ATALANTE 2012

International Conference on Nuclear Chemistry for Sustainable Fuel Cycles

The melting behaviour of oxide nuclear fuels: effects of the oxygen potential studied by laser heating

Dario Manara[a*], Robert Böhler[a], Kostantinos Boboridis[a], Luca Capriotti[a,b], Andrea Quaini[a,b], Lelio Luzzi[b], Franck De Bruycker[a,c], Christine Guéneau[d], Nathalie Dupin[e], Rudy Konings[a]

[a]*European Commission, Institute for Transuranium Elements, P.O. Box 2340, 76125 Karlsruhe, Germany*
[b]*Politecnico di Milano, Department of Energy, "Enrico Fermi" Center for Nuclear Studies, via Ponzio, 34/3 - 20133 Milan, Italy* [c]*CEA Marcoule, DEN/MAR/DRCP/SCPS/LC2A - Bagnols sur Cèze - 30207*
[d]*CEA Saclay – DEN / DANS / DPC / SCP / LM2T – 91191 Gif-sur-Yvette Cedex –France*
[e]*Calcul Thermo – 63670 Orcet – France.*

Abstract

The present work highlights the importance, in nuclear fuel safety and performance, of the very high oxygen potentials of actinide oxides (ThO_2, UO_2, NpO_2, PuO_2) at temperatures close to melting (around 3000 K), i.e. a tendency to oxidize their environment and chemically react with it.

Laser heating coupled with fast pyrometry constitutes an effective approach of studying the melting behaviour of these materials under a controlled atmosphere. Novel results reported in this work show that earlier data are confirmed, with the current technique, only for compounds with a relatively low oxygen potential, such as ThO_2 and UO_2 and their mixed compositions.

Keywords: Actinide Oxides, Melting, Nuclear Fuel, Oxygen Potential, Phase Diagrams.

* E-mail : dario.manara@ec.europa.eu

1. Introduction

The melting behaviour of actinide oxides constituting the main components of many nuclear fuels (both UO_2- and ThO_2-based) is fundamental in the fuel design and safety as it defines the performance limits of a fuel element itself [1].

The melting behaviour of a material largely depends on its nature and the physico-chemical conditions under which the solid/liquid transition takes place, particularly the interaction between the sample and the containment and atmosphere under which melting occurs. This is especially true in materials displaying high volatility at temperatures close to melting, like many refractory oxides. Their oxygen-rich vapour can become even a stable gas in equilibrium with the condensed phases if its total pressure exceeds the ambient pressure. In such a situation, the entire thermodynamic equilibrium of the system is radically altered, with the apparition of new invariant temperatures for the condensed phase/gas transition. The interaction and the mass transport between condensed phases and vapour is also paramount in determining the nature of the phase transformations, especially in case of non-congruent melting and vaporisation. Different precautions must therefore be taken in order to investigate experimentally the melting/freezing behaviour of such kind of materials.

One of the most important parameters in this context is certainly the oxygen potential, defined as the Gibbs free energy associated with the release of one mole of O_2 from the investigated sample into the surrounding environment. Thus the (molar partial) oxygen potential is related with the equilibrium partial pressure p_{O2} (in atm) of molecular oxygen in the studied system by the following relationship:

$$\overline{\Delta G}_{O_2} = RT \ln p_{O2} \tag{1}$$

$\overline{\Delta G}_{O_2}$ increases with temperature according to Eq. (1), where however the dependence of p_{O2} on temperature is not explicit. Its increase with temperature in refractory oxides is well established, but its mathematical dependence can be complex and still needs to be properly defined for the different systems (cf., for example, [2]). The high oxygen potential of oxides signifies their high reactivity with the environment and constitutes a problem in the experimental investigation of these materials at high temperature. This is also a paramount factor for the prediction of the nuclear material behaviour under extreme conditions that might be produced, for example, in a nuclear plant core meltdown mishap, or even just in an accidental power-temperature excursion in the fuel.

