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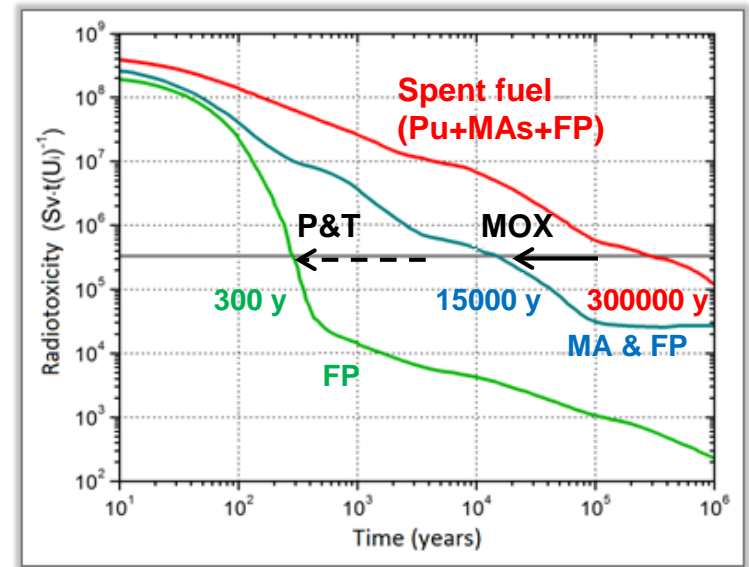
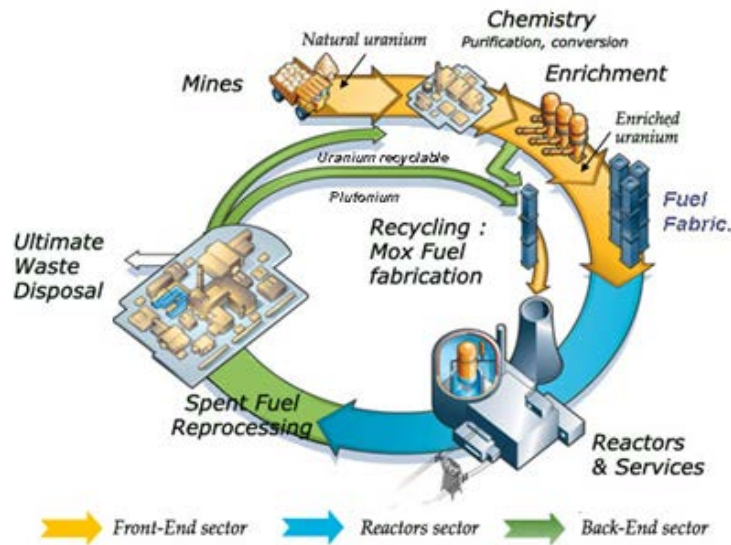


# A THERMODYNAMIC STUDY OF THE U-Am-O TERNARY SYSTEM: MULTIPLE EXPERIMENTAL INVESTIGATIONS FOR CALPHAD MODELING

**E. Epifano<sup>1</sup>**

**P. M. Martin<sup>1</sup>, D. Manara<sup>2</sup>, O. Benej<sup>2</sup>, T. Wiss<sup>2</sup>, F. Lebreton<sup>1</sup>, R. Vauchy<sup>1</sup>, C. Guéneau<sup>3</sup>, L. Ramond<sup>4</sup>, P. Coste<sup>4</sup>, M. Bataille<sup>4</sup>, A. Scheinost<sup>5</sup>, Ch. Valot<sup>1</sup>, S. Pillon<sup>4</sup>, R. Konings<sup>2</sup>**

1. CEA, Nuclear Energy Division, Research Department on Mining and Fuel Recycling Processes/SFMA/LCC, BP 17171 F-30207 Bagnols sur Cèze, France
2. JRC-Karlsruhe (Germany), Nuclear Safety & Security
3. CEA (France), DEN/DPC/SCCME/LM2T
4. CEA, Nuclear Energy Division, Research Department on Mining and Fuel Recycling Processes/SFMA/LFC, BP 17171 F-30207 Bagnols sur Cèze, France
5. ESRF, Rossendorf beamline



- $UO_2$  is the most used nuclear fuel
- The spent fuel has a long-term radiotoxicity due to Pu+MA+FP
- ❑ In France, Pu is recovered and recycled with  $(U,Pu)O_2$  fuel (known as MOX)
- ❑ The next step in order to have a « complete closed » fuel cycle:

