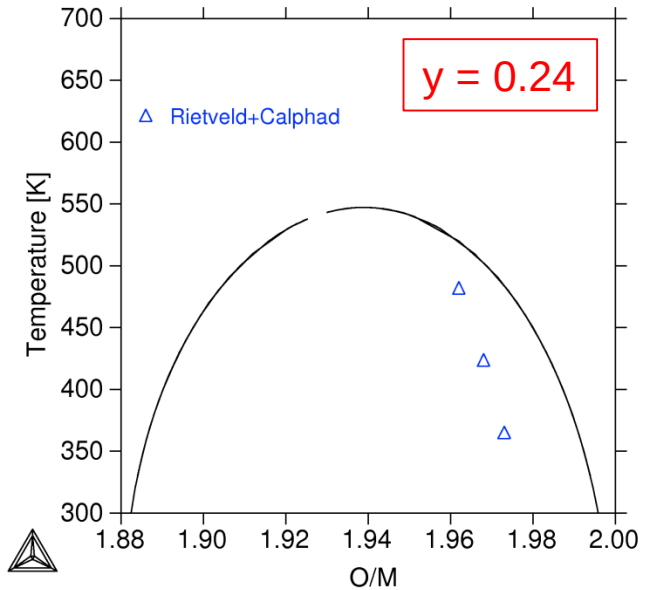
Determination of O/M is possible in certain cases:

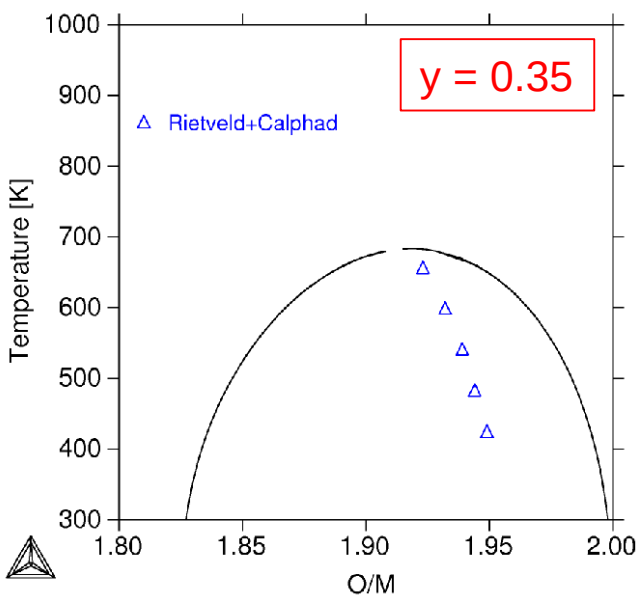
- Biphasic domain → Rietveld refinement + CALPHAD

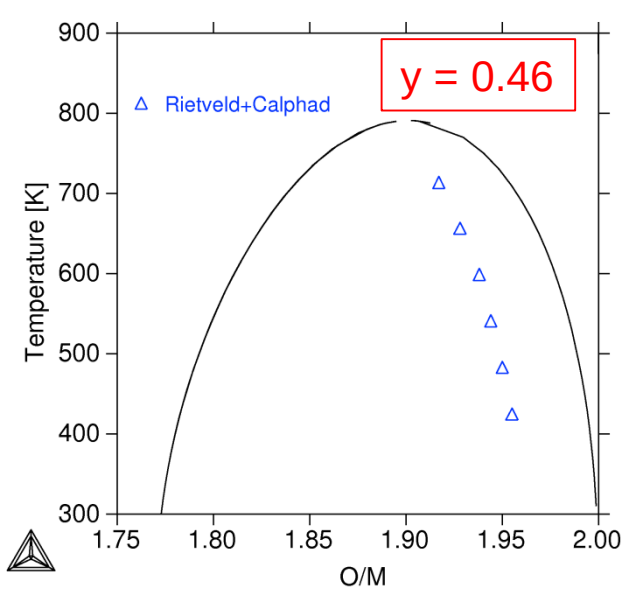
Phase fractions from experiments (peak intensities, Rietveld refinement) = Phase fractions are positioned on the calculated miscibility gap

