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Japan Atomic Energy Agency, Japan  
Lionel Desgranges,  
Commissariat à l'Energie Atomique et aux  
Energies Alternatives (CEA), France

## \*CORRESPONDENCE

C. Gaillard,  
✉ gaillard@ipnl.in2p3.fr

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# Insights into the $UO_{2+x}/U_4O_9$ phase characterization in oxidized $UO_2$ pellets as a function of hyper-stoichiometry

C. Gaillard<sup>1\*</sup>, H. Lotz<sup>1</sup>, L. Sarrasin<sup>1</sup>, Y. Pipon<sup>1,2</sup>, R. Ducher<sup>3</sup> and N. Moncoffre<sup>1</sup>

<sup>1</sup>University Lyon, University Claude Bernard Lyon 1, CNRS/IN2P3, IP2I Lyon, Villeurbanne, France,

<sup>2</sup>University Lyon, University Claude Bernard Lyon 1, IUT Lyon-1, Département Chimie, Lyon, France,

<sup>3</sup>IRSN, LETR-BP3, St-Paul-Lez-Durance Cedex, France

We present new insights into the study of the  $UO_{2+x}/U_4O_9$  equilibrium in  $UO_2$  as a function of the hyper-stoichiometry ( $x$ ) by coupling HERFD-XANES at the uranium  $M_4$ -edge with micro-Raman spectroscopy mapping. XANES allowed the measurement of uranium speciation in the samples, while Raman spectroscopy was used to individually characterize the composition and localization of the different oxide phases.  $UO_2$  pellets were oxidized under dry conditions at temperatures above the  $UO_{2+x}/U_4O_9$  phase transition to reach hyper-stoichiometries in the range of  $0.01 \leq x \leq 0.1$ . Combining both techniques, we could determine the proportions of  $U_4O_9$  and  $UO_{2+x}$ . We show that at a low O/U ratio,  $U_4O_9$  is present as small clusters inside  $UO_2$  grains. As the O/U increases, we found evidence of the formation of a network of  $U_4O_9$  crystallized inside the  $UO_{2+x}$  grains. The variation of the  $UO_{2+x}$  phase hyper-stoichiometry ( $x$ ) was evaluated as a function of the sample oxidation.

## KEYWORDS

$UO_2$ , oxidation,  $U_4O_9$ , Raman spectroscopy, HERFD-XANES

## 1 Introduction

Uranium oxide  $UO_2$  is widely studied because of its use as a nuclear fuel in nuclear pressurized water reactor power plants. An important parameter that can affect the fuel's performance is fuel oxidation, which can occur during normal reactor operations in the case of a defective rod or during reactor accident conditions. Under LOCA (LOss of Coolant Accident) conditions, fuel oxidizes due to high temperatures and the steam environment, affecting its thermal properties and the release of fission products (Horlait et al., 2023; Kudo et al., 2007; Le Gall et al., 2020). Understanding oxidation mechanisms and characterizing formed oxide phases are therefore important to evaluate all consequences of this type of accident. Both the kinetics of oxidation and the crystallographic structures of the U–O oxide phases ( $\alpha$ ,  $\beta$ ,  $\gamma$ -  $U_4O_9$ ,  $U_3O_7$ ,  $\alpha$ ,  $\beta$ -  $U_3O_8$ ) have been studied extensively (Taylor, 2005; Mc Eachern and Taylor, 1998; Rousseau et al., 2006; Desgranges et al., 2011; Garrido et al., 2006; Soulié et al., 2019; Mc Eachern, 1997).  $UO_2$  has a fluorite structure of Fm-3m. At high temperatures,  $UO_2$  oxidation forms a  $UO_{2+x}$  single phase, where oxygen atoms are incorporated into the fluorite structure in interstitial octahedral sites. At lower temperatures,  $UO_{2+x}$  coexists with  $\alpha$ - $U_4O_9$  ( $=UO_{2.25}$ ). In hyper-stoichiometric compounds, the charge balance is made by the valence change of uranium cations from

$U^{4+}$  to  $U^{5+}$ , while interstitial oxygen atoms are accommodated as Willis clusters involving two oxygen vacancies, two oxygen  $O'$  atoms, and two  $O''$  atoms. A further increase in interstitial oxygen atoms leads to a distortion of the unit cell from cubic to tetragonal and ultimately to a monoclinic structure. The formation of  $U_4O_9$  (and  $U_3O_7$ ) involves a slight volume reduction, while the formation of  $U_3O_8$  involves a 36% volume increase.

