

Thermodynamics of nuclear fuel

Case studies:

JOG and (U,Am)O₂ in Fast Neutron Reactors

E. Epifano^{1,4,5}

P. M. Martin¹, D. Manara², C. Guéneau³, A. L. Smith⁴

1. CEA, Nuclear Energy Division, DMRC/SFMA, 30207 Bagnols-sur-Cèze, France
2. European Commission, DG Joint Research Centre, Nuclear Safety & Security, P. 2340, 76125, Karlsruhe, Germany.
3. CEA, Nuclear Energy Division, DPC/SCCME, Université Paris-Saclay, F-91191 Gif-sur-Yvette, France
4. Delft University of Technology, Applied Science, Reactor Physics and Nuclear Materials, Delft, The Netherlands
5. DMAS/LEM, ONERA & CNRS, Chatillon, France



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TU Delft

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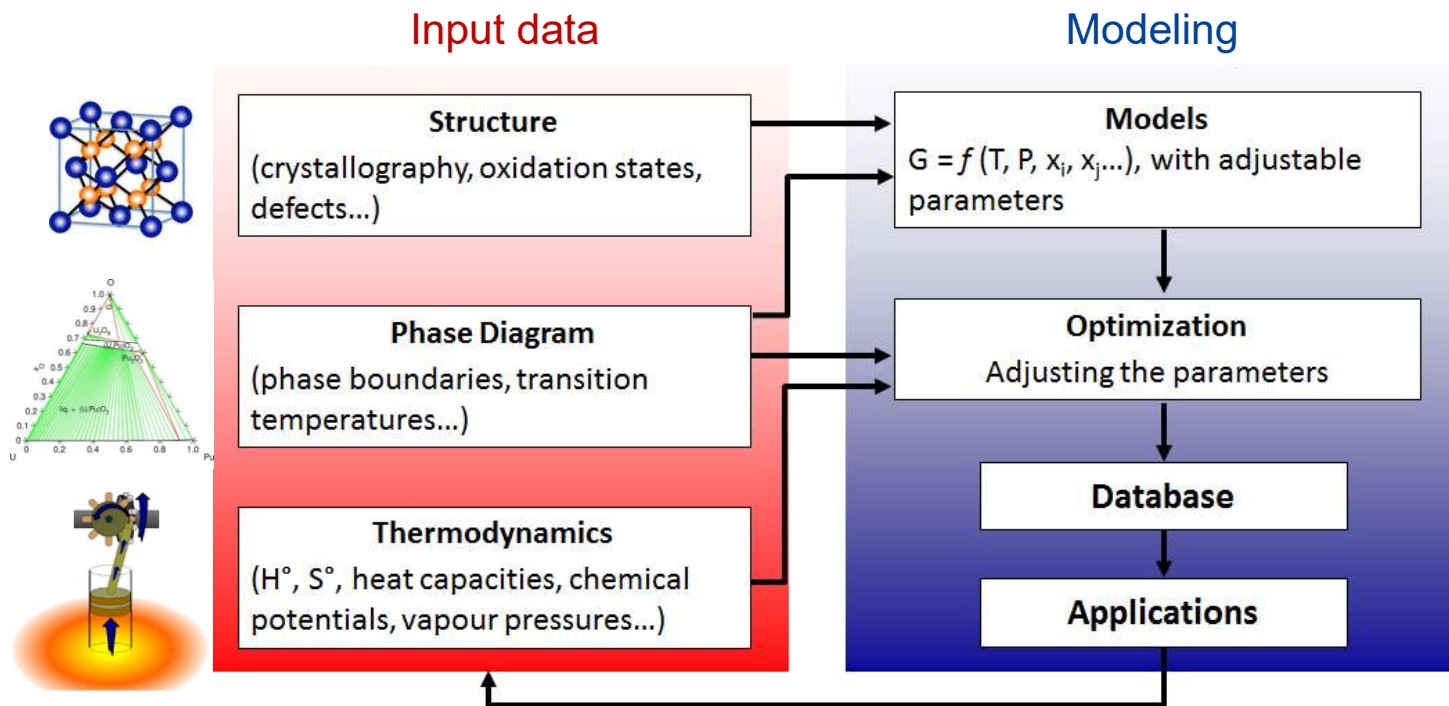
- ❑ **Conclusions**

The CALPHAD method

- The thermodynamic equilibrium at given conditions (P, T, x_i) is found by **minimization of the total Gibbs energy G** , which can be expressed as a linear combination of the G_m^α (Gibbs energy of the α phase):

$$G(T, P, x_i) = \sum_{\alpha} N^{\alpha} G_m^{\alpha}(T, P, x_i^{\alpha})$$

- The G_m^α functions are optimized by least square minimization method using experimental data



Case study 1: the JOG

MOX fuel for FNRs

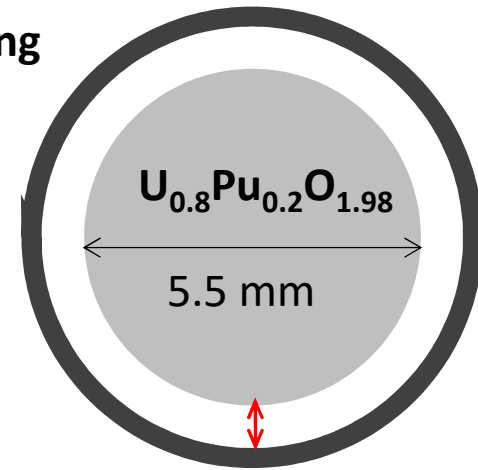
MOX fuel for SFR (Phenix)



M. Tourasse et al., JNM 188 (1992) 49-57

Radial section of fuel pin:

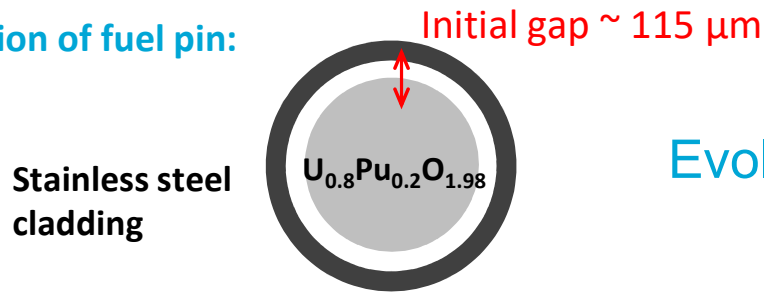
Stainless steel cladding



Initial gap $\sim 115 \mu\text{m}$

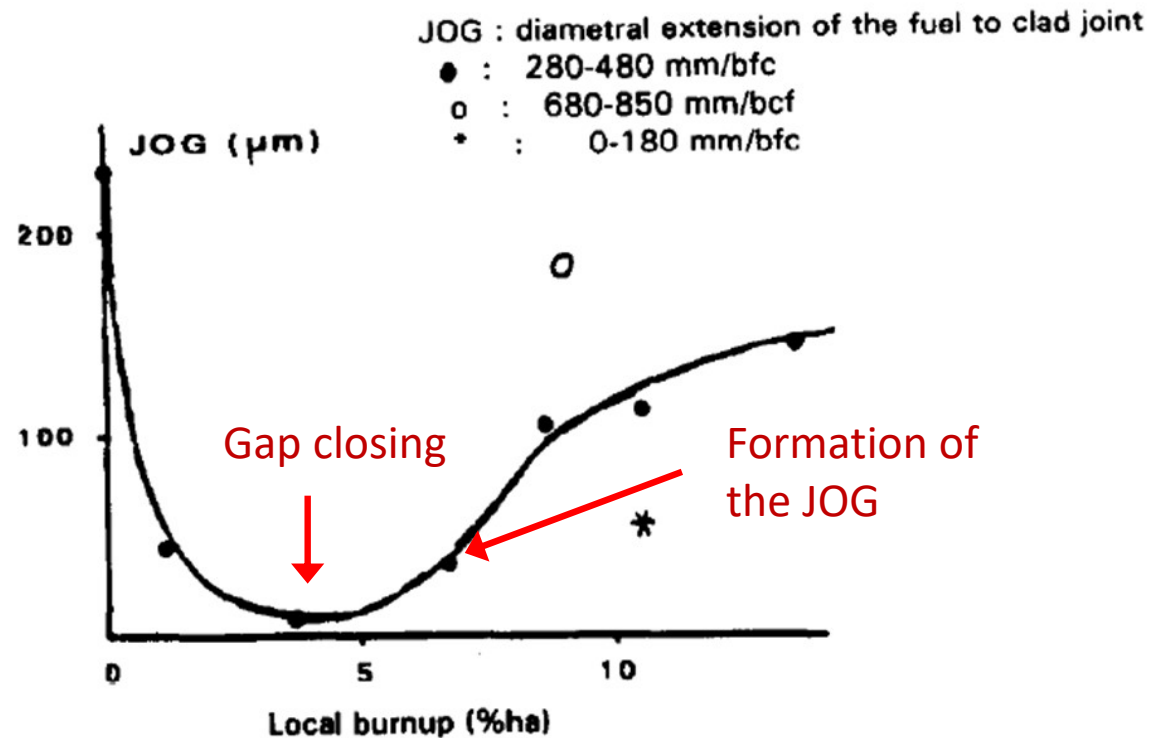
What is the JOG?