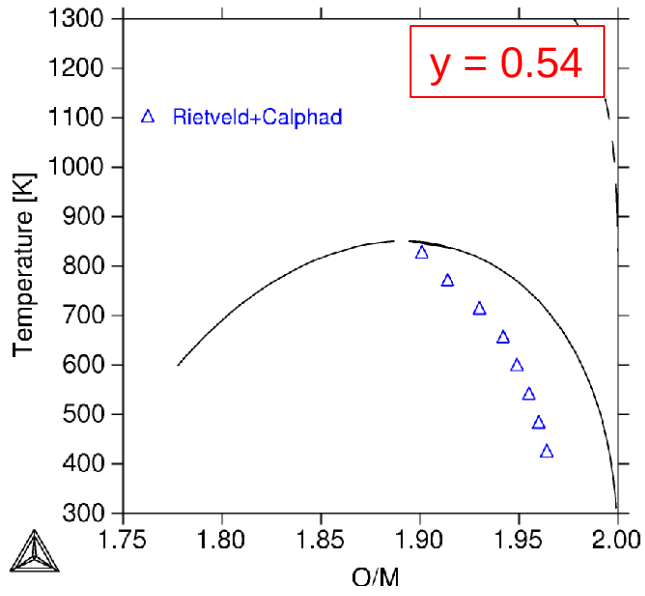
→ O/M value at each T

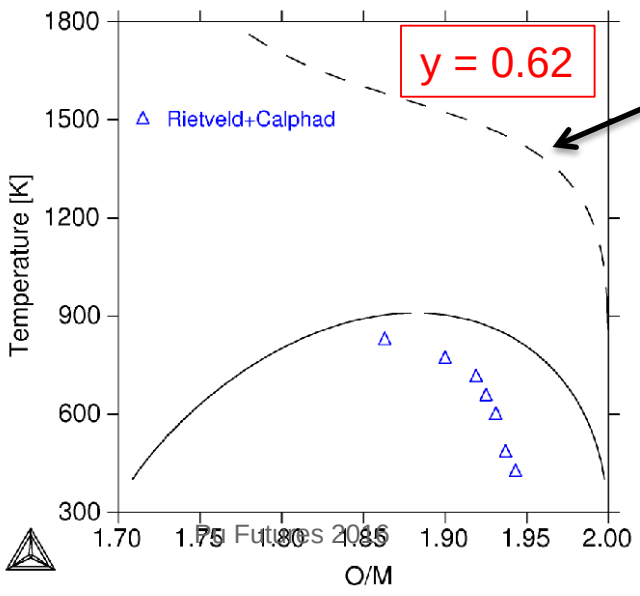
Calculations + Rietveld







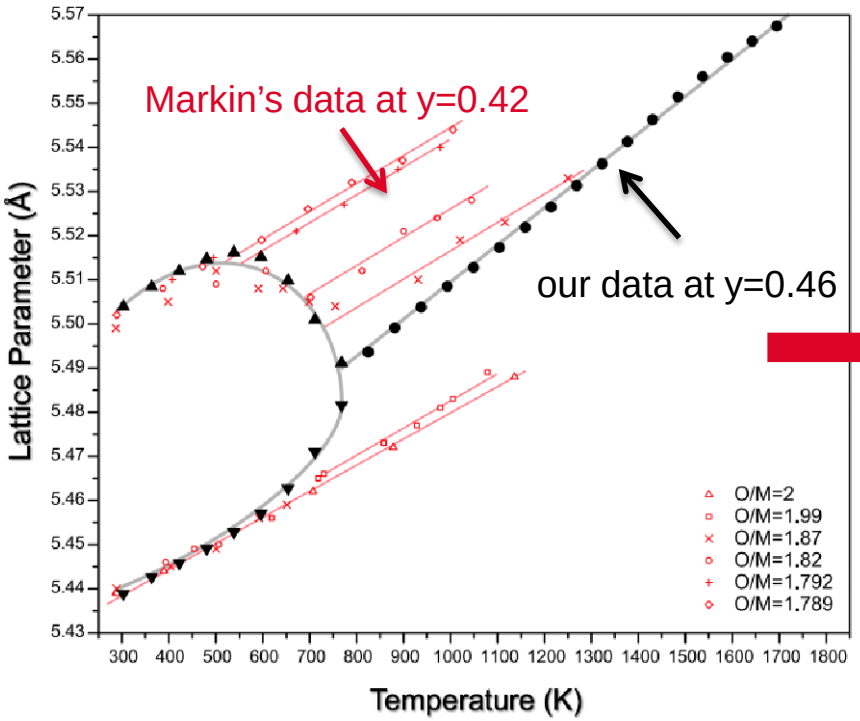


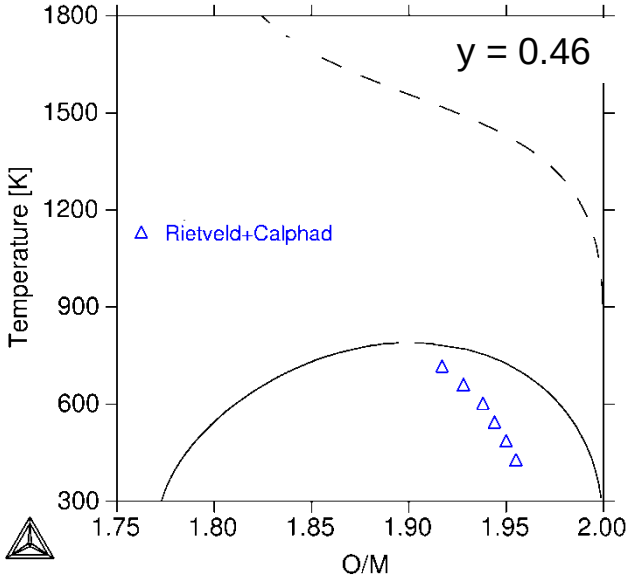


Calculated equilibrium between sample and gas for He/5%H_2 + 15 vpm H_2O

Calculations + literature

- Single phase domain → comparison with literature

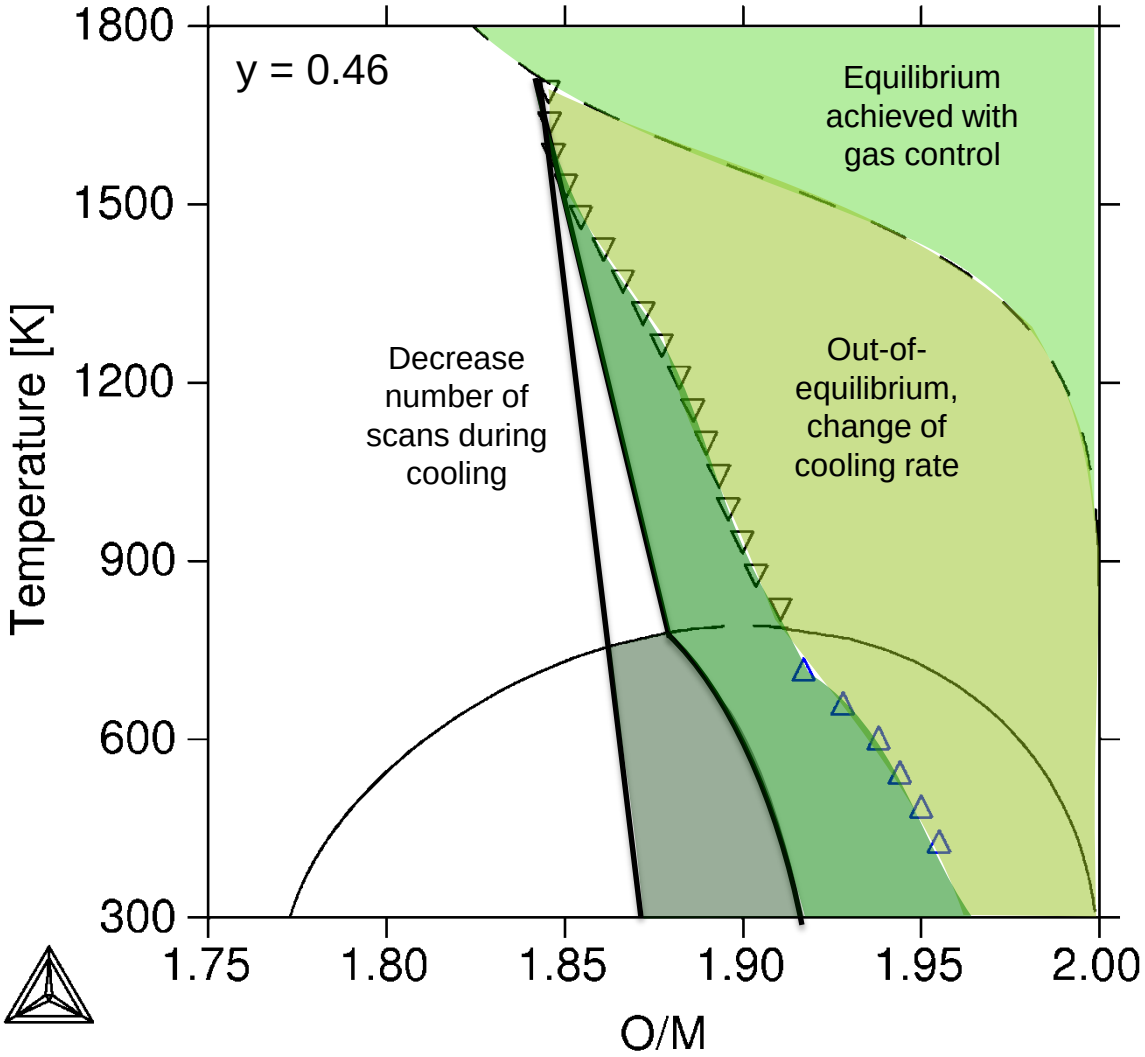




$$\frac{O}{M} = 21{,}3075 + 22{,}78 * 10^{-5} * T - 3{,}565 * a$$

At HT → equilibrium between sample and gas = reduced sample
At LT → equilibrium between sample and gas = stoichiometric sample

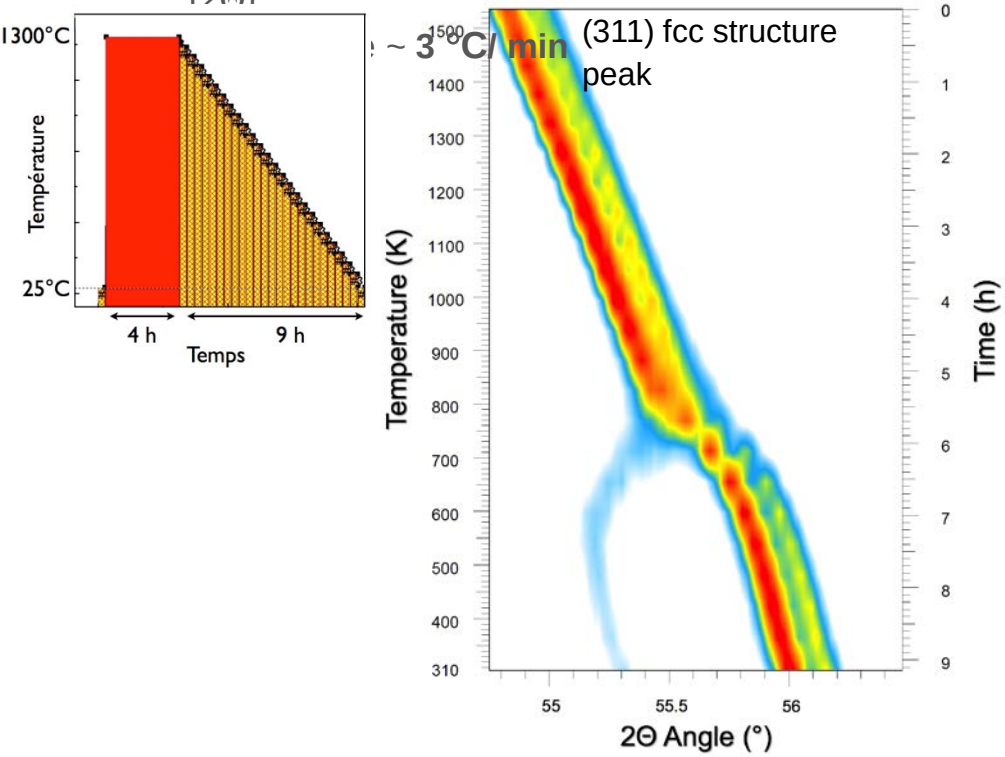
To be or not to be at equilibrium ?