In traditional closed furnace heating techniques oxide samples tend to react with the containment (often metallic) by exchanging oxygen with it. For example, this kind of phenomenon has been shown experimentally in the recent work of Kato et al. [3] on PuO_2 and mixed uranium-plutonium dioxides. On the other hand, in open heating methods the sample tends to lose oxygen in the atmosphere, so that the final melting composition can be significantly reduced (or hypo-stoichiometric) with respect to the original one [4]. In many cases, it is necessary to heat the sample under a suitable over-pressure of oxygen in order to maintain the original composition up to the melting point [4, 5]. However, it is clear that such experimental conditions can create safety issues.

The current research deals with the melting behaviour of some pure and mixed actinide dioxides investigated by fast laser heating under quasi-containerless conditions and controlled atmosphere combined with fast pyrometry [6]. If on one hand this method circumvents some of the already cited experimental issues typical of furnace heating, on the other it presents other potential problems, mostly related with the production of real thermodynamic equilibrium during the experiments. These latter issues can be overcome by suitably setting the experimental parameters (atmosphere, heating power, dwelling time at high temperature) taking as references standard materials whose behaviour is sufficiently well known. The behaviour of actinide (An) dioxides can then be assessed depending of the different oxygen potentials of the given AnO_2 systems, knowing that $\overline{\Delta G}_{O_2}$ increases with the actinide atomic number [7, 8].

The present paper reports the first results obtained on the $UO_2 – ThO_2$ system, the latest investigated with the current technique. Such a study takes place in the renewed interest in thorium-based fuel cycle and the need to

develop a sustainable production of energy through anti-proliferation fuel, such as the mixed $(U, Th)O_2$ fuel based on the use of ^{232}Th as the fertile nuclide for the production of fissile ^{233}U [9]. ThO_2 was also used as blanket mantel in LMFBR [10] with good results. It was also tested as a U-free matrix fuel with the aim of burning Pu-stockpiles without production of new plutonium, showing a good resistance to irradiation as well [11].

The novel results reported in this work show that earlier data are generally confirmed, with the current technique, for ThO_2 and UO_2 and their mixed compositions, certainly due to the relatively low oxygen potential of these compounds compared with the oxides of heavier actinides. It has already been shown in recent publications [12-14], in fact, that the melting/solidification points of quasi-stoichiometric PuO_2 and NpO_2, characterised by a much higher $\overline{\Delta G}_{O_2}$, is considerably higher (by more than 250 K) than previously reported in the literature available.

All these experimental observations stress the paramount importance of oxygen chemistry in determining the high temperature behaviour of these oxides.

2. Experimental

The current approach, already described elsewhere [6], is summarized in the scheme of Figure 1.
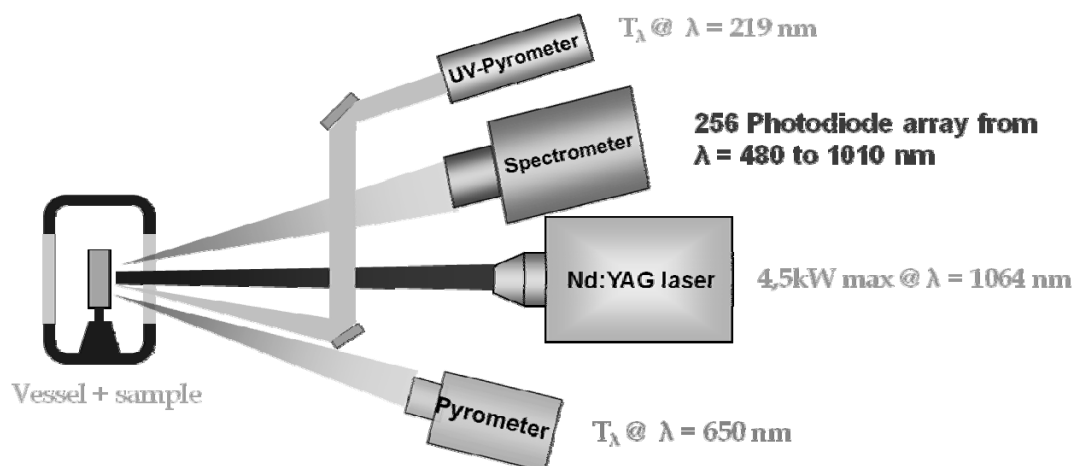

Fig. 1: Schematic of the laser heating and fast multi-wavelength pyrometry set-up used in the current research.

