The melting behaviour of uranium/neptunium mixed oxides

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ABSTRACT

The melting behaviour in the pseudo-binary system (UO₂ + NpO₂) has been studied experimentally for the first time in this work with the help of laser heating under controlled atmosphere. It has been observed that the solidus and liquidus lines of this system follow an ideal solution behaviour (negligible mixing enthalpy) between the well-established solid/liquid transition temperatures of pure UO₂ (3130 K) and that recently assessed for NpO₂ (T = 3070 K). Pre- and post-melting material characterizations performed with the help of X-ray diffraction and Raman spectroscopy are also consistent with ideal mixing of the two end members. Such behaviour follows the similar structure and bonding properties of tetravalent uranium and neptunium and the similar melting points of the two oxides. The interest of this investigation is twofold. From a technological viewpoint, it indicates that the incorporation of NpO₂ in UO₂ fuel or transmutation targets is a viable option to recycle neptunium without inducing any relevant change in the chemical or thermal stability of the uranium dioxide matrix, even up to the melting point. From a more fundamental perspective, it confirms that actinide dioxides, and particularly UO₂, tend to mix in a way closer to ideal, the closer are the atomic numbers, 5-f electron shell filling, atomic radii and oxygen potentials of the metals forming the pure dioxides.

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1. Introduction

Once minor actinides (Am, Np, Cm) are chemically separated (partitioned) from the spent nuclear fuel, they can be transmuted into lighter and less radioactive isotopes in a fast neutron reactor, resulting in a significant reduction of the nuclear waste radiotoxicity, especially on an intermediate time scale (10² to 10³ years).

In this context, two options have been considered for the transmutation of MAs in a sodium-cooled fast reactor: (a) homogeneously adding (2 to 6)% of MAs to the fuel (homogeneous mode) and (b) introducing MAs in higher amounts up to (10 to 30) wt% into transmutation targets (heterogeneous mode) [1].

Basic knowledge on (MAs + O) and (U + MAs + O) systems is thus becoming more and more interesting at high temperature especially for both the transmutation fuel fabrication and its behaviour under irradiation. The present investigation focuses on the thermal stability of neptunium-bearing oxide fuel because data are still scarce in the general (U + Np + O) system. \(^{237}\)Np is produced in a nuclear reactor through neutron irradiation of \(^{238}\)U [2]. A ternary (UO₂ + NpO₂ + U₃O₈) phase diagram is available at \(T = 1273 \text{ K only} \) [3], and the evolution of phase relationships was studied by in situ –high temperature X-ray diffraction by Chollet et al. [4]. Experimental investigations need to be conducted further, especially in the vicinity of the melting transition, since such thermodynamics or physical data are fundamental for modelling the fuel behaviour under irradiation, and the completion of the phase diagram at higher temperatures. This research field is particularly relevant in the safety analysis of fast neutron reactors designed for MA transmutation, especially for the simulation of severe accidents leading to uncontrolled thermal excursions in the fuel.

In recent years, The European Commission’s JRC-ITU in Karlsruhe (Germany) developed an innovative method to measure melting temperature based on quasi-containerless conditions for samples with very short duration of the heating cycles. Ever since, numerous studies have successfully proved the reliability of this technique: UO₂ +x [5,6], \((U, Pu)O₂\) [7,8], PuO₂ [9], NpO₂ [2], \((U, Th)O₂\) [10] melting behaviour and phase diagrams at high temperatures were revisited. It has been proven that earlier values of the melting points of actinide compounds, obtained by traditional furnace heating techniques, were most probably affected by excessive high-temperature interaction between the sample and its containment. The error induced in these melting temperatures could amount to several hundred degrees Kelvin. In particular, this was shown for actinide dioxides such as PuO₂ and NpO₂. The new...
higher value of the solid/liquid transition temperature established for plutonium dioxide naturally led to a full re-assessment of the whole (UO₂ + PuO₂) system at high temperature. For this system, it has been observed that the oxygen potentials of both the pure end members and the intermediate compositions play a paramount role in defining the phase boundaries. These latter are largely affected by oxygen gain and losses, to the point that (urania + plutonia) phase equilibria can only be rigorously assessed within a full thermodynamic description of the ternary (U + Pu + O) system. Similar considerations have been made for the systems (UO₂ + ThO₂) [10] and (ThO₂ + PuO₂) [11], in which, however, the higher chemical stability of thorium dioxide ensured behaviour of the mixed system closer to ideal even in an approximate pseudo-binary description.

Also the melting point of neptunium dioxide has been established to be more than T = 300 K higher than that proposed in earlier research. Its oxygen potential is however closer to that of pure UO₂, when compared to the oxygen potential trends of PuO₂ or ThO₂ and NpO₂ [12], which latter value could be less precise in uranium-rich systems. Similar considerations have been made for the systems (UO₂ + NpO₂) [13], in which however, the higher chemical stability of thorium dioxide ensured behaviour of the mixed system closer to ideal even in an approximate pseudo-binary description.