Fast cooling experiment under He/5%H_2 + ~ 15 vpm (y = 0.46)

Measurements in isothermal conditions

25 min per scan between 22 and 145° (2Θ)

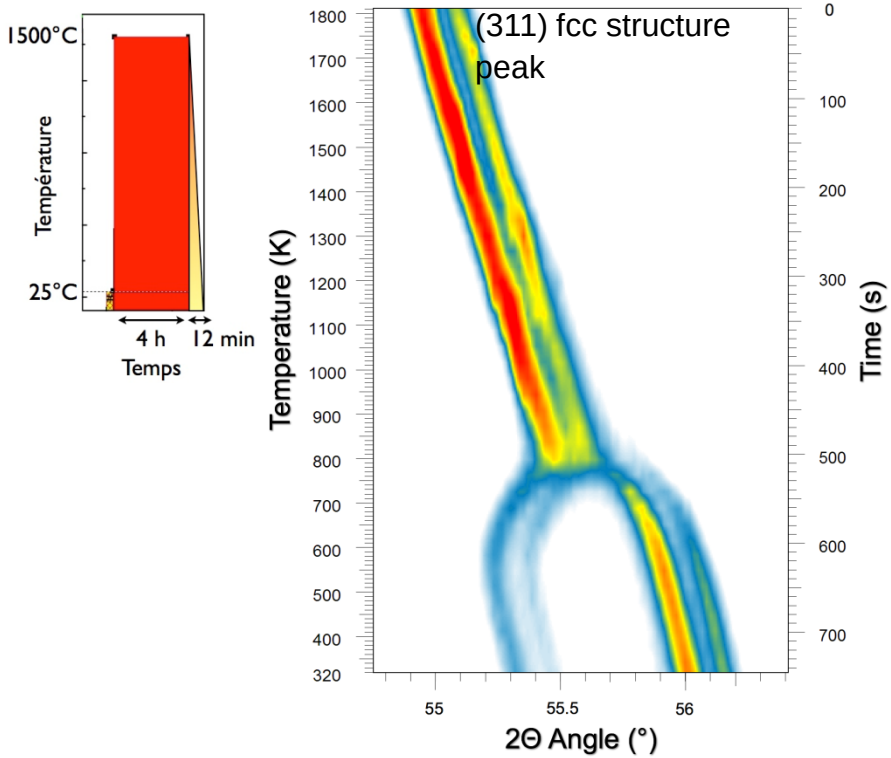


Phase separation at ~ 775 K and 2 fcc a = 5.439(1)Å and 5.504(5)Å

Measurements in fixed-scan (non-isothermal)

14 s per scan on a restricted 3° (2Θ) angular range

Cooling rate ~ **2 °C/ sec**



Phase separation at ~ 775 K and 2 fcc a = 5.439(1)Å and 5.495(5)Å

Almost identical XRD results

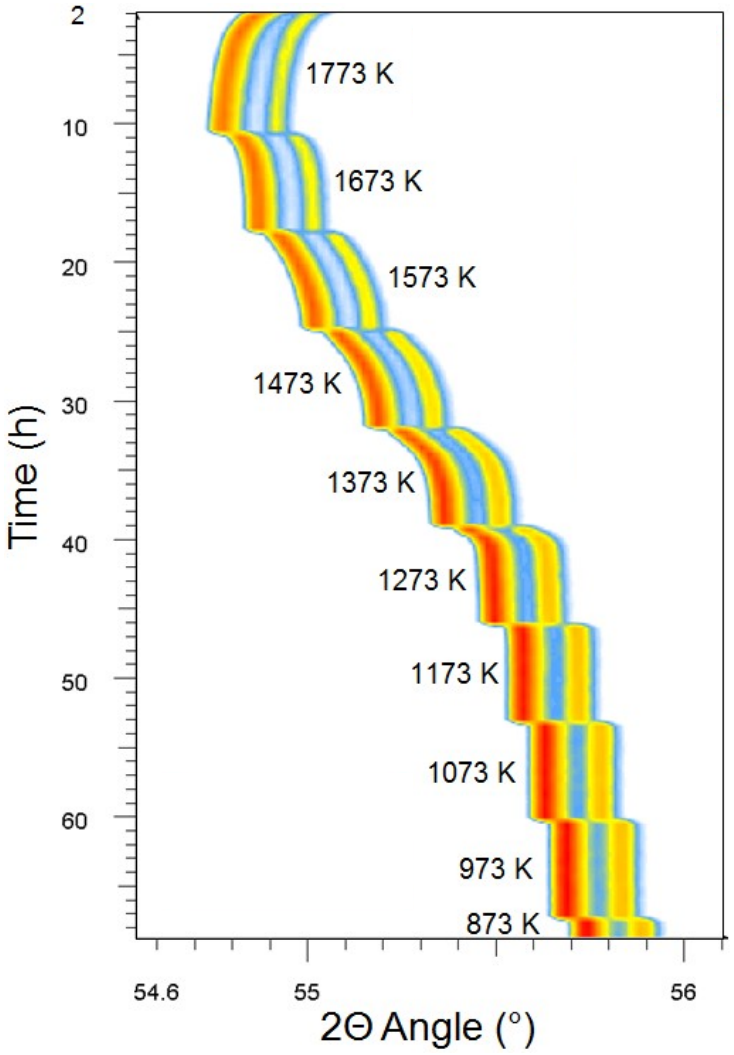
Suggests that the phase separation is mostly governed by oxygen diffusion under both conditions

R. Vauchy, R.C. Belin, A.-C. Robisson, F. Hodaj, J. Eur. Ceram. Soc. 34 (2014)

Slow cooling experiment under He/5%H_2 + ~ 15 vpm (y = 0.46)

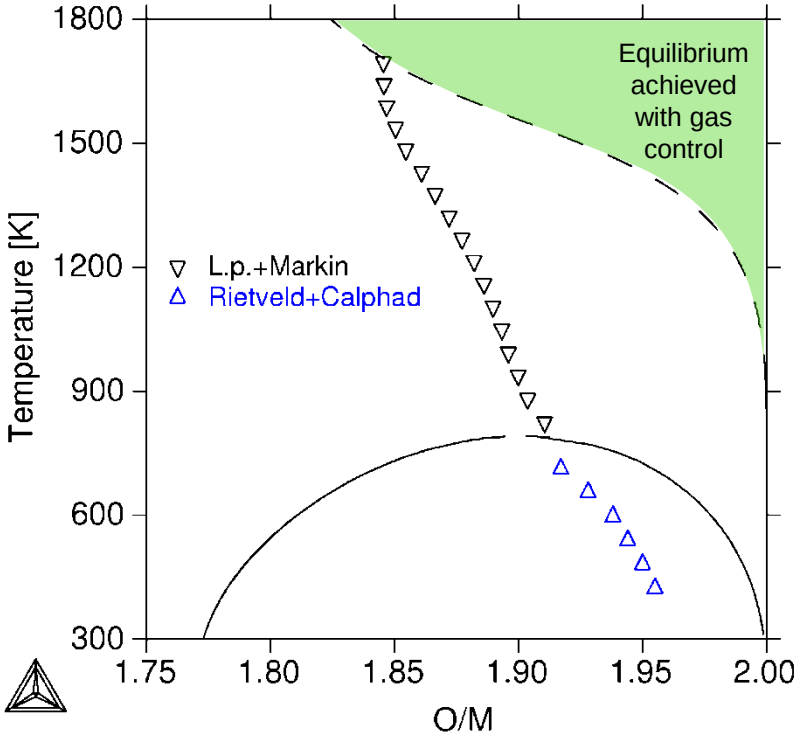
Measurements in isothermal conditions

~ 7 hours at each temperature



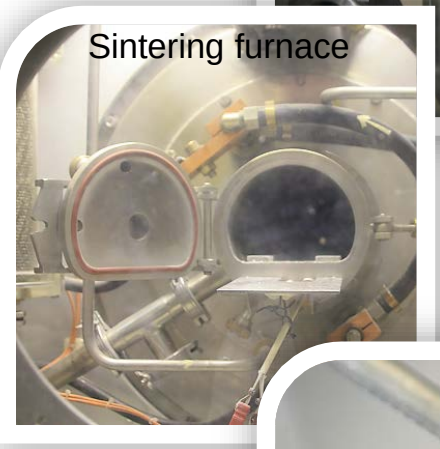
No phase separation is observed

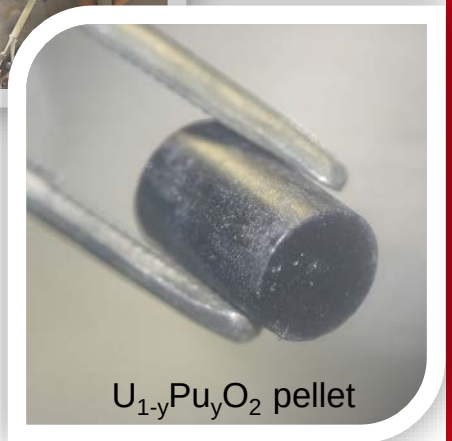
Oxygen stoichiometry (O/M=2) reached at 873K