## Transmutation of Minor Actinides (Am, Cm, Np)

$(U, Am)O_2$  are possible transmutation targets

➔ Need to know the **phase equilibria in the U-Am-O system**

- Fabrication process
- Behavior in reactor
- Storage after irradiation



Development of a **CALPHAD** model

**INTRODUCTION**

**STRUCTURAL PROPERTIES**

**EXPERIMENT**

**HT-ENTHALPIES**

**MELTING-T**

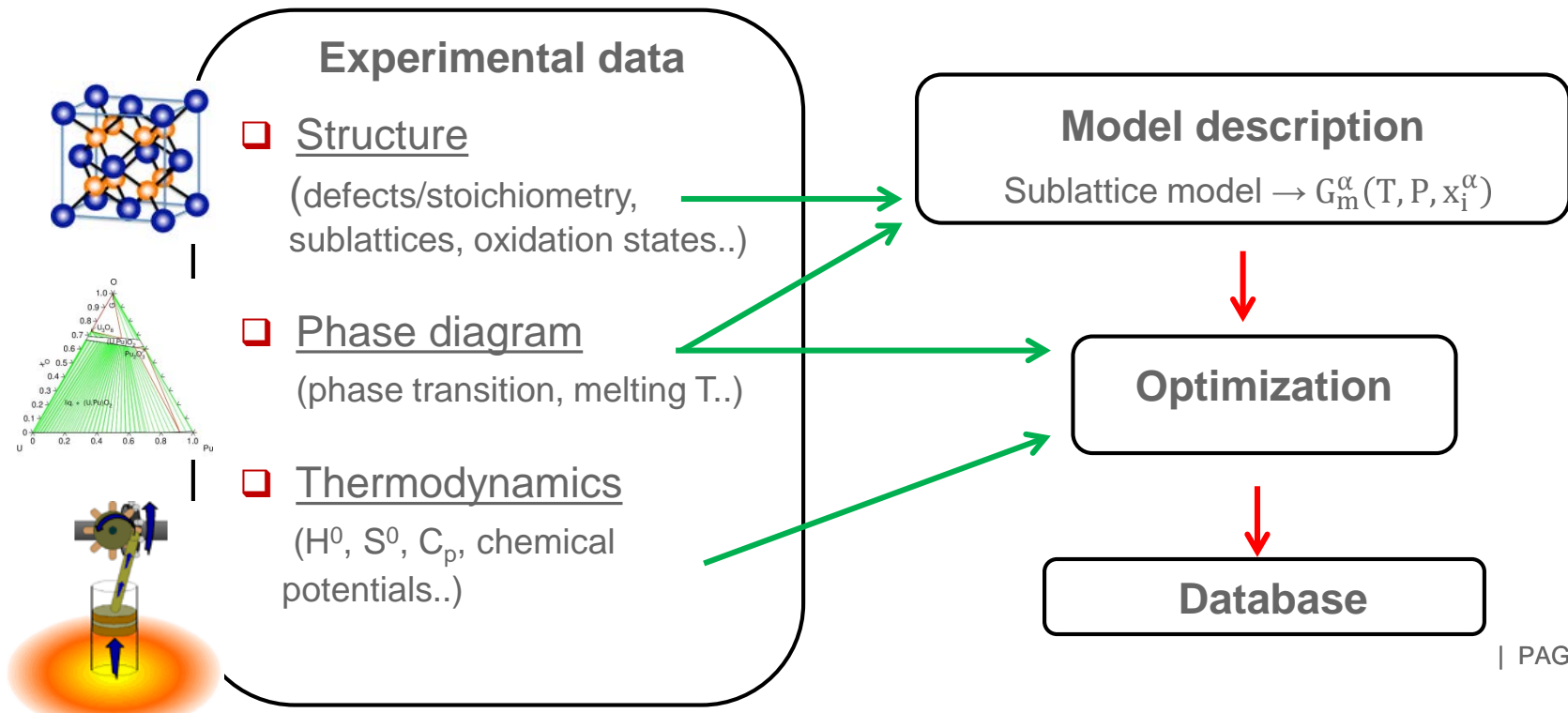
**CONCLUSIONS**

# INTRODUCTION: THE CALPHAD METHOD

- The thermodynamic equilibrium at given conditions ( $p$ ,  $T$ , composition) is found by **minimization of the total Gibbs energy  $G$** , which can be expressed as a linear combination of the  $G_m^\alpha$  (Gibbs energy of the  $\alpha$  phase)

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

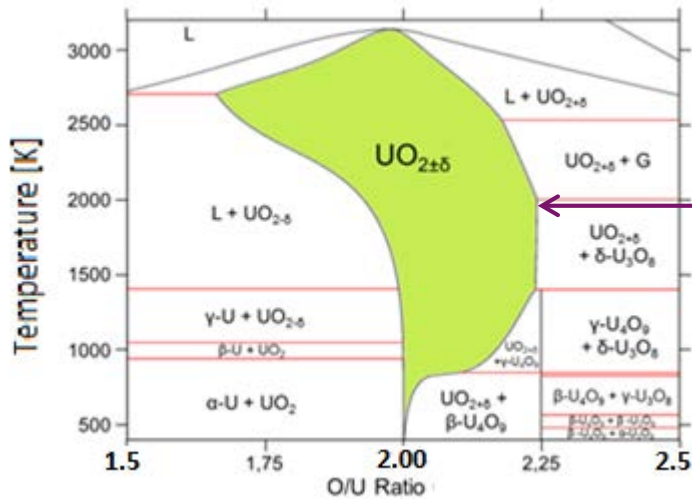
- Each  $G_m^\alpha$  is modeled starting from Structure/Phase Diagram data
- Adjustable parameters are optimized using Phase diagram/Thermodynamics data



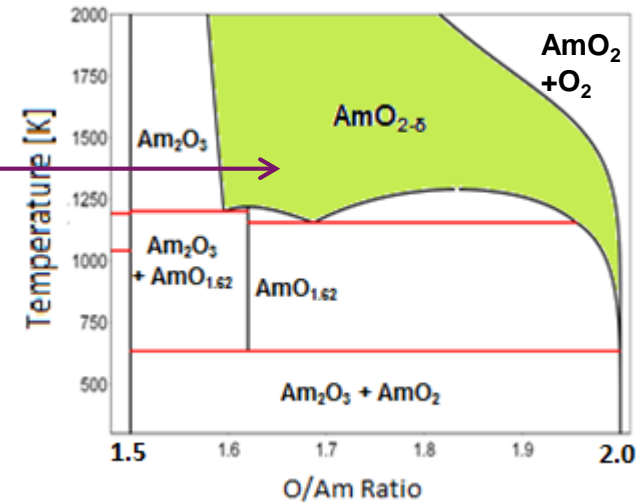
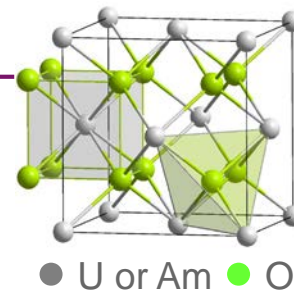
# INTRODUCTION

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

2. Gotcu et al., J. Nucl. Mater. 414 (2011) 408-421



Fluorite structure



■ U oxidation state between +3 and +6

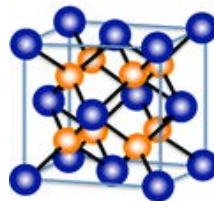
- ❑ Large existence domain of  $UO_{2\pm\delta}$
- ❑ *Hyper-stoichiometric* phases ( $U_4O_9$ ,  $U_3O_8$ ...)

■ Am oxidation states between +3 and +4

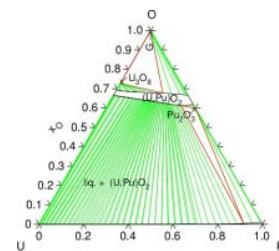
- ❑ Large existence domain of  $AmO_{2-\delta}$
- ❑ *Hypo-stoichiometric* phases

$UO_{2\pm\delta}$  and  $AmO_{2-\delta}$  have different thermodynamic properties  $\Leftrightarrow$  Oxygen/Metal (O/M) ratio  
**(U, Am) $O_2$  solid solution?**

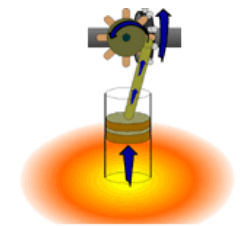
- Few data in the literature
- Contents of this work:



Structural properties:  
Literature and new data



Phase diagram:  
Melting T



Thermodynamics:  
H(T)-H(298.15 K)