TABLE 1

| Material | NpO₂ | UO₂ | UO₂ ITU | (U₁₋₅Np)O₂ ITU |
|----------|------|-----|---------|-----------------|
| Provenance | CEA/VALRHO | Advanced nuclear materials Co. |
| State | Powder | Concentration/
| | mg kg⁻¹ | Pellet | sol-gel liquid |
| | | powder | | solution |
| Li | | | | <1 |
| B | | | | <1 |
| C | | | | 56 |
| N | | | | 11.7 |
| F | | | | 6.8 |
| Na | 400 | § | 6.1 | 15.4 |
| Mg | 400 | ↑ | 208 | 3.2 |
| Al | 400 | ↑ | 1.7 | 4.8 |
| Si | 1.7 | ↓ | 1 | 1 |
| P | | | | 40 |
| S | | | | 44 |
| Cl | | | | 5.7 |
| K | 700 | § | 212 |
| Ca | | | | |
| Ti | | | | |
| V | <0.2 | ↑ | 11.3 |
| Cr | 300 | § | 28.4 |
| Mn | § | | 27 |
| Fe | 1000 | 7.5 | 1.7 |
| Co | | | | |
| Ni | 1.5 | ↑ | 2.3 |
| Cu | | | | |
| Zn | § | | 3.86 |
| As | | | | |
| Y | <1 | | 12.5 |
| Zr | § | | 7.2 |
| Mo | § | | 3.86 |
| In | | | | |
| Sn | <3 | ↑ | 2.1 |
| Sb | | | | |
| W | § | | 3 |
| Pb | § | | 4.98 |
| Bi | <2.3 | | |
| Th | <1.7 | | 5.35 |

*: Sum of those elements is below 2 · 10⁻⁶.
§: Sum of those elements is below 8 · 10⁻⁶.

2. Materials and methods

2.1. Sample preparation

Disks of (U₁₋₅Np)O₂, with y = 0.1, 0.2, 0.3 and 0.7 were prepared at the LEFCA facility (CEA Cadarache, France), starting from UO₂ and NpO₂ powders. Uranium dioxide powder was produced by a wet fabrication route based on the formation of ammonium diuranate (ADU) from uranyl nitrate precipitated with ammonia. The particles obtained were then atomized and dried, leading to spherical-shaped agglomerates of roughly 20 μm. The sum of impurities is below 192 · 10⁻⁶ (Table 1). The purity of the NpO₂ powder, provided in 1995 by CEA/VALRHO, was determined by ICP-AES analysis. It contains less than 0.4 wt% impurities (Table 1). Raw powder was ground and mixed in the appropriate ratios and first calcined under a reducing atmosphere (i.e., Ar/5%H₂) at T = 1773 K for 20 h. Powders subsequently underwent an intermediate grinding before being sieved and pressed into pellets in an automatic press at 390 MPa. Pellets were sintered 24 h at T = 2023 K in an atmosphere of Ar/H₂, leading to 80% density and size of 6 mm in diameter and 2.5 mm in thickness, suitable for the sample holder of melting temperature measurement apparatus. Phase composition and O/M ratios were checked by powder X-ray diffraction (PXRD) [4] with an expanded uncertainty on y reported in Table 2 as U(x(NpO₂)) and U(O/M) = ±0.01 on the O/M ratio. This latter value could be less precise in uranium-rich samples due to the strong tendency to oxidation of uranium dioxide in contact with even low traces of oxygen.

Similar disks with different compositions y = 0.02, 0.05, 0.20, 0.50, 0.75 and 0.85 with an expanded uncertainty Uₜ of ±1% have been prepared by gel-supported precipitation (or sol-gel external gelation) at JRC-ITU Karlsruhe. The purity of the sol-gel liquid solution is provided in Table 1. The uranyl nitrate solution was mixed with an acidic solution of ²³⁸U to achieve a mole stoichiometry Np(U + Np) of 0.02, 0.05, 0.20, 0.50, 0.75 and 0.85. Those ratios have been checked by Inductively Coupled Plasma – Mass Spectrometry. An organic thickener (Methocel, Dow Chemicals Inc.) was added in order to increase the viscosity of the solution. The solution was then dropped in an ammonia bath where the droplet to particle conversion took place thanks to the hydrolysis of the metal ions. The resulting powder was washed, dried and then calcined at T = 873 K in air (2 h) to remove organics and then at T = 973 K in Ar/H₂ (2 h). The disks were then sintered at T = 1923 K (4 h) under Ar/H₂. As detailed elsewhere [14], the O/M ratios of these compounds are equal to (2.00 ± 0.01) (U(O/M)). Pure neptunium dioxide samples were prepared as described by Böhler et al. [2]. The starting material was a 99.87 wt% pure powder. Disks 6 mm in diameter and (1.2 to 1.5) mm in thickness were obtained using a bi-directional press. They were then sintered for 99.3% of ²³⁵U, and for 0.7% of ²³⁵U. Over 99.9% of the current neptunium consisted of ²³⁷Np.
For simplicity, the samples have been labelled with the acronym NOXab, where ab indicates the molar percentage of NpO₂ in the mixed oxide. Thus, for example, NOX30 corresponds to a sample (U₁₋₀.₃NpO₂)O₂ with y = 0.3.