Radial section of fuel pin:



Evolution of the fuel-cladding distance:

- 3-phase process:
 - 1) BU (burn up) < 5% \rightarrow Initial gap closing
 - 2) 5% < BU < 10% \rightarrow sharp increase of the cladding-fuel distance
 - 3) BU > 10% \rightarrow lower rise

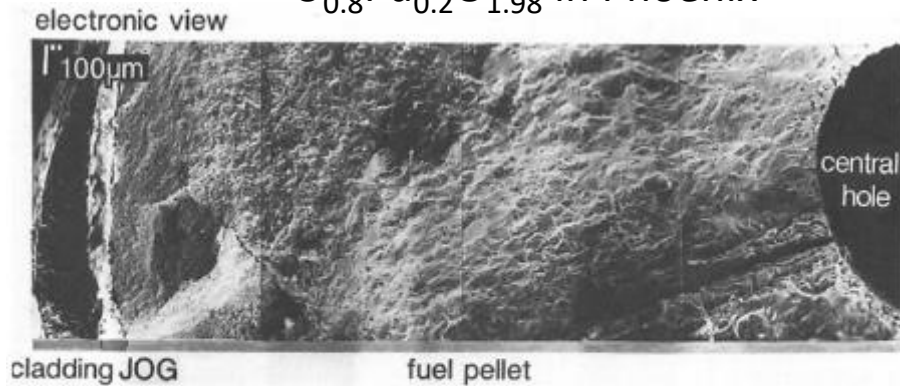


Formation of a layer between fuel and cladding = JOINT-OXIDE-GAINE (JOG)

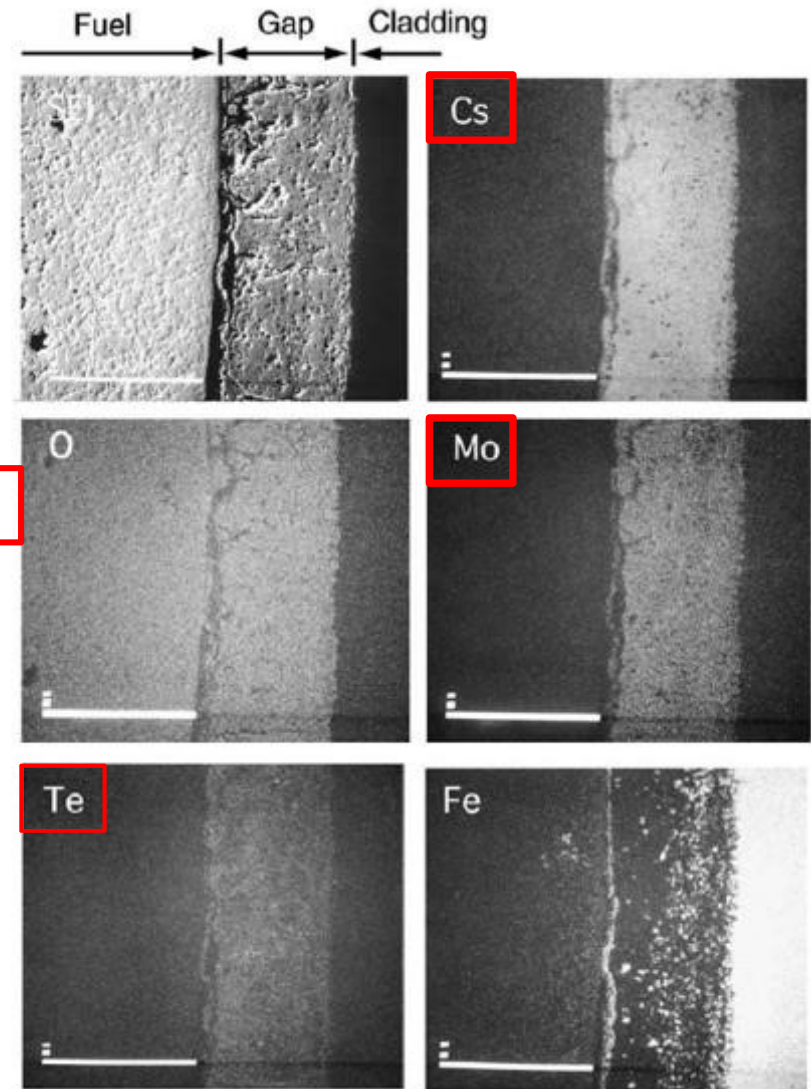
M. Tourasse et al., JNM 188 (1992) 49-57

Chemical composition of the JOG?

$U_{0.8}Pu_{0.2}O_{1.98}$ in Phoenix

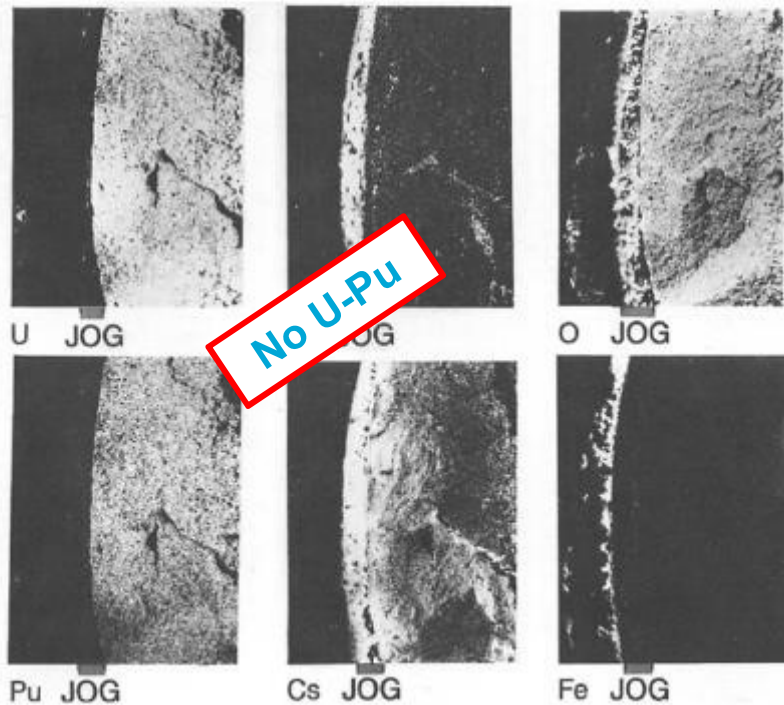


$U_{0.7}Pu_{0.3}O_{1.96}$ in JOYO



OXIDE

No U-Pu



Chemical composition of the JOG

- **Cs, Mo** are the most abundant elements
- **Te, I, Ba, Pd**
- **Oxide** phase
- U, Pu only on the pellet side

JOG formation \leftrightarrow migration of volatile FPs from the inner pellet toward the colder periphery

Expected phases in the JOG

- **Cs₂MoO₄**
- **Cs₂UO₄** – pellet side
- **Cs₂Te** (s) or (l)
- CsI (s), CsI(l) or CsI(g), Cs₂I₂(g)

The thermodynamics of the JOG system is not well known

T. N. PHAM THI, PhD Thesis, Aix-Marseille universite, 2014

Objective: complete thermodynamic description of the

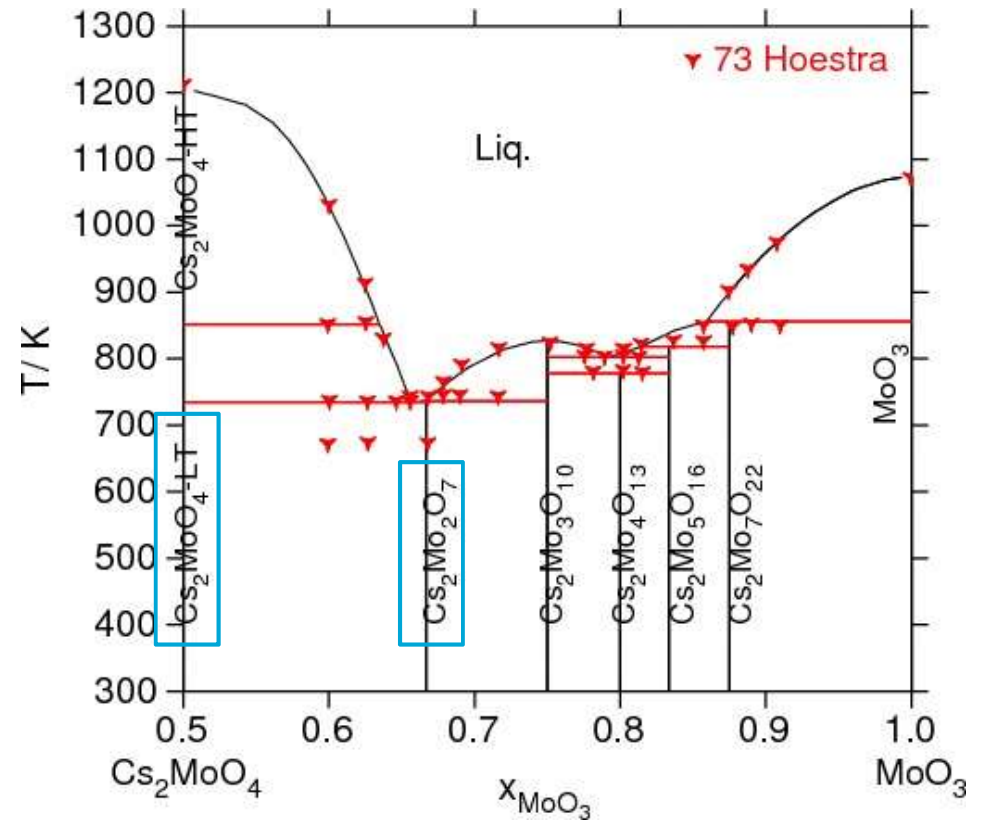
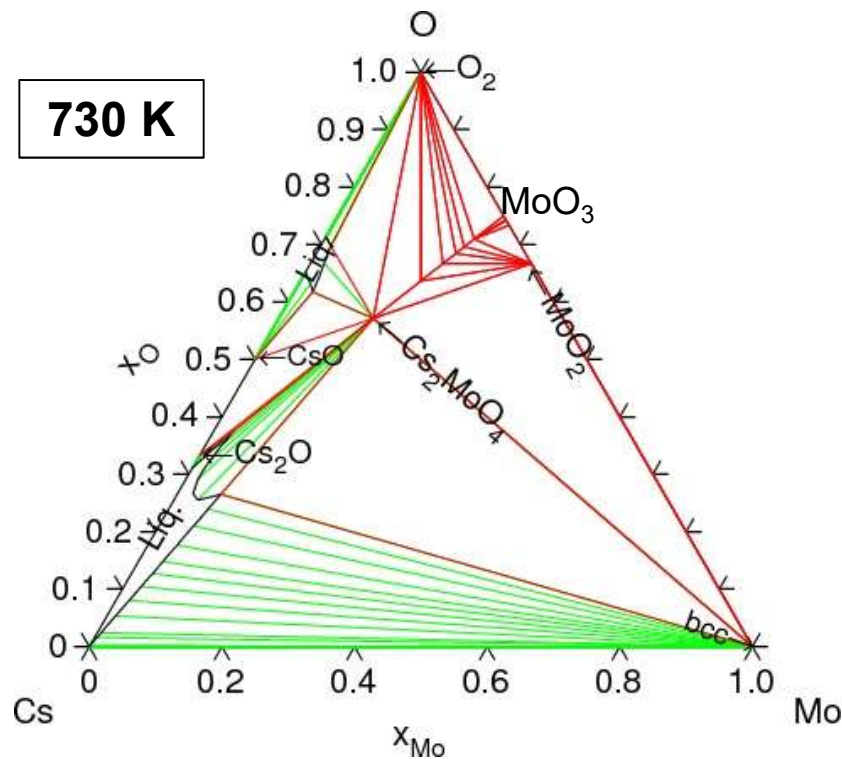
Cs-Mo-Te-I-U-Pu-O system

Cs-Mo-O and Cs-Te-O

TODAY

Short literature review of the Cs-Mo-O system

- Several Cs-Mo oxides
- Cs_2MoO_4 is the main phase expected in the JOG
- A CALPHAD model available in the TAFID, but missing data for some compounds and need for validation