CONCLUSION

- We have developed a high temperature XRD with the capability of performing precise measurements : phases identification, l.p., fractions vs. T and pO_2
- However, we are aware of the constraints of the experimental technique and try to deal with them
- Calculations with the CALPHAD method are useful to overcome experimental limitations (determination of the O/M as a function of T)
- With this HT-XRD, we have provided new experimental data, both in the hyper- and hypo-stoichiometric domains of the U-Pu-O system
- They will contribute to the available knowledge on this phase diagram, possibly ameliorating the currently available thermodynamic database
- The methodology used in the current work might be useful to investigate other oxides systems exhibiting a miscibility gap





Thank you for your attention

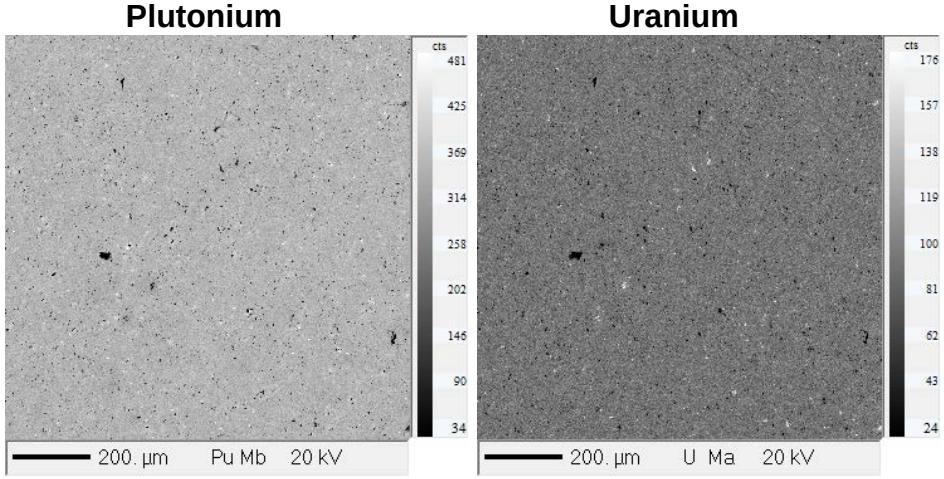
Recent publications :

R. Vauchy *et al. JNM 469, 2016, 125-132*
R. Vauchy *et al. Inorg. Chem. 55(5), 2016, 2123-2132*
R. Vauchy *et al. Appl. Mater. Today 3, 2016, 87-95*

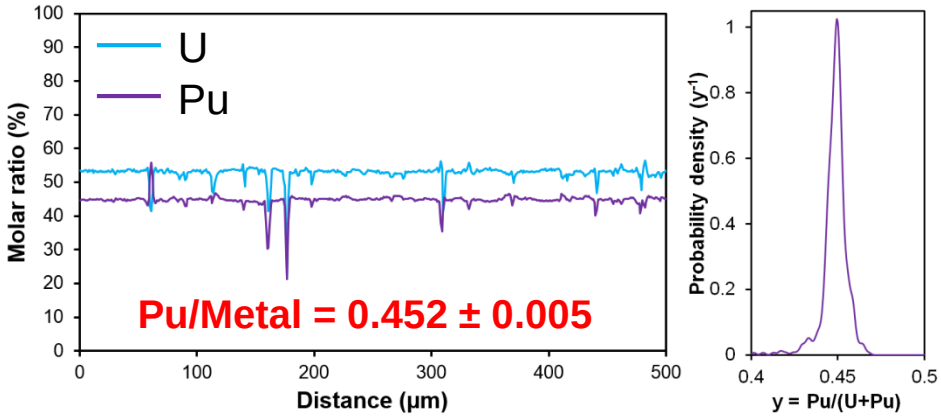
Sample manufacturing

- **Manufacturing of $U_{0.55}Pu_{0.45}O_2$ pellets by powder metallurgy [1]**

Objective #1 : homogeneous U-Pu distribution

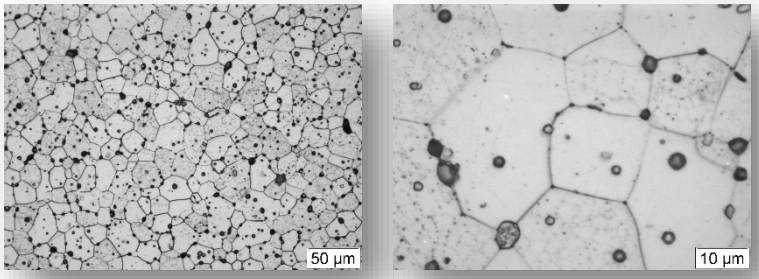


EPMA X-ray mapping in gray levels of Pu and U in $U_{0.55}Pu_{0.45}O_2$ [2]



Elementary U and Pu profils over 500 µm and integrated Pu/M [2]

Objective #2 : dense pellets with big grains for diffusion study

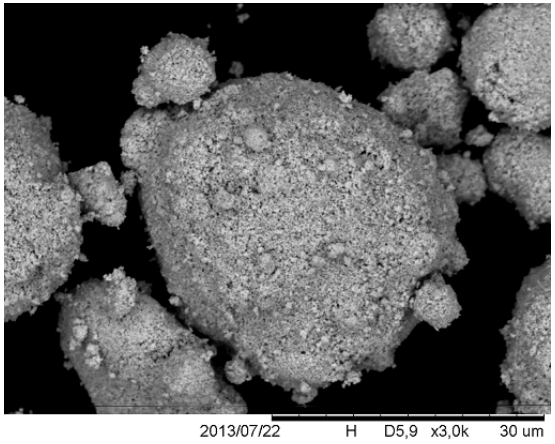


$\rho_{apparent}$ ($\%\rho_{theo}$)	Grain size (µm)
95.6(3)	30-40

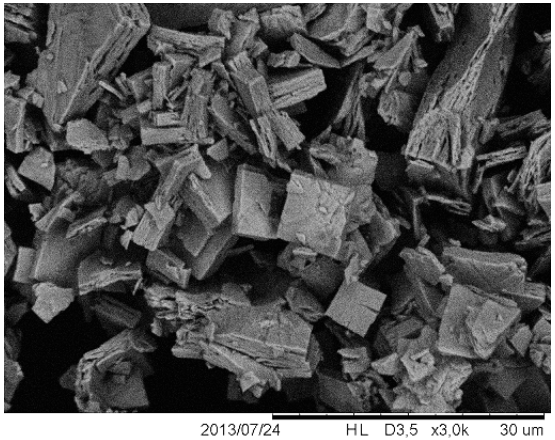
[1] *R. Vauchy et al.* ***Ceram. Int.****, 40(7B), 2014, 10991-10999*
[2] *R. Vauchy et al.* ***JNM****, 456, 2015, 115-119*

Optimized ceramic processing

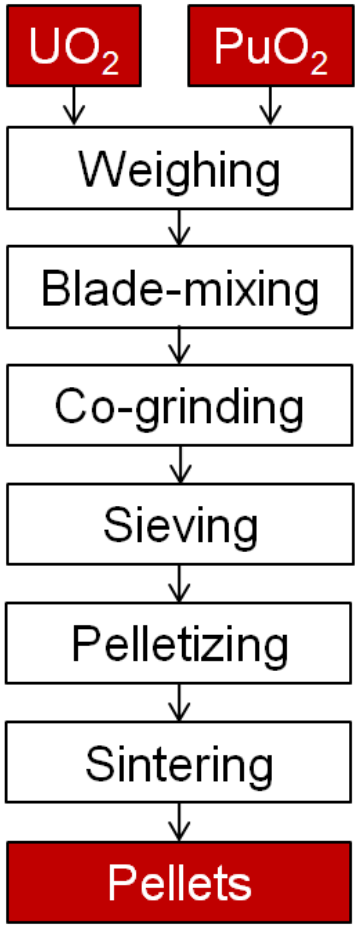
- Optimization of a powder metallurgy process [1]



SEM on raw UO_2 powder [2]



SEM on raw PuO_2 powder [2]



