



## **Partitioning And Transmuter Research Initiative in a Collaborative Innovation Action**

# PATRICIA

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### **DELIVERABLE**

#### **D4.3 Measurements and atomic scale calculations in U-Pu-Am-Np-O systems**

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### DOCUMENT SUMMARY

A thorough knowledge of the thermal-physical and thermo-chemical properties of transmutation type fuels is key for the safety assessment of transmutation concepts, such as Accelerator Driven Systems (ADS) (MYRRHA prototype) or fast reactor concepts such as Sodium-cooled Fast Reactors (SFR) (ASTRID-type) or Lead-cooled Fast Reactors (LFR) (ALFRED). In this work, we report experimental measurements on (U,Np)O<sub>2</sub> and (Pu,Np)O<sub>2</sub> oxides, including synthesis and characterization by X-ray diffraction, chemical analysis, Raman spectroscopy, as well as the determination of enthalpy increments and heat capacity by drop calorimetry, and melting temperatures by a laser flash technique. In addition, lattice parameters, enthalpy increments, heat capacity and melting temperatures of (U,Am)O<sub>2-x</sub> oxides are calculated using atomic scale modelling methods. The results obtained will serve as input to develop a comprehensive model of the U-Pu-Am-Np-O system, as will be presented in deliverable D4.4.

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## Summary

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## Glossary

|        |                                              |
|--------|----------------------------------------------|
| ADS    | Accelerator Driven System                    |
| DSC    | Differential Scanning Calorimetry            |
| ICP-MS | Inductively Coupled Plasma Mass Spectrometry |
| EPMA   | Electron Probe Microanalyser                 |
| FPC    | Fuel Performance Code                        |
| KEMS   | Knudsen Effusion Mass Spectrometry           |
| LAF    | Laser Flash                                  |
| LFR    | Lead-cooled Fast Reactor                     |
| MA     | Minor Actinide                               |
| PPMS   | Physical Property Measurement System         |
| SFR    | Sodium-cooled Fast Reactor                   |
| XRD    | X-Ray Diffraction                            |

## 1 Introduction

Transmutation of Minor Actinide (MA) is planned in several Generation IV systems, including the specific Accelerator Driven Systems (ADS) combining an accelerator and a lead-cooled Fast Reactor (LFR) (MYRRHA prototype) and fast reactor concepts such as Sodium-cooled Fast Reactors (SFR) (ASTRID-type) or LFR (ALFRED). It requires the incorporation of MAs into the fuel and both metallic and oxide fuels are potential candidates as fuel for transmutation. In Europe, based on historical experience and know-how from the current fleet of Light Water Reactors, oxide fuels have emerged as the shorter-term solution to meet the Generation IV assigned performances and reliability goals.

Transmutation of MA can be done by homogeneous recycling, with MA diluted at a low content (< 5%) in the standard driver fuel (U,Pu)O<sub>2</sub>, or by heterogeneous recycling with higher MA content (10%-15%) in UO<sub>2</sub> based fuels located into the radial blankets (outer part of the core). Americium, in particular the <sup>241</sup>Am isotope, is the main contributor to the heat load of long-lived high-level radioactive waste. For this reason, studies on americium in the framework of partitioning and transmutation require dedicated research efforts.

The Domain 2 of PATRICIA is dedicated to the safety assessment of transmutation type fuels, in particular Am-bearing fuels, under normal operating conditions, but also under off-normal and accidental conditions. It is commonly assumed that the thermal and thermo-chemical properties of the fuel yield the dominant contribution to the uncertainties in thermal evaluation within Fuel Performance Codes (FPCs). Key thermal-physical and thermal-chemical properties are thus investigated here, with the aim to enhance the reliability of fuel behaviour calculations and contribute to the design of safer fuel elements with lower uncertainties.

More specifically, experimental measurements and atomic scale calculations were performed on selected mixed oxides in the U-Pu-Am-Np-O system. The data obtained will serve as input to develop thermodynamic models of the U-Am-O, U-Np-O, Pu-Am-O, Pu-Np-O ternary systems, and higher order U-Pu-Am-Np-O system, as will be presented in Deliverable D4.4. The development of a comprehensive model for the highly complex U-Pu-Am-Np-O system is key for the understanding and prediction of the behaviour of fast reactor/ADS fuels including minor actinides (Am,Np) and a high Pu content.

A brief literature review of all the data available on the aforementioned ternary systems is first included in this report, followed with an explanation of the experimental and computational methods used. The measured properties on (U,Np)O<sub>2</sub> and (Pu,Np)O<sub>2</sub> oxides are then presented, followed by the calculated properties on (U,Am)O<sub>2</sub>.

## 2 Literature review

### 2.1 Ternary U-Np-O system

#### 2.1.1 Thermodynamic data

- Melting temperatures

The melting behaviour of  $U_{1-y}Np_yO_2$  with  $y=0.02, 0.1, 0.2, 0.3, 0.5, 0.7, 0.75$  and  $0.85$  was characterized using a laser heating technique under controlled atmospheres (argon or air) in quasi-container-less conditions by Chollet et al. [2015Chollet]. The melting temperatures reported are in very good agreement with the reported melting points for the pure dioxides,  $T = (3130 \pm 30)$  K for  $UO_2$  [2005Manara] and  $T = (3070 \pm 67)$  K for  $NpO_2$  [2012Böhler].

- Heat capacities

Yamashita et al. [1997Yamashita] derived high temperature heat capacities for  $U_{1-y}Np_yO_2$  solid solutions based on experimental thermal expansion data and the relation  $C_p = \beta V / K_a \gamma$ , where  $\beta$  is the isobaric volumetric expansion,  $V$  is the molar volume,  $K_a$  is the adiabatic compressibility, and  $\gamma$  is the Grüneisen constant. Approximations were made for the values of the coefficients  $K_a$ ,  $\gamma$  and  $V$ , that are not available in the literature.  $K_a$  and  $\gamma$  were assumed to be independent of temperature. After calculation, the  $C_p$  curves for the solid solutions were found between those of  $UO_2$  and  $NpO_2$  (Figure 1). However, the accuracy of the method was not estimated.

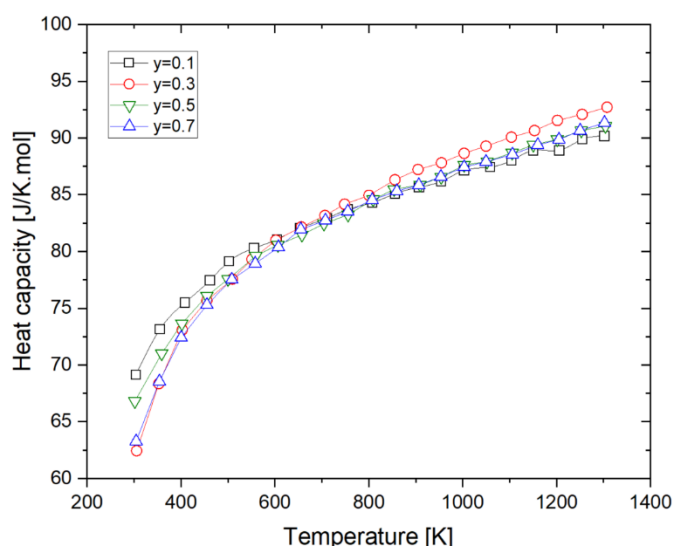


Figure 1 Estimated heat capacities of  $NpO_2$  and  $Np_yU_{1-y}O_2$  solid solution plotted against temperature [1997Yamashita].

Moreover, measurements of enthalpy increment were performed at JRC in 2015 on a series of  $(U,Np)O_2$  samples using the drop calorimetry technique (unpublished data). Samples prepared by CEA (20%, 30% and 70% Np) and JRC (5%, 20%, 75% [incomplete campaign]) were measured. Some of these results are discussed in the results section.

- Vapour pressures

Vapour pressure data were collected at JRC in 2015 using the Knudsen Effusion Mass Spectrometry (KEMS) technique (unpublished data). The measurements were performed in a tungsten cell under vacuum on  $(U,Np)O_2$  solid solutions with Np contents of 10%, 20%, 30%, 50%, 70% and 85%.

### 2.1.2 Phase diagram data

Yamashita et al. studied the ternary  $\text{UO}_2$ - $\text{U}_3\text{O}_8$ - $\text{NpO}_2$  phase diagram at 1273 K using high temperature X-Ray diffraction and thermogravimetry [1994Yamashita]. The authors' results are shown below in Figure 2. They suggested that a wide and homogeneous  $(\text{U,Np})\text{O}_{2+x}$  solid solution exists in the range  $\text{UO}_2$ - $\text{U}_4\text{O}_9$ - $\text{U}_{0.4}\text{Np}_{0.6}\text{O}_{2.27}$ - $\text{NpO}_2$ . [1970Paul] also reported that the phase boundary of  $\text{MO}_{2+x}$  ( $\text{M}=\text{U}_{1-y}\text{Np}_y$ ) was  $y=0.55$  at 1373 K in 1 atm  $\text{O}_2$ , which is in fair agreement with this data.

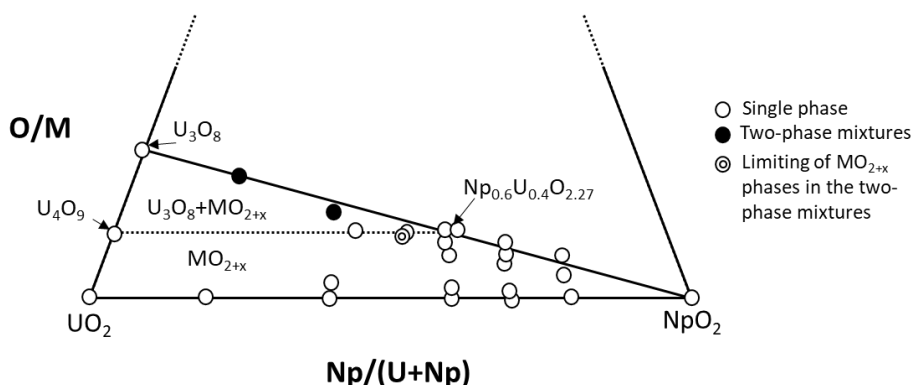


Figure 2 Sketch of the ternary U-Np-O phase diagram at 1273 K, as reported by Yamashita et al. [1994Yamashita].

As mentioned in section 2.1.1, Yamashita et al. performed high temperature X-Ray diffraction measurements on various  $\text{U}_{1-y}\text{Np}_y\text{O}_2$  solid solutions ( $y=0.1, 0.3, 0.5, 0.7$ ) from room temperature up to 1273 K [1997Yamashita]. The measurements were carried out under He-8 vol% $\text{H}_2$ , starting from 1273 K and decreasing the temperature progressively by 50 or 100 K. The authors found that the lattice parameters increased smoothly up to 1300 K indicating that no phase transitions occurred or nor any other orderings happened in this temperature range.

Chollet et al. also studied  $\text{U}_{1-y}\text{Np}_y\text{O}_2$  ( $y=0.1, 0.3$  and  $0.7$ ) solid solutions by high temperature X-Ray diffraction up to 1373 K in air [2013Chollet]. The authors performed in situ- oxidation of the solid solutions, which revealed various oxidation steps. A single phase  $\text{U}_{1-y}\text{Np}_y\text{O}_2$  was observed between 300 and 573 K, irrespective of the Np content. For  $y=0.1$  and  $0.3$ , a two phase mixture ( $\text{MO}_{2+x}+\text{M}'_4\text{O}_{9-z}$ ) appeared at 573 K. A metastable phase  $\text{M}''_3\text{O}_7$  also appeared at 673 K which disappeared at 773 K. Moreover Chollet et al. suggested the composition of  $\text{MO}_{2+x}$  should be very close to  $(\text{U}_{0.3}\text{Np}_{0.7})\text{O}_{2+x}$  in this temperature range (573-773 K). Regarding the  $y=0.7$  composition, a single phase exists in the range (573-773 K) with the composition  $(\text{U}_{0.3}\text{Np}_{0.7})\text{O}_{2+x}$ . For all three compositions,  $y=(0.1,0.3,0.7)$ , a two phase mixture ( $\text{MO}_{2+x}+\text{M}''_3\text{O}_8$ ) was observed in the range (773-1373 K). For  $y=0.1$  and  $0.3$ , a U/Np segregation was suggested in the  $\text{M}''_3\text{O}_8$  phase with a composition close to  $(\text{U}_{0.9}\text{Np}_{0.1})\text{O}_8$ . The 10% incorporation of neptunium in the  $\text{U}_3\text{O}_8$  phase is more than suggested by [1994Yamashita] (insoluble) and Paul [1970Paul] (less than 3.5%), but less than synthesized by [2003Finch] (33 %), see hereafter. It is probable that the maximum solubility decreases as the temperature increases. For  $y=0.7$ , the  $\text{M}''_3\text{O}_8$  composition should correspond to  $\text{U}_3\text{O}_8$ . For all compositions, the  $\text{MO}_{2+x}$  composition was reported close to  $(\text{U}_{0.3}\text{Np}_{0.7})\text{O}_{2+x}$ .