The solid sample is mounted in a pressurized cell with a controlled atmosphere inside a α-shielding glove-box. It is held in place by three radially arranged graphite screws, so that its contact with the mount is minimized. The heating agent is a TRUMPF® Nd:YAG continuous − wave laser radiating at 1064.5 nm, programmable with a complex power/time profile of variable duration and a maximum power of 4.5 kW. Laser pulses of a few tens ms to a few seconds consist of an initial power ramp, designed to reduce the thermal shock, followed by a constant-power plateau. The sample is heated beyond the melting point and then allowed to cool naturally and re-solidify. The sample temperature is detected by fast multi-channel pyrometers allowing a real-time radiance analysis, including also the determination of the sample normal spectral emissivity [6]. Phase transitions are detected from the resulting thermogram analysis, by the observation of characteristic thermal arrests. Heating cycles are performed under air, air mixed with argon, pure argon, Ar + 2 volume % H2 slightly pressurized up to 0.3 MPa or helium up to 100 MPa. For the latter case, a slightly modified experimental set-up has to be employed, not

reported in the present paper. Quasi-containerless conditions are achieved by directly heating only a limited area of approximately 3 to 8 mm in diameter on the sample surface. The variable size of the laser-irradiated spot allows investigating samples of different shape. The molten volume is contained by the outer periphery of colder solid material, thus preventing contamination by foreign material. Several experimental parameters can be varied in order to check the impact of the different factors (atmosphere, heating cycle duration, laser spot size, etc.) on the observed melting behaviour.

The melting points of pure metals (W, Ta, Mo, Nb, V) have been taken as primary and secondary references for the latest definition of the International Temperature Scale (ITS 1990) [15, 16]. In fact, many of the issues listed in the previous section, like the different diffusion rates, segregation phenomena and non-congruent phase transitions, are irrelevant in the case of pure elements (metals in particular), which makes them good standard materials. Since many additional sources of uncertainty arise in compounds, in the current research the melting point of pure uranium dioxide has been taken as an additional reference. Such phase transition has been measured here at (3115 ± 30) K, in good agreement with recommended values [8].

For the present investigation, a series of six composition of mixed $(U, Th)O_2$ samples from 5 to 100 mol % ThO_2 ($0.5 \leq x(ThO_2) \leq 0.95$) were prepared, in addition to the pure uranium and thorium dioxides. The starting material was powder obtained by gel-supported solidification (SOL-GEL) (cf. [13]). The samples were cut and pasted to obtain cylindrical pellets successively sintered in a dry $Ar+H_2$ (2%) atmosphere and annealed in air at 1500°C to reach the exact stoichiometry O / Metal = 2. The goodness of the nominal $x(ThO_2)$ of the samples was checked by X-Ray Diffraction (XRD) analysis, which gave values for the lattice parameters in agreement with Vegard's law and earlier literature data [17]. The samples were then analysed after the laser heating experiments by XRD, Raman spectroscopy and thermo-gravimetric analysis (TGA). All these characterisation methods ensured that eventual composition shifts (segregation), occurring during the melting/freezing cycles, were well below the uncertainty bands reported for the final results. The results reported in the next section can therefore be considered as segregation-independent within such reported uncertainty bands.