Recent experimental data on $\text{Cs}_2\text{Mo}_2\text{O}_7$: standard entropy

- CALPHAD model for a solid stoichiometric phase:

$$G_m(T) = \Delta_f H_m^\circ(298.15\text{K}) - S_m^\circ(298.15\text{K})T + \int_{298}^T C_{p,m}(T) dT - T \int_{298}^T \frac{C_{p,m}}{T} dT$$

Standard enthalpy of formation

Standard entropy

$$\int_0^{298\text{K}} \frac{C_p}{T} dT$$

Low-T heat capacity

Heat capacity

$$C_{p,m}(T) = a + bT + cT^2 + dT^{-1} + eT^3 + \dots$$

S_m° of $\text{Cs}_2\text{Mo}_2\text{O}_7$ was missing in the literature:

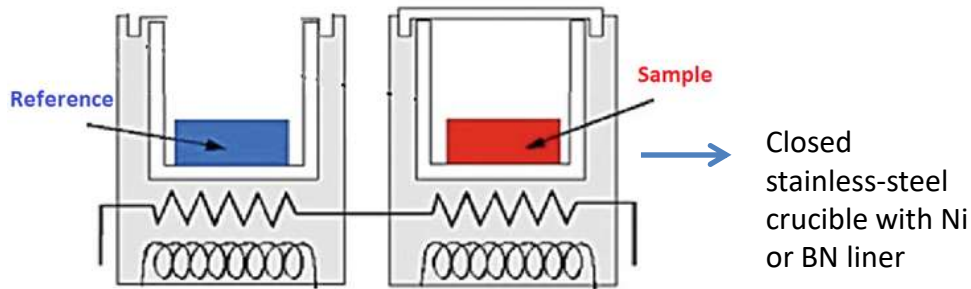
- $C_{p,m}^0(298.15\text{ K}) = 211.9 \pm 2.1 \text{ J K}^{-1} \text{ mol}^{-1}$
- $S_m^0 = 317.4 \pm 4.3 \text{ J K}^{-1} \text{ mol}^{-1}$**
 = **332** $\text{J K}^{-1} \text{ mol}^{-1}$ from **CALPHAD calculations (TAFID)**!



A. Smith et al., *Journal of solid state chemistry* 253, (2017), 89-102

Experimental results on $\text{Cs}_2\text{Mo}_2\text{O}_7$: enthalpy of melting

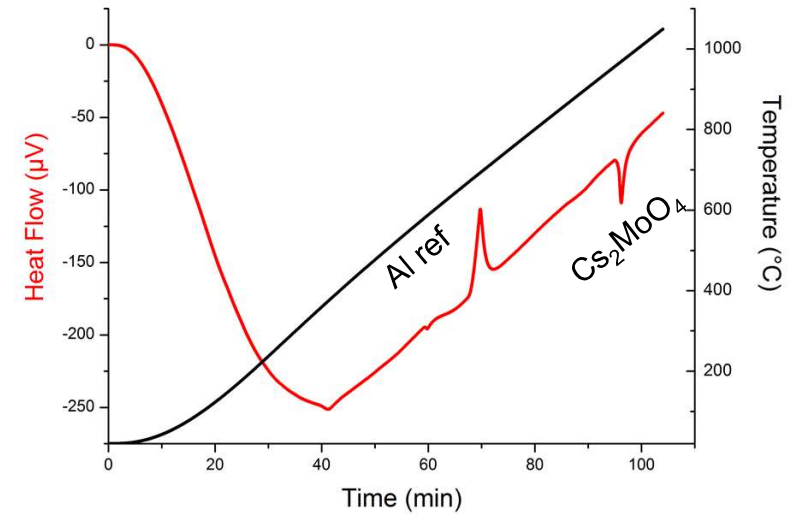
- Differential Scanning Calorimetry (DSC)



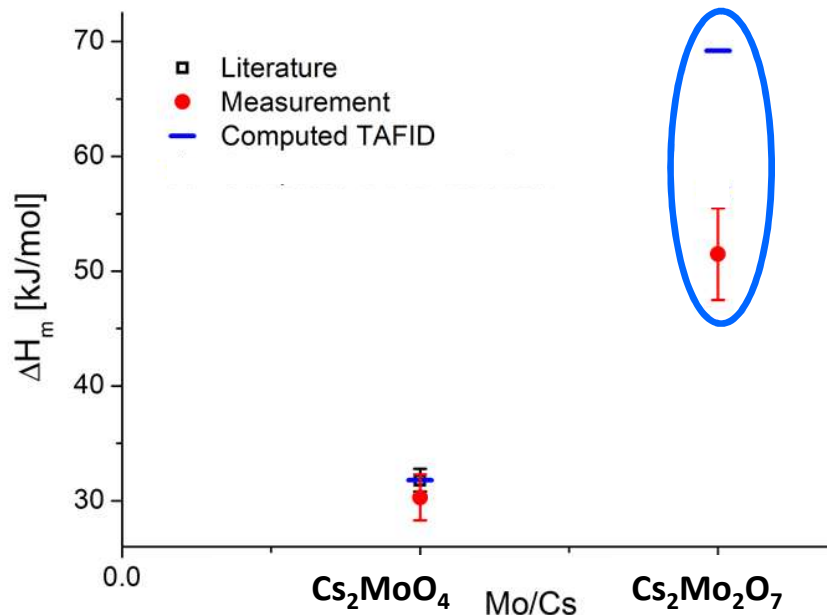
sensitivity $\rightarrow s = \frac{A}{\Delta H}$

A ← Peak area

ΔH ← Enthalpy of the transition



- Results



Big difference between the previous CALPHAD model and the experimental value!

Consistent with the S° experimental value

L. Denielou et al., J. Chem. Thermodyn., 7 (1975) 901.

Short literature review of the Cs-Te-O system

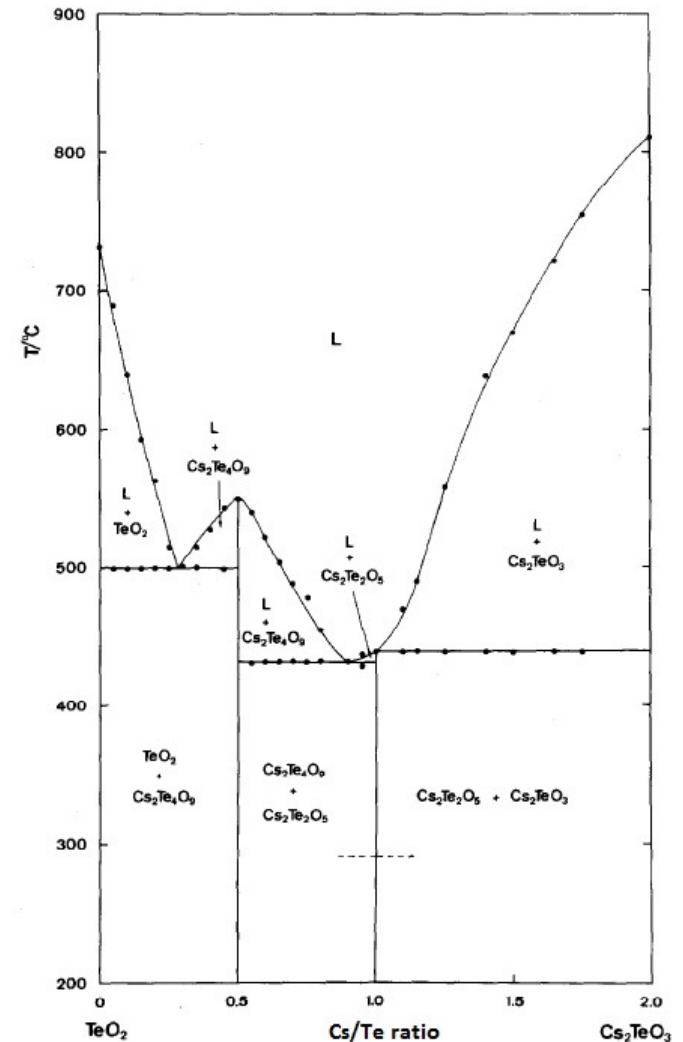
- Tellurium generally observed as Cs_2Te in the JOG
- NO CALPHAD model available
- However, tellurites and tellurates exist:

	Structure	T range	$\Delta_f H^\circ$	S°
Cs_2TeO_3	P321	≤ 810 °C	●	X
$\text{Cs}_2\text{Te}_2\text{O}_5$	<i>Pbca</i>	≤ 439 °C	●	X
$\text{Cs}_2\text{Te}_4\text{O}_9$	I-42d	≤ 549.5 °C	●	X
Cs_2TeO_4	Pnma		●	X
$\text{Cs}_2\text{Te}_4\text{O}_{12}$	R-3m		X	X