In 2003, Finch et al. synthesized  $\text{Np}_x\text{U}_{3-x}\text{O}_8$  with  $x$  between 0 and 0.33, and performed SEM, XRD and XAS measurements on the compounds [2003Finch]. The authors showed that  $\text{Np}_x\text{U}_{3-x}\text{O}_8$  exists between  $\alpha$ - $\text{U}_3\text{O}_8$  and  $\text{NpU}_2\text{O}_8$ . Based on comparison with  $\text{NpF}_4$  standard, the XANES results suggested that Np was tetravalent in those compounds. As  $\text{Np(IV)}$  fraction increases in  $\text{Np}_x\text{U}_{3-x}\text{O}_8$ , the ratio of pentavalent U to hexavalent U must then decrease to maintain electroneutrality. Moreover, they suggest that tetravalent Np incorporating in  $\alpha$ - $\text{U}_3\text{O}_8$  induces a structural change from the alpha type structural sheet to a structural sheet resembling that of  $\beta$ - $\text{U}_3\text{O}_8$ . This suggests that if  $\text{NpU}_2\text{O}_8$  is a valid compound, it may be isostructural with  $\beta$ - $\text{U}_3\text{O}_8$ . But confirmation would require the synthesis of this latter compound

and the determination of its structure. Furthermore, Chollet et al. have analysed a sample of  $(U_{0.9}Np_{0.1})O_{2+x}$  by X-Ray Diffraction. Their results show the presence of two phases: a FCC phase and an oxidized orthorhombic  $(Np,U)_3O_{8\pm x}$  phase.

More recent studies also report XANES measurements on  $U_{1-y}Np_yO_2$  [2014Martel, 2016Chollet]. The latter studies show that for compositions with y up to 0.85, U and Np have an oxidation state of (IV). Chollet et al. also studied  $(U_{0.9}Np_{0.1})O_{2+x}$  by XAS [2016Chollet]. For this compound, the oxidation state for U is between  $U_3O_8$  and  $U_4O_9$  and for Np stays IV. However, XANES analysis does not always provide conclusive evidence of the presence of Np(V) in a heterogeneous system, Np(V) could then be deduced by EXAFS analysis [2005Denecke]. The EXAFS analysis of the oxidized compound show that the amplitude of this peak is apparently weaker than for the  $NpO_2$  and stoichiometric samples. This difference could be explained by the higher oxygen disorder in the oxidized sample, the neptunium cation appears to be in the same symmetry and so the Np cation is also at the (IV) oxidation state in this compound.

## 2.2 Ternary Pu-Np-O system

There is no data available in the literature on this system.

## 2.3 Ternary U-Am-O system

- Melting temperature

Melting temperature measurements of  $(U,Am)O_{2\pm x}$  oxides were reported by Epifano et al. up to 70 mol% Am under various atmospheres. The melting temperatures were found to be significantly lower (around 2700 K) in a strongly oxidizing atmosphere (compressed air at  $0.300 \pm 0.005$  MPa), compared to the melting temperatures (beyond 3000 K) obtained in an inert environment (pressurized Ar).

- Heat capacities

*Enthalpy increment data were measured on a series of  $(U,Am)O_{2\pm x}$  solid solutions using drop calorimetry in the temperature range (475-1790 K) by Vălu et al. [2014Vălu] for Am/(Am+U) ratios equal to 0.0877 and 0.1895, and in the temperature range (470-1750 K) by Epifano et al. [2017aEpifano] for Am/(Am+U) ratios equal to 0.32, 0.39, 0.49, 0.58 and 0.68. The heat capacity functions were obtained by derivation of the enthalpy increment data and are listed in*

Table 1.

| Am/(Am+U) ratio | Cp(298.15 K)                           | Cp(T) = a + bT + cT <sup>-2</sup> [J K <sup>-1</sup> mol <sup>-1</sup> ] |                    |                   | Ref.           |
|-----------------|----------------------------------------|--------------------------------------------------------------------------|--------------------|-------------------|----------------|
|                 | [J K <sup>-1</sup> mol <sup>-1</sup> ] | a                                                                        | b·10 <sup>-3</sup> | c·10 <sup>6</sup> |                |
| 0.0877          | 63.66                                  | 74.172                                                                   | 14.601             | -1.321384         | [2014Vălu]     |
| 0.1895          | 63.73                                  | 62.367                                                                   | 23.0544            | -0.489837         | [2014Vălu]     |
| 0.32            | 63.81                                  | 79                                                                       | 6                  | -1.567            | [2017aEpifano] |
| 0.39            | 63.88                                  | 85                                                                       | 8                  | -2.122            | [2017aEpifano] |
| 0.49            | 63.95                                  | 82                                                                       | 11                 | -1.902            | [2017aEpifano] |
| 0.58            | 64.02                                  | 74                                                                       | 16                 | -1.313            | [2017aEpifano] |
| 0.68            | 64.09                                  | 71                                                                       | 19                 | -1.137            | [2017aEpifano] |

Table 1: Heat capacity functions of  $(U,Am)O_2$  oxides

- Vapour pressures

Vapour pressure measurements were reported in the PhD theses of Lebreton [2014Lebreton] and Epifano [2017bEpifano] using KEMS under vacuum. The work of Lebreton focused on  $U_{1-y}Am_yO_{2-x}$  samples with Am/(Am+U) ratios of 0.3, 0.4 and 0.5, measured in isothermal conditions at about 2300 K to reach congruent vaporization (likely not reached during the experiments). However, the final

composition of the samples could not be determined, and the presented results therefore are referring to the initial americium content.

The work of Epifano focused on Am/(Am+U) ratios of 0.6 and 0.7. Epifano also re-analysed the data obtained by Lebreton and two other samples with Am/(Am+U) ratios of 0.1 and 0.2 measured independently at JRC. The derived total and partial pressures at 2320 K for all compositions are listed in Table 6.5 and shown in Figure 6.10 of the PhD thesis of Epifano. Epifano reports a relative uncertainty of at least 30% on those values, given the uncertainties on the temperature ( $\pm 20$  K) and the data treatment (notably the choice of ionization cross sections and interpretation of the dissociation processes).

## 2.4 Ternary Pu-Am-O system

### • Melting temperature

The only measurement was performed by Fouquet-Métivier on  $\text{Pu}_{0.49}\text{Am}_{0.51}\text{O}_{2-x}$  mixed oxide using the laser melting technique [2022Fouquet-Métivier]. An oxygen probe was used to estimate the variation of the O/M ratio along the successive laser shots. The results are compared to the CALPHAD model developed by Fouquet-Métivier [2022Fouquet-Métivier] in Figure 3.

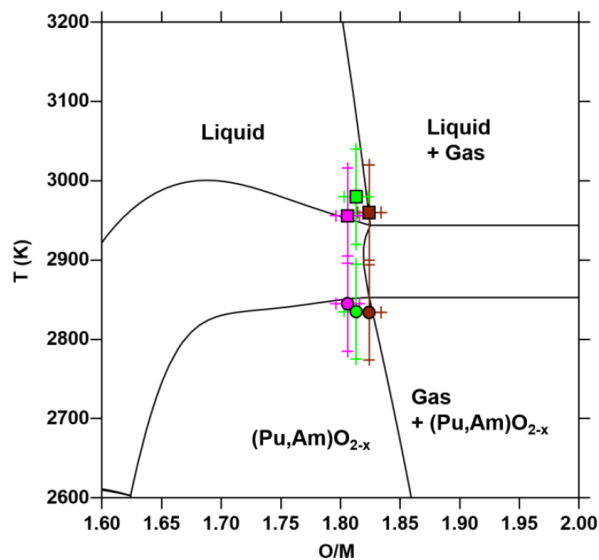


Figure 3 Calculated isopleth section for  $\text{Pu}_{0.49}\text{Am}_{0.51}\text{O}_{2-x}$  compared to the solidus/liquidus temperatures and associated O/M ratios. (Figure 6-23 of PhD thesis by [2022Fouquet-Métivier]).

The solidus/liquidus temperatures do not vary much with the O/M ratio of the sample, that is slightly reduced under argon atmosphere. The solidus/liquidus temperatures are consistent with the trend when considering the pure end-members, i.e.  $T_{\text{melt}}(\text{UO}_2) > T_{\text{melt}}(\text{PuO}_2) > T_{\text{melt}}(\text{AmO}_2)$ .

### • Heat capacities

In the EUROTRANS European project, heat capacity for mixed oxides  $(\text{Pu},\text{Am})\text{O}_{2-x}$  with Am/(Pu+Am) ratio of 0.2, 0.5 and 0.8 were measured by Differential Scanning Calorimetry (DSC) in the temperature range 400-1400 K [2009Ottaviani]. The uncertainty of the measurements was of  $\sim 5\%$ . The heat capacity of the three oxides appeared to be very close from each other. The following correlation was deduced from these three measurements:

$$C_p(T, (\text{Pu}, \text{Am})\text{O}_2) = 469.3 - 3.821 \times 10^{-1} \times T + 1.949 \times 10^{-4} \times T^2 - 195.246 \times 10^{-5} \times T^{-2}$$

These values are close to the reduced phases  $\text{Pu}_2\text{O}_3$  and  $\text{Am}_2\text{O}_3$ , which is consistent with the fact that the oxides were sintered under reducing atmosphere. However the exact O/M ratio of the samples is not known.

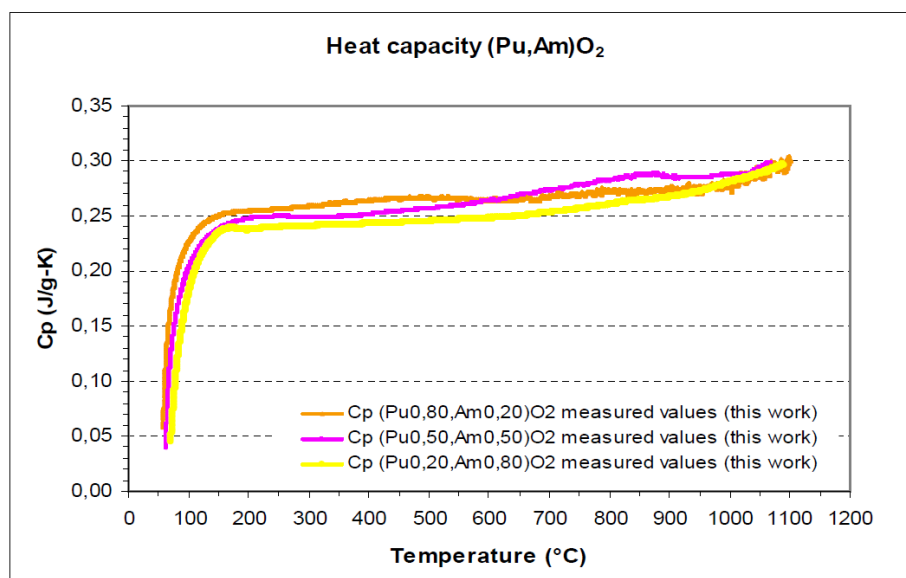


Figure 4 Heat capacity of  $(\text{Pu},\text{Am})\text{O}_2$  mixed oxides with Am/(Pu+Am) ratio of 0.2, 0.5 and 0.8 [2009Ottaviani].

- Vapour pressures

In the frame of the EUROTRANS European project, a mixed oxide with 6.1 % of Am was studied by KEMS. The vaporization of Pu, PuO and  $\text{PuO}_2$  started at 1950 K [2010Staicu].

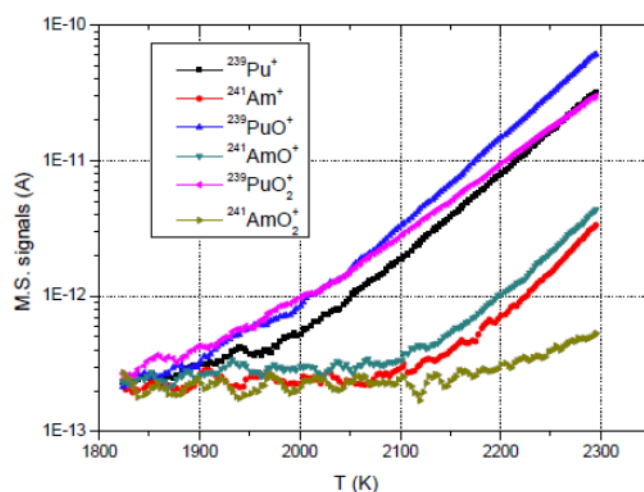


Figure 5 Mass spectrometric signal of gaseous species above  $\text{Pu}_{0.939}\text{Am}_{0.061}\text{O}_{2-x}$  sample as function of temperature measured by KEMS.