Experimental values determined for both CEA and JRC sample batches have been compared in order to obtain better statistics on their reproducibility.

2.2. Melting temperature measurements

Details of the laser-heating setup used in this research have been reported in previous publications [6], although the technique has been partially modified in the present work. During the shots, a mixed oxide disk was held in a sealed autoclave under controlled atmosphere slightly pressurised by air or argon at (0.35 ± 0.02) MPa, the uncertainty being extended to two standard deviations. Such a controlled atmosphere permitted, together with the relative short duration of the experiments, minimisation of the deviations. Such a controlled atmosphere has been prepared in the present work. During the shots, a mixed oxide disk was held in a sealed autoclave under controlled atmosphere slightly pressurised by air or argon at (0.35 ± 0.02) MPa, the uncertainty being extended to two standard deviations. Such a controlled atmosphere permitted, together with the relative short duration of the experiments, minimisation of the deviations.

For the current (UO₂ + NpO₂) mixed samples (composition derived from the Raman analysis).

| Sample | NpO₂ mole fraction (x(NpO₂)) | Origin | Average measured melting/solidification temperature/K | Atmosphere in which heating was performed. Pressure = (0.35 ± 0.02) MPa | T₂g Raman peak position/(cm⁻¹) | Mole fraction after melting (x(NpO₂) ± 0.05) |
|--------|-----------------------------|--------|-----------------------------------------------------|--------------------------------------------------------------------------------|--------------------------------|------------------------------------------|
| UO₂    | 0 ± 0.0002                 | ITU    | 3130 ± 25                                           | Ar                                                                          | 444                          | 445                                      |
| NOX2   | 0.02 ± 0.001               | ITU    | 3094 ± 30                                           | Ar                                                                          | 446                          | 450                                      | 0.25                                    |
| NOX5   | 0.05 ± 0.001               | ITU    | 3129 ± 83                                           | Ar                                                                          | 449                          | 449.5                                    | 0.225                                   |
| NOX10  | 0.10 ± 0.001               | CEA    | 3124 ± 26                                           | Ar                                                                          | 450                          | 451                                      | 0.3                                     |
| NOX20  | 0.20 ± 0.002               | CEA/ITU| 3112 ± 25                                           | Ar                                                                          | 459                          | 460                                      | 0.75                                    |
| NOX30  | 0.30 ± 0.002               | CEA    | 3100 ± 25                                           | Ar                                                                          | 465                          | 464                                      | 1                                       |
| NOX50  | 0.50 ± 0.005               | ITU    | 3125 ± 27                                           | Air                                                                         | 469                          | 460                                      | 0.75                                    |
| NOX70  | 0.70 ± 0.005               | CEA    | 3087 ± 32                                           | Air                                                                         | 464                          | 464                                      | 1                                       |
| NOX75  | 0.75 ± 0.007               | ITU    | 3091 ± 32                                           | Air                                                                         | 464                          | 464                                      | 1                                       |
| NOX85  | 0.85 ± 0.008               | ITU    | 3087 ± 30                                           | Air                                                                         | 464                          | 464                                      | 1                                       |
| NpO₂   | 1 ± 0.0005                 | ITU    | 3070 ± 25                                           | Air                                                                         | 464                          | 464                                      | 1                                       |

Notes: Raman measurements performed on sample NOX50 were unsuccessful due to poor surface reflectivity. Reported uncertainties are absolute extended uncertainties, i.e. they correspond to two standard deviations, with a 95% confidence. U(T) is expressed in K; U(y) in the Raman peak position is ±1 cm⁻¹; U(P) = ±0.02 MPa; U(x(NpO₂)) is given for pure compounds and mixed compositions by case in case in the second column. In the last column, the local composition determined by Raman spectroscopy is affected by a larger uncertainty, deduced from the uncertainty in the localisation of the T₂g Raman peak, yielding U(x(NpO₂)) = 0.05.

a) Due to impurities.

Table 2
Experimental melting/solidification points and Raman T₂g peak positions for the current (UO₂ + NpO₂) mixed samples (composition derived from the Raman analysis).