**INTRODUCTION**

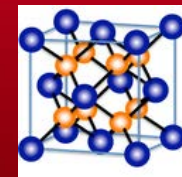
**STRUCTURAL PROPERTIES**

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**MELTING-T**

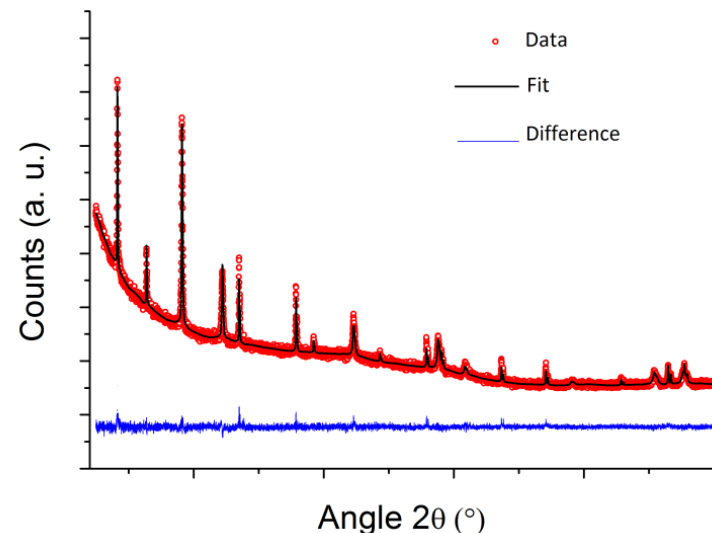
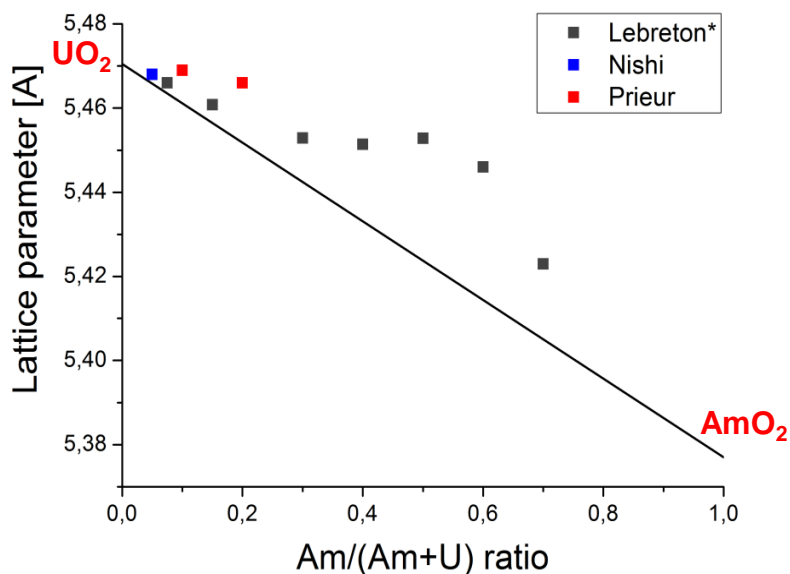
**CONCLUSIONS**



■ **Monophasic  $U_{1-x}Am_xO_{2\pm\delta}$**  compounds with FCC fluorite structure have been reported in the literature for  $x \leq 0.7$  (confirmed by XRD)

■ **Peculiarities** of  $U_{1-x}Am_xO_{2\pm\delta}$  compounds<sup>3, 4</sup>:

□ **Lattice parameter  $a$**  evolution with Am content:

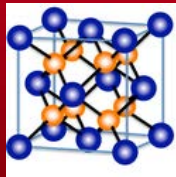


Diffraction pattern of a  $U_{0.5}Am_{0.5}O_2$  sample and corresponding fit with a single fluorite structure

3.D. Prieur et al, *Inorg. Chem.* 50 (2011) 12437-12445  
4. F. Lebreton et al, *Inorg. Chem.* 54 (2015) 9749-9760.

■ Further investigations by X-ray absorption spectroscopy (XAS)...

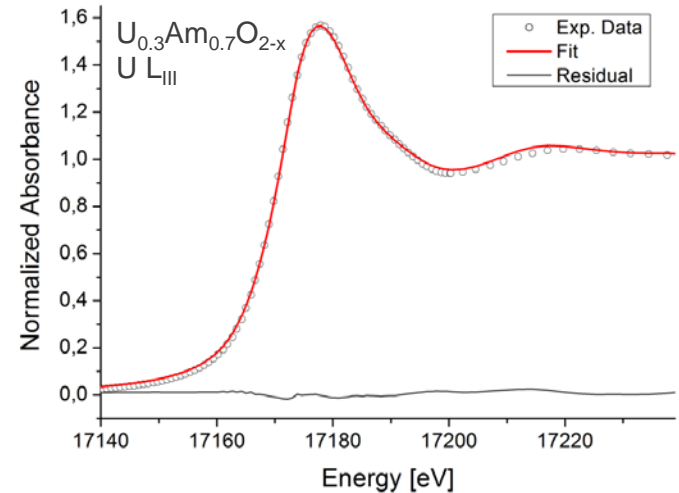
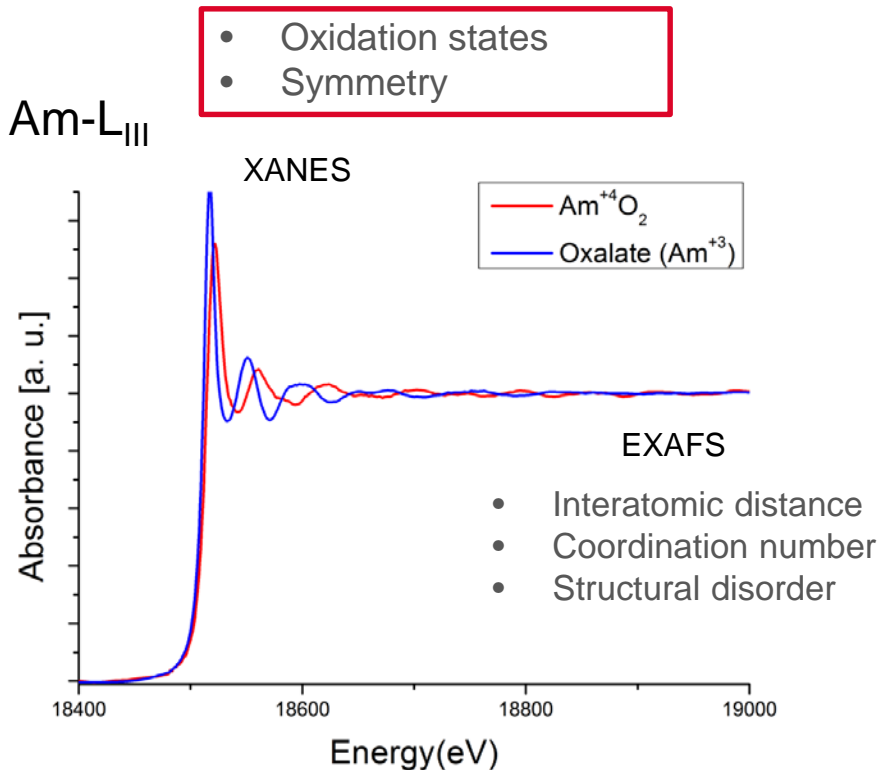
\*Values corrected by self-irradiation