The transition mechanism from  $UO_{2+x}$  to  $U_4O_9$  has been widely investigated in terms of phase transition, establishing the U–O equilibrium phase diagram (Bannister and Buykx, 1974; Blackburn, 1958; Gronvold, 1955; Guéneau et al., 2002; Higgs et al., 2007; Ishii et al., 1970; Lierde et al., 1970; Matsui and Naito, 1975). However, few have studied the morphological changes in polycrystalline  $UO_2$  after oxidative treatments. Whillock and Pearce studied the distribution and percentage of  $U_4O_9$  in oxidized  $UO_2$  (total O/U ratio between 2.05 and 2.12) (Whillock and Pearce, 1990). They found different types of morphology for  $U_4O_9$  in  $UO_2$ , from needles to starbursts or massive blocks, as the  $U_4O_9$  proportion varies from 20% to 40%. Schaner studied the  $UO_2$ – $U_4O_9$  equilibrium phase diagram between  $UO_{2.006}$  and  $UO_{2.176}$  on polycrystalline  $UO_2$  pellets using metallographic techniques (Schaner, 1960), finding that  $U_4O_9$  solubility in  $UO_{2+x}$  depends on temperature. In addition, photomicrographs of the sample surfaces taken after different oxidative treatments at 900 °C show that the  $U_4O_9$  morphology inside  $UO_{2+x}$  grains depends on the O/U ratio and on the experimental procedure used to cool the samples at ambient temperature (slow temperature decrease or quenching below the phase transition limit).

In this study, we contribute to the study of the  $UO_{2+x}/U_4O_9$  equilibrium in  $UO_2$  as a function of hyper-stoichiometry by coupling HERFD-XANES at the uranium  $M_4$ -edge with micro-Raman spectroscopy mapping. XANES allows the measurement of uranium speciation in the samples, while Raman spectroscopy individually characterizes the composition and localization of the different oxide phases in  $UO_2$  pellets. Combining both techniques, we could determine the proportion between  $U_4O_9$  and  $UO_{2+x}$  and evaluate the variation of the  $UO_{2+x}$  phase stoichiometry (x) as a function of the sample oxidation.

## 2 Materials and methods

### 2.1 Sample preparation

Depleted  $UO_2$  pellets (diameter 9 mm × 1.6 mm thick) of high bulk density (97.5% of the theoretical density) sintered at 1750 °C under reducing conditions (Ar/H<sub>2</sub> 5%) for 5 h were provided by Framatome. Their average grain size was 11 μm, which is comparable to that of the PWR nuclear fuel. The pellets were polished on one side by the PRIMEVerre company (Montpellier, France) with a ¼ μm diamond paste. The samples were then annealed in a PECKLY<sup>®</sup> tubular furnace at 1000 °C for 10 h under vacuum (10<sup>-7</sup> mbar) to de-gas adsorbed species on the pellets. Second, annealing at 1600 °C for 4 h in a NABERTHERM<sup>®</sup> tubular furnace was performed under a Ar/H<sub>2</sub> 5% gas mixture flowing through ultrahigh capacity oxygen and moisture traps. This thermal treatment allowed annealing of the polishing defects while avoiding  $UO_2$  oxidation.

$UO_2$  oxidation was performed by thermal annealing under a dry atmosphere using different protocols according to the samples (Table 1). Before and after each annealing, the pellets were weighted with a Sartorius μ-balance with a ±2 μg accuracy. The O/U ratio was calculated from the mass gain of the samples during annealing, with an error of ±0.001.