The sample cooled naturally when the laser beam was switched off during the thermal cycle. Thermal arrests corresponding to exothermic phase transitions were then observed on the thermograms recorded by the fast pyrometers. These operate in the visible-near infrared range between (488 and 900) nm. The reference pyrometer wavelength was here 655 nm and was calibrated according to the procedure already reported in previous work [6]. The normal spectral emissivity (NSE) of the current dioxides, necessary for the determination of the sample temperature, has already been studied in detail in earlier publications [2]. The NSE of mixed dioxide samples has been studied employing the same multi-wavelength pyrometry approach [6]. Given the experimental uncertainty on the NSE (±5% of the absolute NSE value), it has been observed that the assumption of a constant value of NSE = (0.825 ± 0.04) is reasonable for all the compositions investigated. This value has been used to correct the radiance signal recorded by the pyrometers and convert it, through Planck’s blackbody law, into real absolute temperature.

Uncertainty of the temperature measurements was calculated according to the error propagation law [6], taking into account the uncertainty associated to pyrometer calibration, the emissivity, transmittance of the optical system and the accuracy in detecting the onset of vibrations in the RLS signal. The estimated cumulative uncertainty is thus lower than ±1% of the reported temperatures in the worst cases, with a 2-k coverage factor (corresponding to one standard deviation around the average value).
excitation of a silicon single crystal, set at microscope with a 50-fold magnification and long focal distance for all the compositions. Spectra were measured in a confocal the Kr+ laser was the best-compromise excitation source to study the sample surface. It was finally found that the 647 nm line of optimise the signal/noise ratio (by minimising the material flu- wavelength and power were chosen at each measurement in order spectra were considered not to affect the present analysis. The difficulty in separating these few mg from the non-molten material matrix.

2.5. Raman spectroscopy Analysis of the material microstructure evolution before and after the melting/freezing cycles was performed by micro-Raman spectroscopy, a less demanding technique in terms of sample preparation and a more suited one for the local analysis of melted and non-melted portions of the sample surface. Raman spectra were measured with a Jobin–Yvon® T64000 spectrometer used in the single spectrograph configuration. Used excitation sources were the (488 and 514) nm lines of an Ar+ Coherent® laser, as well as the 647 nm and the 752 nm lines of a Kr+ Coherent® laser. Eventual polarisation effects on the Raman spectra were considered not to affect the present analysis. Actual wavelength and power were chosen at each measurement in order to optimise the signal/noise ratio (by minimising the material fluorescencescence) and reducing undesirable oxidation/burning effects on the sample surface. It was finally found that the 647 nm line of the Kr+ laser was the best-compromise excitation source to study the present mixed oxides under the same experimental conditions for all the compositions. Spectra were measured in a confocal microscope with a 50-fold magnification and long focal distance (1 cm). This feature yielded a good spectral resolution \( (U_y = \pm 1 \text{ cm}^{-1} \text{ with } 95\% \text{ confidence level}) \) with a spatial resolution of 2 \( \mu \text{m} \times 2 \mu \text{m} \). The spectrometer detector angle was calibrated daily with the \( T_{24} \) excitation of a silicon single crystal, set at 520.5 \( \text{cm}^{-1} [18] \).

2.6. Scanning electron microscopy Secondary and backscattered electron images were recorded on a Philips XL40 scanning electron microscope operated at 25 kV and installed in a glove-box.

3. Results

3.1. Thermal analysis Figure 1 displays the pyrometer-recorded thermogram relative to a series of three laser shots on a NOX20 sample. It can be observed that the three laser shots have different intensity and duration. This makes the comparison between the temperatures of melting and freezing statistically more significant. A rapid thermal arrest, preceded by a slight undercooling is visible during the cooling stage. This is interpreted as the solidification of the compound upon recalescence following the same behaviour observed in recent laser melting investigations [2,5–9].

Non-congruent melting, where the solid and liquid phases coexist with different compositions, is expected for the mixed compositions. However, solidus and liquidus temperatures of \((U_1,Np)_2O_5\) samples cannot be clearly distinguished in the current thermograms, even with the help of the RLS technique. Solidus and liquidus points are most probably too close together to be discriminated within the present experimental uncertainty.

Table 2 and figure 2 contain a summary of the observed melting/solidification points for the compositions investigated, along with the corresponding absolute expanded uncertainty bands (two standard deviations). These are obtained by combining the instrumental uncertainty (estimated to be \( T = \pm 25 \text{ K at } 3100 \text{ K} \)) with the data spread for each composition. The uncertainty bands reported in table 2 for the pure dioxides refer to the current measurements, not to those reported by us in earlier publications. They are in perfect agreement with the approximately congruent melting points of the pure dioxides, \( T = (3130 \pm 30) \text{ K for } UO_2 \) and \( T = (3070 \pm 67) \text{ K for } NpO_2 \), recently assessed [2,5]. Consistently with the close atomic numbers and oxygen potential trends of uranium and neptunium [12], these transition temperatures are rather similar and the difference between them is comparable with the current experimental uncertainty. The measured solid/liquid transition temperatures appear to evolve with a rather regular trend between the two end members within such error bands. The only partial exception is constituted by the case of NOX5. For this composition, the sample broke during laser heating and only two relatively successful melting point measurements could be performed, yielding two very different values, \( T = (3070 \text{ and } 3183) \text{ K. Although such values are obviously affected by a large and not quantifiable uncertainty, their average is in line with the transition temperatures recorded for the other compositions.}