Moreover in 2011, Gotcu et al. performed KEMS measurements on  $\text{Pu}_{0.756}\text{Am}_{0.244}\text{O}_{2-x}$  [2011Gotcu-Freis].  $\text{PuO}_2(\text{g})$  and  $\text{PuO}(\text{g})$  were found to be the major species in the gas phase. A CALPHAD model was also developed on the Pu-Am-O system. Phase diagram and thermodynamic data, however, are scarce. The experimental vapour pressure data are well reproduced. Thus, significant uncertainties remain and new measurements are required.

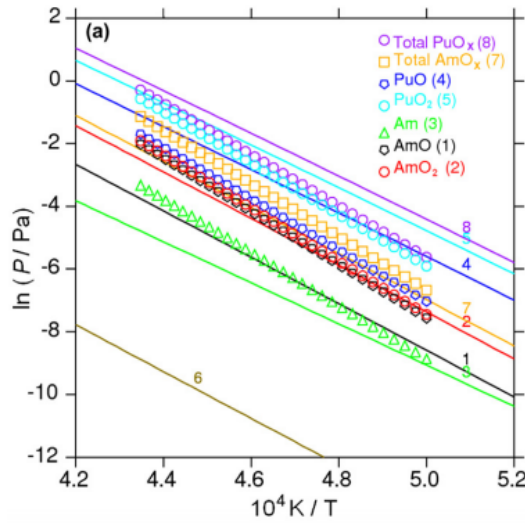


Figure 6 Calculated and experimental vapour pressure data on  $Pu_{0.756}Am_{0.244}O_{2-x}$  [2011Gotcu-Freis].

#### • Oxygen potential

Fouquet-Métivier [2022Fouquet-Métivier] improved the CALPHAD model published by Gotcu-Freis in 2011. A comparison with the existing experimental oxygen potential data is presented in Figure 7.

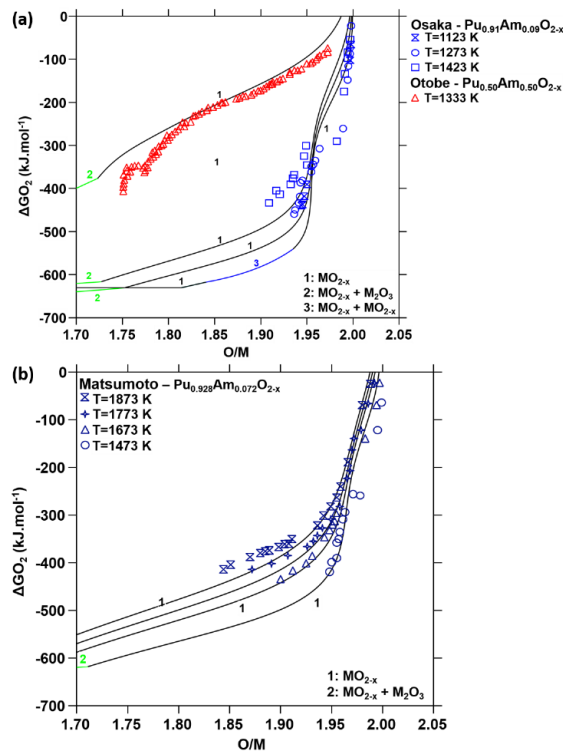


Figure 7 Oxygen potential data calculated using the updated model, compared to experimental data of (a) Osaka et al. and Otake et al. and (b) Matsumoto et al. (Figure 6-17 of PhD thesis by [2022Fouquet-Métivier]).

Fouquet-Métivier [2022Fouquet-Métivier] performed oxygen potential measurements using TGA on  $Pu_{0.77}Am_{0.23}O_{2-x}$  at 1673 K. The author compared the results to the thermodynamic model of Gotcu-Freis [2011Gotcu-Freis] and to her own model [2022Fouquet-Métivier] below. The models tend to underestimate the oxygen potential data for this composition.

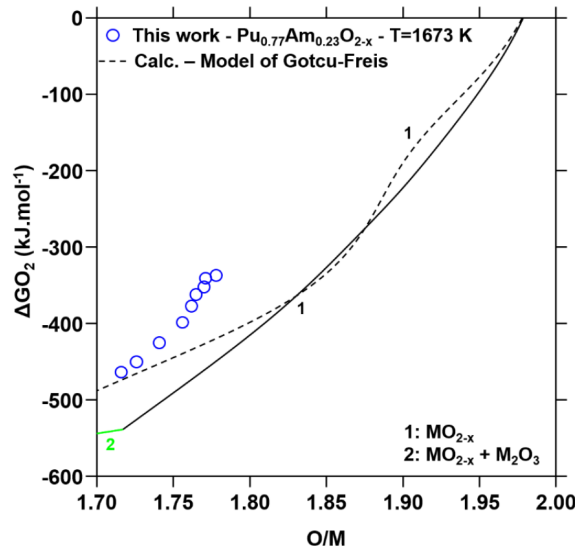


Figure 8 Calculated oxygen potentials for  $\text{Pu}_{0.77}\text{Am}_{0.23}\text{O}_{2-x}$ , compared to the experimental values and the model of Gotcu-Freis et al. (Figure 6-21 of PhD thesis by [2022Fouquet-Métivier]).

### • Phase diagram

The phase diagram data are very scarce on the Pu-Am-O system. Moreover the phase equilibria in this ternary system are quite complex due to the existence of intermediate oxide compounds between the sesquioxides and the dioxides in both Pu-O and Am-O binary systems.

Miwa et al. [2007Miwa] measured phase diagram data in  $\text{Pu}_{0.91}\text{Am}_{0.09}\text{O}_{2-x}$  region using DTA and x-ray diffraction. However there are no detailed information in [2007Miwa]. The CALPHAD model of Fouquet-Métivier [2022Fouquet-Métivier] is compared to the experimental data in Figure 9. Figure 9 is an isopleth section of  $\text{Pu}_{0.91}\text{Am}_{0.09}\text{O}_{2-x}$ , compared to the experiments of Miwa et al. [2007Miwa].

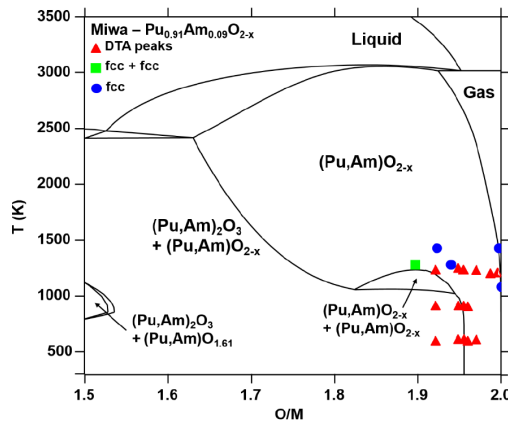


Figure 9 Isopleth section of  $\text{Pu}_{0.91}\text{Am}_{0.09}\text{O}_{2-x}$ , compared to the experiments of Miwa et al. [2007Miwa]. (Figure 6-16 of PhD thesis by [2022Fouquet-Métivier]).

Fouquet-Métivier [2022Fouquet-Métivier] studied the phase equilibria in three samples with 20, 50 and 80% Am using HT-XRD. The identification of the phases was very tricky and in most of the cases impossible. Only phase equilibria could be deduced in the sample containing 20% Am as shown in the calculated phase diagram using the CALPHAD model of Fouquet-Métivier [2022Fouquet-Métivier] in Figure 10. A two phase region between the sesquioxide and the dioxide was highlighted. A tentative isothermal section calculated at 1273 K is also shown in Figure 11.

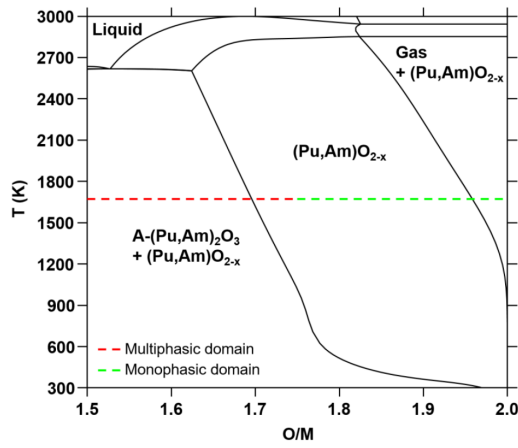


Figure 10 Isoleth section for  $\text{Pu}_{0.77}\text{Am}_{0.23}\text{O}_{2-x}$  compared to the domains evidenced by HT-XRD and TGA for the Pu/Am 80/20 sample (Figure 6-22 of PhD thesis by [2022Fouquet-Métivier]).

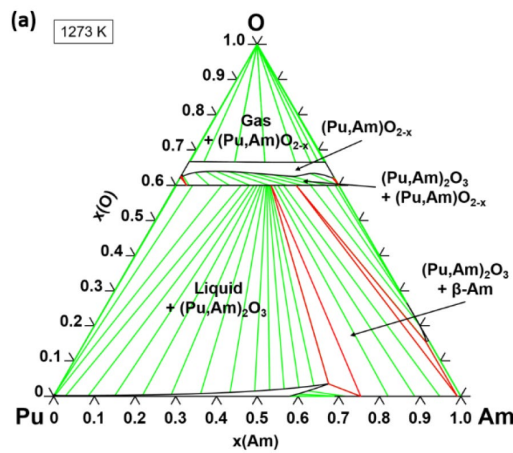


Figure 11 Tentative isothermal section of the Pu-Am-O system at 1273 K.

New phase diagram measurements are mandatory to improve the knowledge and the modelling on this system.

### 3 Experimental methods

#### 3.1 Sample synthesis

$\text{NpO}_2$ ,  $\text{UO}_2$  or  $\text{PuO}_2$  were mixed in the appropriate stoichiometric ratios and calcined under argon.

Table 2 summarizes the parameters of the calcination for each sample. The resulting powders were subsequently pressed (500 MPa) into pellets, after which the pellets were sintered. Sintering conditions are listed in

Table 2.

| Type of sample                                                         | Calcination conditions                             | Sintering conditions                                              |
|------------------------------------------------------------------------|----------------------------------------------------|-------------------------------------------------------------------|
| $\text{U}_{1-y}\text{Np}_y\text{O}_{2\pm x}$<br>y: 0.20, 0.50 and 0.75 | 4h at 800°C under Ar/H <sub>2</sub>                | 6h at 1650°C under Ar/H <sub>2</sub>                              |
| $\text{U}_{1-y}\text{Np}_y\text{O}_{2\pm x}$<br>y: 0.01 and 0.05       | 1h at 80°C then 1h at 600°C with a ramp of 100°C/h | 4 h at 1700°C under Ar/H <sub>2</sub> + 100 ppm H <sub>2</sub> O  |
| $\text{Pu}_{1-z}\text{Np}_z\text{O}_2$<br>z: 0.30 and 0.69             | 1h at 80°C then 1h at 600°C with a ramp of 100°C/h | 4 h at 1700°C under Ar/H <sub>2</sub> + 1200 ppm H <sub>2</sub> O |

Table 2 Parameters of calcination and sintering for each sample

Table 3 gives an overview of the synthesized compositions, and the corresponding characterizations.

| Type of sample          | y or z          | Characterizations                |
|-------------------------|-----------------|----------------------------------|
| $U_{1-y}Np_yO_{2\pm x}$ | 0.20 and 0.75   | Drop calorimetry                 |
|                         | 0.01 and 0.05   | Laser heating, laser flash       |
|                         | 0.03            | Laser flash                      |
|                         | 0.50            | KEMS                             |
| $Pu_{1-z}Np_zO_2$       | 0.30* and 0.69* | Laser heating, KEMS, EPMA, Raman |

Table 3 Summary of the different compositions prepared and characterizations performed. \* values determined by ICP-MS

### 3.2 ICP-MS

ICP-MS measurements were performed with a nuclearised Element2 instrument (Thermo Scientific<sup>®</sup>) equipped with Ni cones, a cyclonic spray chamber and a self-aspirating PFA nebulizer. [2005Walker], [2013Krachler] and [2014Krachler] provide more information on the technique. Samples were prepared by dissolving approximately 5 mg of (Pu,Np)O<sub>2</sub> in a solution of HNO<sub>3</sub>.

### 3.3 X-Ray Diffraction (XRD)

Room-temperature XRD measurements were carried out with a BRUKER D8 diffractometer with Bragg-Brentano geometry implemented in a glove-box. The X-ray beam is supplied by a conventional Cu radiation tube source (40KeV, 40 mA).