Samples  $UO_2_{ox1\_A}$  and  $UO_2_{ox1\_B}$  correspond to the same initial pellet. For  $UO_2_{ox1\_A}$ , the pellet was annealed in a NABERTHERM<sup>®</sup> tubular furnace at 1600 °C under an Ar/O<sub>2</sub> 5 ppm gas flow over 4 h, with a ramping of 300°/h for heating and cooling. After annealing, the pellet was weighed and analyzed by Raman spectroscopy. It was then oxidized a second time following the same experimental protocol (sample  $UO_2_{ox1\_B}$ ) to reach a final O/U ratio of 2.010. The sample  $UO_2_{ox2}$  was submitted to the same annealing treatment as  $UO_2_{ox1\_B}$  to reach a 2.010 stoichiometry. Then, it was annealed in a steel tubular furnace at 900 °C for an hour under an Ar/O<sub>2</sub> 5 ppm gas flow. According to the O/U phase diagram (Guéneau et al., 2002; Lindemer and Besmann, 1985), this annealing condition allows the dissolution of any  $U_4O_9$  phase that might be present in the sample to form the sole  $UO_{2+x}$  phase. Sample quenching was then performed to keep this  $UO_{2+x}$  phase at an ambient temperature. This rapid sample cooling, from 900 °C to room temperature, was achieved in 10 minutes under the same atmospheric conditions as those during the annealing (Ar/O<sub>2</sub> 5 ppm gas flow). After this quenching, no mass variation was detected on the pellet, so we can assume that its final stoichiometry was the same as before quenching (2.010). Sample  $UO_2_{ox3}$  was prepared by annealing at 1600 °C under an Ar/O<sub>2</sub> 5 ppm gas flow for 15 h. Sample  $UO_2_{ox4}$  was obtained using a SETARAM<sup>®</sup> thermobalance. The  $UO_2$  pellet was placed in a quartz boat suspended in an oven. The analyzer was placed in a vacuum for 30 min and then filled with a carrier gas to avoid any gaseous pollution. The gases used were He and Ar/O<sub>2</sub> 100 ppm, the introduction of O<sub>2</sub> being controlled by an oxygen sensor. In order to reach the O/U ratio = 2.10, oxidation was performed at 850 °C. A ramp of 10°C.min<sup>-1</sup> was programmed up to 850 °C, then plateaued at 850 °C until the mass gain was reached, and finally the heating was switched off. O<sub>2</sub> was added only during the plateau at 850 °C, while the increase and decrease in temperature were performed under He. The mass gain was achieved in 3.5 h. Supplementary Figure S1 displays the mass gain variation with time and temperature; these curves show that the mass gain of the pellet is linear with time at 850 °C. The change of atmosphere at the end of the plateau combined with the decrease of temperature (approximately 30 °C/min) probably limited the oxidation to a negligible level during the cooling stage.

### 2.2 HERFD-XANES measurements at the U $M_4$ -edge

High Energy Resolution Fluorescence Detected XANES (HERFD-XANES) data were measured at the MARS beamline of the SOLEIL synchrotron (Saint-Aubin, France) (Sitaud et al., 2012) on pellets. Spectra were measured at room temperature at the U  $M_4$ -edge (3728 eV) using a double-crystal monochromator (DCM) equipped with a pair of Si(111) crystals. Higher harmonic rejection and vertical focusing were achieved using the Si strip of

TABLE 1 Summary of the sample oxidative treatments.

Sample ID	O/U ratio	Sample oxidative treatment
UO <sub>2</sub>	2.000	—
UO <sub>2_ox1_A</sub>	2.007	4h-1600°C - Ar/O <sub>2</sub> 5 ppm
UO <sub>2_ox1_B</sub>	2.010	4 h + 4h-1600°C - Ar/O <sub>2</sub> 5 ppm
UO <sub>2_ox2_BQ</sub>	2.010	4 h + 4h-1600°C - Ar/O <sub>2</sub> 5 ppm
UO <sub>2_ox2_AQ</sub>	2.010	4 h + 4h-1600°C - Ar/O <sub>2</sub> 5 ppm, quenching at 900 °C
UO <sub>2_ox3</sub>	2.050	15h-1600°C - Ar/O <sub>2</sub> 5 ppm
UO <sub>2_ox4</sub>	2.100	2h-850°C - Ar/O <sub>2</sub> 100 ppm during plateau temperature