3.2. Morphology of the melted and re-solidified surface With the current experimental approach, only a limited part of the sample mass undergoes a melting/freezing process. The rather complex melting/solidification dynamics involved have been extensively studied for analogous systems, with the help of non-equilibrium thermodynamics and phase field modelling [8,19,20]. It has been shown, in particular, that local thermody-namic equilibrium conditions are produced in the centre of the melted pool, where the temperature is recorded by the pyrometers on a spot about \( 10^4 \) times smaller than the whole material volume
involved in the melting/freezing process. Laser irradiation on a limited spot of the sample results in the formation of a “self-contained” liquid pool in direct contact with solid walls of non-molten material. These walls act, during the rapid solidification process, as preferential 3-dimensional nucleation sites for the formation of the new solid phase, fostering the growth of large crystalline grains (several \( \mu m^3 \)) despite the high cooling rates (>\( 10^4 \) K \( \cdot s^{-1} \)). Such a feature has been observed also in the present investigation with the help of electron microscopy imaging (Figure 3). Large cohesive grains of about 10 \( \mu m^3 \) are visible in the molten zone in Figure 3(a) and (b) relatively to very fine grains of the non-molten porous material. The thickness of the molten zone is several tens of \( \mu m \) (Figure 3c).

3.3. Raman spectroscopy

Figure 4 shows the Raman spectra of some compositions among those investigated in this work. Three main spectral features can be identified in the spectra. The only Raman active mode foreseen by the Factor Group theory for this kind of fluorite-like compounds is the \( T_{2g} \) metal – oxygen stretching vibration clearly visible here around 450 cm\(^{-1} \) [21]. The peaks centred at (580 and 1150) cm\(^{-1} \) were recently assigned, respectively, to 1 longitudinal optical (LO) and 2 LO phonons in pure uranium dioxide by Livneh and Sterer [22]. These authors soundly proved, with the help of energy- and pressure-dependent Raman scattering, that the broader peak located at 1160 cm\(^{-1} \) is a Raman resonant overtone of the LO phonon band intersecting the \( \Gamma \) limit of the Brillouin zone at 580 cm\(^{-1} \). Manara et al. [23] showed that the 2LO peak can be regarded as a fingerprint of a quasi-perfect fluorite structure in UO\(_2\). Because, as confirmed by PXRD for the current sample, the fcc fluorite structure is maintained for all compositions in the (UO\(_2\) + NpO\(_2\)) system, the assignment of these Raman modes can be extended to the samples investigated here. It should be noted that, since the bands at (580 and 1160) cm\(^{-1} \) are lattice extensions of the \( T_{2g} \) IR active vibration, which is not Raman active, their appearance in the Raman spectrum can only be related to the presence of oxygen defects in the lattice, and more precisely clustered oxygen vacancies [24]. Their spectral position and their shape are independent on the sample composition. Therefore, these modes (and particularly the most intense line at 580 cm\(^{-1} \)) can only be used in the present research for a qualitative investigation of oxygen defect formation during the melting/freezing process. On the other hand, the position of the \( T_{2g} \) Raman peak does vary monotonically from 445 cm\(^{-1} \) (pure UO\(_2\)) to 464 cm\(^{-1} \) (pure NpO\(_2\)) as a function of composition (Figure 5). In particular, this peak looks symmetrical at all compositions, unlike the same peak recently reported for the mixed oxides (UO\(_2\) + ThO\(_2\)) [25]. The vibrational mode of the present (UO\(_2\) + NpO\(_2\)) system seems therefore to follow one-mode behaviour, as foreseen for mixed crystals of this type by the Modified Random Element Isodisplacement (MREI) model proposed by Chang et al. [26]. According to such a model, the \( T_{2g} \) peak position shifts in an approximately linear fashion between the positions relative to the pure end members, and no split in the vibrational line is observed in the mixed oxides. This makes the Raman active mode an ideal tool for the semi-quantitative analysis of the local sample composition, which constitutes the main objective of the current Raman analysis. More details about vibrational spectroscopy of the present mixed oxides will be left to further research.

The first-approximation linear correlation between the \( T_{2g} \) Raman peak position and \( x(\text{NpO}_2) \) in the current samples is shown in Figure 5. The uncertainty bars reported in Figure 5 represent the relative standard deviation \( u \), of the peak position recorded in several different measurements.