Tank : 40 rpm
Blades : 3000 rpm
30 min

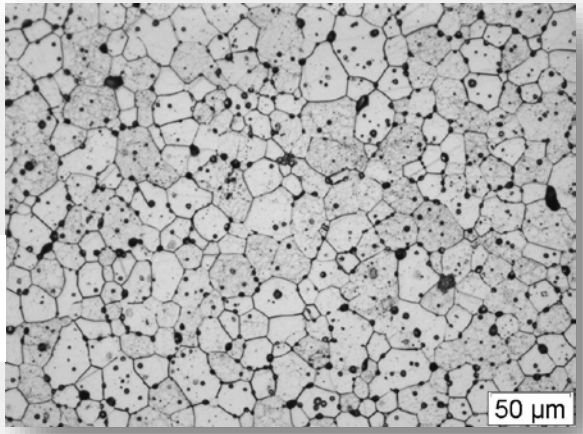
Ball-mill
300 min

160 µm

Automatic, uni-axial, mono-punch press
~300 MPa

2023 K, 24 h
↗100 K.h^{-1} ↘50 K.h^{-1}
Ar + 5% H_2 + 1500 ppm H_2O

Apparent density> 95% ρ_{theo} ⟹ Diffusion
Homogeneous U-Pu distribution ⟹ U-Pu-O

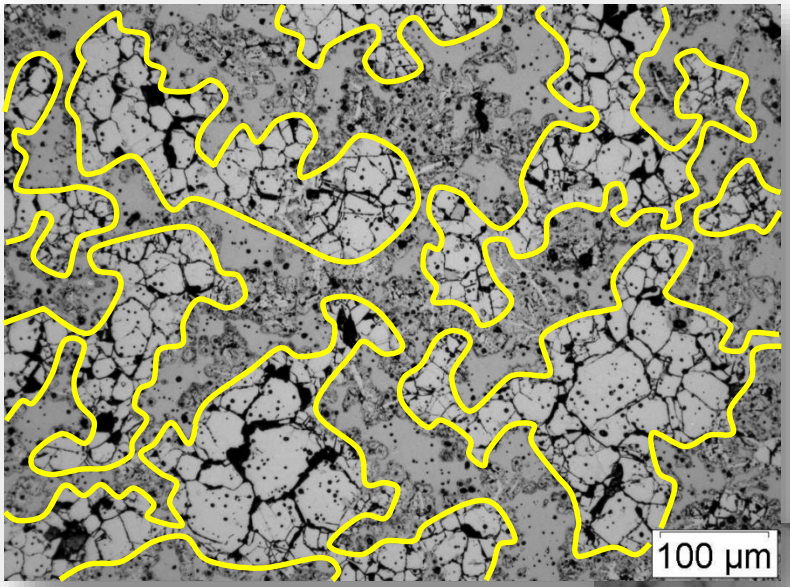


Optical micrography of $U_{0.55}Pu_{0.45}O_{2.000}$ after chemical etching

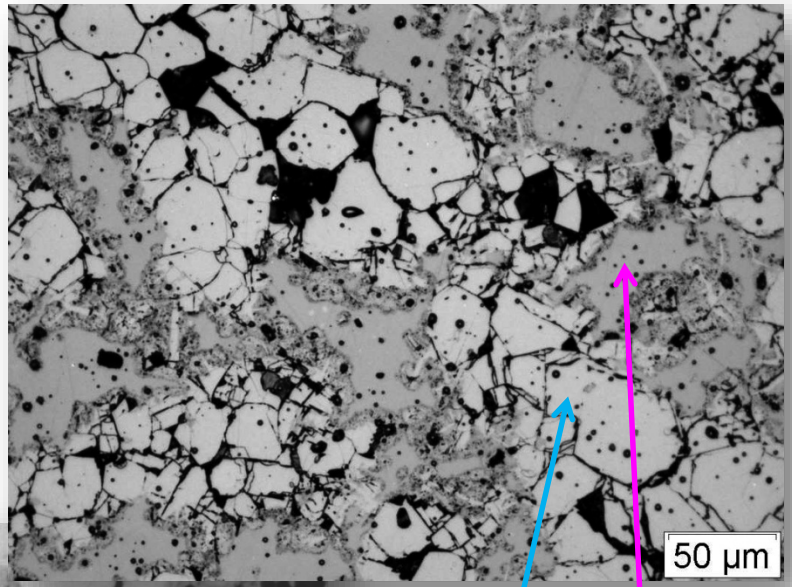
$\rho_{apparent}$ (%ρ_{theo})	Grain size (µm)
95.6(3)	30-40

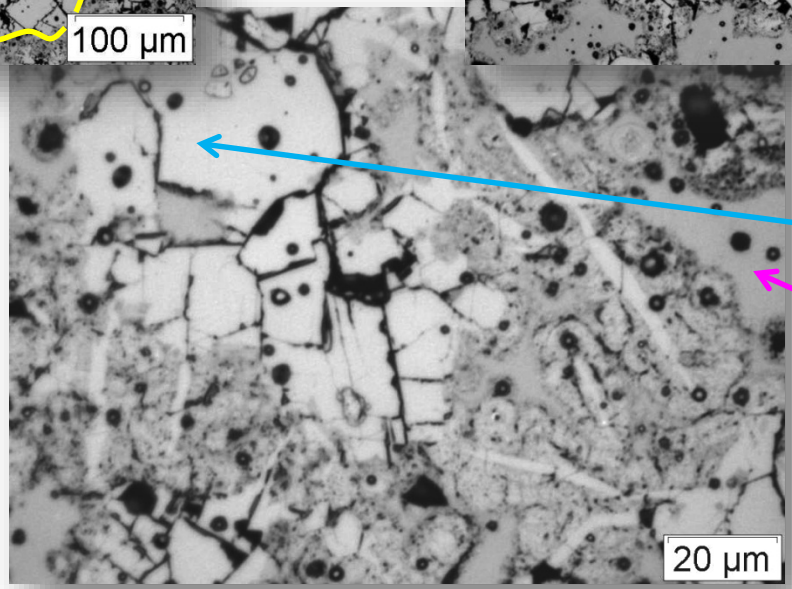
[1] *R. Vauchy et al., Ceram. Int. 40, 2014, 10991-10999*
[2] *S. Berzati, Thèse, 2013*

Microstructural effects of phase separation



↘ ~0.05 K.s^{-1}





High-oxygen phase (O/M≈2.0)

Low-oxygen phase (O/M<<2.0)

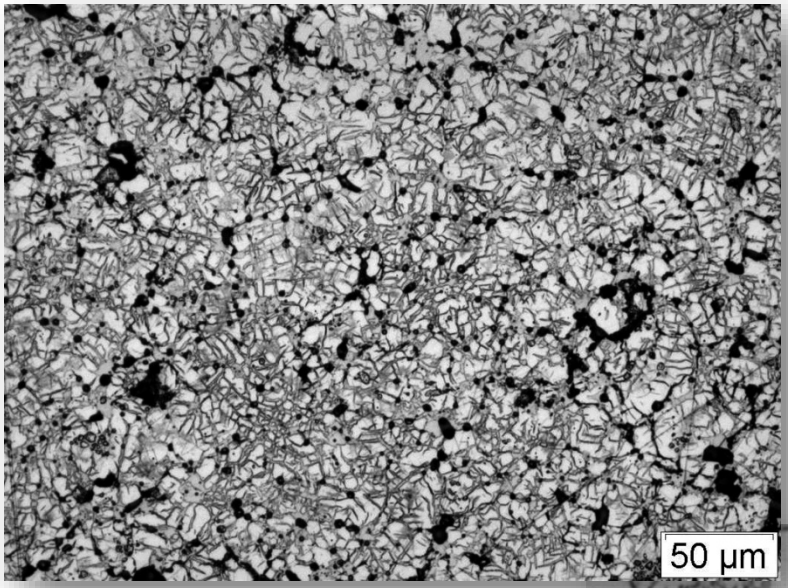
Two distinct zones **even before** chemical etching

↓

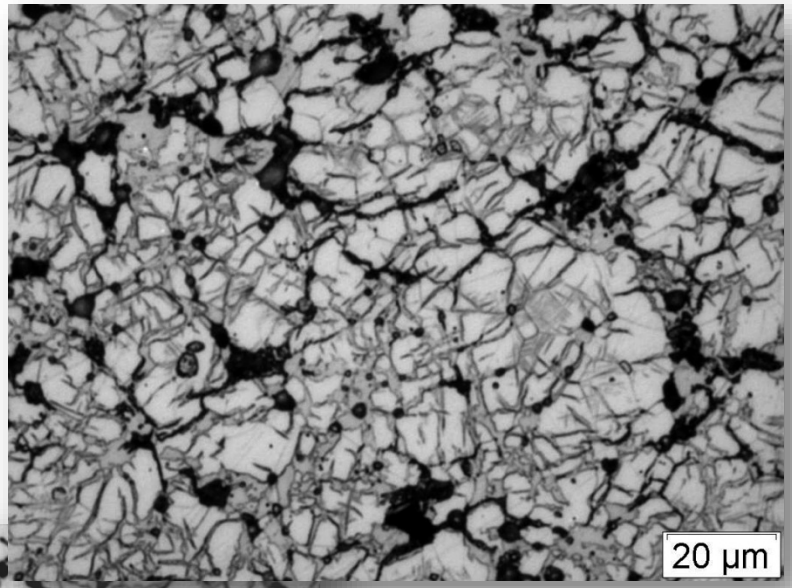
Related to the **two phases** observed by XRD