Iso-structural with Cs_2MoO_4

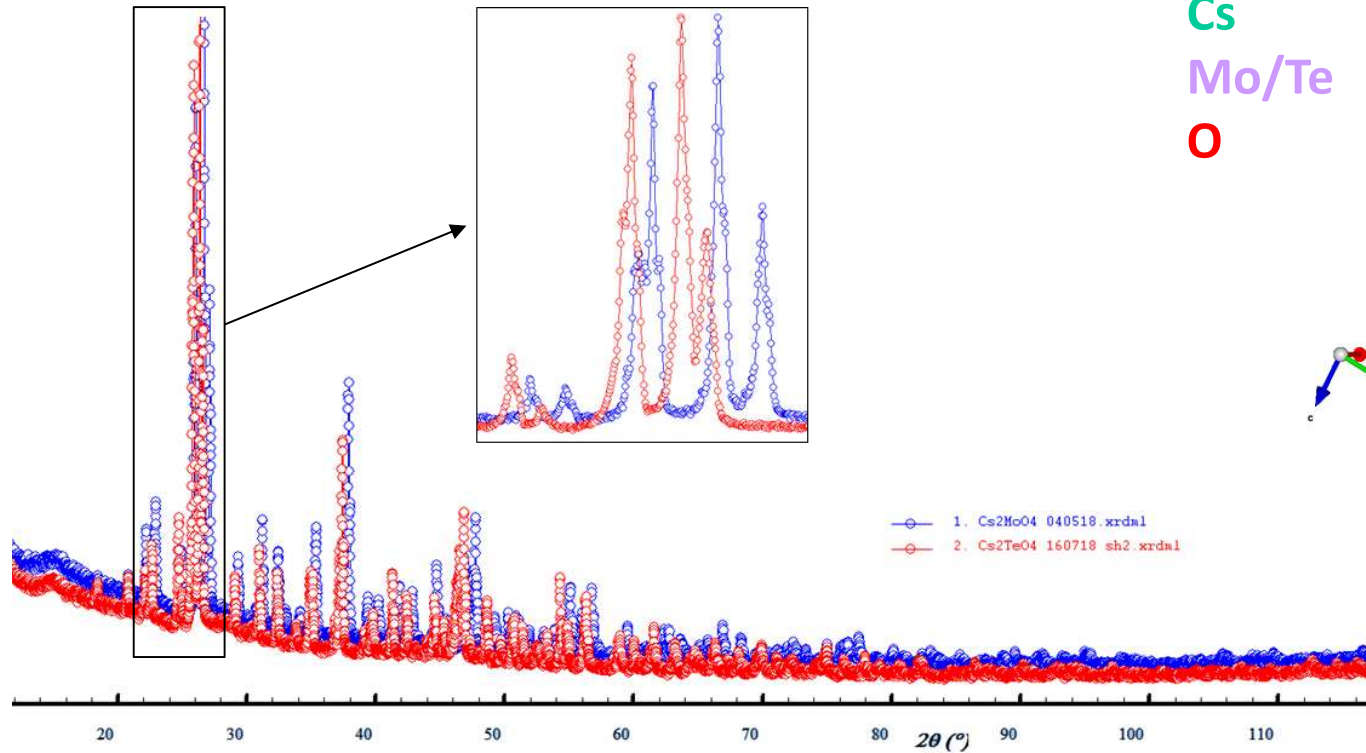


Study of solubility



Experimental data on $\text{Cs}_2(\text{Mo},\text{Te})\text{O}_4$

- XRD pattern of a $\text{Cs}_2\text{MoO}_4 + \text{Cs}_2\text{TeO}_4$ mixture

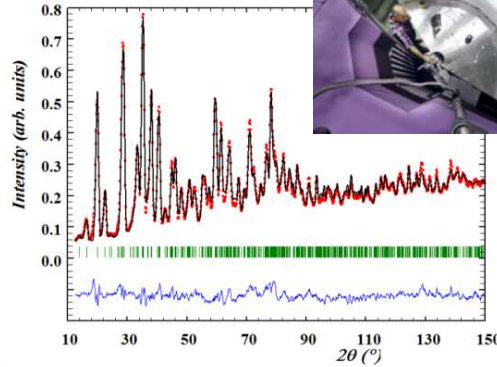
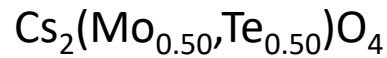


Cs_2MoO_4 :
 $a = 8.501(2) \text{ \AA}$
 $b = 6.555(2) \text{ \AA}$
 $c = 11.593(2) \text{ \AA}$

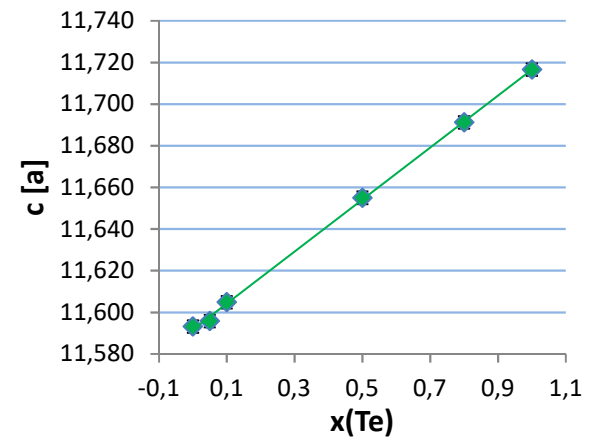
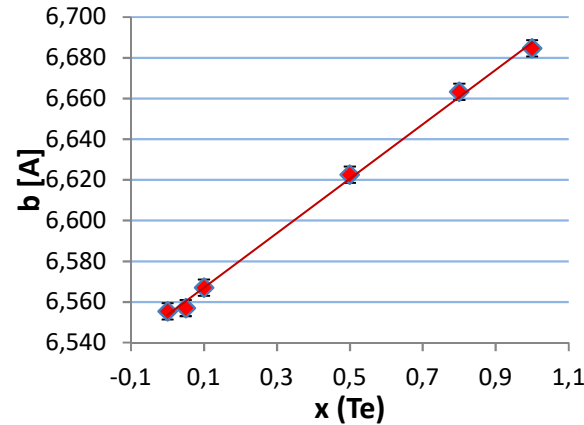
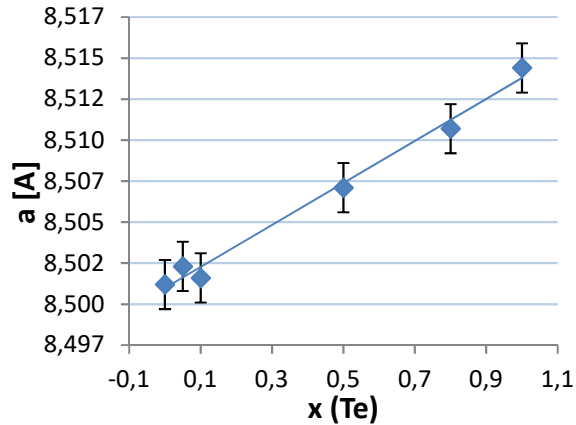
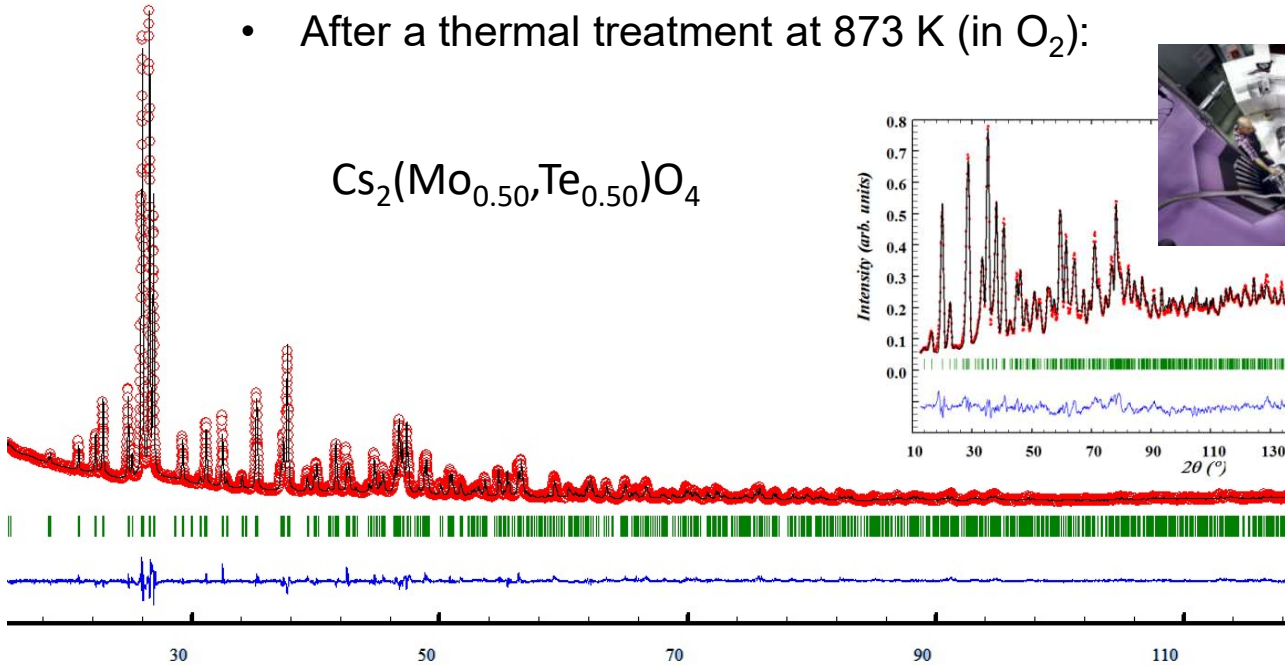
Cs_2TeO_4 :
 $a = 8.514(2) \text{ \AA}$
 $b = 6.684(2) \text{ \AA}$
 $c = 11.716(2) \text{ \AA}$

Experimental data on $\text{Cs}_2(\text{Mo},\text{Te})\text{O}_4$

- After a thermal treatment at 873 K (in O_2):



- One single phase obtained for all the compositions
- Lattice parameters follow Vegard's law

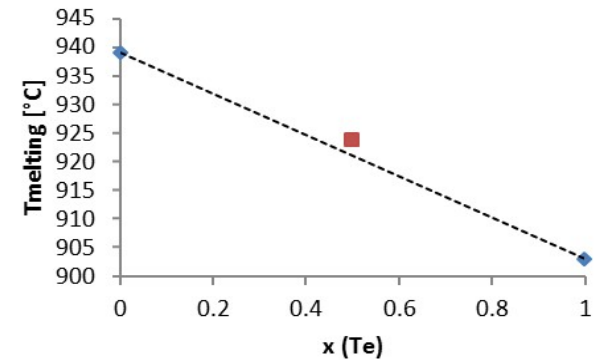


Experimental data on $\text{Cs}_2(\text{Mo},\text{Te})\text{O}_4$

$\text{Cs}_2(\text{Mo},\text{Te})\text{O}_4$: implications for reactor

Melting Temperature

- $T_m(\text{Cs}_2\text{MoO}_4) = 1220 \pm 10 \text{ K}$
- $T_m(\text{Cs}_2\text{TeO}_4) = 1177 \pm 10 \text{ K}$
- Cs_2TeO_4 has a lower melting point
- Measurements on the solid solution on going

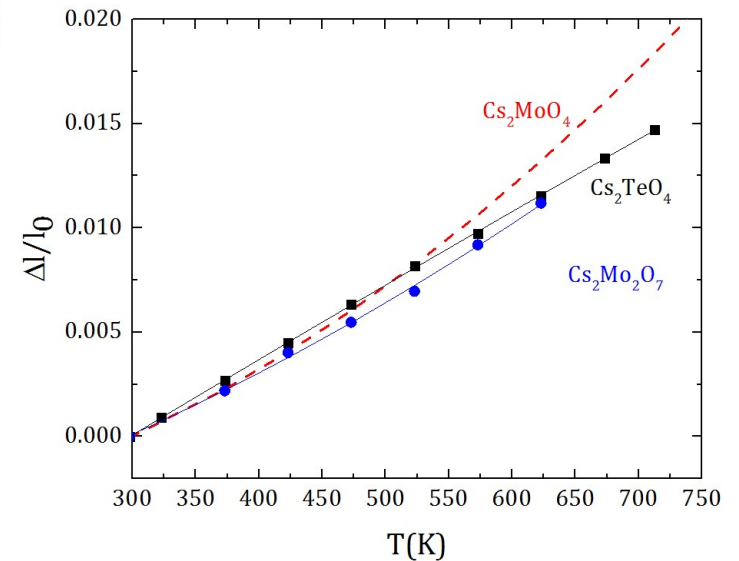


A. Volfi, Master thesis, Politecnico di Milano

Thermal expansion (HT-XRD)

Study of the compounds thermal expansion

- $\alpha_a = 36.3 \cdot 10^{-6} \text{ K}^{-1}$
- $\alpha_b = 39.1 \cdot 10^{-6} \text{ K}^{-1}$
- $\alpha_c = 32.8 \cdot 10^{-6} \text{ K}^{-1}$



Conclusions on case study 1

- The **JOG** is characteristic of FNRs and it is formed because of the migration of volatile FPs due to high thermal gradients
- Need to have a thermodynamic description of the **U-Pu-Cs-Mo-Te-O** system → **CALPHAD** method
- Recent investigations on **Cs-Mo-O**
 - CALPHAD model existing
 - New experimental data: S° and ΔH_m of **Cs₂Mo₂O₇**
 - The two experiments are consistent one with the other
 - Need to update the existent CALPHAD model
- Recent investigations on **Cs-Mo-Te-O**
 - A **Cs₂TeO₄** compound iso-structural with **Cs₂MoO₄** exists
 - The existence of a **Cs₂(Mo,Te)O₄** solid solution has been shown
 - The effects need to be investigated!