4. Discussion

4.1. Segregation effects

It has been observed that, in the case of strongly non-congruent melting, the rapid cooling process can lead, in the vicinity of the boundary between the two phases, to segregation effects both in the non-molten solid and in the melted and refrozen liquid. Such segregation effects can be experimentally observed by post-melting material characterization. For example, clear local compositional changes have been detected after melting/freezing cycles in the systems (UO\(_2\) + ThO\(_2\)), (UO\(_2\) + PuO\(_2\)) and (ThO\(_2\) + PuO\(_2\)) [8,10,11], in particular for the compositions where the solidus and liquidus temperatures were observed to be the furthest apart, i.e. where the equilibrium compositions of coexisting solid and liquid differed the most. On the other hand, fast diffusion in the liquid ensures the restoration of the initial equilibrium composition in the central part of the liquid pool, where the thermal analysis is performed.

The fact that solidus and liquidus points in the pseudo-binary (UO\(_2\) + NpO\(_2\)) system are not distinguishable within the current experimental uncertainty suggests that the melting/freezing process occurs in an approximately congruent manner at all intermediate compositions. Thus, also possible segregation effects upon fast cooling from the liquid phase should be very limited. Such segregation effects have been checked in the present investigation by micro-Raman spectroscopy. This technique has been shown to be more effective than, for example, PXRD, for the local analysis of a melted and refrozen surface, where segregation effects can be visible on small areas (of the order of a few tens \( \mu m \)) in the vicinity of the boundary between the melted and the non-melted material [10].

The Raman \( T_{2g} \) peak correlation reported in Figure 5 was then used to measure, locally, the sample composition in samples laser heated beyond melting and refrozen to room temperature. Results of such analysis are reported in Table 2. They show occasional variations in the sample composition after the melting/freezing process only in a couple of uranium-dioxide rich samples. In some particular cases, where the sample integrity was maintained after the high power laser shots, the same technique could be employed in order to line-map the sample composition across the
melted-non-melted material boundary. An example of such line mapping is reported in figure 6, for a NOX70 sample. Although the experimental uncertainty affecting these measurements is rather large (in average ±0.05 on the reported molecular fractions, depending on the data spread), their results give an idea about possible segregation phenomena occurring at high temperature. Although laser irradiated samples appear to be slightly enriched in NpO$_2$ on the surface, such phenomena are quite limited. In most cases a composition very close to the initial one is maintained (within the experimental uncertainty) throughout the melting–freezing and quenching process. This is not entirely true for uranium-rich compositions, where the melted and re-solidified part is enriched in NpO$_2$ beyond the analysis uncertainty, particularly for the sample NOX10. It is therefore reasonable to assume that the solidus and liquidus points might be further apart in this compositional range. They should however still remain within the uncertainty of the current experimental temperature determination (on average ±30 K at 3000 K).

4.2. Phase diagram considerations

Figure 7 reports the experimental melting/freezing points measured in this work, together with the relative $U_r$ uncertainty bands. Temperature uncertainty bands have been estimated as described in Section 2.2 above. The horizontal (composition) uncertainty bands combine the 95% confidence bands ($U_r$) in the nominal sample composition with the possible segregation effects analysed in the previous section. These bands are therefore asymmetric. Combination of the two uncertainty bands gives (with a 2-k coverage factor) a 95% confidence limit for the exact position of the measured melting points. The same graph reports also the solidus and liquidus curves calculated for the (UO$_2$ + NpO$_2$) pseudo-binary system in the assumption of ideal solution mixing in both the solid and liquid solutions. Within this hypothesis, configurational entropy is the only thermodynamic effect of mixing the two dioxides, and no energy (enthalpy) contribution is generated by the

**Figure 3.** Secondary Electron (SE) microscopy imaging of a sample NOX 30 laser-melted in this work. Large cohesive grains of about 10 $\mu$m³ are visible in the molten zone in (a) and (b) relative to very fine grains of the solid porous material (a). The thickness of the molten zone reaches several tens of $\mu$m (c).

**Figure 4.** Selected Raman spectra recorded on the current uranium–neptunium mixed oxides. Excitation source was a Kr$^+$ laser radiating at 647 nm, with an approximate power of 10 mW at the sample surface, on a 2 $\mu$m × 2 $\mu$m spot.

**Figure 5.** The spectral position of Raman-active T$_{2g}$ peak as a function of composition in the current samples before and after melting. Uncertainty bands reflect the ±1 cm$^{-1}$ instrumental uncertainty combined with the data spread at each composition. Raman analysis was unsuccessful on sample NOX50 due to its poor reflectivity.