### 3.4 Raman spectroscopy

Raman spectroscopy measurements were carried out using a Jobin-Yvon<sup>®</sup> T64000 spectrometer. Measurements were performed with 2 lasers: a diode laser ( $\lambda = 532$  nm) and a Kr+ Coherent<sup>®</sup> laser ( $\lambda = 647$  nm). The laser beams were focused on the sample though a long focal distance objective with 50x magnification. The laser spot size on the samples was of the order of 1  $\mu\text{m}^2$ . The calibration was done routinely by measuring the Raman spectrum of monocrystalline Si. The measurements were performed on  $Pu_{1-z}Np_zO_{2\pm x}$  (z: 0.30 and 0.69). A specific sample holder was used due to the radioactivity of the samples. The description of the instrument design is available in [2015Naji].

### 3.5 Drop calorimetry

Enthalpy increment measurements were carried out using a nuclearized Setaram Multi Detector High Temperature Calorimeter (MDHTC 96 type) operating in drop mode. More details on the instrument are provided in [2011Beneš]. Calibration of the calorimeter temperature scale was performed using high purity ( $\geq 99.95\%$ ) standard materials (Au, Pb, Al, Sn, Ag and In).

### 3.6 Low temperature heat capacity

Low-temperature heat capacity measurements were performed using thermal relaxation calorimetry with a Physical Property Measurement System (PPMS) instrument at applied magnetic fields ( $B=0, 1, 7, 10$  and  $14$  T) in the temperature ranges  $T=(7.8-288)$  K for  $Pu_{0.70}Np_{0.30}O_{2\pm x}$  and  $T=(3.5-289)$  K for  $Pu_{0.31}Np_{0.69}O_{2\pm x}$ . Details of the apparatus are available in [2022Griveau].

### 3.7 Laser heating

Laser heating experiments were performed to determine melting temperatures using a set-up developed and installed at JRC Karlsruhe. Details of the experimental set-up can be found in several publications [2005Manara], [2008Manara], [2011aDe Bruycker], [2011bDe Bruycker], [2014Böhler].

Table 4 shows the experimental conditions for the measurements on (U,Np)O<sub>2±x</sub> and (Pu,Np)O<sub>2±x</sub>.

|                                | (U,Np)O <sub>2±x</sub> | (Pu,Np)O <sub>2±x</sub> |              |
|--------------------------------|------------------------|-------------------------|--------------|
| Atmosphere                     | Air                    | Argon                   | Air          |
| Sample size                    | Disc (D~5mm)           | quarter disc (D~4 mm)   | Disc (D~5mm) |
| Diameter of the melted surface | 4.8 mm                 | 2 mm                    | 4.8 mm       |

Table 4 Experimental conditions as a function of sample type

### 3.8 Electron Probe MicroAnalyzer (EPMA)

EPMA analyses for Np, Pu and O were carried out with a shielded Cameca SX100. The experimental conditions were 15 kV for the acceleration potential. More information about the technique are available in [2017Pöml], [2018Vigier] and [2023Colle], [2017Pöml]. (Pu,Np)O<sub>2±x</sub> samples were examined by EPMA before and after the laser heating experiments. For that purpose, the samples were embedded in epoxy resin, polished and coated with a 20 nm conductive layer of aluminium to ensure electrical conductivity. PuO<sub>2</sub> and NpO<sub>2</sub> samples were used as reference materials.

## 4 Atomic scale modelling methods

### 4.1 The Cooper-Rushton-Grimes empirical interatomic potential

The Cooper-Rushton-Grimes (CRG) potential [2014Cooper] combines two types of interactions to calculate the potential energy of atoms: pair interactions and N-body interactions in the Embedded Atom Method (EAM) formalism [1983Daw,1984Daw]. The potential energy of an atom  $i$  is written as:

$$E_i = \frac{1}{2} \sum_{j \neq i} \varphi_{\alpha\beta}(r_{ij}) - G_\alpha \sqrt{\sum_{j \neq i} \sigma_\beta(r_{ij})} \quad (1)$$

Where,  $\alpha$  and  $\beta$  correspond to the type of the chemical species. The pair potential  $\varphi_{\alpha\beta}(r_{ij})$  is the sum of the long-range Coulomb potential  $\varphi_C(r_{ij})$ , as well as short-range potentials in the Morse [1929Morse] and Buckingham [1938Buckingham] formalisms, noted  $\varphi_M(r_{ij})$  and  $\varphi_B(r_{ij})$ , respectively. An 11 Å cut-off range is used so that interactions between distant atoms are not computed.

$$\varphi_{\alpha\beta}(r_{ij}) = \varphi_C(r_{ij}) + \varphi_M(r_{ij}) + \varphi_B(r_{ij}) \quad (2)$$

$$\varphi_C(r_{ij}) = \frac{Q_\alpha Q_\beta}{4\pi\epsilon_0 r_{ij}} \quad (3)$$

$$\varphi_M(r_{ij}) = D_{\alpha\beta} \left[ \exp\left(-2\gamma_{\alpha\beta}(r_{ij} - r_0)\right) - 2 \exp\left(-\gamma_{\alpha\beta}(r_{ij} - r_0)\right) \right] \quad (4)$$

$$\varphi_B(r_{ij}) = A_{\alpha\beta} \exp\left(\frac{-r_{ij}}{\rho_{\alpha\beta}}\right) - \frac{C_{\alpha\beta}}{r_{ij}^6} \quad (5)$$

An EAM term is added to take into account that the environment around atoms modifies slightly the pairwise interaction between them. This is required to reproduce the Cauchy violation ( $C_{12} \neq C_{44}$ ) observed for actinide oxides.  $\sigma_\beta(r_{ij})$  is defined as:

$$\sigma_\beta(r_{ij}) = \left(\frac{\eta_\beta}{r_{ij}^8}\right) \frac{1}{2} \{1 + \text{erf}[20(r_{ij} - 1.5)]\} \quad (6)$$

An error function with a 1.5 Å cut-off range is added to prevent EAM forces from overcoming short-range repulsion, which would result in non-physical forces.  $A_{\alpha\beta}$ ,  $\rho_{\alpha\beta}$ ,  $C_{\alpha\beta}$ ,  $D_{\alpha\beta}$ ,  $\gamma_{\alpha\beta}$ ,  $r_0$ ,  $\eta_\beta$  and  $G_\alpha$  are the parameters fitted for the potential. The first part of this work was the optimization of terms for the  $\text{Am}^{3+}$  and  $\text{U}^{5+}$  oxidation states present in actinide oxides to allow for the systematic study of their properties using classical molecular dynamics. The optimization and validation of the potential terms have been published [2023Labonne].

## 4.2 Simulation techniques

The CRG potential can be used to systematically determine the structural and thermodynamic properties of actinide oxides using several simulation techniques. In order to obtain the structural and thermodynamic properties as a function of temperature, the Heat Until it Melts (HUM) method [1987Carnevali,1991Ercolessi] is commonly used. It consists in a progressive increase of the simulation temperature at a constant pressure. Properties such as the lattice parameter and enthalpy content as well as the simulation temperature and pressure are extracted over all the duration of the simulation. From these basic data, other properties can be calculated, such as the density, thermal expansion coefficient, specific heat capacity, enthalpy of mixing and fusion enthalpy.

Although melting can be observed using the HUM method, the transition temperature is significantly overestimated due to finite-size effects as well as to the relatively short duration of the simulation. Thus, another technique is used specifically to estimate the melting temperature, though the general case is the existence of a solidus and a liquidus. The Moving Interface (MI) method [1994Morris,1994Belonoshko] uses a supercell which is split between a solid part and a liquid part of the same composition. The temperature and pressure are then imposed on the entire cell, and the position of the solid/liquid interface is monitored. Depending on the movement of the interface, and thus on the relative amount of atoms in each phase, one can conclude whether the simulation was performed above or below the melting temperature. By performing several simulations at different final temperatures, the pseudo-melting temperature can be bounded.

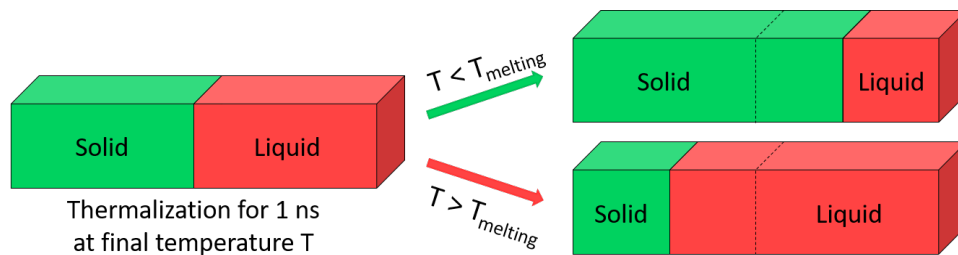


Figure 12 Illustration of the Moving Interface Method

## 5 Experimental investigation of the U-Np-O system

### 5.1 Heat capacity determination at high temperatures

Enthalpy increment data on  $\text{U}_{1-y}\text{Np}_y\text{O}_{2\pm x}$  (with  $y$ : 0.20 and 0.75) were previously acquired at JRC in 2015 (unpublished data) using drop calorimetry. The aim of the work performed in PATRICIA was to

complement the data already collected by performing measurements over a wider range of temperatures to improve the knowledge on the heat capacity of these two mixed oxides, which can be obtained by deriving the enthalpy increment data. The data obtained in this work and those previously acquired at JRC are shown in Figure 13, as well as the enthalpy functions of  $\text{UO}_2$  and  $\text{NpO}_2$  [2014Konings] for comparison. This figure shows that the enthalpy increments of the two mixed oxides and those of the two end-members  $\text{UO}_2$  and  $\text{NpO}_2$  follow a similar trend with temperature.

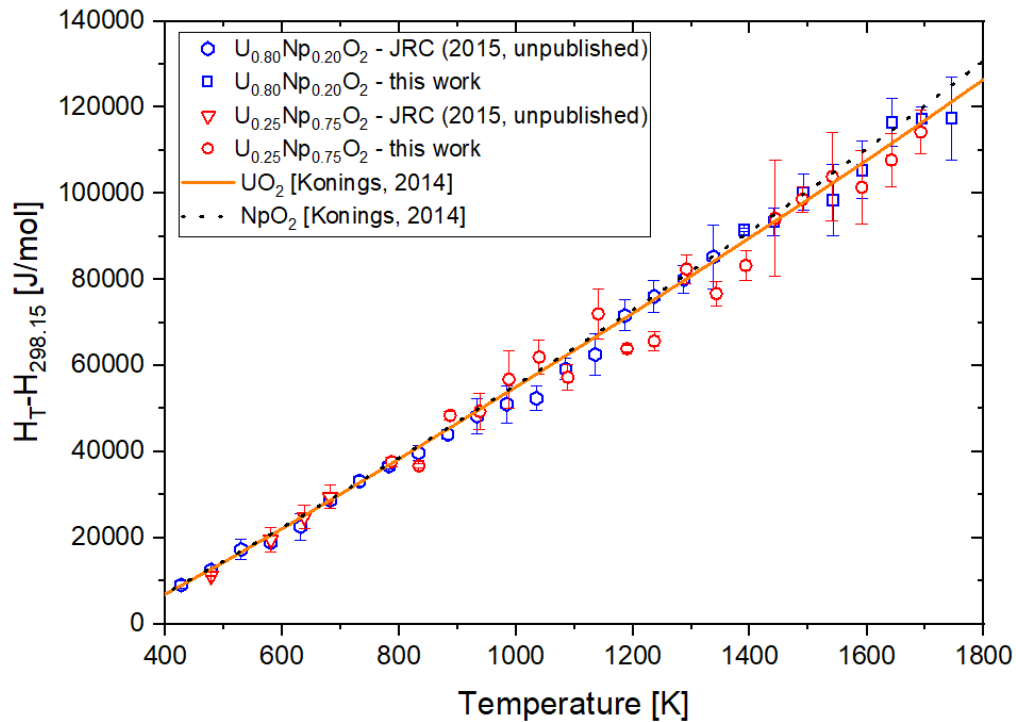


Figure 13 Enthalpy increments of  $\text{U}_{1-y}\text{Np}_y\text{O}_{2\pm x}$  ( $y$ : 0.20 and 0.75) obtained in this work compared with the data obtained previously at JRC (unpublished data) (blue and red), and the data of  $\text{UO}_2$  (orange) and  $\text{NpO}_2$  (black).

The heat capacity functions for  $\text{U}_{1-y}\text{Np}_y\text{O}_{2\pm x}$  (with  $y$ : 0.20 and 0.75) were subsequently derived using a linear regression of all the enthalpy increment data (those previously collected at JRC in 2015, and those obtained in this work). For the fit, the Maier-Kelley polynomial relation was used [1932Maier]:

$$C_p = a + b \cdot T + c \cdot T^{-2}$$

where  $T$  is the temperature in Kelvin,  $a$ ,  $b$  and  $c$  are the parameters to be optimized.

Moreover, the fit was constrained to match  $C_p$  values measured by thermal relaxation calorimetry at low temperatures (between 130 and 270 K) (unpublished data JRC), as well as the derived  $C_p$  value at 298.15 K (itself determined using the low-temperature data).