3. Results

Figure 2a reports the cooling stages of two thermograms recorded by the current experimental method on a UO_2 and a ThO_2 sample laser heated beyond melting. It can be seen that the solidification temperature of thorium dioxide (around 3620 K in this particular measurement) is much higher than the one of UO_2 (3120 K). This result reproduces well data already assessed for UO_2, and the most recent measurements published on ThO_2 [7, 18]. Figure 3b shows the solidus and liquidus lines for the pseudo-binary $UO_2 – ThO_2$ system, published in the 1950s [17], compared with the current new experimental data obtained by laser heating on three of the intermediate compositions prepared in this work, with nominal values $x(ThO_2)$=0.05, 0.20 and 0.95. The vertical error bands associated with the current results are mainly due to the experimental data scatter and an estimated 1% relative uncertainty in the pyrometric temperature determination. The horizontal ones take into account, conservatively, possible segregation effects occasionally observed by post-melting XRD analysis. Both uncertainty bands account for a 2-σ coverage. It can be noted that the current data agree fairly well with existing ones. The results of Lambertson et al. [17] were rather accurate, but they were refined by Latta et al. [19] who found that the melting point had probably a minimum value for small ThO_2 contents, around $x(ThO_2)$=0.05. The present data seem to confirm the existence of such a minimum melting temperature, although its actual value, close to 3050 K, still needs to be thoroughly established. The solidus and liquidus lines drawn in the present work (solid lines in Figure 2b) are only a guide for the eye, and they still need to be assessed by thermodynamic optimisation (CALPHAD). The corresponding lines of Lambertson et al. (dotted in Figure 2b) have been corrected to take into account the existence of the mentioned minimum fusion temperature and the higher value of the melting point of pure ThO_2 more recently measured by Ronchi and Hiernaut [18] and also confirmed by the current study.
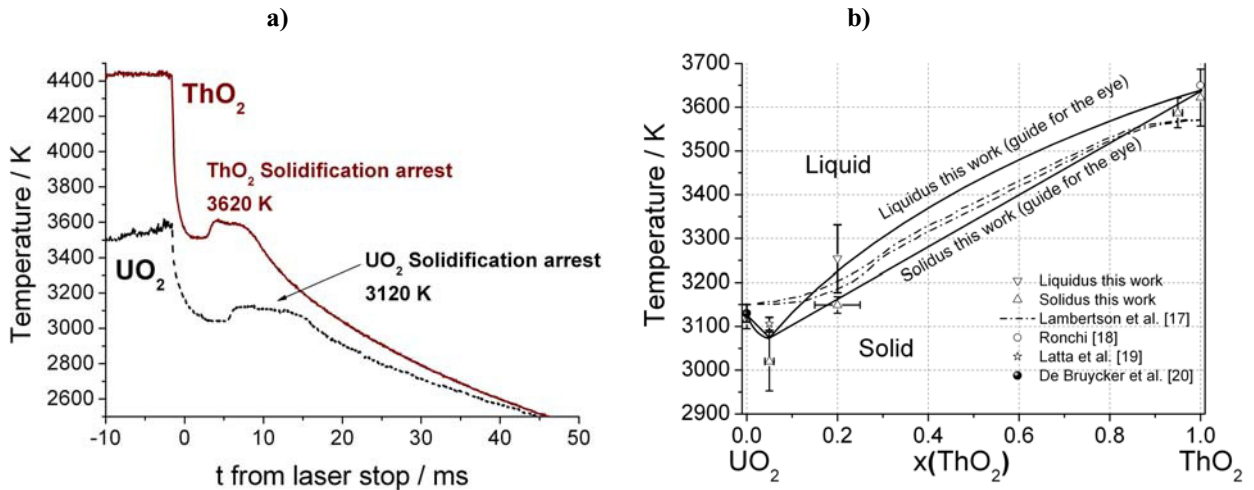
a)

b)

Fig. 2a: The solidification arrests of ThO_2 and UO_2. Fig. 2b: The $UO_2 – ThO_2$ section of the ternary U-Th-O phase diagram taking into account results obtained in the current research. Solidus and liquidus lines are a guide for the eye only.

4. Discussion

Novel results on the UO2 - ThO2 mixed system are compared here with recently published results on the mixed UO2 – PuO2 system [12, 13, 20, 21], in order to give an idea of the different melting behaviour observed in systems characterized by different oxygen potentials.