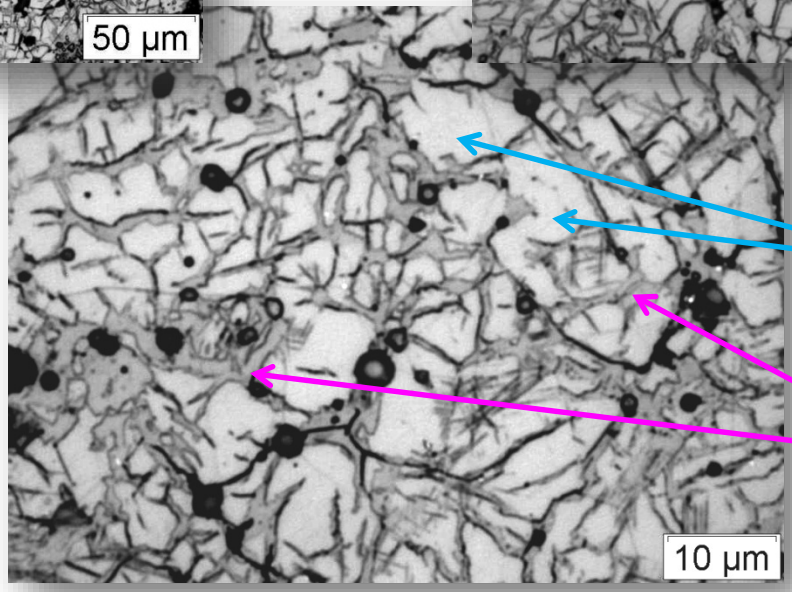
Damaged microstructure (cracks) owing to mechanical strains induced by the phase separation

Microstructural effects of phase separation



↘ ~300 K.s^{-1}





Two zones clearly visible **after** chemical etching and at a **different scale** than the slowly cooled sample

Damaged microstructure by cracks (not visible here)

High-oxygen phase (O/M≈2.0)

Low-oxygen phase (O/M<<2.0)

DE LA RECHERCHE À L'INDUSTRIE

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Samples fabrication and characterization