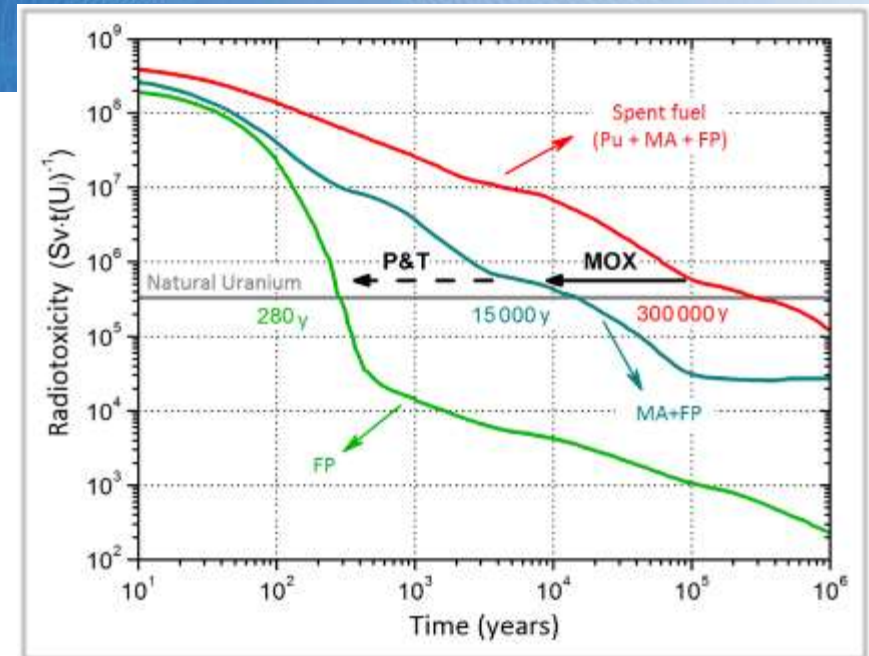
Case study 2:

$(U,Am)O_2$ oxides

Why (U,Am)O₂?

- Spent fuel: long-term **radiotoxicity** due to
 - Pu
 - MAs, in particular ²⁴¹Am
- Pu → already recovered to produce MOX
- Next step for a sustainable **nuclear fuel cycle**:

Partition & Transmutation of MAs



(U,Am)O₂ are possible transmutation targets

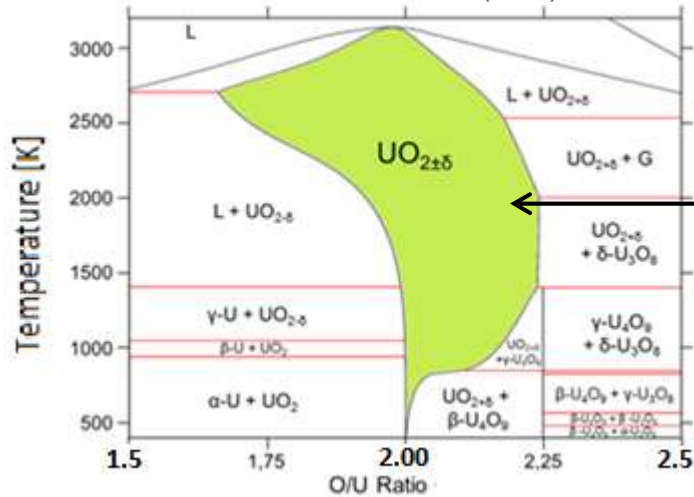
- ➔ **Need to know the phase equilibria in the U-Am-O system**
- Fabrication process
 - Behavior in reactor

Investigate the thermodynamics of the U-Am-O system
and develop a thermodynamic database

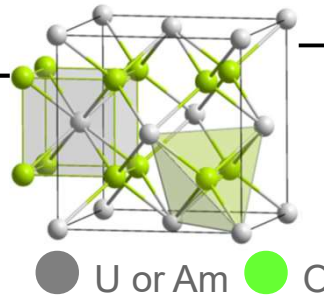
Introduction: the U-O and the Am-O systems

1. C. Guéneau et al., *J. Nucl. Mater.* 419 (2011) 145-167

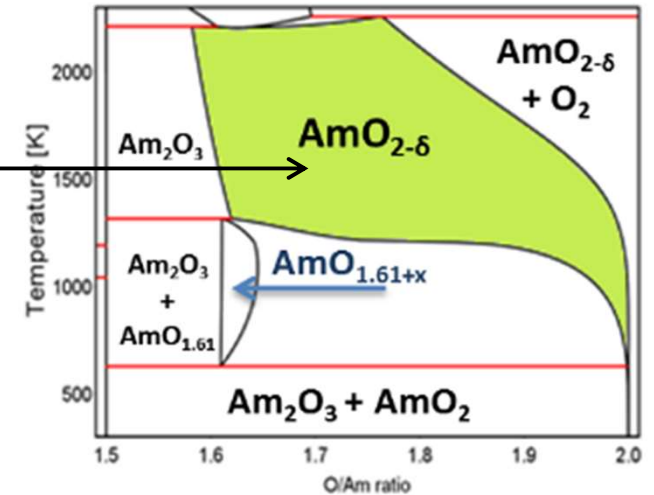
2. E. Epifano et al., *Inorg. Chem.* 56 (2017) 7416-7432



Fluorite structure



● U or Am ● O

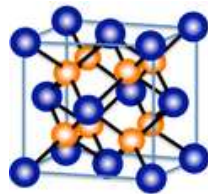


- U oxidation state between +3 and +6
- Large existence domain of $\text{UO}_{2\pm\delta}$
- *Hyper-stoichiometric* phases (U_4O_9 , U_3O_8 ...)

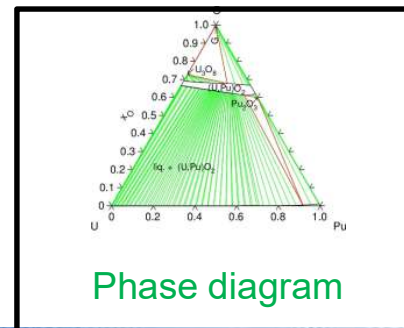
- Am oxidation states between +3 and +4
- Large existence domain of $\text{AmO}_{2-\delta}$
- *Hypo-stoichiometric* phases

$\text{UO}_{2\pm\delta}$ and $\text{AmO}_{2-\delta}$ have different thermodynamic properties \Leftrightarrow Oxygen/Metal (O/M) ratio
(U,Am)O₂ solid solution?

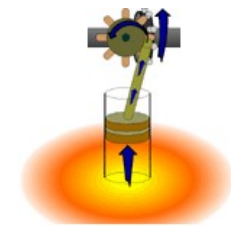
- Few data in the literature



Structural properties



Phase diagram

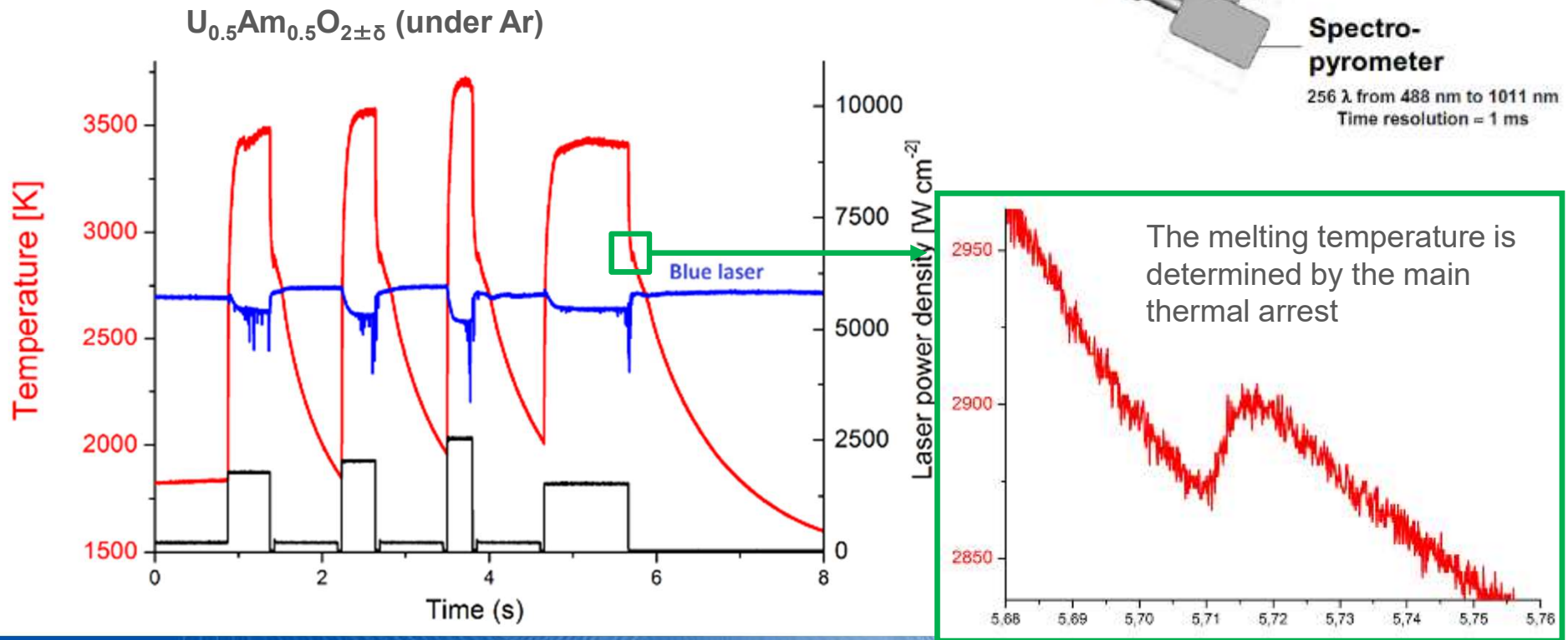
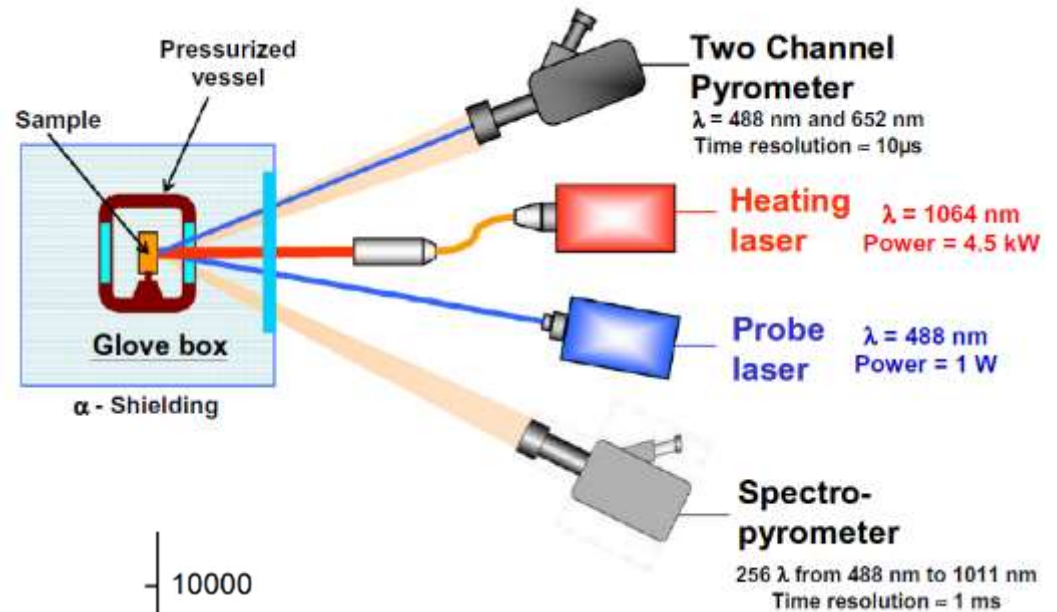