## ■ BM20 beamline at ESRF (Grenoble, France)

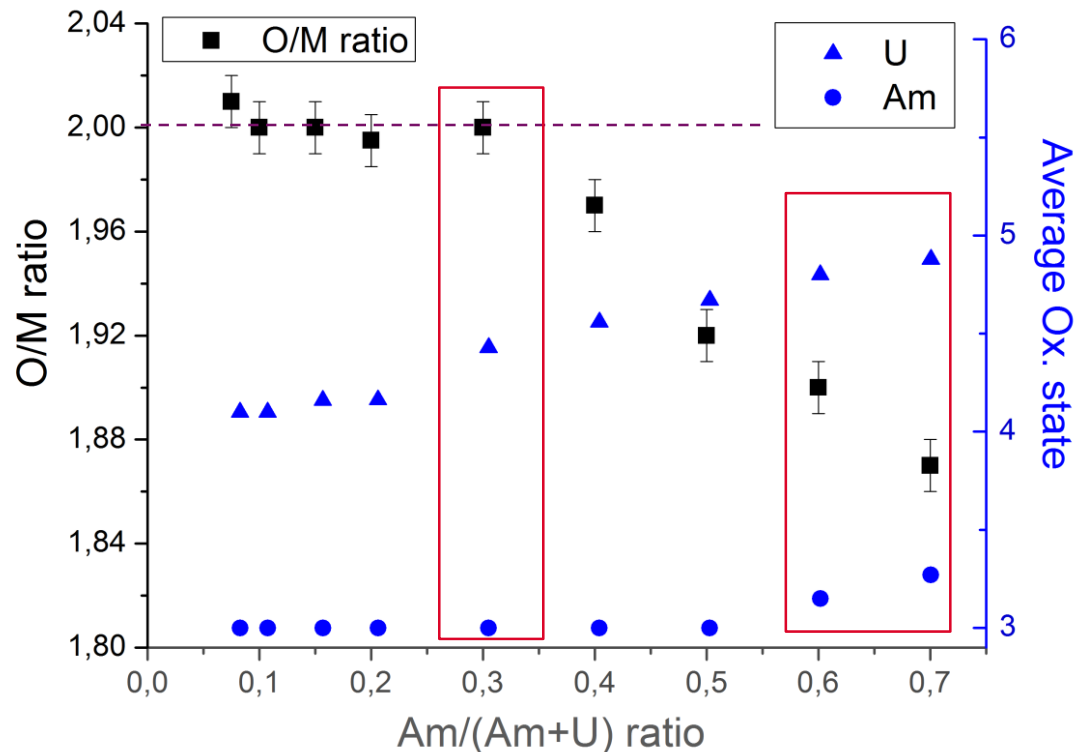
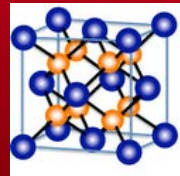
- ❑ Spectra acquired in both transmission and fluorescence mode at the **U L<sub>III</sub>**, **U L<sub>II</sub>** and **Am L<sub>III</sub>** edges
- ❑ Calibration of energy using Y, Zr and Mo foils during the acquisition

XANES: linear combination fit with reference samples → **Oxidation state**



	Americium		Uranium	O/M ratio
Am%	Am <sup>+3</sup>	Am <sup>+4</sup>	Av Oxid. state	O/M
<b>30%</b>	0.30	0	4.43	<b>2.00</b>



STRUCTURAL PROPERTIES OF  $U_{1-x}Am_xO_{2\pm\delta}$ 

\* Samples prepared by the UMAC process (powder metallurgy) and stocked for few months under air

3. T. Dela et al., *J. Nucl. Mat.* 432 (2013) 305-312

4. D. Prieur et al, *Inorg. Chem.* 50 (2011) 12437-12445  
 5. F. Lebreton et al, *Inorg. Chem.* 54 (2015) 9749–9760.

- Am/(Am+U) < 0.5: purely  $Am^{+3}$ ,  $U^{+4}/U^{+5} \Leftrightarrow$  charge compensation mechanism
- $Am^{+4}$  partially present in samples with  $Am/(Am+U) = 0.6$  and  $0.7$
- The average oxidation state of U increases with the Am content
- $Am/(Am+U) \geq 0.4 \Leftrightarrow O/M < 2$
- Decrease of O/M as Am content increases

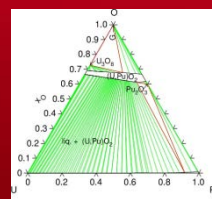
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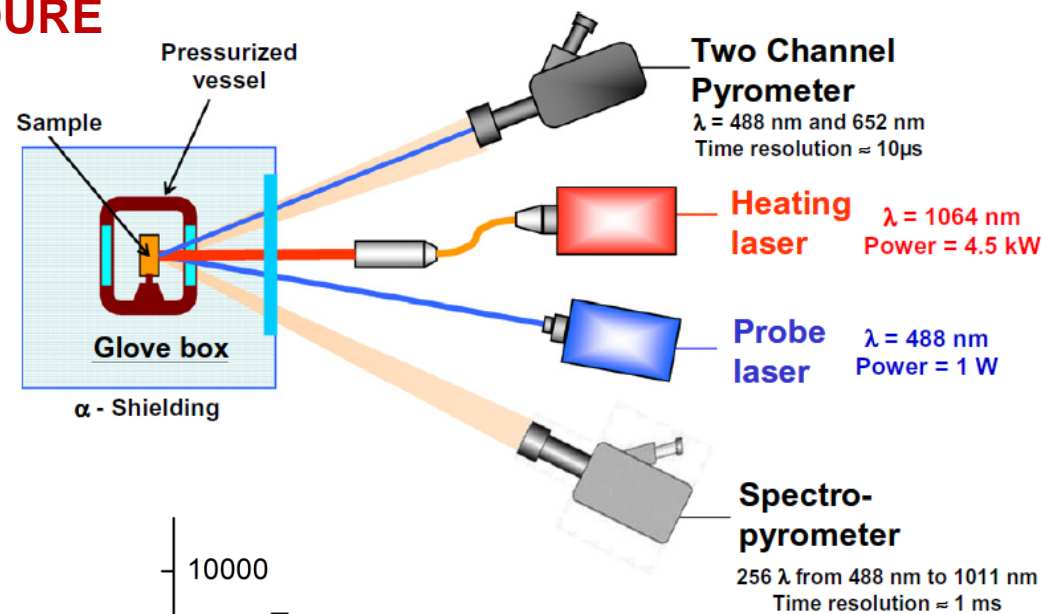
HT-ENTHALPIES