Samples fabrication and characterization

Starting samples

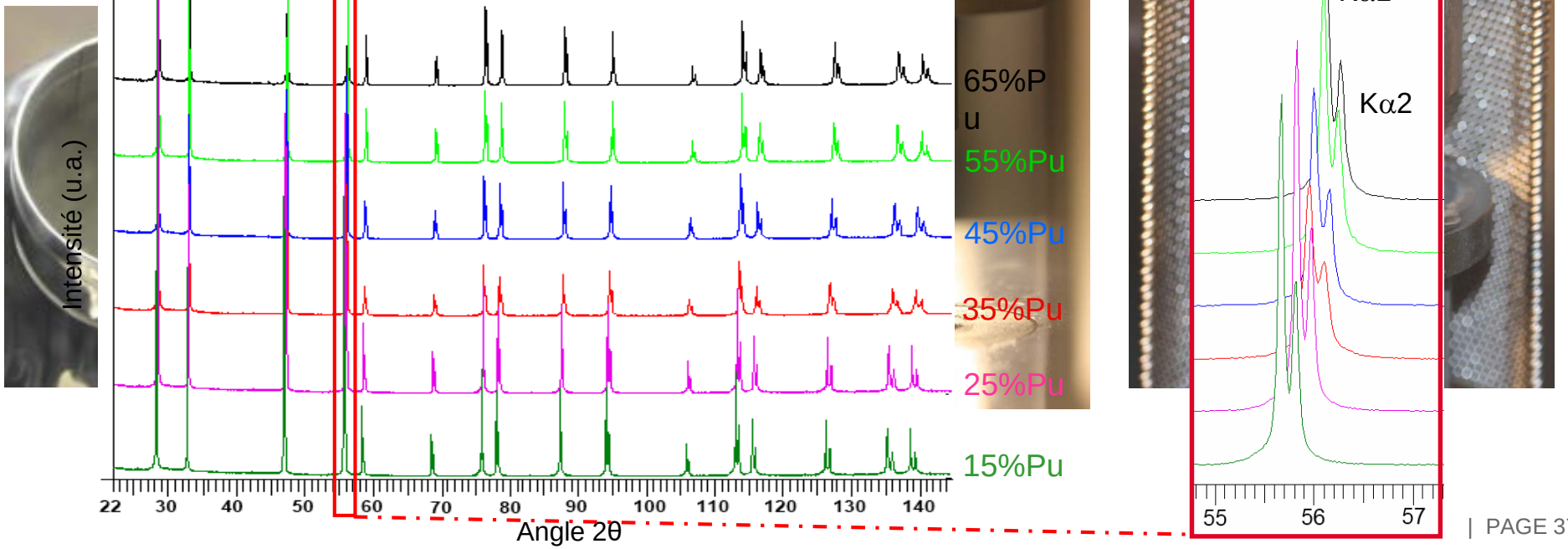
Co-grinding process

$(U_{1-x},Pu_x)O_2$ solid solution

HT- XRD characterization

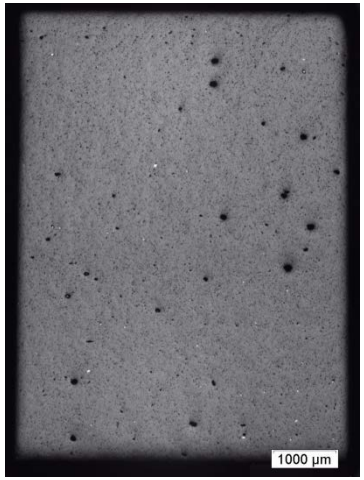
Air

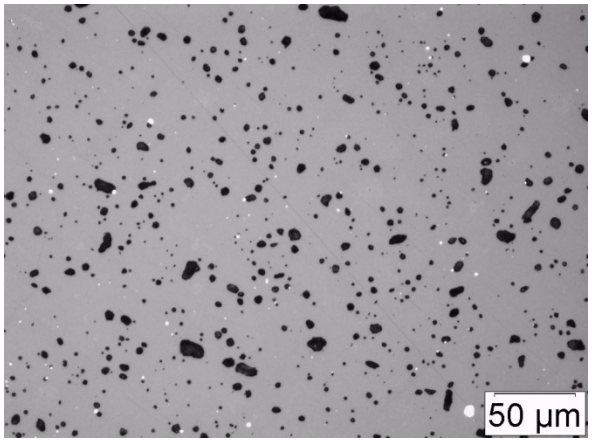
He + 5%H_2
+ 10 ppm residual H_2O

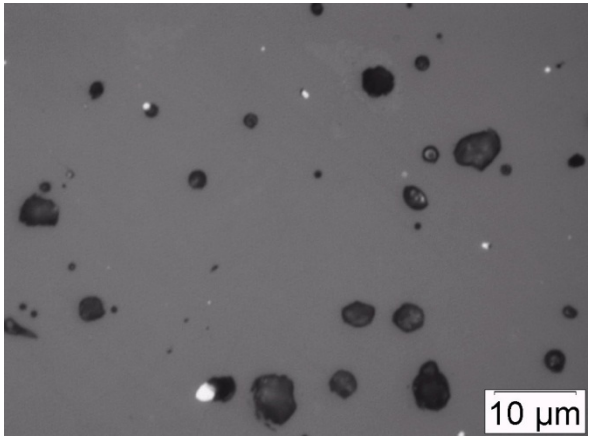


Microstructure of starting samples

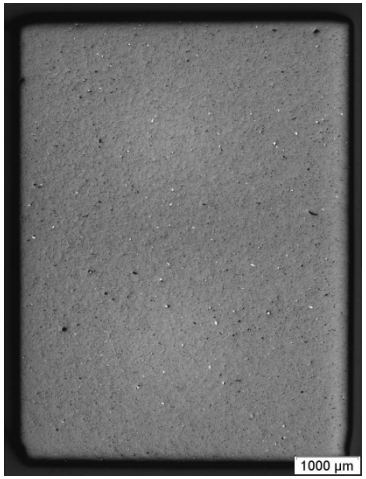
15% Pu

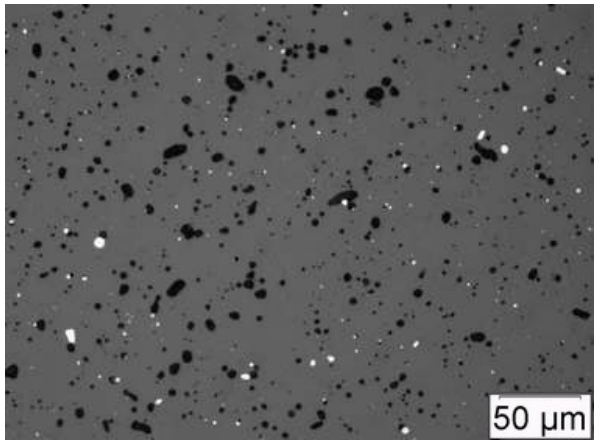


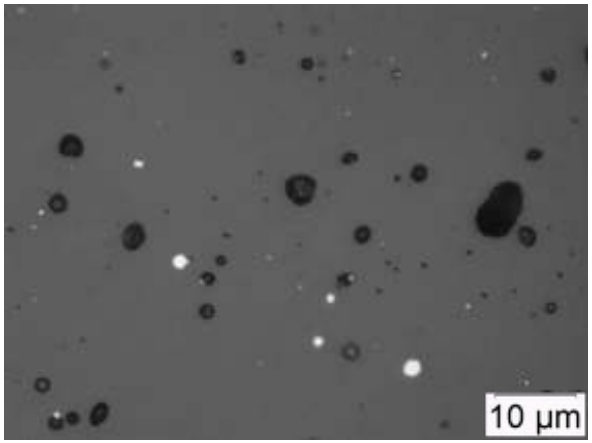




65% Pu



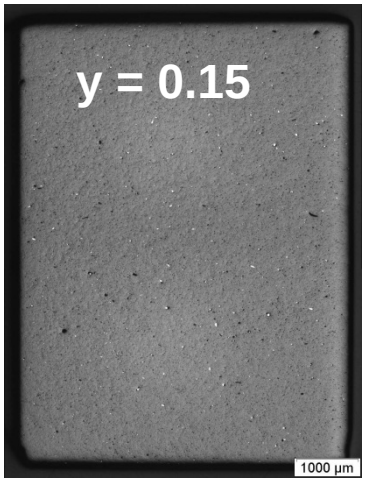




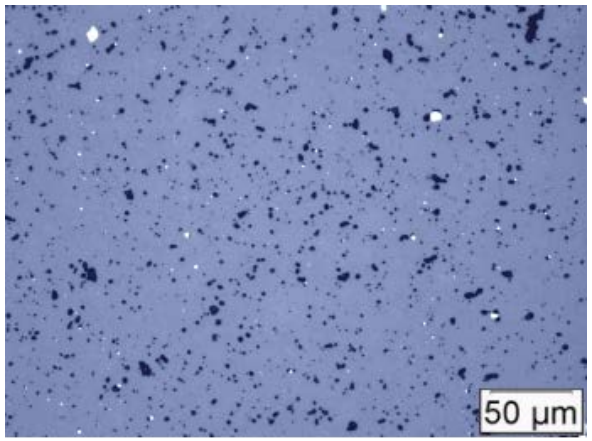
- Dense samples
- Homogeneous microstructure for all Pu content

Effect of the phase separation on the microstructure

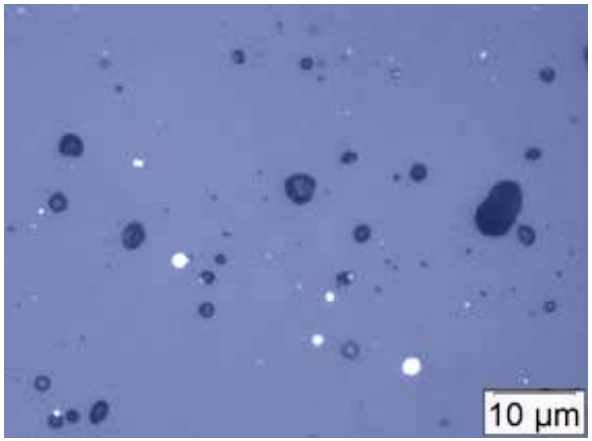
Monophasic sample



macrography

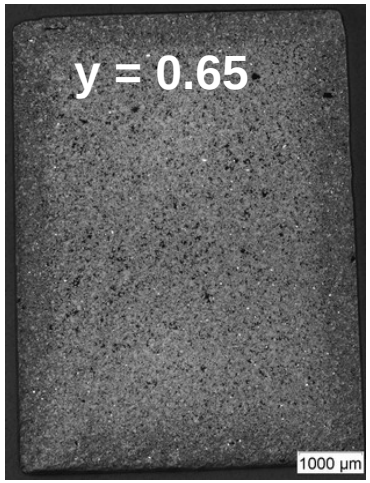


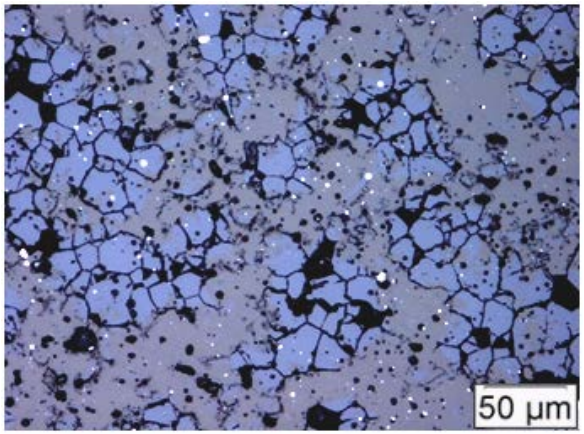
X20 zoom

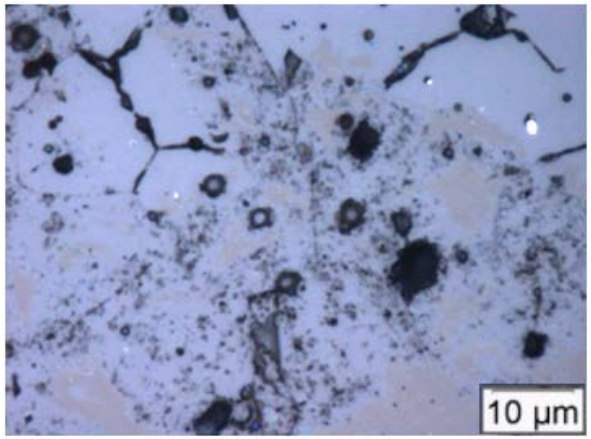


X100 zoom

Biphasic sample



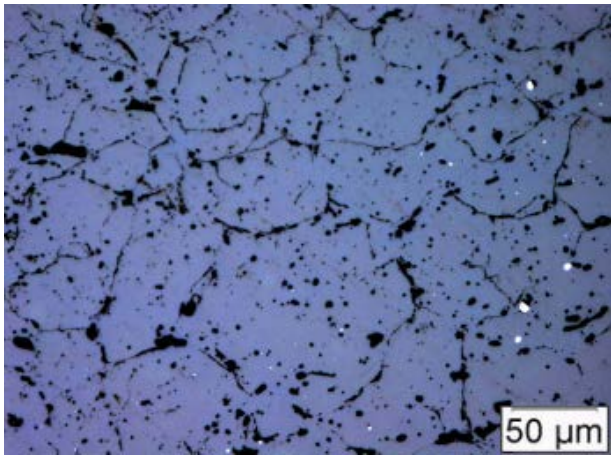




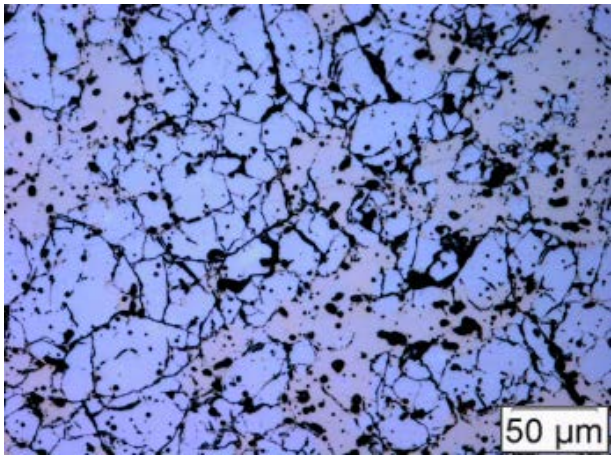
- Cracked material after phase separation
- Appearance of a new type of microstructure