Thermodynamics

Melting-T: experimental set-up and procedure



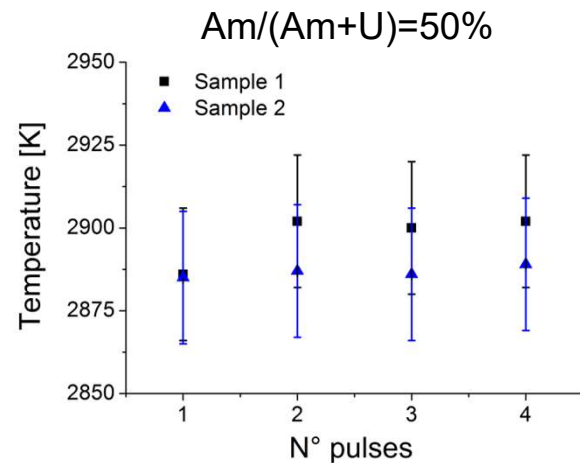
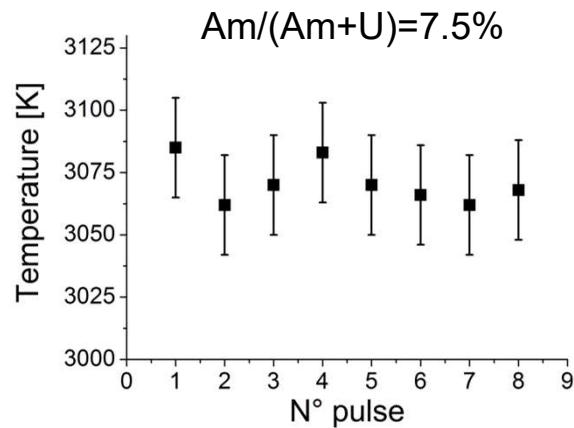
- Nd:YAG Heating laser (~4.5 kW) ⇔ melting
- Fast Pyrometer ⇔ thermogram acquisition
- Probe Laser ⇔ Reflected Signal Technique to detect the melting
- Spectro-pyrometer (check on the ϵ value)



Melting-T: experimental results

Argon

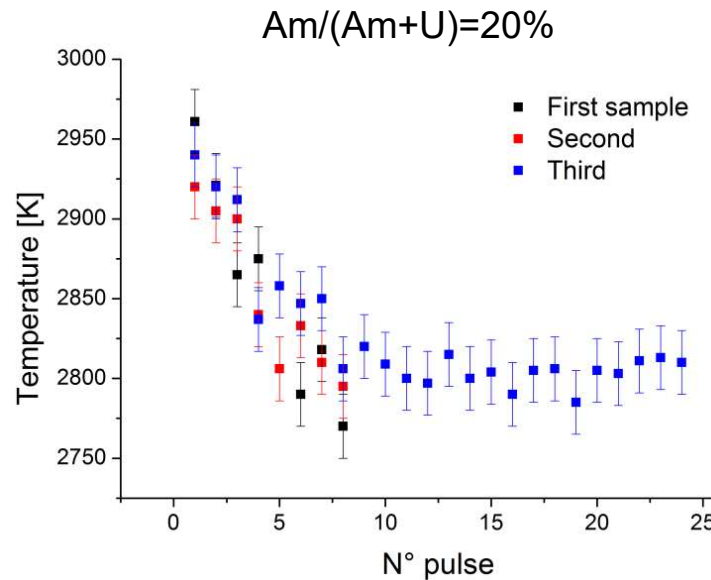
Repeatability of all the measurements



Air

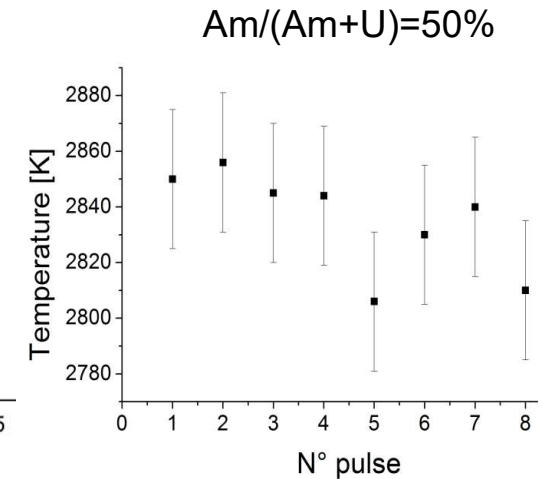
$7.5\% \leq Am/(Am+U) \leq 20\%$

Initial decrease of T_m



$Am/(Am+U) = 30\%, 50\%$

Fair repeatability of the measurements, but higher data dispersion



Exception: Am/(Am+U)=70%, only 1 measurement under air (technical difficulties)

Melting-T: experimental results

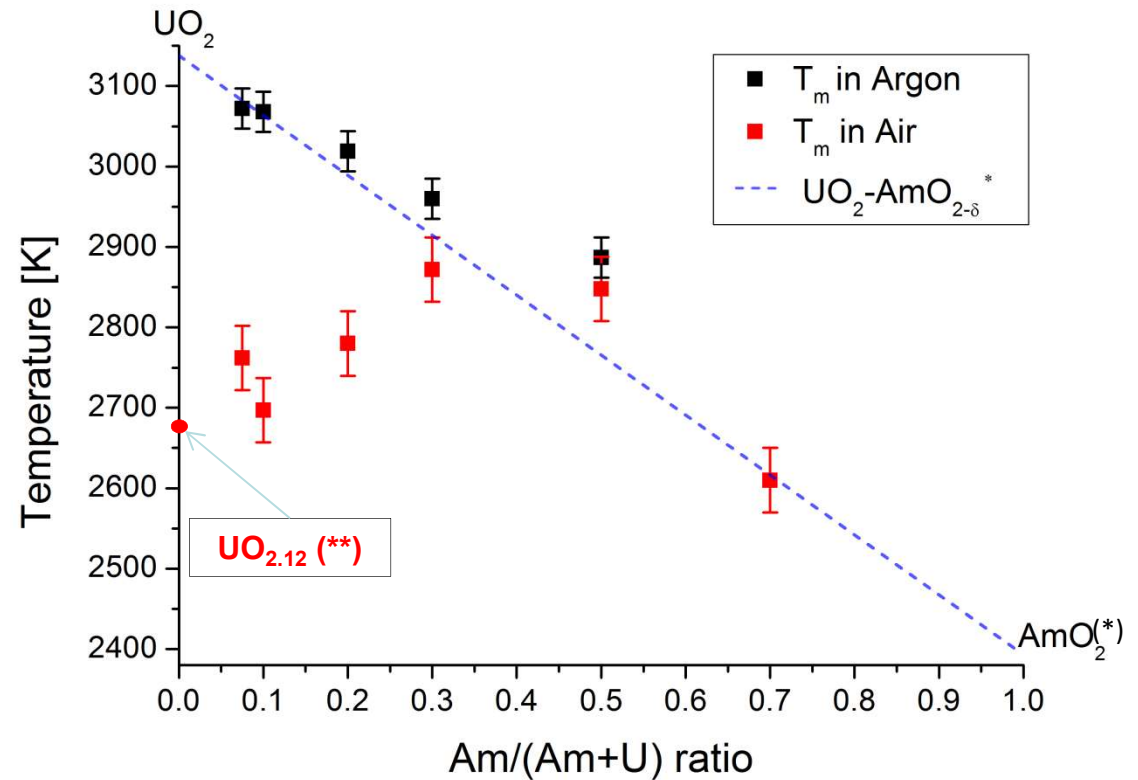
Results

□ Under argon

- almost **linear decrease** of T_m with the Am/(Am+U) ratio

□ Under air

- Generally lower T_m than in Ar
- $T_m > T_m$ (UO_{2+x} in air)
- No monotonic variation with Am/(Am+U) ratio
- Highest T_m for Am/(Am+U)=0.3 and 0.5
- For Am/(Am+U)=0.5, very similar value in Ar and in Air



(*) R. McHenry, *Trans. Am. Nucl. Soc.* 8, (1965) 75.

(**) D. Manara et al, *J. Nucl. Mater.* 342 (2005) 148-163
C. Guéneau et al., *J. Nucl. Mater.* 419 (2011) 145-167

Final composition of the samples?