Table 5 summarizes the constraints applied, and optimized parameters of the fits.

In Figure 14, our results are compared with the heat capacity of  $\text{UO}_2$  and  $\text{NpO}_2$  presented in [2014Konings]. The curve obtained for  $\text{U}_{0.80}\text{Np}_{0.20}\text{O}_{2\pm x}$  follows the trend of  $\text{UO}_2$  until 1300 K. Above this temperature, the heat capacity is lower than  $\text{UO}_2$ . This difference can be explained by the fact that for the mixed oxide, the influence of defects (Frenkel pair formation) is not taken into account. On the contrary, the heat capacity of  $\text{U}_{0.25}\text{Np}_{0.75}\text{O}_{2\pm x}$  does not follow the expected trend compared to  $\text{NpO}_2$  or  $\text{UO}_2$ . The  $C_p$  values are lower until 900 K then higher than the two end-members. Further optimization of parameters  $a$ ,  $b$  and  $c$  may be necessary for this composition.

|                                                     | $C_{p298.15}^*$<br>[J·K <sup>-1</sup> ·mol <sup>-1</sup> ] | a<br>[J·K <sup>-1</sup> ·mol <sup>-1</sup> ] | b·10 <sup>-3</sup><br>[J·K <sup>-2</sup> ·mol <sup>-1</sup> ] | c·10 <sup>6</sup><br>[J·K·mol <sup>-1</sup> ] |
|-----------------------------------------------------|------------------------------------------------------------|----------------------------------------------|---------------------------------------------------------------|-----------------------------------------------|
| U <sub>0.80</sub> Np <sub>0.20</sub> O <sub>2</sub> | 63.99                                                      | 79±11                                        | 7±1                                                           | -1.500±0.0848                                 |
| U <sub>0.25</sub> Np <sub>0.75</sub> O <sub>2</sub> | 64.23                                                      | 59±5                                         | 29±2                                                          | -0.281±0.008                                  |

Table 5 Constraints and parameters for the fit of the high temperature heat capacity according to a Maier-Kelley polynomial. \*Value determined by thermal-relaxation calorimetry (JRC, unpublished data).

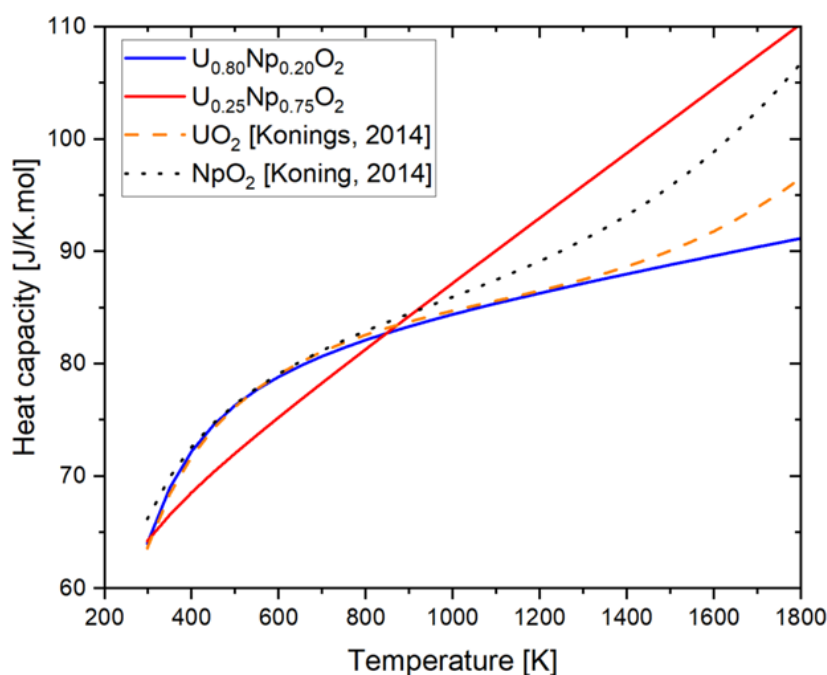


Figure 14 Heat capacity functions of U<sub>0.80</sub>Np<sub>0.20</sub>O<sub>2</sub> and U<sub>0.25</sub>Np<sub>0.75</sub>O<sub>2</sub> derived from the enthalpy increments obtained by drop calorimetry compared with the heat capacities of UO<sub>2</sub> and NpO<sub>2</sub> [2014Konings].

## 5.2 Melting behaviour

### 5.2.1 Melting measurements under air

Figure 15 and Figure 16 show the thermograms obtained under air for U<sub>0.99</sub>Np<sub>0.01</sub>O<sub>2±x</sub> and U<sub>0.95</sub>Np<sub>0.05</sub>O<sub>2±x</sub>, respectively. Due to technical problems, no values were obtained for the two first shots for the first sample of U<sub>0.95</sub>Np<sub>0.05</sub>O<sub>2±x</sub>. Moreover, the thermogram for the second shot of the third sample of U<sub>0.95</sub>Np<sub>0.05</sub>O<sub>2±x</sub> is not complete, as the sample broke during measurement. Several conclusions can be drawn from these results. First, the solidification temperatures of the first shots are similar for both compositions and are close to those of UO<sub>2</sub>. Second, the temperatures obtained for subsequent shots are lower, which is probably due to the oxidation of the molten zone. Finally, for U<sub>0.99</sub>Np<sub>0.01</sub>O<sub>2±x</sub>, two or three thermal arrests are observed during cooling. This could be related to a segregation of U and Np in oxidizing conditions. SEM-EDX measurements are in progress and may help to clarify the phenomena involved.

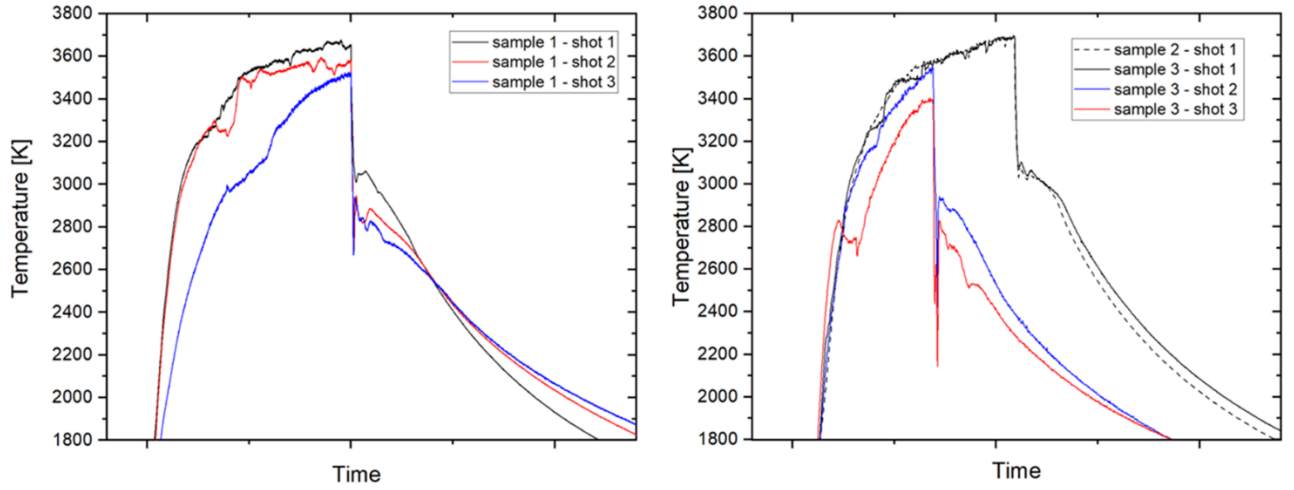


Figure 15 Thermograms of three different  $U_{0.99}Np_{0.01}O_{2\pm x}$  samples

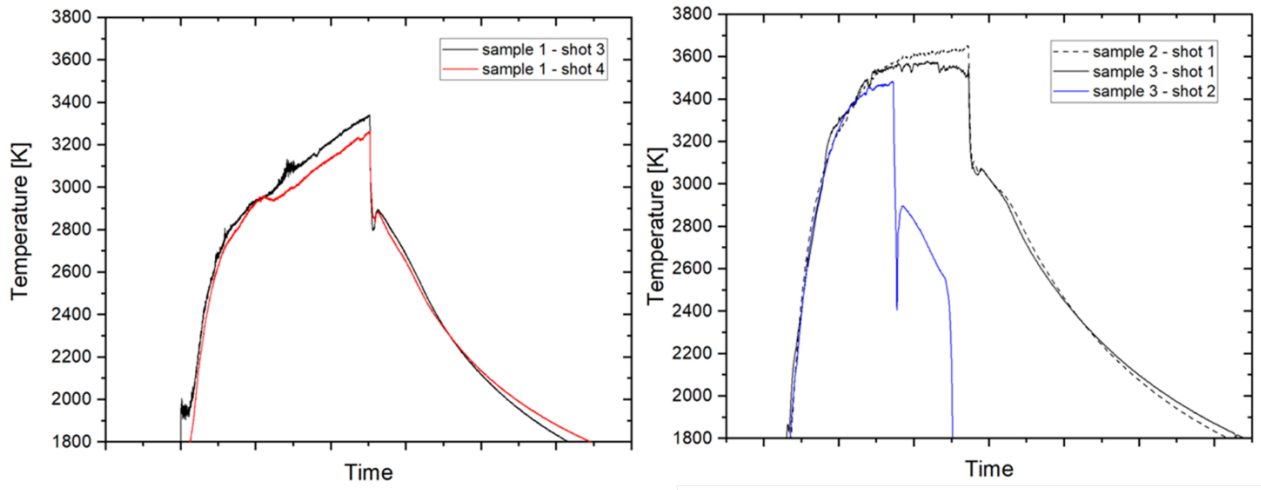


Figure 16 Thermograms of three different  $U_{0.95}Np_{0.05}O_{2\pm x}$  samples

### 5.2.2 Melting measurements under argon

Figure 17 shows the recorded solidification temperatures of the  $U_{0.97}Np_{0.03}O_{2\pm x}$  sample, along with the corresponding absolute expanded uncertainty bands. The solidification temperature values for  $UO_2$  and  $NpO_2$  from [2015Chollet] are also given for comparison. The value measured in this study is in agreement with that determined by Chollet et al. in the same atmosphere ( $U_{0.98}Np_{0.02}O_{2\pm x}$ :  $3094 \pm 30$  K and  $U_{0.95}Np_{0.05}O_{2\pm x}$ :  $3129 \pm 83$  K).

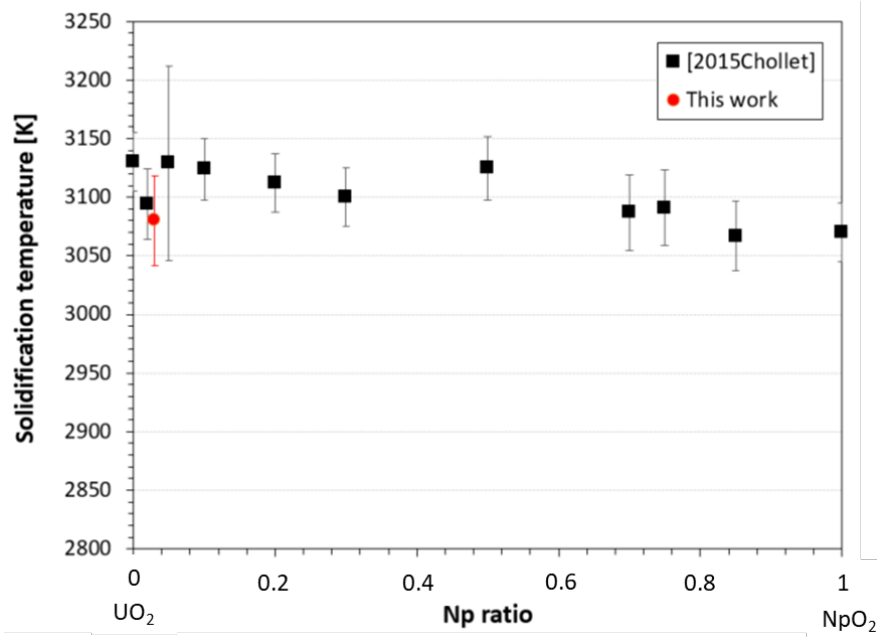


Figure 17 Solidification temperature for  $U_{0.97}Np_{0.03}O_{2\pm x}$  measured under Ar (in red) compared with the solidification temperatures from [2015Chollet] (in black).

## 6 Experimental investigation of the Pu-Np-O system

### 6.1 Structural characterization

Two mixed oxides  $Pu_{1-z}Np_zO_2$  (with  $z=0.30$  and  $0.69$ ) were synthesized and characterized using XRD at room temperature in order to check the quality and purity of the resulting powder. The refined lattice parameters for  $Pu_{0.31}Np_{0.69}O_2$  are  $a = 5.4077 \text{ \AA}$  and for  $Pu_{0.70}Np_{0.30}O_2$  are  $a = 5.4213 \text{ \AA}$ , in good agreement with Vegard's law between  $PuO_2$  and  $NpO_2$  (Figure 17), confirming the solid solution and the stoichiometry of the synthesized compounds.