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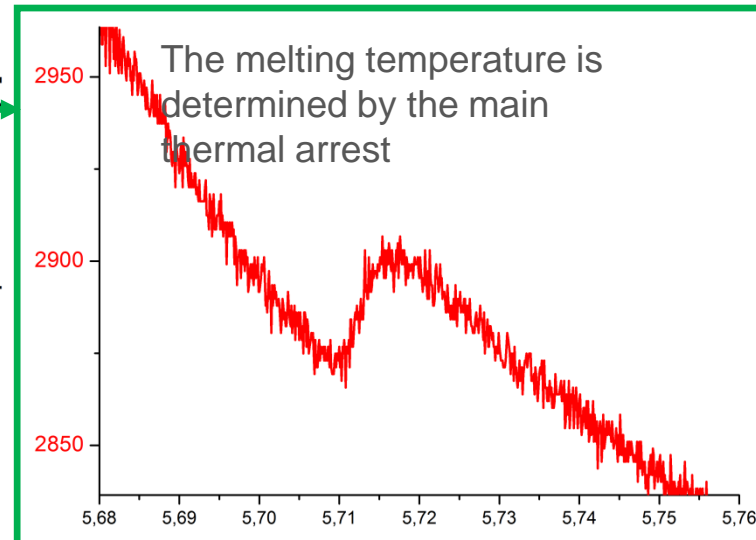
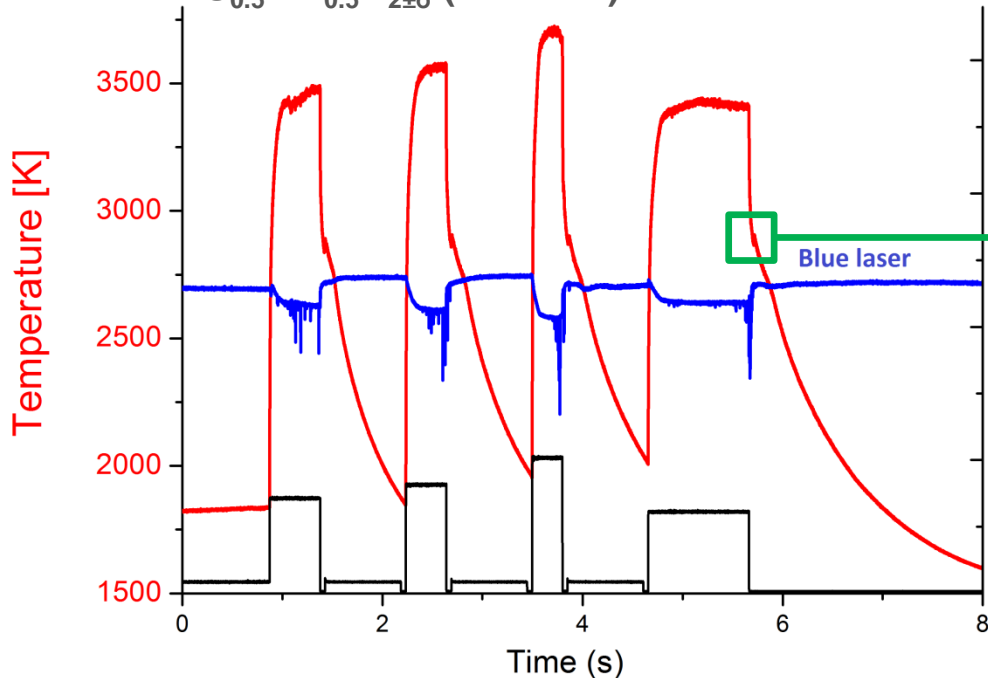
## EXPERIMENTAL SET-UP & PROCEDURE

- 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  $\epsilon$  value)



Example:

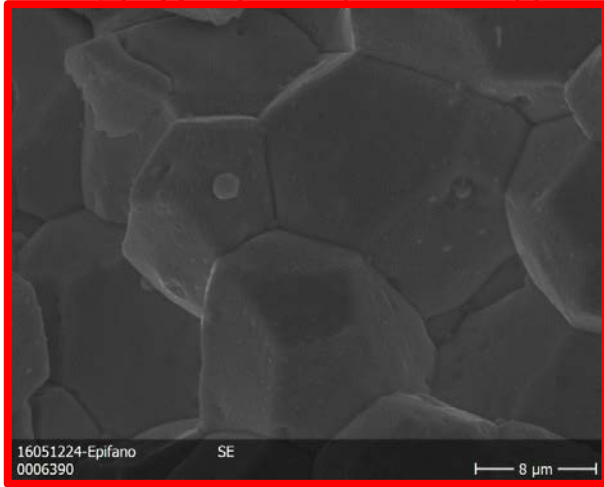
$\text{U}_{0.5}\text{Am}_{0.5}\text{O}_{2\pm\delta}$  (under Ar)



# MELTING-T MEASUREMENTS

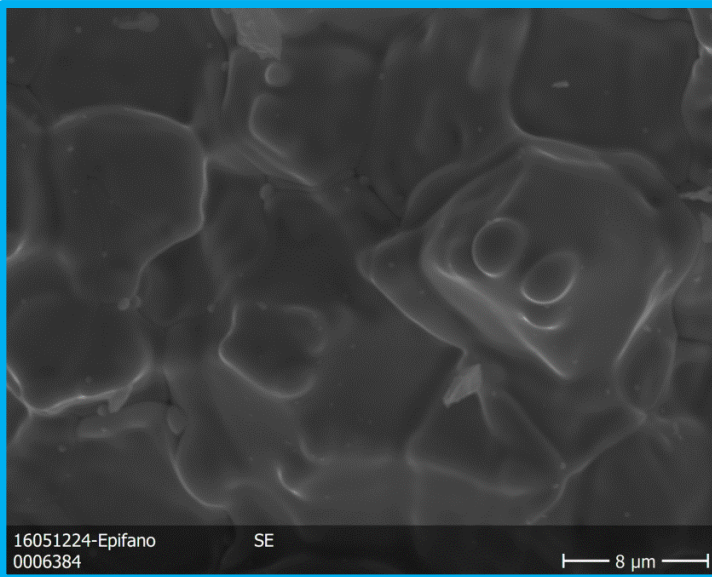
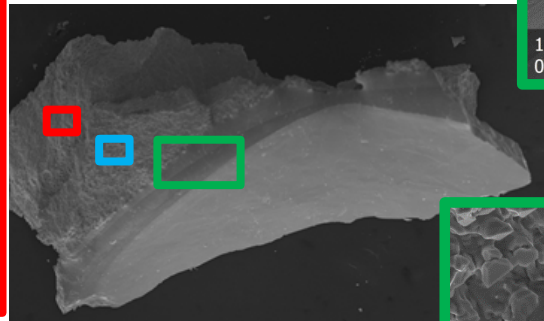
## Laser heating advantages:

- ❑ Short measurement duration



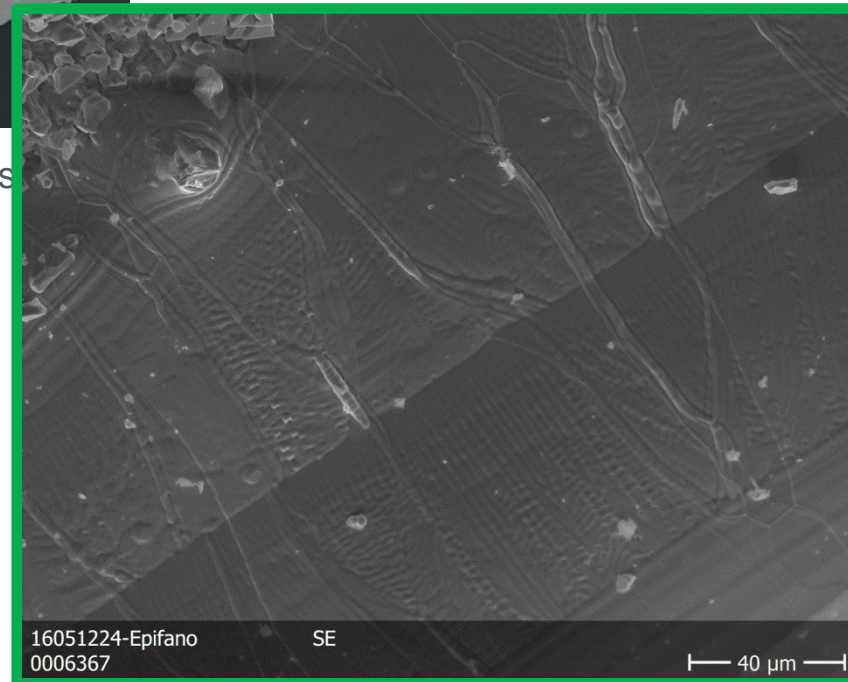
Far region

Melted region

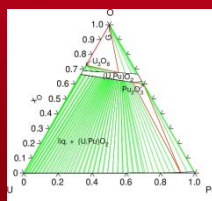


SEM image of a melted s

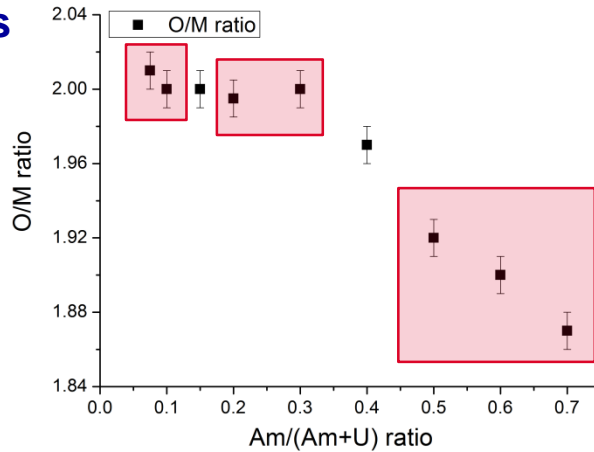
Intermediate region



# MELTING-T ( $T_m$ ) MEASUREMENTS



## Samples



## Atmosphere

- Argon
- Air

6. D. Manara et al, J. Nucl. Mater. 342 (2005) 148-163  
7. R. McHenry, Trans. Am. Nucl. Soc. 8, (1965) 75.

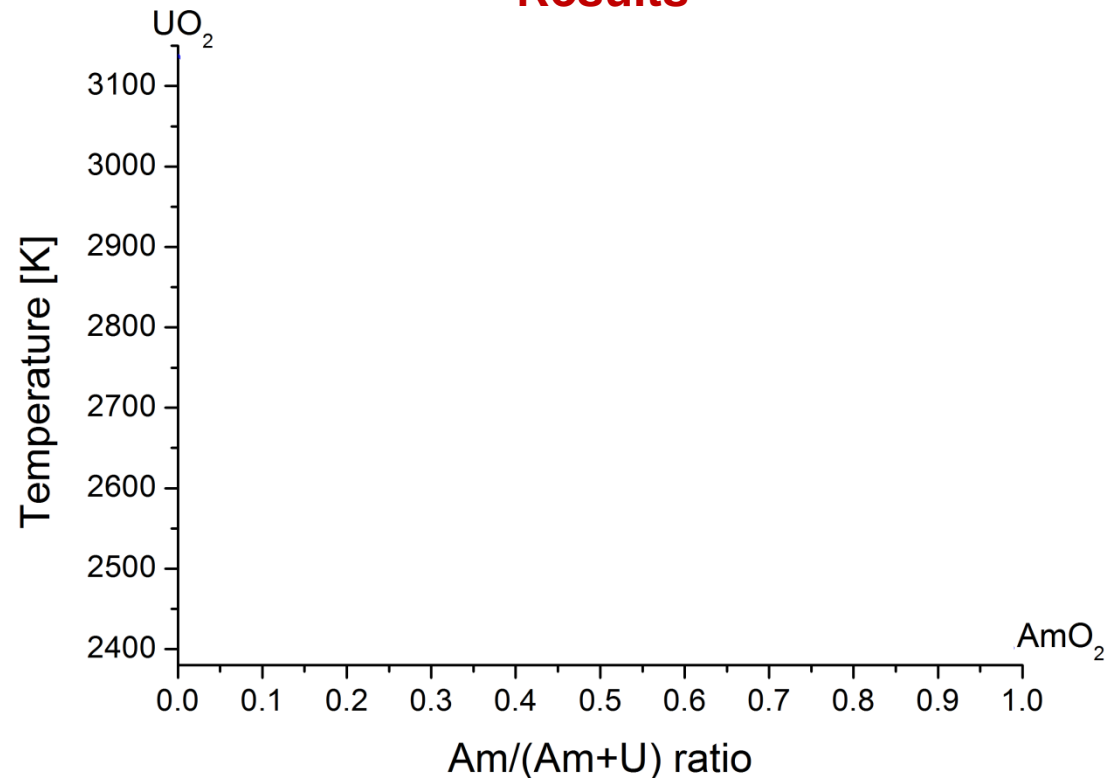
□ Under argon: almost **linear decrease** of  $T_m$  with the  $Am/(Am+U)$  ratio

□ Under air

- Lower  $T_m \rightarrow$  variation (increase) of the O/M
- No monotonic variation with  $Am/(Am+U)$  ratio
- Highest  $T_m$  for  $Am/(Am+U)=0.3$  and 0.5