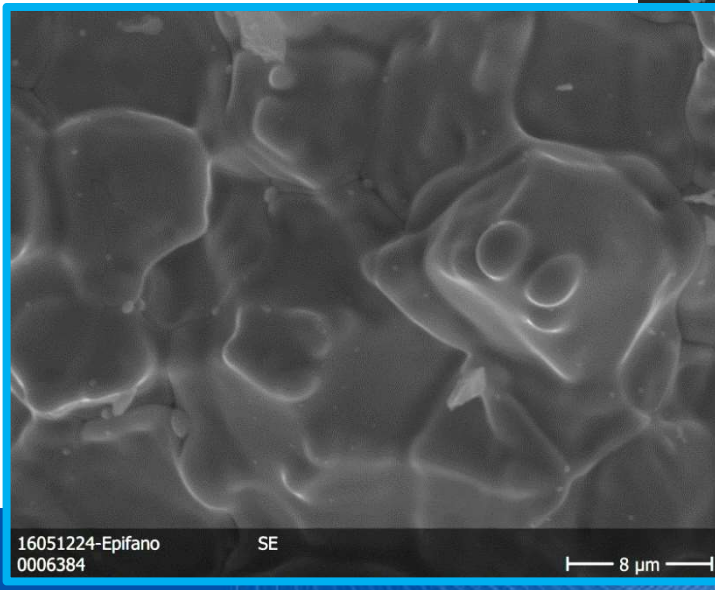
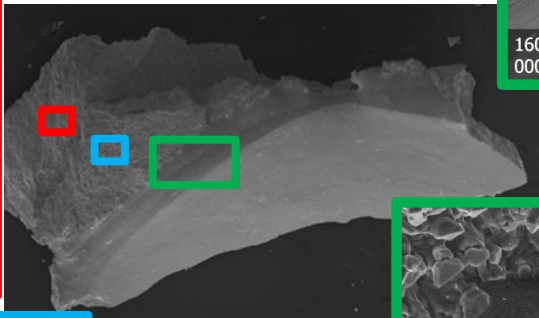
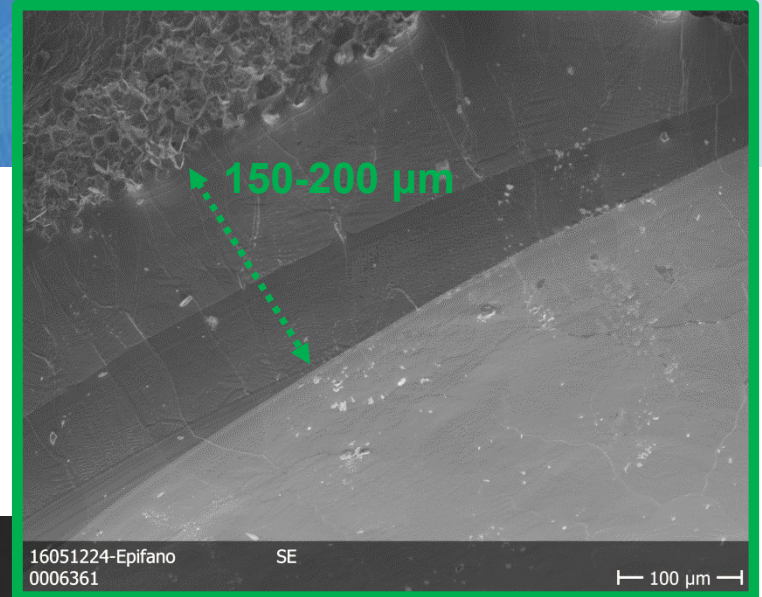
Post-melting characterization (at RT!!!)

Laser heating advantages:

- ❑ Short measurement duration

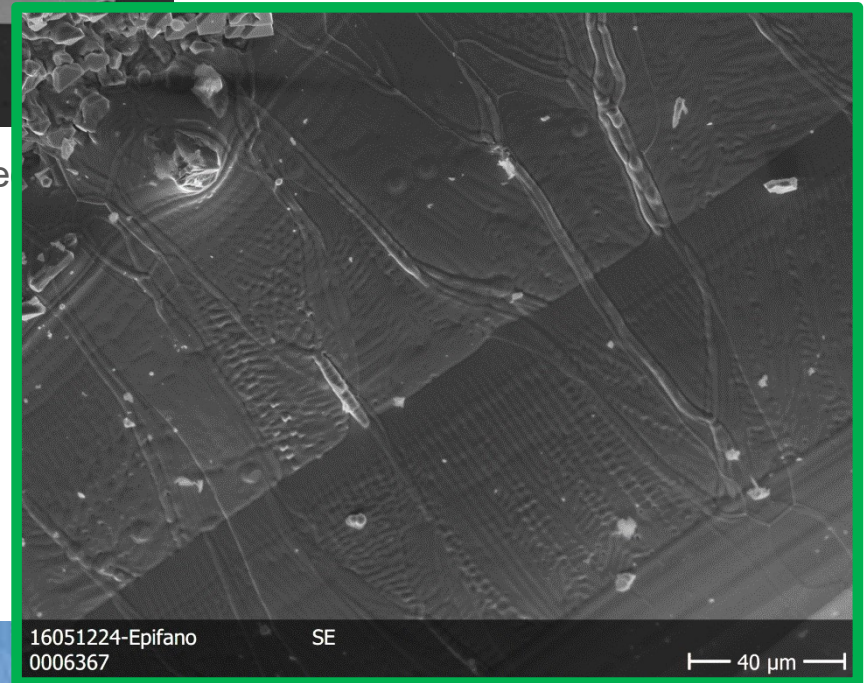


Far region **Melted region**



SEM image of a melted

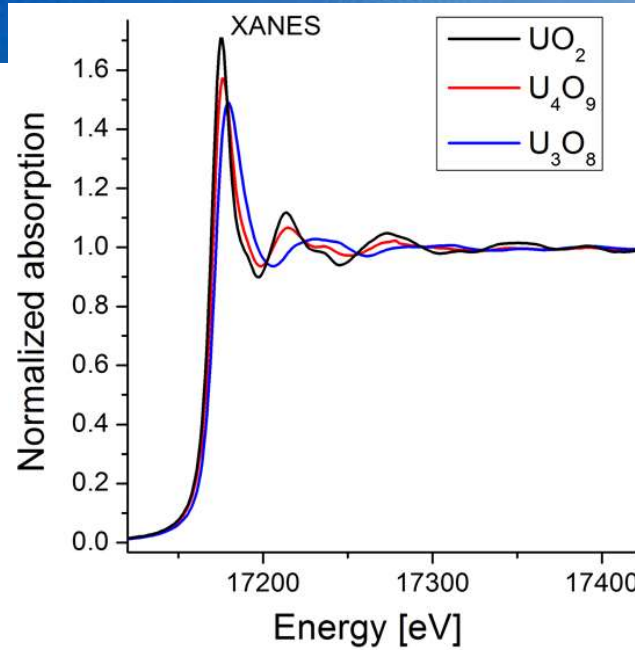
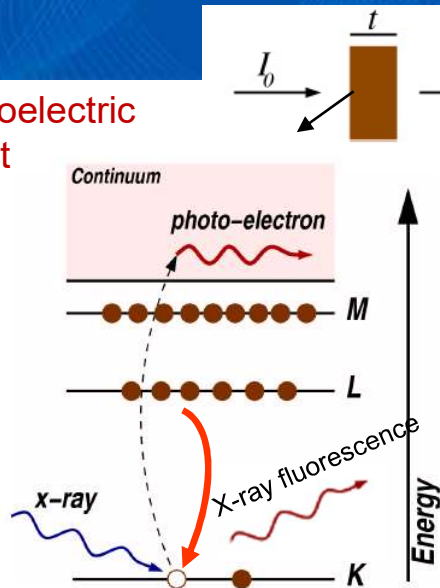
Intermediate region



Post-melting characterization: XAS (RT!!!)



Photoelectric effect

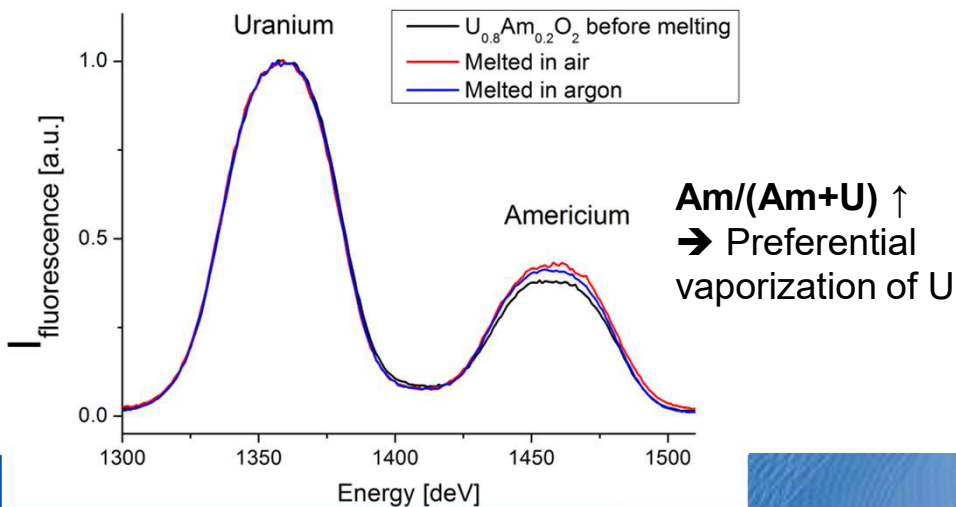


- Characteristic of the element
- Absorption edge is dependent on the **oxidation state**