The system UO2 – PuO2 has been extensively studied due to its wide employment as nuclear fuel. Recent experiments [3, 12, 13, 20], including some performed by means of the current experimental approach, have shown that the melting point of plutonium dioxide had been underestimated in traditional furnace heating studies [22] by more than 300 K. Such a discrepancy could be attributed to extensive interaction between the sample and its containment (generally tungsten), as confirmed by the elegant experimental study recently performed by Kato et al. [3]. The pseudo-binary UO2 – PuO2 system has been shown [20, 21] to be characterized by the presence of a stable gas phase (oxygen) in equilibrium with the condensed fcc (U, Pu)O2 solid solution in the PuO2-rich part of the phase diagram. A minimum melting point has been suggested to occur in the ternary U-Pu-O system at a composition around x(PuO2)= 50% in the UO2 - PuO2 plane [20]. The effect of the oxygen potential has been highlighted by changing the experimental atmosphere, whereby results were interpreted with the help of CALPHAD calculations to ensure thermodynamic consistency with the ternary U-Pu-O phase diagram [21]. It has been concluded that whereas uranium dioxide tends to melt congruently under a slightly reducing atmosphere (argon), at a stoichiometric composition (UO2.00 approximately), plutonium dioxide melts quasi-congruently at (3017 ± 28) K at a slightly hypo-stoichiometric composition (PuO1.98±0.02) only in a strongly oxidizing atmosphere (air pressurized at 0.3 MPa). Under reducing conditions, plutonium dioxide would massively loose oxygen before melting, whereas in an oxidizing atmosphere uranium dioxide would become hyper-stoichiometric UO2+x and quickly vaporize before melting at a much lower temperature than reported for stoichiometric UO2. Finally, the UO2-PuO2 section of the ternary U-Pu-O phase diagram reproduced in Figure 3 has been proposed [21]. One can notice that the current phase boundaries agree fairly well with previous data only for x(PuO2) < 0.5.
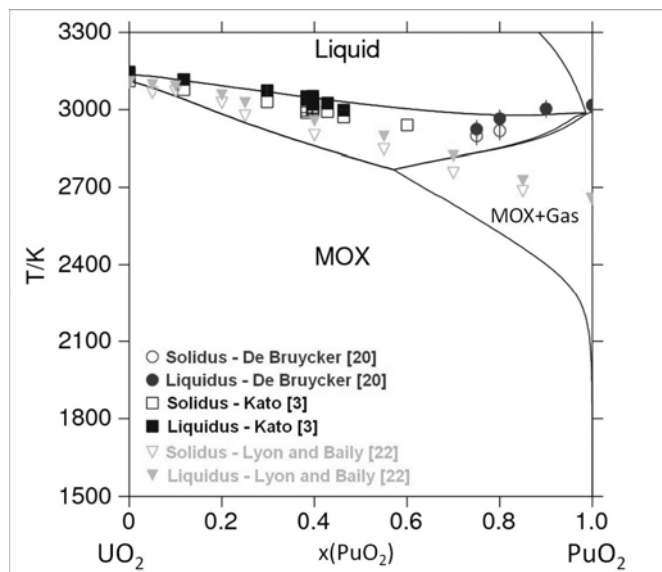
Fig. 3: The UO_2-PuO_2 section of the ternary U-Pu-O phase diagram optimized by CALPHAD (after [21]) taking into account recent experimental results. The UO_2-PuO_2 solid solution is indicated as MOX. Empty and full red circles represent data points obtained with the present experimental approach [20].

Similarly, a very recent study [14] performed with the present experimental approach has shown that the congruent melting/freezing point of neptunium dioxide occurs at a composition $NpO_{1.98\pm0.02}$ and 3070±62 K, once more about 250 K higher than previously assessed.

Figure 4 shows the melting/solidification data measured in the current research in the actinide dioxide series compared with previous results.

It can be easily seen that the disagreement between current and older data increases with the actinide atomic number and, more significantly, with the oxygen potential $\overline{\Delta G}_{O_2}$ of the corresponding dioxide at a given temperature. The results presented in the current paper on (U, Th)O_2 mixed dioxides and those recently published on the mixed (U, Pu)O_2 composition reveal a similar behaviour for mixtures: the higher the oxygen potential of the mixed oxides, the larger the discrepancy between current experimental data and older results measured in traditional W − furnace heating. This shows the suitability of the current quasi-containerless and fast heating/cooling approach for the investigation of these materials.