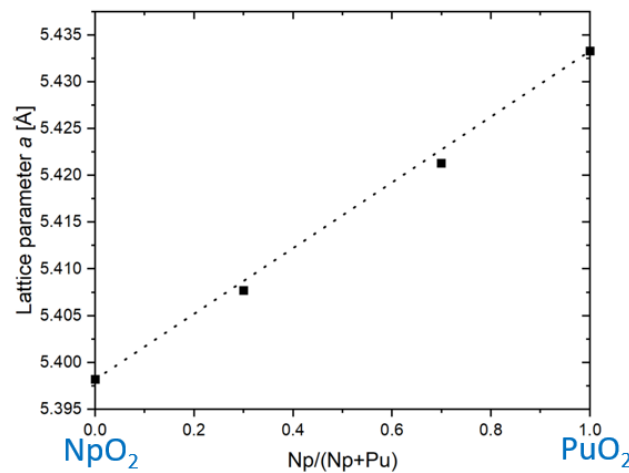


Figure 18 XRD patterns  $Pu_{0.31}Np_{0.69}O_2$  (left) and  $Pu_{0.70}Np_{0.30}O_2$  (right).

### 6.2 Raman measurements

Figure 19 shows the Raman spectra of the solid solutions  $Pu_{1-z}Np_zO_{2\pm x}$  (with  $z=0.30$  and  $0.69$ ) recorded with two excitation sources (532 nm and 647 nm), compared to reference spectra of  $NpO_2$  and  $PuO_2$ .

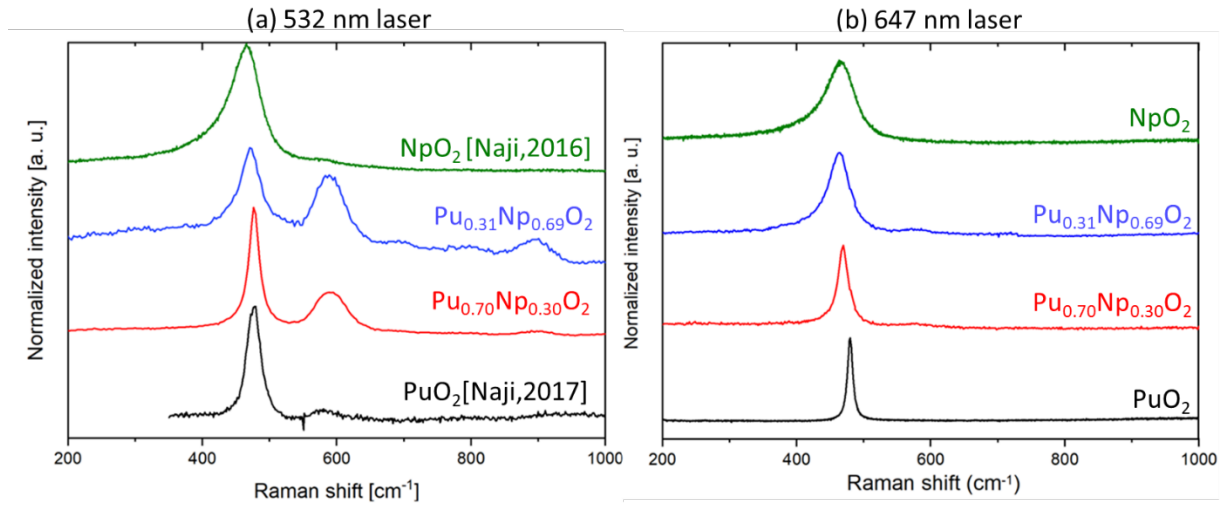


Figure 19 Raman spectra of  $\text{Pu}_{1-x}\text{Np}_x\text{O}_2$  ( $x=0.30$  in red and  $0.69$  in blue) recorded with a  $532\text{ nm}$  (a) and  $647\text{ nm}$  (b) excitation source, compared with 2 references  $\text{NpO}_2$  (green) and  $\text{PuO}_2$  (black). The  $\text{NpO}_2$  and  $\text{PuO}_2$  of (a) were acquired with a  $514\text{ nm}$  excitation source and are taken from [2016Naji] and [2017Naji], respectively.

First, it should be noted that all of the spectra collected at different locations in the samples are identical, confirming the homogeneity of the mixed oxide samples. The mixed oxide spectra show three main features that are well-known for fluorites: a  $T_{2g}$  peak at  $471\text{ cm}^{-1}$  for  $x=0.70$  and  $476\text{ cm}^{-1}$  for  $x=0.30$ , which dominates for two excitation energies, a  $1\text{LO}$  peak around  $590\text{ cm}^{-1}$ , and a  $2\text{LO}$  peak around  $1160\text{ cm}^{-1}$  for the two compositions. Another band is observed around  $895\text{ cm}^{-1}$  that is not yet assigned. Medyk et al. [2020Medyk] also observed a band around  $900\text{ cm}^{-1}$ , and assumed it could correspond to the second harmonic of the  $T_{2g}$  line.

It is also observed that the position of the  $T_{2g}$  peak shifts as function of the Np content: its wavelength becomes lower when the Np content increases. Differences in the shape of the  $T_{2g}$  peak can also be noticed: for a higher content of Np the peak is larger and more asymmetrical. Previous studies on  $\text{NpO}_2$  have reported that the  $T_{2g}$  peak in this oxide was asymmetric in the lower energy part [1990Begun, 2012Sarsfield, 2016Naji]. Thus, this feature seems to be a characteristic of the  $\text{NpO}_2$  lattice.

Finally, the bands around  $590\text{ cm}^{-1}$ ,  $895\text{ cm}^{-1}$  and  $1160\text{ cm}^{-1}$  are more pronounced for the sample with 69% Np. This could be explained by higher lattice distortions in this sample (non-perfect fluorite structure), caused by the partial substitution of Np atoms by Pu atoms [2017Elorrieta]. Furthermore, these three last bands are more visible with the  $532\text{ nm}$  laser. It was shown by Villa-Aleman et al. that this laser can provide a better differentiation among the defect bands [2019Villa-Alaman].

### 6.3 Heat capacity determination at low temperature

The measured low temperature heat capacity data of  $\text{Pu}_{0.70}\text{Np}_{0.30}\text{O}_{2\pm x}$  and  $\text{Pu}_{0.31}\text{Np}_{0.69}\text{O}_{2\pm x}$  are shown in Figure 20. Based on these data, values of heat capacities at  $298.15\text{ K}$  are determined to be:  $72.74\text{ J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$  for  $\text{Pu}_{0.70}\text{Np}_{0.30}\text{O}_{2\pm x}$  and  $69.79\text{ J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$   $\text{Pu}_{0.31}\text{Np}_{0.69}\text{O}_{2\pm x}$ . An anomaly is observed around  $14\text{ K}$  for  $\text{Pu}_{0.31}\text{Np}_{0.69}\text{O}_{2\pm x}$ , which can be related to the rank 5 triakontadipolar order observed in  $\text{NpO}_2$  [2006Santini].

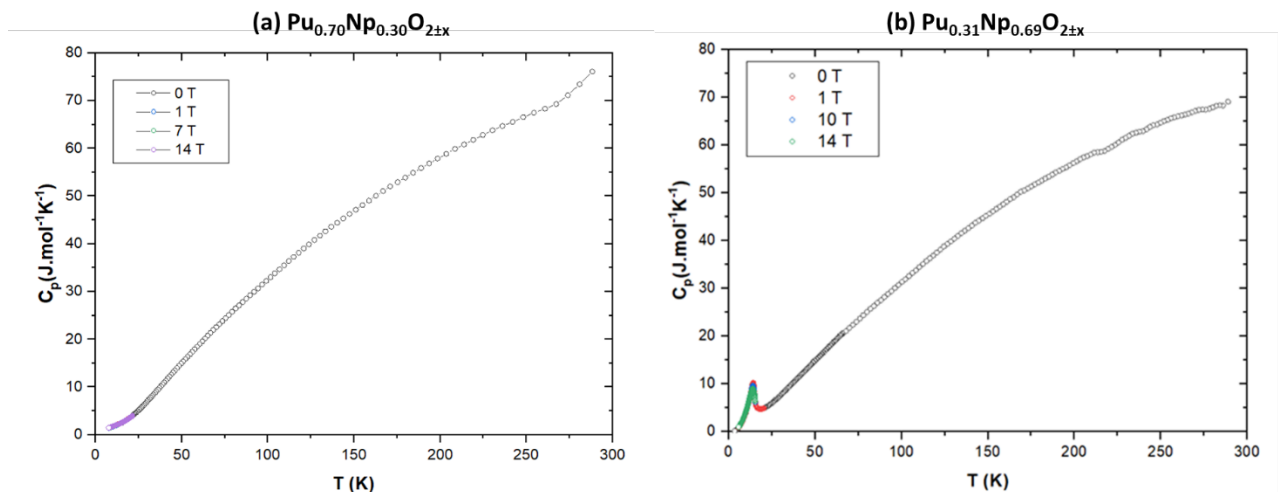


Figure 20 Heat capacity of  $\text{Pu}_{1-z}\text{Np}_z\text{O}_{2\pm x}$  (with  $z=0.30$  and  $0.69$ ) measured with different magnetic fields

## 6.4 Melting behaviour

### 6.4.1 Measurements under air

Figure 21 shows the recorded solidification temperatures for the  $\text{Pu}_{0.7}\text{Np}_{0.3}\text{O}_{2\pm x}$  sample, along with the corresponding absolute expanded uncertainty bands. SEM-EDX characterization of the molten area is underway to obtain information on the evolution of the microstructure and composition of the sample after the laser shots.

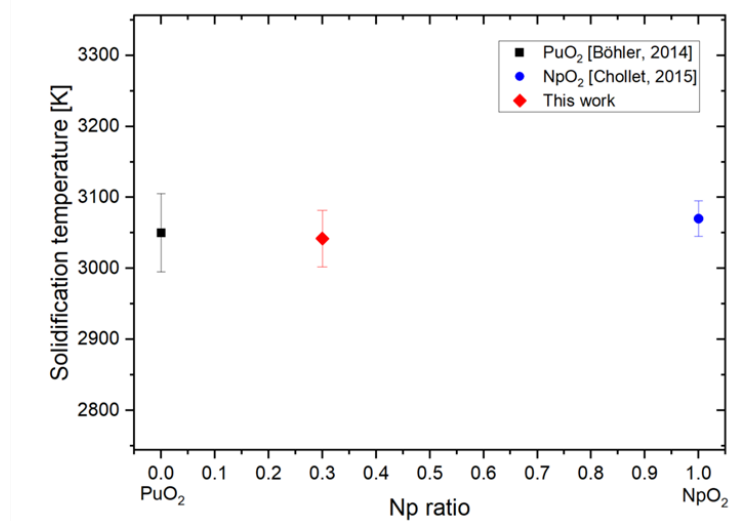


Figure 21 Solidification temperature for the  $(\text{Pu},\text{Np})\text{O}_2$  mixed oxide samples measured under air in red. The solidification temperature of  $\text{NpO}_2$  measured under air by [205Chollet] is shown in blue.

### 6.4.2 Measurements under argon

Melting measurements were also performed under argon atmosphere on quarter of discs. Because of the small size of the laser spot, only the temperatures determined by the spectropyrrometer are considered reliable, and are thus taken into account.

#### Solidification temperatures

Figure 22 shows the recorded solidification temperatures for the compositions investigated ( $3051 \pm 40$  K for  $\text{Pu}_{0.70}\text{Np}_{0.30}\text{O}_2$  and  $3088 \pm 35$  K for  $\text{Pu}_{0.31}\text{Np}_{0.69}\text{O}_2$ ), along with the corresponding absolute expanded uncertainty bands. These are obtained by combining the instrumental uncertainty (estimated to be  $\pm 25$  K at 3100 K) with the standard deviation for each composition.