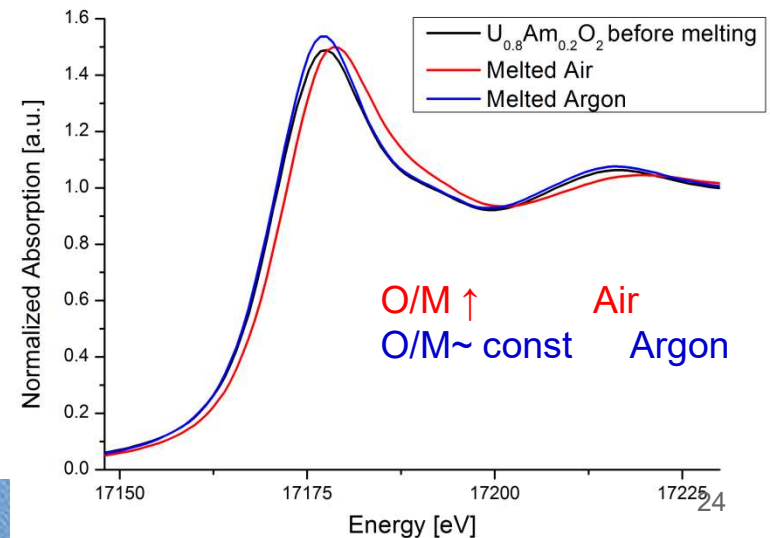
↓
U, Am oxidation state

Am/(Am+U) ratio

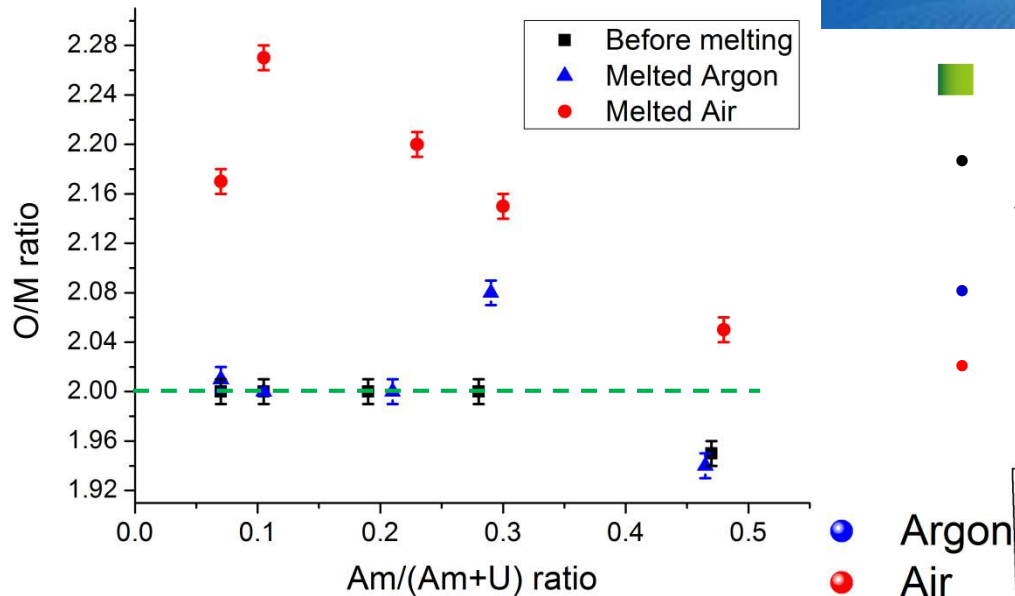
$E \gg E_{\text{edge}} \rightarrow I_f$ is proportional to the mass of element



→ O/M ratio



Post-melting characterization: XAS

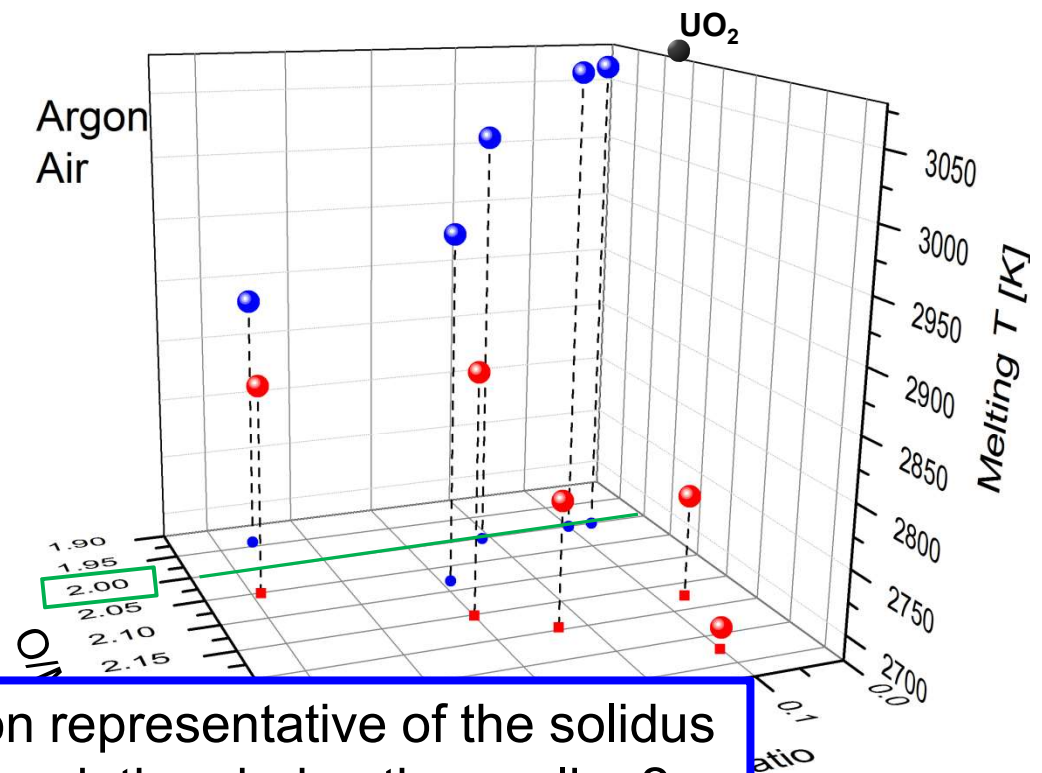


Composition change during melting

- Slightly increase of Am/M → preferential vaporization of U species
- O/M ratio ~ const., Argon
- O/M increase, Air

Melting T

- In Argon, Increase of Am/(Am+U) → T_m decrease
- $O/M > 2$ → $T_m \downarrow \downarrow$
- In Air, high Am content → O/M closer to 2 → higher T_m



Stabilization of the oxidation

Is the final composition representative of the solidus or there is a further variation during the cooling?

CALPHAD thermodynamic modeling

To model the melting behaviour, we need:

- **GAS** phase → no ternary molecular species → extrapolation from the binaries
- The **(U,Am)O₂** → 3-sublattice model*



$$G = \sum_I P_I(Y) \cdot G_I^0 + G_{mix}^{ideal} + G_{mix}^{xs}$$

- The **LIQUID** → partially ionic 2-sublattice liquid model



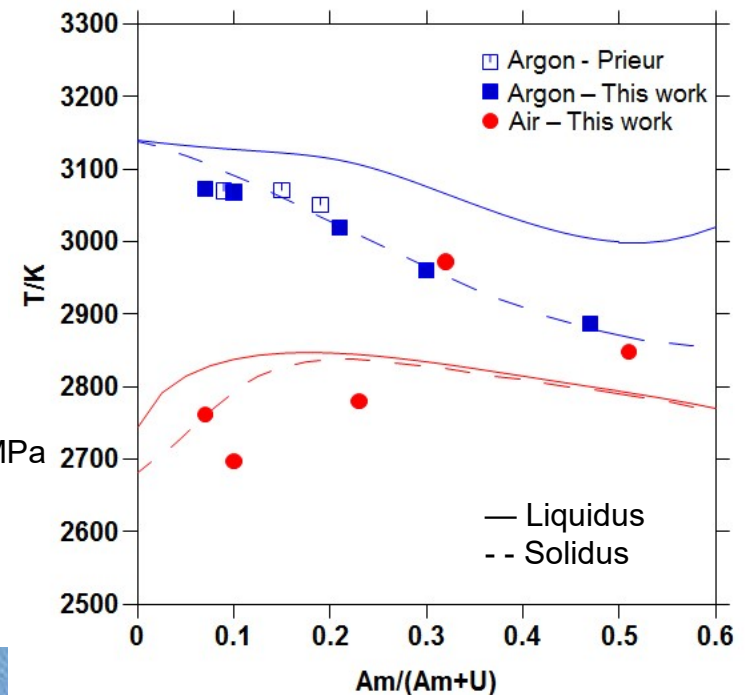
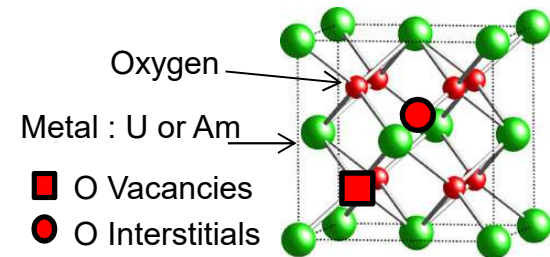
$$P = \sum_j v_j y_{A_j} + Q_{yva}$$

$$Q = \sum_i v_i y_{C_i}$$

- Optimized fitting the melting-T
- Gas-Solid-Liquid equilibrium calculated (not imposed composition of the phases!):

Ex: $n(Am)=0.5$, $n(U)+n(Am)=1$, $n(O)=2$, $n(Ar)=5$, $P=0.30$ MPa

Close reproduction of complex experiments!



* E. Epifano, « Study of the U-Am-O system », PhD thesis, Paris 2017

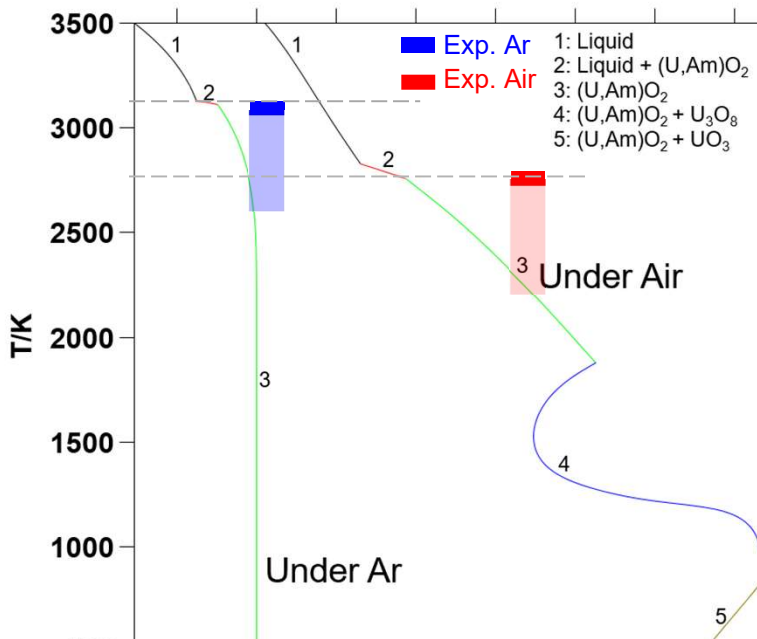
CALPHAD computations

Is the final composition representative of the solidus or there is a further variation during the cooling?

- **Calculated solidification paths**
 - The total composition of the system was fixed (and the total P)
 - The composition of the phases was let to vary:

$Am/(Am+U)=7 \text{ at.}\%$

(Similar results for the other compositions)



The calculations indicate a change in composition during the cooling (after the re-solidifications)

Case study 2 : Conclusions

- $(U,Am)O_2$ are possible transmutation targets
- T_m measurements by laser-heating + **post-melting characterizations**
 - T_m decreases when $O/M > 2$
 - T_m decrease with the Am content, in reducing conditions
 - The Am doping improves the resistance toward the oxidation
- The new experimental data were used for the **CALPHAD modeling** of the **liquid phase** of the U-Am-O system
- **The CALPHAD method allows simulating and better understanding complex experiments**

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...And thank you for the attention