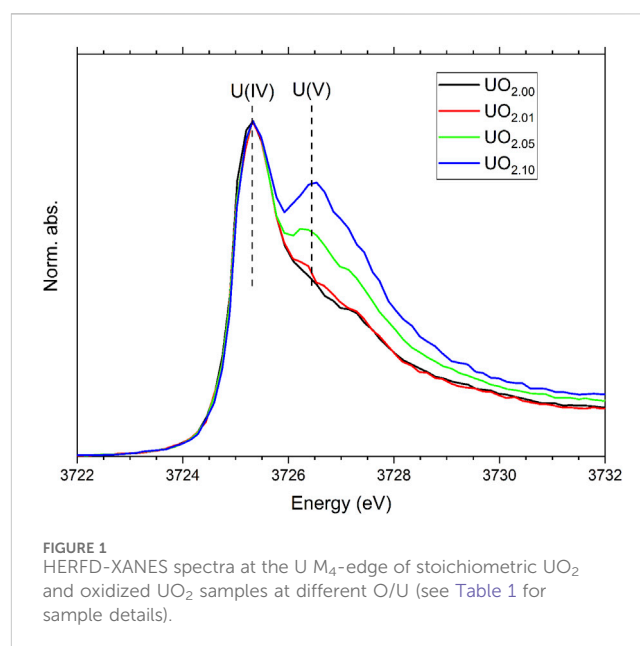
each mirror inserted before and after the DCM with a 4 mrad incidence angle. The beam size was  $250 \times 150 \mu\text{m}$ . The incident energy was calibrated using the absorption K-edge of potassium of a KBr pellet (3608.4 eV). HERFD-XANES was performed using the crystal-analyzer emission spectrometer in the Rowland geometry and a KETEK single-element silicon solid-state detector. The  $M_{\beta}$  emission line of U (3339 eV) was analyzed using the 220 reflection of an Si (220) bent, diced crystal analyzer with a curvature radius of 1 m. The samples were oriented at  $45^\circ$  with respect to the incident beam. An He-filled balloon was used to reduce the scattering of the incident and emitted X-rays by the air between the sample and the crystal analyzer and the detector. No evolution of the spectra was observed during measurements under the beam. Collected spectra were normalized using ATHENA software (Ravel and Newville, 2005). The contributions of U(IV) and U(V) were derived from the linear combination of UO<sub>2</sub> and U<sub>4</sub>O<sub>9</sub> reference spectra.

## 2.3 Raman analysis

Raman spectroscopy analyses were performed on a Renishaw Invia Qontor equipped with a 1800 gr/mm grating using a He-Ne laser (633 nm). Mapping was recorded using a  $\times 50$  objective from 200 to 1300  $\text{cm}^{-1}$ . Great care was taken to ensure that the laser did not induce any structural modification during the measurements. Starting with low to high laser powers, analyses were repeated on the same point on a pellet surface to optimize our measurement parameters and verify that Raman spectra did not change under the effect of the beam. The incident laser power was thus fixed to 0.9 mW. A silicon standard was used to calibrate the spectrometer with its line frequency fixed at 520.5  $\text{cm}^{-1}$ . Raman mapping was performed on UO<sub>2</sub> pellets with a spatial resolution of  $1 \times 1 \mu\text{m}^2$ . Each mapping covered at least ten grains and the depth probed was estimated to be 3–5  $\mu\text{m}$  (Griffiths and Hubbard, 1991). Data were processed on WIRE 5.4 software.

## 2.4 AFM

Atomic force microscopy (AFM) was performed on a NaioAFM microscope (Liestal, Switzerland) fitted with a 190 Al cantilever tip with the following dimensions: length, 225  $\mu\text{m}$ ; width, 38  $\mu\text{m}$ ; tip radius, 10 nm. The cantilever spring constant was 48  $\text{N m}^{-1}$ . Data analysis was performed using Nanosurf, Naio control software in the dynamic



mode. The AFM images were recorded in air and at room temperature. Data treatment was performed using Gwyddion software.