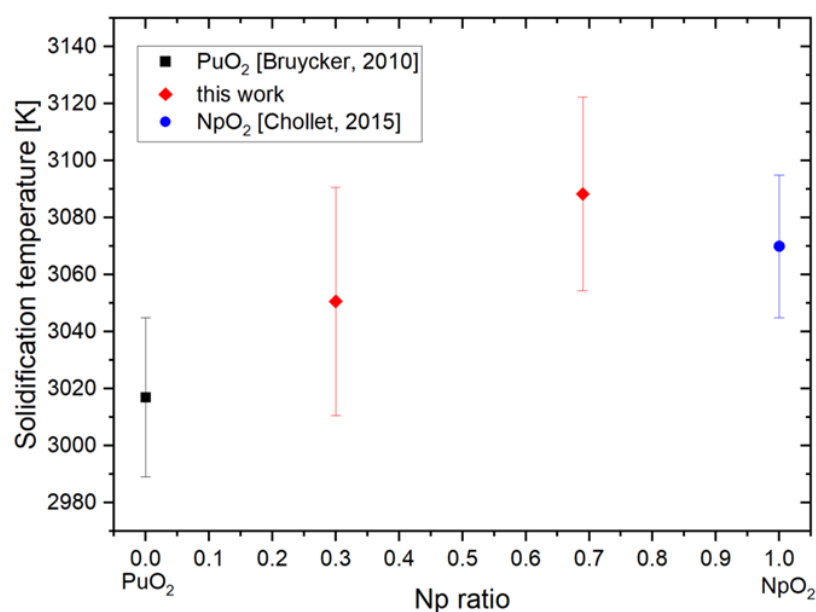


Figure 22 The solidification temperature for the (Pu,Np)O<sub>2</sub> mixed oxide samples measured under argon in red.

### Evolution of the oxygen-to-metal (O/M) ratio

Two oxygen gauges (at the entrance and exit of the measurement chamber) allow us to determine the oxygen-to-metal ratio (O/M) after each shot. The assumption is made that the variation in the oxygen partial pressure measured during the experiments is directly related to changes in the O/M ratio of the sample. It is thus assumed that only the sample can react with the oxygen present in the chamber. Moreover, a ratio of 2.00 ratio before the measurements is assumed for the two compositions studied.

For both compositions, a reduction of the sample was observed during the measurements. Moreover it is observed that the shots 2 and 3 lead to a higher oxygen release compared to the first shot. The O/M ratio seems to stabilise around 1.95 after 3 shots for Pu<sub>0.70</sub>Np<sub>0.30</sub>O<sub>2</sub>, and 1.96 after 4 shots for Pu<sub>0.31</sub>Np<sub>0.69</sub>O<sub>2</sub>, respectively. Additional measurements should be done to confirm this result. It is also important to note that the O/M ratio is estimated here at room temperature after the shots, and may not be representative of the actual O/M ratio at which the melting occurs.

|                                                      | Shot                           | 1                     | 2                     | 3                     | 4                     | 5                     |
|------------------------------------------------------|--------------------------------|-----------------------|-----------------------|-----------------------|-----------------------|-----------------------|
| Pu <sub>0.70</sub> Np <sub>0.30</sub> O <sub>2</sub> | n(O <sub>release</sub> ) (mol) | 9.51x10 <sup>-8</sup> | 3.08x10 <sup>-7</sup> | 1.59x10 <sup>-7</sup> | 7.99x10 <sup>-8</sup> | 2.15x10 <sup>-8</sup> |
|                                                      | O/M ratio                      | 1.993                 | 1.969                 | 1.957                 | 1.951                 | 1.950                 |
| Pu <sub>0.31</sub> Np <sub>0.69</sub> O <sub>2</sub> | n(O <sub>release</sub> ) (mol) | 6.44x10 <sup>-8</sup> | 2.14x10 <sup>-7</sup> | 1.43x10 <sup>-7</sup> | 7.99x10 <sup>-7</sup> |                       |
|                                                      | O/M ratio                      | 1.995                 | 1.976                 | 1.968                 | 1.962                 |                       |

Table 6 Values of n(O<sub>release</sub>) and O/M ratio determined for each shot for Pu<sub>0.7</sub>Np<sub>0.3</sub>O<sub>2</sub> and Pu<sub>0.31</sub>Np<sub>0.69</sub>O<sub>2</sub> samples. The uncertainties on the calculated O/M are ± 0.005.

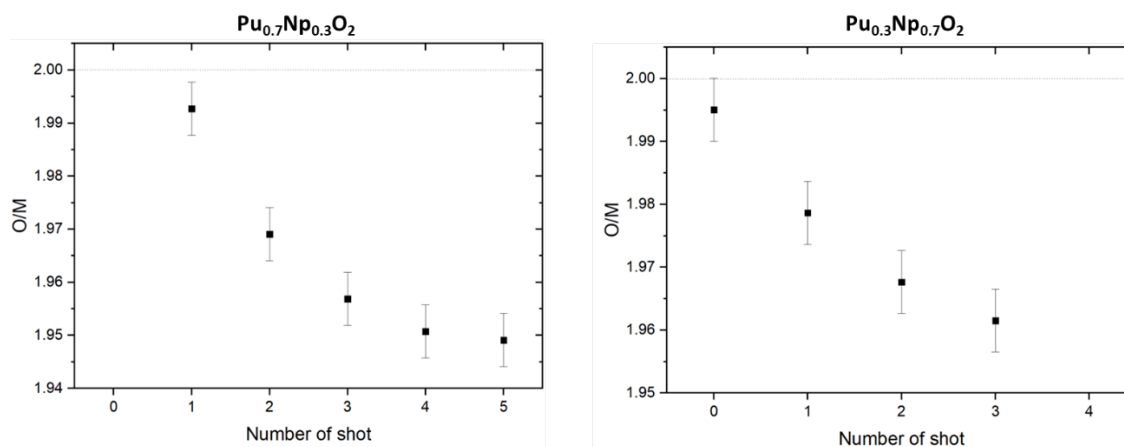


Figure 23 Evolution of the O/M ratio in function of the number of shots for both (Pu,Np)O<sub>2</sub> mixed oxide samples

## 6.5 Chemical characterization before and after melting

EPMA analyses were performed on the Pu<sub>0.70</sub>Np<sub>0.30</sub>O<sub>2</sub> and Pu<sub>0.31</sub>Np<sub>0.69</sub>O<sub>2</sub> samples as-synthesized and after laser heating measurements. Secondary electron (SE) images of these samples are shown in Figure 24 and Figure 25. The as-synthesized Pu<sub>0.70</sub>Np<sub>0.30</sub>O<sub>2</sub> sample exhibits many pores and cracks, as seen in Figure 24, while the as-synthesized Pu<sub>0.31</sub>Np<sub>0.69</sub>O<sub>2</sub> samples contains pores but only a few cracks (see Figure 25 (a)). During the sample preparations carried out in this work, it was observed that Pu<sub>0.70</sub>Np<sub>0.30</sub>O<sub>2</sub> samples were more brittle, which is in agreement with these observations. In Figure 25 (b), only a small part of the molten area of the Pu<sub>0.31</sub>Np<sub>0.69</sub>O<sub>2</sub> sample is visible. This zone has a higher density (indicated by a white circle). During laser heating measurements, the sample undergoes high thermal stress, which favours fracturing. Figure 26 shows a back scattering electron (BSE) image of Pu<sub>0.31</sub>Np<sub>0.69</sub>O<sub>2</sub> in the molten and unmolten zones. The grain size in the molten area is smaller (diameter: 2 – 10 μm) than in the unmolten area (diameter: 20 – 45 μm).

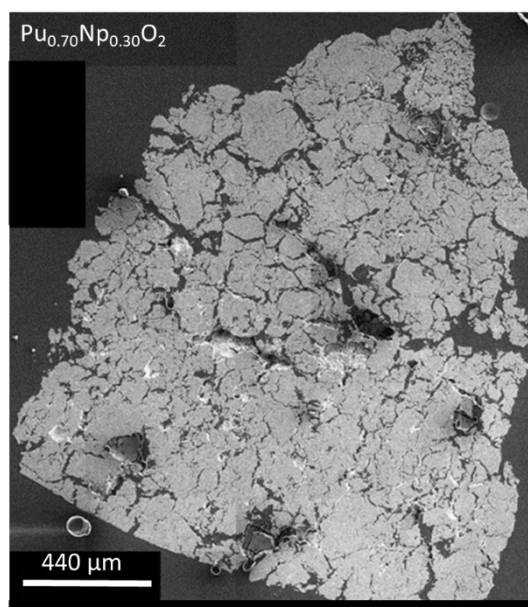


Figure 24 SE image of Pu<sub>0.70</sub>Np<sub>0.30</sub>O<sub>2</sub> sample as-synthesized

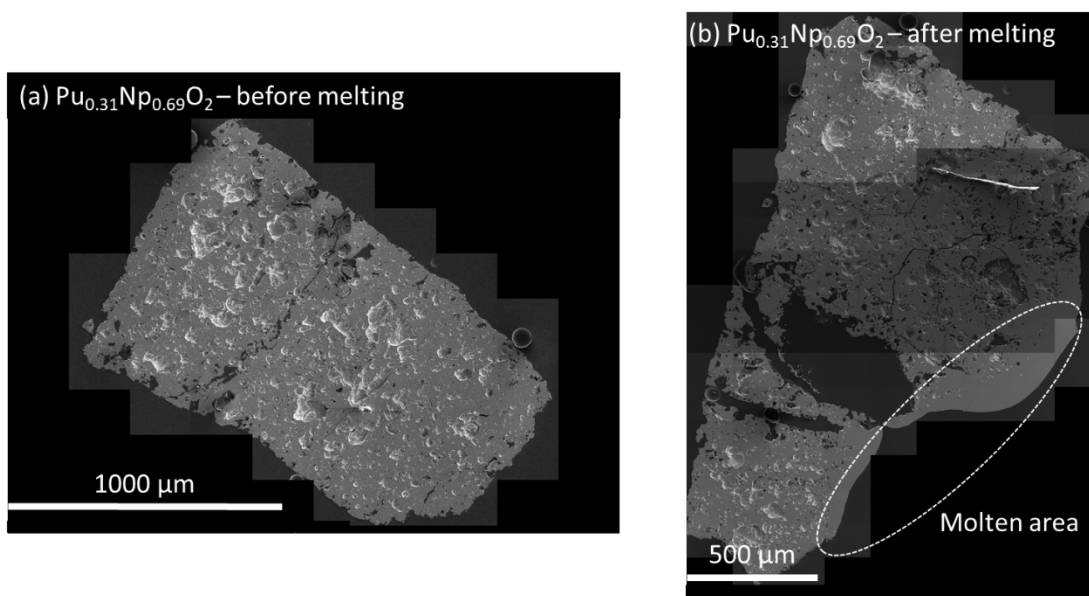


Figure 25 SE images of  $\text{Pu}_{0.31}\text{Np}_{0.69}\text{O}_2$  sample as-synthesized (a) and after the laser heating measurement (b)

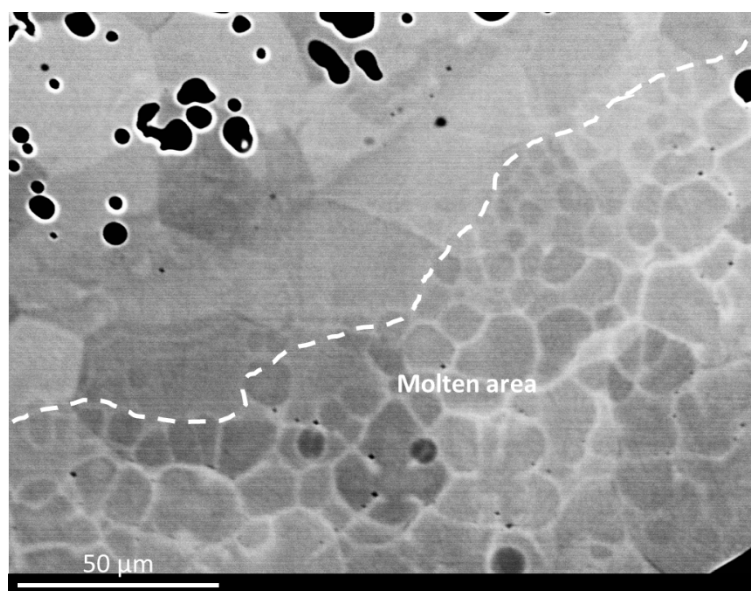


Figure 26 BSE Image of  $\text{Pu}_{0.31}\text{Np}_{0.69}\text{O}_2$  sample after laser heating measurement

Table 7 summarizes the results of quantitative EPMA in this study. For each sample, measurements were performed at various locations to check homogeneity. For the as-synthesized samples, the EPMA results confirm the ICP-MS measurements. The study of the molten area shows that this zone is homogenous and has the same composition as the unmolten part.

|                                                                  | Np at%         | Pu at%         | O at%          |
|------------------------------------------------------------------|----------------|----------------|----------------|
| $\text{Pu}_{0.70}\text{Np}_{0.30}\text{O}_2$ as-synthesized      | $10.0 \pm 0.4$ | $23.5 \pm 0.3$ | $66.5 \pm 0.2$ |
| $\text{Pu}_{0.31}\text{Np}_{0.69}\text{O}_2$ as-synthesized      | $23.0 \pm 0.3$ | $10.5 \pm 0.4$ | $66.5 \pm 0.2$ |
| $\text{Pu}_{0.70}\text{Np}_{0.30}\text{O}_2$ after laser heating | $23.3 \pm 0.2$ | $10.3 \pm 0.1$ | $66.4 \pm 0.1$ |

Table 7 summary table of Np and Pu results obtained by EPMA

The analysis showed no clear difference in oxygen content between melted and unmolten areas. This technique, however is not suitable for the oxygen analysis. XANES analysis is required to complete this

study and provide information on the oxidation states of uranium and plutonium, and thus the O/M ratio. Such measurements are planned at the ROBL beamline of the ESRF in February 2024.