It is important to conclude that the melting behaviour of actinide dioxides is therefore strongly dependent on the chemical environment in which they are heated through the solid/liquid transition. More precisely, the oxygen potential and the volatility of each actinide dioxide determine the chemical form under which the compound reaches its melting temperature. Dioxides AnO$_2$ with high $\overline{\Delta G}_{O_2}$, such as PuO_2 and NpO_2, are most likely to partially decompose at high temperatures, but still lower than melting, according to the reaction

$$2AnO_2 \rightarrow 2AnO_{2-x} + xO_2 \tag{2}$$

This kind of equilibria cannot be neglected in the simulation of the nuclear fuel behaviour under extreme (accidental) conditions. Of course, this behaviour is not limited to actinide dioxides only. For example, it has extensively been studied and assessed in non-active compounds such as CeO_2 [5] and in CaO [23]. The melting/freezing point of this latter oxide, one of the most common in nature and technology, is still largely controversial, due to its recognized dependence on the chemical environment (reducing, oxidizing) in which the solid/liquid transition occurs.
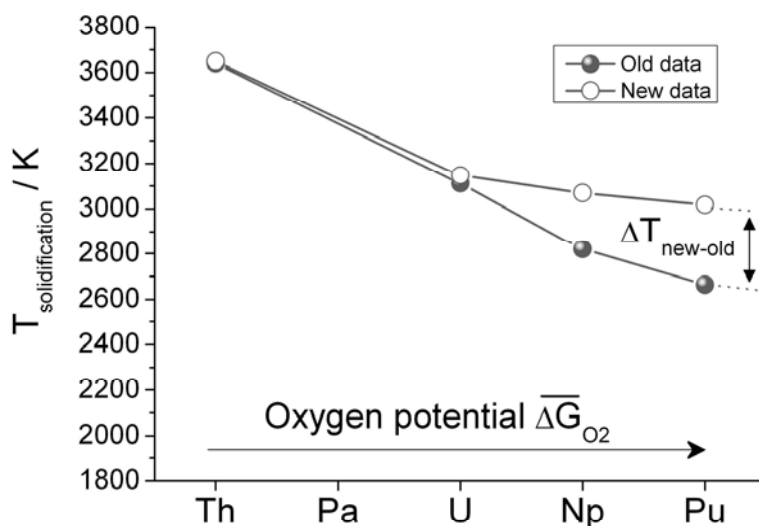
Fig. 4: The melting/solidification data measured by fast quasi-containerless laser heating in
the actinide dioxide series compared with previous results (cf. [14]).

5. Conclusions

A first reassessment of the melting behaviour of UO_2, ThO_2 and some mixed $(U, Th)O_2$ compositions has been carried out in this work by means of fast laser heating under quasi-containerless conditions, controlled atmosphere and fast multi-wavelength pyrometry. The current results have been compared both with similar data recently measured on other pure and mixed actinide dioxides with the same experimental method and with previous literature data obtained by more traditional tungsten furnace heating techniques. Clearly, the current technique allows reproducing fairly well older results only in oxides characterized by a relatively low oxygen potential. Such a critical comparison highlights that the melting behaviour of these compounds is largely dependent on the chemical environment in which the solid/liquid transition takes place. In particular, compounds with high oxygen potential tend to lose oxygen and partially vaporize at temperatures lower than melting, behaviour already observed in previous research on non-radioactive refractory oxides.

These results encourage further research on other materials, whose behaviour at very high temperature might result to be more complex than one might believe on the basis of traditional furnace heating experiments only.

Acknowledgements

References

[1] D. R. Olander: "Fundamental Aspects of Nuclear Reactor Fuel Elements", Technical Information Center, Office of Public Affairs-Energy Research and Development Administration, 1976, ISBN 0870790315, 9780870790317, 613 pp.