## 3 Results

### 3.1 Chemical state of uranium in oxidized samples

HERFD-XANES at the U  $M_4$ -edge probes the 5f unoccupied states, and it has been shown to be suitable for differentiating U(V) species from U(IV) and U(VI) (Kvashnina and Butorin, 2022). Therefore, we used this technique on UO<sub>2</sub> oxidized samples in order to determine the uranium oxidation state. It must be noted that at this edge, the UO<sub>2</sub> pellet is probed only over the first micrometer. Figure 1 displays the HERFD-XANES spectrum of a stoichiometric UO<sub>2</sub> compared with spectra of oxidized samples with different O/U ratios. The first peak at 3725.3 eV corresponds to U(IV), while the second peak observed at 3726.4 eV corresponds to the presence of U(V). This latter peak is thus the signature of hyperstoichiometry.

TABLE 2 Proportion of U(IV) and U(V) and stoichiometries in  $\text{UO}_2$  oxidized samples, obtained by linear fitting of HERFD-XANES spectra using reference compounds  $\text{UO}_2$  and  $\text{U}_4\text{O}_9$ . The average O/U ratio was obtained by mass gain measurements after oxidation treatments.

Sample ID	Average O/U*	% $\text{UO}_2$	% $\text{U}_4\text{O}_9$	% U(IV)	% U(V)	XANES O/U ratio ( $\pm 0.01$ ) on the first $\mu\text{m}$
$\text{UO}_2$	2.000	100	0	100	0	2.00
$\text{UO}_2\text{-ox1\_B}$	2.010	90	10	95	5	2.02
$\text{UO}_2\text{-ox3}$	2.050	70	30	85	15	2.08
$\text{UO}_2\text{-ox4}$	2.100	35	65	67	33	2.16

\*obtained by mass gain measurements.

$\text{UO}_2$  oxidation can lead to the formation of different species:  $\text{UO}_{2+x}$ , which is a mixture of U(IV) and U(V);  $\text{U}_4\text{O}_9$  composed of 50% U(IV) and 50% U(V);  $\text{U}_3\text{O}_8$  containing a mixture of U(V) and U(VI) (Leinders et al., 2020). We did not consider the latter oxide as we had no evidence of a U(VI) signal, which was further confirmed by Raman analysis (see below). Thus, spectra were fitted by a linear combination of U(IV) and U(V) reference spectra in order to determine the proportion between uranium oxidation degrees. Table 2 gives these results and the O/U ratio calculated from this proportion. The less oxidized sample  $\text{UO}_2\text{-ox1\_B}$  contained approximately 10%  $\text{U}_4\text{O}_9$ . Sample  $\text{UO}_2\text{-ox3}$  contained 30%  $\text{U}_4\text{O}_9$  and a stoichiometry at the surface which was slightly higher than the average obtained by mass gain measurements (O/U = 2.08 vs. 2.05). Analysis of the  $\text{UO}_2\text{-ox4}$  sample showed a noticeable higher hyperstoichiometry at the extreme surface (2.16) than average (2.10), and the presence of 65%  $\text{U}_4\text{O}_9$ .

### 3.2 Speciation of uranium oxide phases by Raman spectroscopy

Raman spectroscopy was used to identify the different crystallographic phases that may be present in samples after oxidation. Three phases were expected: stoichiometric  $\text{UO}_2$ ,  $\text{UO}_{2+x}$ , and  $\text{U}_4\text{O}_9$ . Their respective Raman spectra are shown in Supplementary Figure S2, and Raman mappings of stoichiometric  $\text{UO}_2$  were published in Gaillard et al. (2024). For stoichiometric  $\text{UO}_2$ , the most intense band is the  $T_{2g}$  band located at  $444.6\text{ cm}^{-1}$ , typical of the fluorite structure. This triply degenerate mode corresponds to the symmetrical vibration of oxygen atoms around an uranium atom (Keramidas and White, 1973). The second most intense band located at  $\sim 1150\text{ cm}^{-1}$  corresponds to the 2LO band, an overtone of the first-order LO phonon (Livneh and Sterer, 2006; Elorrieta et al., 2018). Recent studies (Gaillard et al., 2024; Livneh, 2022) have shown that this band has a second weak contribution at  $1196\text{ cm}^{-1}$ ; we did not take this into account in this study as it does not give additional information. Indeed, this band has the same behavior as the  $1196\text{ cm}^{-1}$  one upon the formation of  $\text{U}_4\text{O}_9$ . Bands of very weak intensities are noticeable between  $500$  and  $700\text{ cm}^{-1}$ . These so-called U bands are correlated with the presence of defects in the  $\text{UO}_2$  crystallographic structure and to the formation of domains having a local symmetry lower than that of perfect  $\text{UO}_2$  (Guimbretière et al., 2012; Simon et al., 2023). The  $\text{UO}_{2+x}$  spectrum is similar in shape to the  $\text{UO}_2$  spectrum. A slight blueshift of the  $T_{2g}$  band is expected as the result of the  $\text{UO}_2$  lattice contraction (Spino and Peerani, 2008; Allen et al., 1982; He and Shoesmith, 2010). The