➔ Am stabilizes the solid solution in oxidizing conditions

## Results



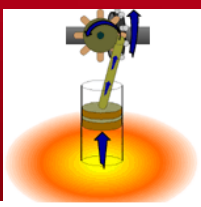
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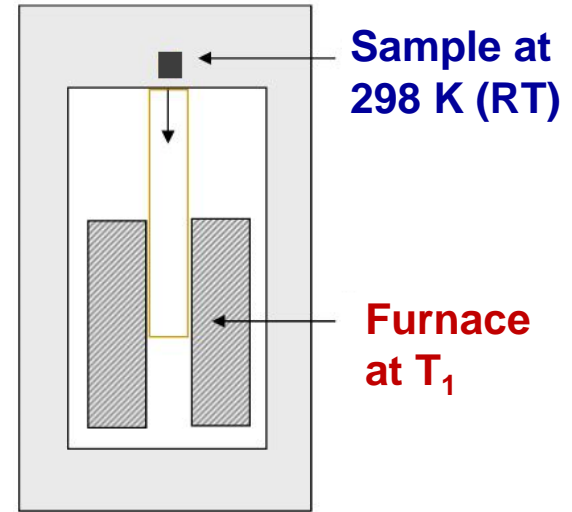
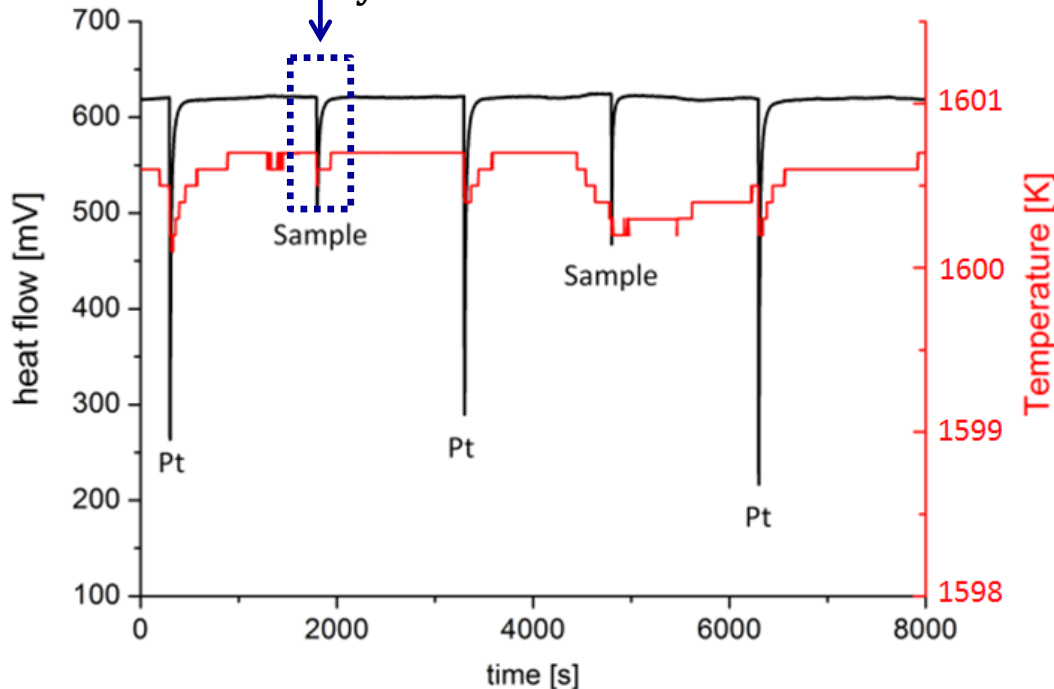


- Furnace programmed to maintain a **constant  $T_1$**
- **RT** samples are dropped in the furnace
- The energy necessary to heat the sample from RT to  $T_1$  is recorded:

$$Q_{meas} = H_{T_1} - H_{RT}$$

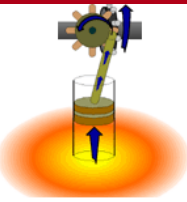
Example:

$$\int \text{heat flow}$$

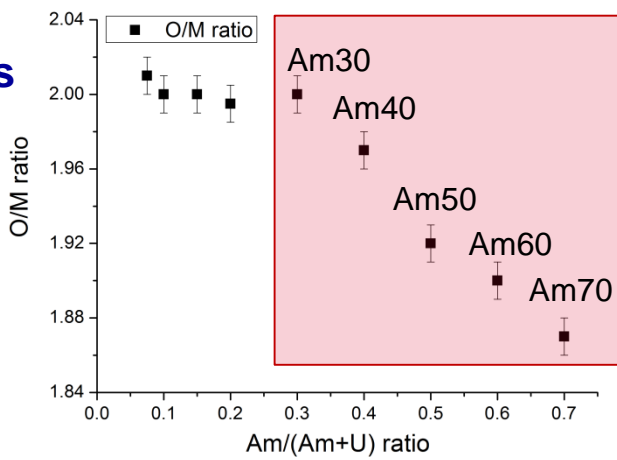


- Before/After each sample a **reference material (Pt)** is dropped to determine the **sensitivity** of the calorimeter (signal/heat ratio)

# HT-ENTHALPY MEASUREMENTS



## Samples

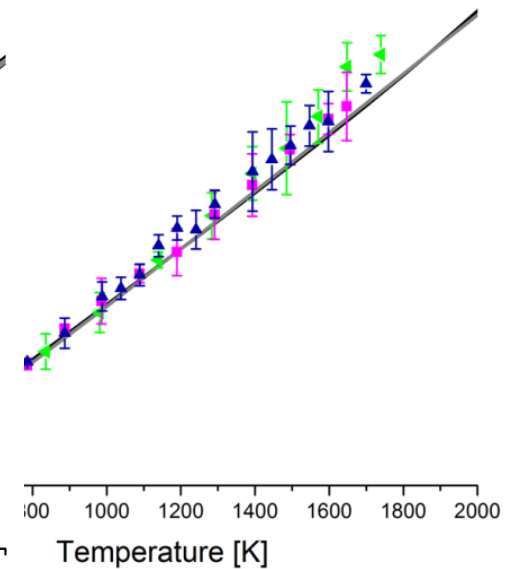
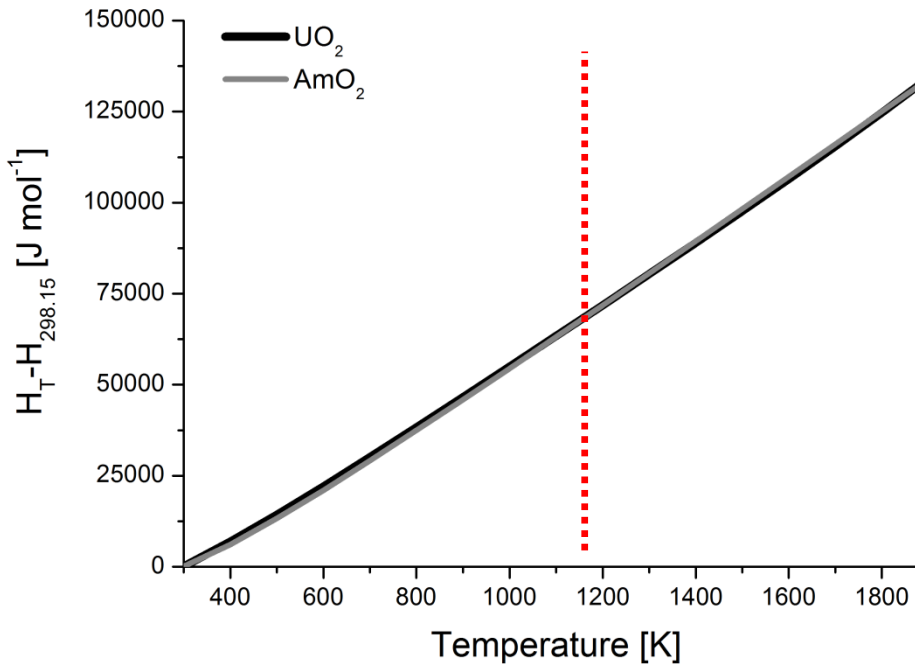
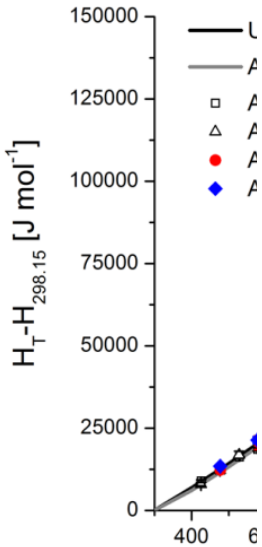