[2] T.M. Besmann and T.D. Lindemer, *J Nucl Mater 1985*; **130**:489-504.

[3] M. Kato, K. Morimoto, H. Sugata, K. Konashi, M. Kashimura, T. Abe, *J Nucl Mater 2008*; **373**:237-245.

[4] B. Riley, *Sci Ceram 1970*; **5**: 83-95.

[5] M. Zinkevich, D. Djurovic, F. Aldinger, *Solid State Ionics 2006*; **177**: 989-1000.

[6] D. Manara, M. Sheindlin, W. Heinz, C. Ronchi, *Rev Sci Instrum 2008*; **79:** 113901-8.

[7] H. Kinoshita, D. Setoyama, Y. Saito, M. Hirota, K. Kurosaki, M. Uno, S. Yamanaka, *J Chem Thermodyn 2003*; **35**: 719-731.

[8] C. Guéneau, A. Chartier, L. V. Brutzel, "*Thermodynamic and Thermophysical Properties of the Actinide Oxides*", in: R. J. M. Konings (Ed.). Compre. Nucl. Mater., first ed. Elsevier, Amsterdam *2012*.

[9] C. Lombardi, L. Luzzi, E. Padovani and F. Vettraino, *Prog. in Nucl. Energy 2008*; **50**: 944- 953.

[10] "*Thorium fuel cycle – Potential benefits and challenges*", IAEA-TECDOC-1450, *2005*.

[11] Ch. Hellwig, M. Streit, P. Blair, T. Tverberg, F.C. Klaasen, R.P.C. Schram, F. Vettraino and T. Yamashita, *J Nucl Mater 2006*; **352**: 291-299.

[12] F. De Bruycker, K. Boboridis, D. Manara, P. Poeml, M. Rini and R.J.M. Konings, *Materials Today 2010*; **13**: 52-55.

[13] F. De Bruycker, K. Boboridis, P. Poeml, R. Eloirdi, J. Somers, R.J.M. Konings and D. Manara, *J Nucl Mater 2011*; **416**: 166-172

[14] R. Böhler, M. J. Welland, F. De Bruycker, K. Boboridis, A. Janssen, R. Eloirdi, R.J.M. Konings and D. Manara, *J Appl Phys 2012*; **111**, 113501-09.

[15] H. Preston-Thomas, *Metrologia 1989*; **27**: 3-25. (amended version)

[16] R. E. Bedford, G. Bonnier, H. Maas, F. Pavese, *Metrologia 1996*; **33**: 133-154.

[17] W. A. Lambertson, M. H. Mueller and F. H. Gunzel, Jr., *J Am Ceram Soc 1953*; **36**: 397-401.

[18] C. Ronchi and J. P. Hiernaut, *J Alloys Compounds 1996*; **240**: 179-185.

[19] R. E. Latta, E. C. Duderstadt and R. E. Fryxell, J. Nucl. Mater., 35 (1970), 347-349.

[20] F. De Bruycker, K. Boboridis, R.J.M. Konings, M. Rini, R. Eloirdi, C. Guéneau et al., *J Nucl Mater 2011*; **419**: 186-194.

[21] C. Guéneau, N. Dupin, B. Sundman, C. Martial, J.-C. Dumas, S. Gossé, S. Chatain, F. De Bruycker, D. Manara, R. J.M. Konings, *J Nucl Mater 2011*;**419**: 145-165.

[22] W.L. Lyon, W.E. Baily, *J Nucl Mater 1967*; **22**: 332-339.

[23] T. Yamada, M. Yoshimura, and S. Somiya, *J Am Ceram Soc 1986*; **69**: C-243-250.

Nomenclature

An	Actinide
$\overline{\Delta G_A}$	Partial molar Gibbs free energy of species A
MOX	The UO_2-PuO_2 solid solution
p_{O2}	Oxygen partial pressure (referred to the standard reference pressure of 1 atm = 101325 Pa)
σ	Standard deviation
T	Absolute temperature (in K)
x(A)	Molar fraction of species A in a mixture or solution.