TABLE 3 Summary of the  $T_{2g}$  band position and width in  $\text{UO}_2/\text{UO}_{2+x}$  and  $\text{U}_4\text{O}_9$  phases (BQ = before quenching, AQ = after quenching, cf. part 2.2).

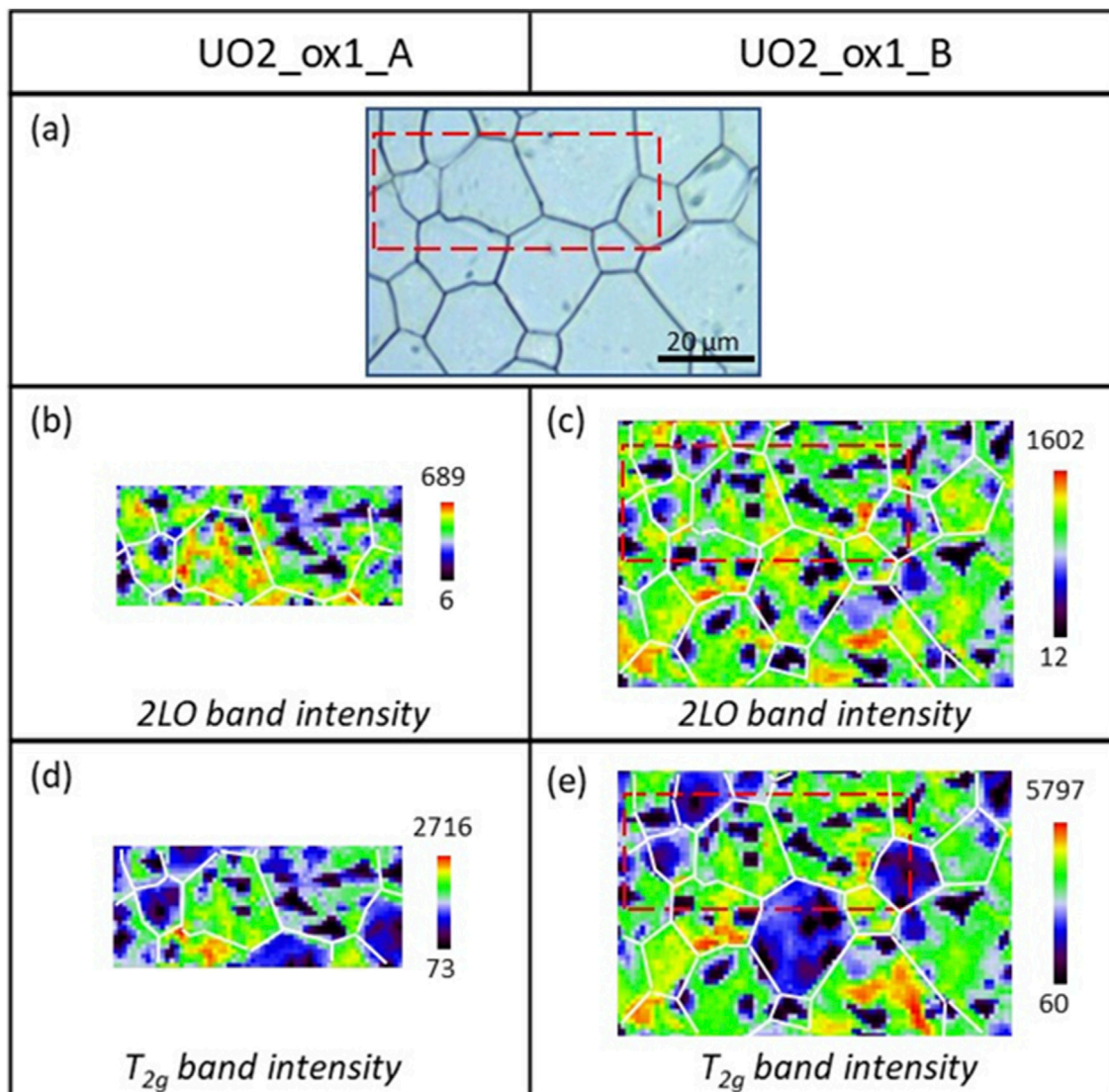
	$\text{UO}_2 - \text{UO}_{2+x}$ phase		$\text{U}_4\text{O}_9$ phase	
	Position ( $\text{cm}^{-1}$ )	Width ( $\text{cm}^{-1}$ )	Position ( $\text{cm}^{-1}$ )	Width ( $\text{cm}^{-1}$ )
$\text{UO}_2$	444.6	15.7	-	-
$\text{U}_4\text{O}_9$	-	-	455	45
$\text{UO}_2\text{-ox1\_A}$	444.7	15.7	448	27
$\text{UO}_2\text{-ox1\_B}$	444.7	15.7	449	30
$\text{UO}_2\text{-ox2 BQ}$	444.8	15.8	452	40
$\text{UO}_2\text{-ox2 AQ}$	444.9	16.2	-	-
$\text{UO}_2\text{-ox3}$	445.1	15.8	450	30
$\text{UO}_2\text{-ox4}$	445.7	16.8	457	45