**Figure 6.** An example of Raman T$_{2g}$-mode line map across the non-melted /melted boundary (of the type shown in figure 3a) recorded on a NOX70 sample. Uncertainty bands report on the composition the ±1 cm$^{-1}$ instrumental uncertainty combined with the data spread. Within the uncertainty, no clear segregation can be deduced in the two zones. A slight average enrichment in NpO$_2$ can be observed in the melted zone, probably due to preferential vaporisation of uranium oxides at high temperatures.
interaction of the different chemical species. When one assumes such an ideal mixing for both the solid and the liquid (UO2 + NpO2) solutions, the solidus and liquidus lines can be obtained by solving the following system of equations [27,28]:

\[
\begin{align*}
\Delta_{\text{fus}} H(\text{UO}_2) \left( \frac{1}{n_{\text{mol}(\text{UO}_2)}} - \frac{1}{x} \right) &= R \ln \left( \frac{1-x}{x} \right) , \\
\Delta_{\text{fus}} H(\text{NpO}_2) \left( \frac{1}{n_{\text{mol}(\text{NpO}_2)}} - \frac{1}{x} \right) &= R \ln \left( \frac{x}{1-x} \right).
\end{align*}
\]

In (1), R is the ideal gas constant (8.3144621 kJ · K\(^{-1}\) · mol\(^{-1}\)), x\(_i\) and x are the NpO\(_2\) mole fractions on the, respective, liquidus and solidus curves at a given absolute temperature \(T (T_{\text{fus}(\text{NpO}_2)} < T < T_{\text{fus}(\text{UO}_2)})\). The \(\Delta_{\text{fus}} H(A)\) and \(T_{\text{fus}(A)}\) are respectively the melting enthalpy and the melting temperature of the pure dioxide A. The values recently assessed by Konings et al. [29] for all these parameters have been retained here. The entropic equations of system (1) obviously imply that the heat capacity of the current samples is independent of temperature and composition in the vicinity of the melting transition. This is somewhat a rough assumption. It has actually been established in this kind of solid dioxides that the formation of oxygen defects, and in particular of Frenkel pairs, leads to an abrupt increase of the heat capacity as temperature approaches the melting point [30,31]. In the case of UO\(_2\) and ThO\(_2\), even a pre-melting order–disorder “lambda” transition has been proposed by certain authors [32–34].

The creation of oxygen defects is actually likely to occur in uranium-rich samples, because U has a partially filled 5-f electron shell and can therefore easily assume the valences +3, +4, +5 and +6 even in the condensed oxide phases [35]. Neptunium (four 5-f electrons) is mostly present in the solid oxide form as Np\(^{4+}\) and Np\(^{5+}\), only under certain circumstances as Np\(^{6+}\) in the form Np\(_2\)O\(_5\) [29]. In the stoichiometric dioxide form, NpO\(_2\) is known to have a higher oxygen potential than UO\(_2\) at a fixed temperature [12]. The NpO\(_2\) actually tends to lose oxygen and become hypo-stoichiometric (with O/Np < 2) more than UO\(_2\) does. The intense Raman peak detected at 580 cm\(^{-1}\) in all mixed oxides, and not in the pure dioxides, indicates that mixing and sintering the two oxides results in the formation of oxygen vacancies. It has been pointed out that these vacancies tend to cluster and result in structural modifications of the coordination polyhedra around the cations rather than remaining simple point defects [24]. On the other hand, the slight over-oxidation of uranium-rich compositions cannot be excluded at very high temperature even in the presence of only small traces of oxygen. The consequent formation of uranium-rich, volatile oxides on the sample surface, such as M\(_2\)O\(_4\) (where M is mostly uranium, but can contain also traces of Np [4]), would result in their rapid vapourisation and in a slight Np-enrichment of the condensed phases, as observed here by Raman spectroscopy.

None of the mentioned phenomena is explicitly taken into account in the present data assessment, considering that their impact on the melting behaviour of mixed uranium–neptunium dioxides is probably smaller than the intrinsic experimental uncertainty of the reported experiments.

This is consistent with the fact that the current experimental data points and the (solidus + liquidus) lines calculated from an ideal solution model agree within such an experimental uncertainty. In other words, the melting/solidification points measured in this work are not consistent, within the experimental uncertainty, with any significant or systematic deviation from ideal solution behaviour in the system (UO\(_2\) + NpO\(_2\)). One can easily estimate, using the heat capacity data available in the literature for melting UO\(_2\) and NpO\(_2\) [29], that the excess enthalpy contribution due to non-ideal mixing, defect formation or surface vapourisation of M\(_2\)O\(_4\) should exceed a magnitude of approximately 5 kJ · mol\(^{-1}\) in order to have an effect, on the observed melting temperature, larger than the current experimental uncertainty. Such non-ideal enthalpy contributions can therefore be summarised in a single \(\Delta H^{\text{excess}}\) term, estimated to be

\[|\Delta H^{\text{excess}}| < 5 \text{ kJ · mol}^{-1}.\]

On the other hand, both the observed oxygen defect formation and the likely formation and vapourisation of a more oxidised phase on the very surface suggest that a more complete thermodynamic description of this type of materials would require a full assessment (CALPHAD) of the ternary (U + Np + O) system.