Effect of the phase separation on the microstructure

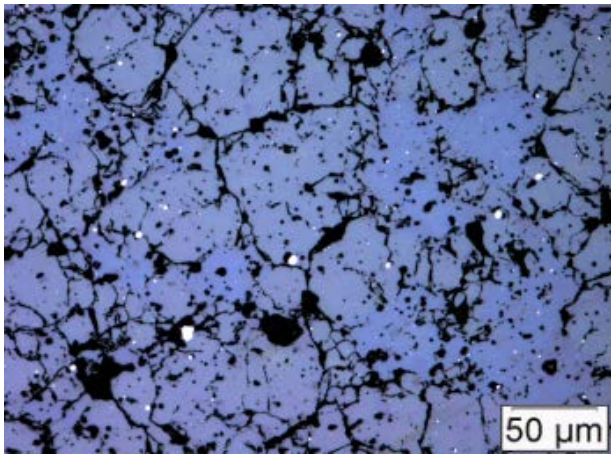
25%Pu



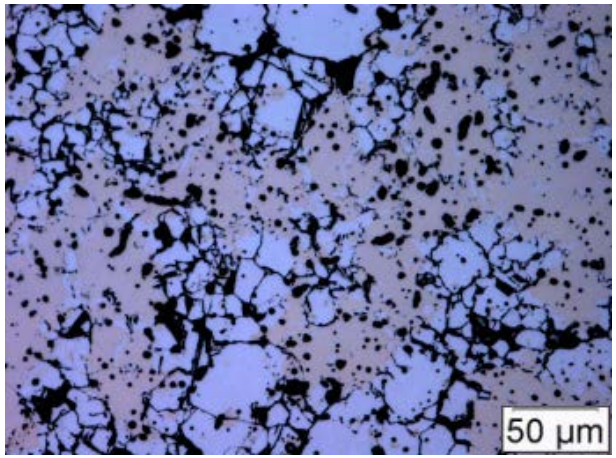
35%Pu

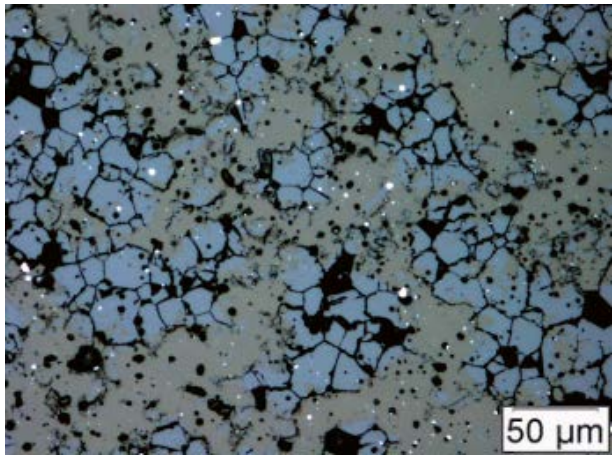


45%Pu



55%Pu



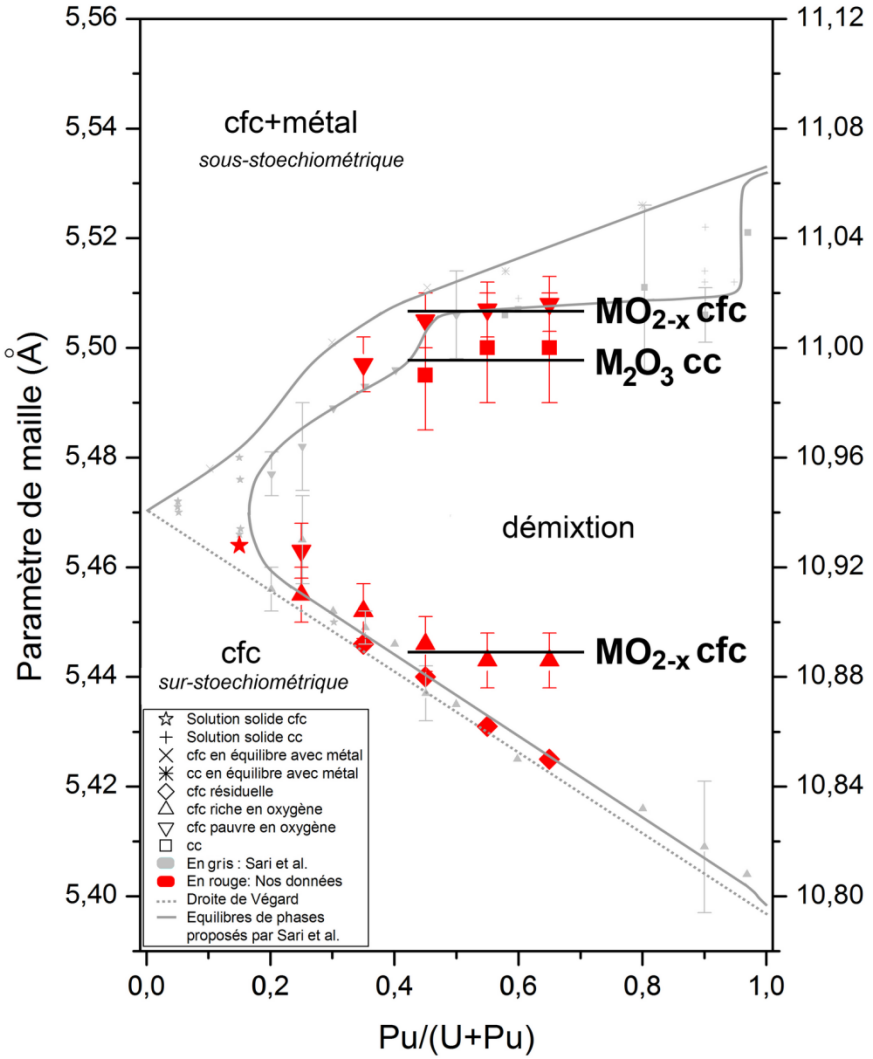


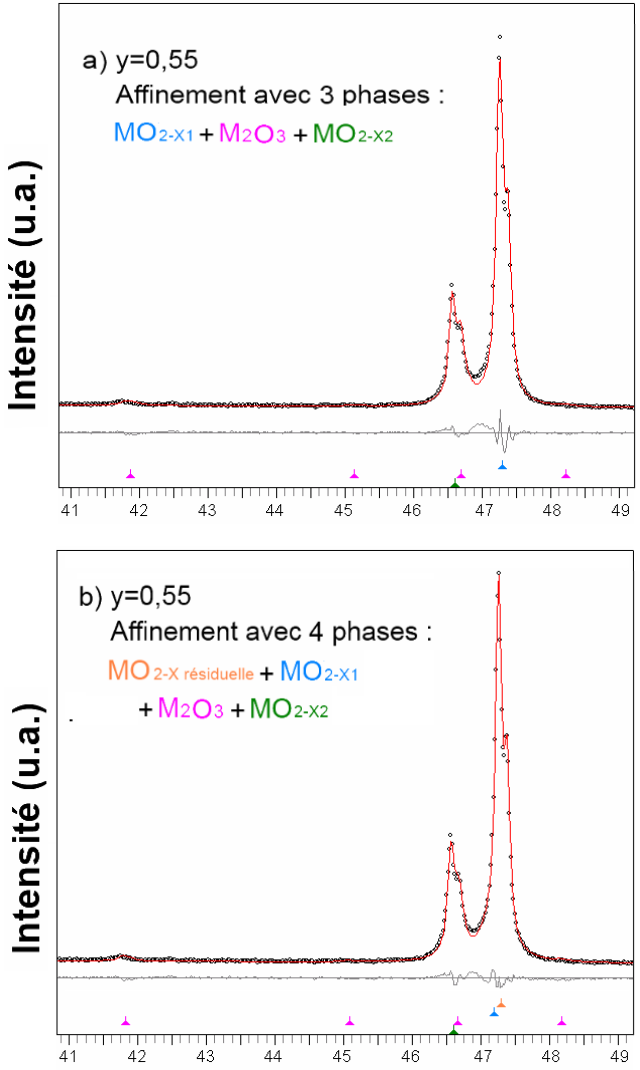
65%Pu

❖Significant impact on the microstructure

❖ The higher the Pu content, the more cracks are observed

Affinement Rietveld : triphasé + phase résiduelle





➢ Affinement compatible avec un équilibre triphasé

Affinement Rietveld : triphasé + phase résiduelle