## 7 Atomic scale modelling of the Am-U-O system

The CRG potential including terms for  $\text{Am}^{3+}$  and  $\text{U}^{5+}$ , described in section 4.1, was used in combination with the simulation techniques explained in section 4.2 to systematically determine the structural and thermodynamic properties of uranium-amerium mixed oxides for americium contents ranging from 0% ( $\text{UO}_2$ ) to 100% ( $\text{AmO}_{2-x}$ ) for O/M ratios comprised between 2.00 and 1.90. The maximum deviation from stoichiometry is limited by the americium content, as some cases would require the introduction of  $\text{U}^{3+}$  for which the potential interaction terms do not exist. All simulations were performed using the LAMMPS code [2022Thompson].

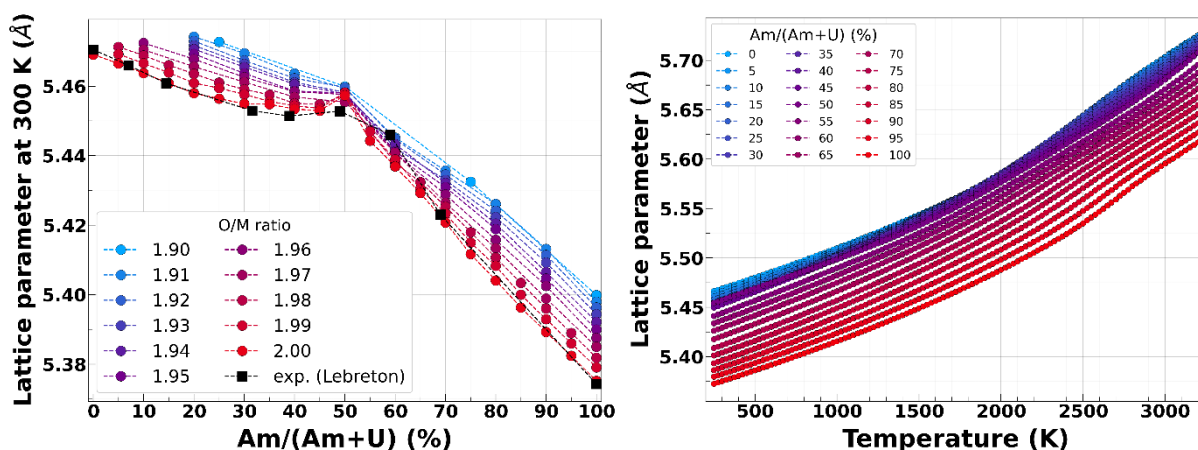


Figure 27: Room temperature lattice parameter as a function of Am content (left) and lattice parameter as a function of temperature (right)

Figure 27 shows the room-temperature lattice parameter as a function of americium content for several O/M ratios as well as the lattice parameter as a function of temperature for stoichiometric compositions. We see the deviation from Vegard's law observed experimentally [2014Lebreton] at room temperature for stoichiometric compounds is very well reproduced by the calculations. In addition, we see the deviation from O/M = 2.00 induces an expansion of the lattice parameter, with a smaller impact on middle americium contents than on low and high concentration oxides. The evolution of the lattice parameter with temperature, *i.e.* the thermal expansion coefficient, is very similar for all compositions up to 2000 K. The change in the slope taking place at higher temperatures is a first hint of the prediction by the potential of a Bredig transition in these compounds, better observed in the derivative properties such as the specific heat capacity. The lattice parameter is of great importance as it is directly related to the density and can thus affect fuel performance in reactor.

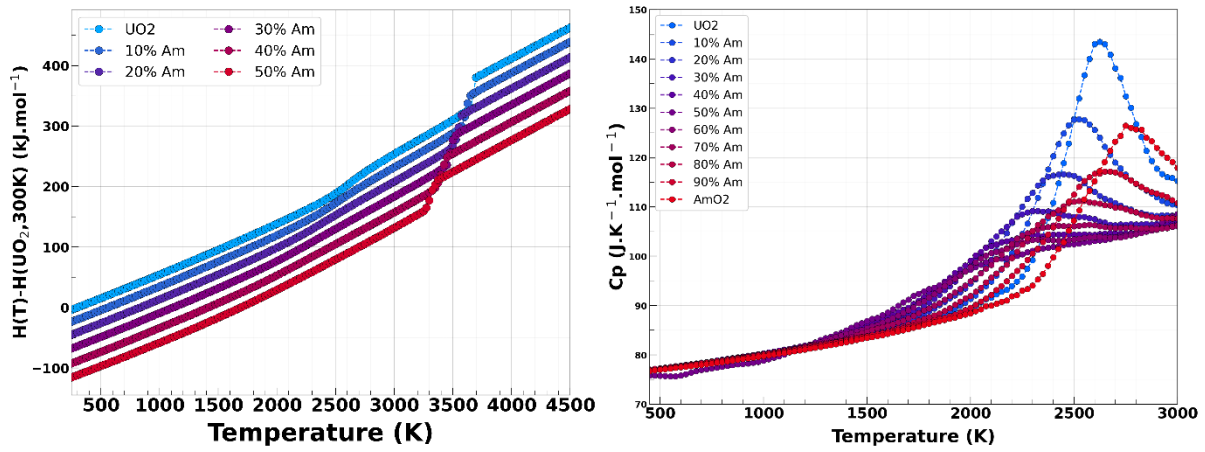


Figure 28: Computed enthalpy increment (left) and specific heat capacity (right) as a function of temperature for various americium contents

Figure 28 shows the computed specific heat capacities as well as part of the computed enthalpy increments from which they are derived using the finite difference method. We clearly observe a peak for most compositions, in particular for low and high americium contents. The existence of a peak in the middle-range concentrations is difficult to establish due to its small amplitude as well as to the increasingly large fluctuations. The specificity of these compositions is their greater proportion of  $\text{Am}^{3+}$  and  $\text{U}^{5+}$  cations, which is probably the cause of the change at 50% Am in the evolution with americium content of most properties. The peaks in the specific heat capacity are a clear indication of the prediction by the potential of a Bredig transition [1968Dworkin], experimentally observed for many fluorite-type materials including  $\text{UO}_2$  [1985Ralph,1983Hiernaut,2017Pavlov], in most uranium-amerium mixed oxides. This transition has been predicted in  $\text{UO}_2$ ,  $\text{PuO}_2$  and MOX using the CRG potential [2020Cheik Njifon,2020Takoukam] and could have an impact on fuel performance during power transient.

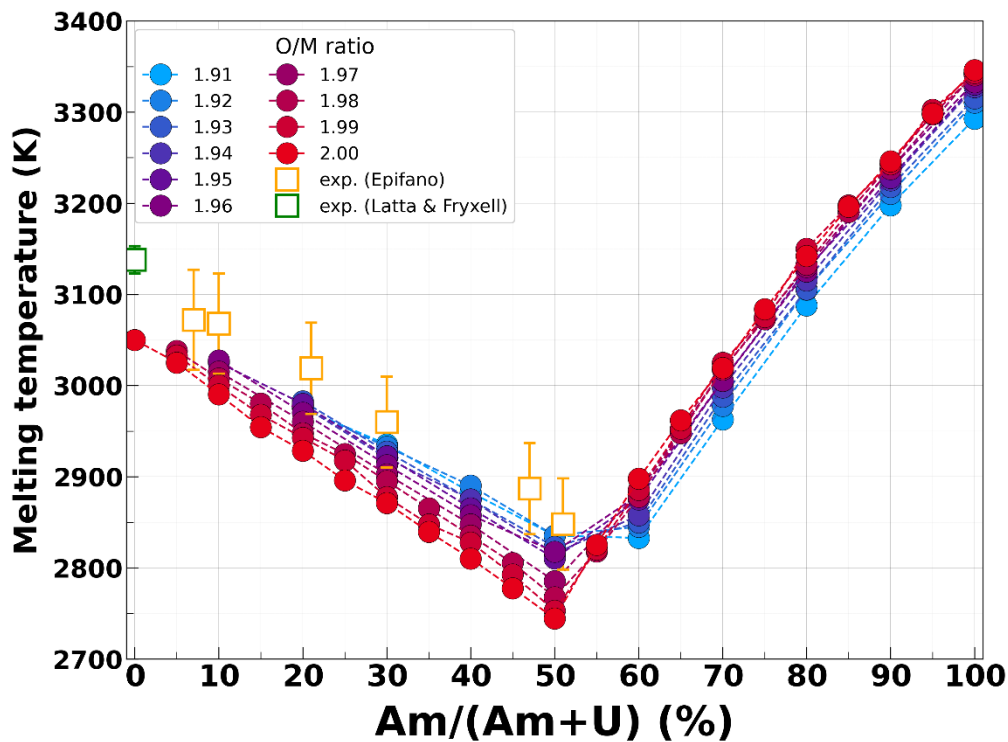


Figure 29: Estimate of melting temperature as a function of Am content

Figure 29 shows the melting temperature estimated using the MI method as a function of americium content for all investigated O/M ratios. Two trends are clearly visible for the stoichiometric compositions: on the one hand, the melting temperature decreases from  $\text{UO}_2$  to  $\text{U}_{0.5}\text{Am}_{0.5}\text{O}_2$ ; on the other hand, it increases from  $\text{U}_{0.5}\text{Am}_{0.5}\text{O}_2$  to  $\text{AmO}_2$ , leading to an estimated melting temperature of about 3350K for  $\text{AmO}_2$ . This is in contradiction with the only melting temperature measurement performed on the  $\text{AmO}_{2-x}$  system [1965McHenry] (2386 K) but the experimental sample likely deviated largely from O/M = 2.00 due to the tendency of americium to reduce easily, especially in temperature.

For americium contents up to 50%, the computed melting temperature is in good agreement with the experiments [2020Epifano] but systematically underestimated by about 90 K. This underestimation is consistent with that known for  $\text{UO}_2$  [1970Latta] using the CRG potential. Since this underestimation is virtually constant, the slope of the predicted melting temperatures is in very good agreement with the experimental one. No reliable data is available for compositions bearing more than 50% americium. A few measurements in this composition range would bring significant insight into the mechanisms at play in the U-Am-O system and are necessary to validate our results.

Regarding the effect of stoichiometry, again, two trends are visible. For compositions with less than 50% Am, deviation from stoichiometry increases the melting temperature, whereas it decreases the melting temperature for americium-rich compositions. This can be explained by the oxidation states present in these compounds:  $\text{U}^{5+}$  is reduced to  $\text{U}^{4+}$  in  $\text{U}_{1-y}\text{Am}_y\text{O}_{2-x}$  with  $y \leq 0.5$ , and since the melting temperature of  $\text{UO}_2$ , which includes only  $\text{U}^{4+}$ , is higher than that of the mixed oxides bearing a  $\text{U}^{4+}/\text{U}^{5+}$  mixture, deviation from stoichiometry increases the melting temperature for these compounds. On the opposite,  $\text{Am}^{4+}$  is reduced to  $\text{Am}^{3+}$  in  $\text{U}_{1-y}\text{Am}_y\text{O}_{2-x}$  with  $y > 0.5$  and the melting temperature of  $\text{AmO}_2$  is higher than that of the mixed oxides including both  $\text{Am}^{4+}$  and  $\text{Am}^{3+}$ . Thus, deviation from stoichiometry decreases the melting temperature for americium-rich mixed oxides.

All these results emphasize that the good comprehension of the oxidation states present in a compound is fundamental to the accurate modelling of their properties. The lack of data regarding high temperatures and americium-rich  $(\text{U},\text{Am})\text{O}_{2-x}$  properties has revealed to be an obstacle to the modelling of these compounds and the present results could be completed by a very limited number of specific measurements such as melting temperatures. Perspective of this work include the optimization of empirical interatomic potential terms for the systematic study of the Pu-Am-O and U-Pu-Am-O systems.

## 8 Conclusion

Experimental measurements on  $(\text{Pu},\text{Np})\text{O}_2$  oxides are reported for the first time in this work, while results on  $(\text{U},\text{Np})\text{O}_2$  oxides were also collected that will complement the existing knowledge on this system. Empirical interatomic potentials on  $(\text{U},\text{Am})\text{O}_2$  have yielded a large number of results regarding the properties of complex systems over a wide range of conditions (composition, pressure and temperature). They allow one to extend the knowledge acquired by experiments and can thus bring significant insight into the behaviour of the studied materials. They have therefore become an essential complement to experimental works.

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