### 4.3. Comparison with other actinide dioxide systems

The upper value set for the non-ideal enthalpy contribution in inequality (2) suggests that \(\Delta H^{\text{excess}}\) can have values probably close to those recently reported in the systems (UO\(_2\) + ThO\(_2\)) and (PuO\(_2\) + ThO\(_2\)). However, due to the more different properties (heat capacity, melting point, melting enthalpy) of the pure end members in those cases, such small non-ideal enthalpy contributions were shown to be sufficient to justify a clear deviation from the ideal solution behaviour and even a minimum melting point for low ThO\(_2\) contents (around 5 mol% in both systems). On the other hand, recent comprehensive studies on the system (UO\(_2\) + PuO\(_2\)) have shown much larger deviations from ideal mixing behaviour in that system [7,8,13]. In that case, besides the occurrence of oxygen defects, the non-ideal character of the solid/liquid phase boundaries is largely linked to the high volatility of even stoichiometric dioxide phases. The (urania + plutonia) system can only be understood as a ternary (U + Pu + O), and hardly as an over-simplified pseudo-binary (UO\(_2\) + PuO\(_2\)). In contrast, the (urania + neptunia) system investigated here has a melting behaviour which can be described satisfactorily with an ideal solution model, at least in the limits of the experimental uncertainty. This is probably mostly due to the rather similar properties of the pure end members (NpO\(_2\) and UO\(_2\) melting temperatures differ only by 60 K). The fact, however, that possible deviations from ideality have been mostly observed in urania-rich compositions indicates that NpO\(_2\) can have a sort of stabilizing effect on the solid solution, with respect to the reduction–oxidation behaviour leading to the
formation of oxygen defects and non-ideal enthalpy contributions. In this respect, neptunium dioxide can play a role similar to that already observed for thorium dioxide in the systems (UO₂ + ThO₂) and (PuO₂ + ThO₂). A sort of stability and stabilising effect (in mixed oxides) order can thus be proposed for the actinide dioxide series:

\[ \text{ThO}_2 > \text{NpO}_2 > \text{PuO}_2 > \text{UO}_2 > \text{AmO}_2 \].

In this series, it is important to consider uranium dioxide as hyper-stoichiometric, in order to take into account its strong tendency to accommodate excess oxygen and increase its cation valence, and americium dioxide as hypo-stoichiometric, due to its very high oxygen potential. The series follows then the oxygen potential trend assessed by Guéneau et al. [12] for the various dioxides. It is on the basis of such a trend that ThO₂ is given the first position and americium dioxide the last. A more systematic assessment of the high temperature behaviour of such mixed actinide oxides, including also AmO₂, obviously calls for further research.

The present work is useful, from a practical viewpoint, in showing that the addition of neptunium dioxide to a uranium dioxide matrix has only a very limited effect on its melting behaviour, both in terms of solid/liquid transition temperature and segregation effects.

5. Conclusions

The melting behaviour of the pseudo-binary (UO₂ + NpO₂) system has been experimentally studied for the first time in this work, by laser heating and fast pyrometry. Other auxiliary methods, such as electron microscopy, X-ray diffraction and Raman spectroscopy, have been used for pre- and post-melting material characterisation. The following conclusions can be drawn:

1. From a thermodynamic viewpoint, the melting behaviour of the (UO₂ + NpO₂) system is satisfactorily described by an ideal solution model (negligible mixing enthalpy). The present experimental data points provide no direct evidence, within the experimental uncertainty, of any significant or systematic deviations from ideal solution behaviour.

2. Post-melting analysis, and in particular Raman spectroscopy results, indicate that slight segregation phenomena can occur during the melting/freezing process, particularly for UO₂-rich compositions. These phenomena are probably related to the formation, on the sample surface, of more volatile oxides of the M₂O₈ type. Therefore, they will be thermodynamically better described in an assessment of the ternary (U + Np + O) system rather than in the pseudo-binary (UO₂ + NpO₂) section.

3. Pre- and post-melting Raman spectroscopy shows that blending and sintering UO₂ and NpO₂ results in the formation of oxygen defects (probably clustered vacancies) in the thus-obtained solid solution at all mixed compositions. No effect on the presence of these defects has been observed following the melting/freezing process.

4. It can be concluded that, thanks to the similar solid/liquid dioxide transition temperature and ionic radius of uranium and neptunium, the addition of NpO₂ to a UO₂ matrix has little influence on its melting behaviour, both in terms of solid/liquid transition temperature and segregation effects.

The formation and evolution of oxygen and structural defects and their effect on the stability and behaviour of this kind of oxides at high temperature remains a fascinating scientific challenge.

From a technological viewpoint, the current results are important for the safety and the performance assessment of possible transmutation fuels in fast nuclear reactors. The high temperature (melting, vapourisation) behaviour of UO₂-based mixed dioxides containing more minor actinides (Am, Cm...) remains an open challenge for further research.

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