## Atmosphere

- Argon (Am30, Am40, Am50)
- Air (Am60, Am70)

7. J. K. Fink, *J. Nucl. Mater.* 279 (2000) 1-18  
 8. T. Nishi et al., *J. Nucl. Mater.* 414, (2011) 109-113.  
 9. O. S. Valu et al., *J. All. Comp.* 614 (2014), 144-150

## Results

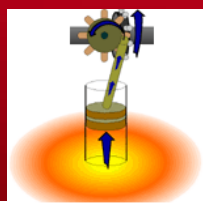


with T

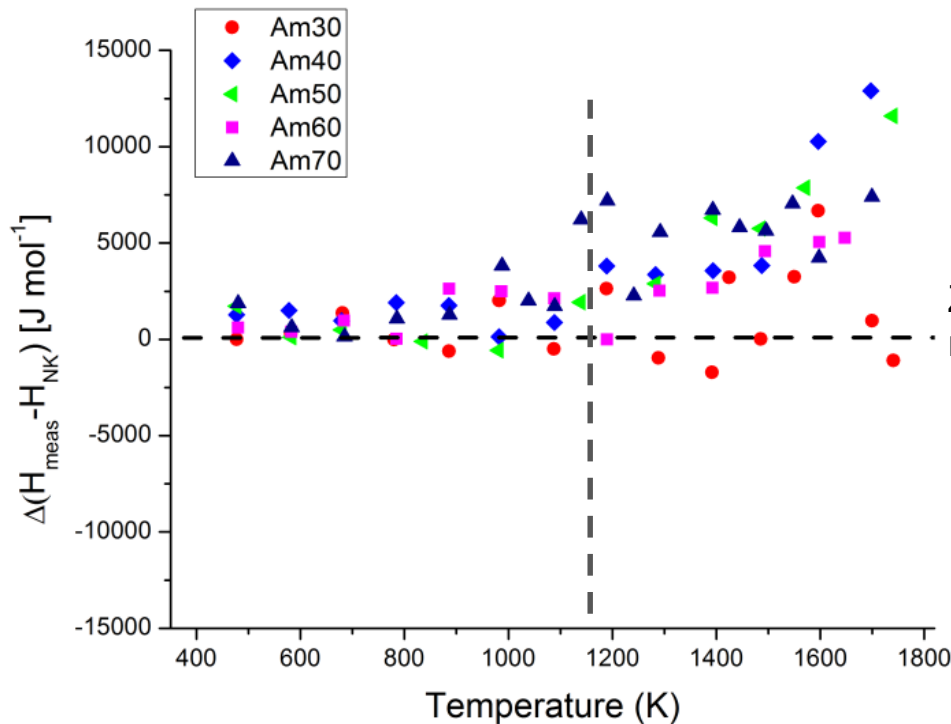
The binary an

Am/(Am+U) > 0.4 & T > 1100 K, higher ΔH than UO<sub>2</sub> and AmO<sub>2</sub>





- The experimental enthalpies  $H_{meas}(T)=H(T)-H(298.15)$  are compared to the ideal values obtained applying the **Neumann-Kopp rule  $H_{NK}(T)$**
- The resulting difference  $\Delta(H_{meas}-H_{NK})$  as a function of T:



~~Zero difference NK rule  $UO_2-AmO_2$~~

We should use a NK rule  $UO_2-AmO_{2-\delta}$

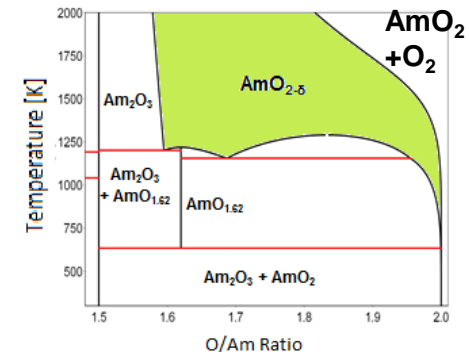
**But no data on  $AmO_{2-\delta}$**

## ■ Excess contribution?

Oxygen vacancies



- $AmO_2 \rightarrow AmO_{2-\delta}$  for  $T > 1180$  K
- Same  $H_p$  for high-Am content mixed oxides



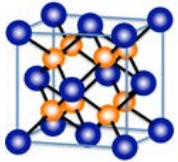
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## Structural properties

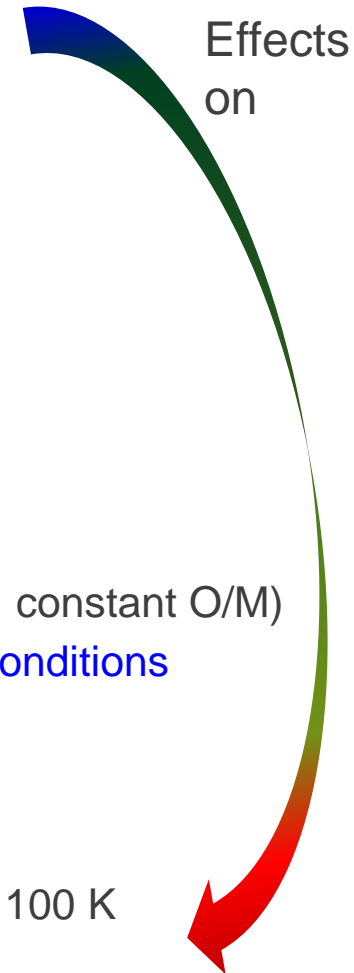
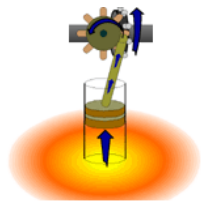
- Fluorite structure ( $\text{Am}/(\text{Am}+\text{U}) \leq 0.7$ )
- Peculiar structural properties
  - $\text{Am}^{+3}$  stability
  - $\text{U}^{+4}/\text{U}^{+5}$
  - $\text{Am}/(\text{Am}+\text{U}) \geq 0.4 \Leftrightarrow$  stable O/M ratio < 2

## Phase diagram properties

- Melting temperature
  - $T_m$  decrease with  $\text{Am}/(\text{Am}+\text{U})$  content Ar (hp: constant O/M)
  - Higher  $T_m$  for high Am contents in oxidizing conditions

## Thermodynamic properties

- High temperature enthalpy increments
  - $\Delta H^{\text{mixed}} > \Delta H^{\text{UO}_2}$ , for  $\text{Am}/(\text{Am}+\text{U}) > 0.4$  and  $T > 1100$  K
  - O/M decrease effects  $\Leftrightarrow$  O vacancies



Perspectives: integration of the data in a CALPHAD model