insertion of oxygen atoms in the  $\text{UO}_2$  fluorite structure entails the presence of defects in the material, which is seen on the Raman spectrum by a slight widening of the  $T_{2g}$  peak and an increase of the intensity of the U defect bands. Different features are observed on the  $\text{U}_4\text{O}_9$  spectrum. A strong decrease of the  $T_{2g}$  intensity and increase of the U band intensity are observed, while the 2LO band is no longer visible. We also observe a strong width widening of the  $T_{2g}$  band, which shifts from  $\sim 445\text{ cm}^{-1}$  in  $\text{UO}_2$  to  $\sim 454\text{ cm}^{-1}$  in  $\text{U}_4\text{O}_9$ .

Thus, strong differences are present between  $\text{U}_4\text{O}_9$  and  $\text{UO}_2/\text{UO}_{2+x}$  Raman spectra. In particular, the absence/presence of the 2LO band at  $1150\text{ cm}^{-1}$  was used to detect the presence of  $\text{U}_4\text{O}_9$  in the oxidized pellets. Table 3 summarizes the  $T_{2g}$  band position and width measured, respectively, in the  $\text{UO}_{2+x}$  and  $\text{U}_4\text{O}_9$  phases of each oxidized sample.

#### 3.2.1 $\text{UO}_2$ microstructure at low O/U ( $\leq 2.010$ )

Figure 2 presents Raman mappings of the  $\text{UO}_2\text{-ox1}$  sample oxidized twice consecutively. The first oxidation (on the left of the figure) led to an O/U ratio of 2.007 (sample  $\text{UO}_2\text{-ox1\_A}$ ), while the second oxidation (on the right of the figure) led to a 2.010 stoichiometry (sample  $\text{UO}_2\text{-ox1\_B}$ ). For both O/U ratios, the same region was analyzed by Raman spectroscopy in order to study the evolution of the sample surface morphology. On the optical image (Figure 2A), the region analyzed on sample  $\text{UO}_2\text{-ox1\_A}$  is indicated with a red rectangle, while the region analyzed on sample  $\text{UO}_2\text{-ox1\_B}$  corresponds to the whole optical picture. Mappings of the 2LO band intensity are displayed in Figures



**FIGURE 2** Raman mapping of the 2LO and  $T_{2g}$  band intensities at the surface of sample *UO2\_ox1* after two oxidations (samples *UO2\_ox1\_A* on the left and *UO2\_ox1\_B* on the right). (A) Optical picture of the analyzed region; (B) and (C) Raman mapping of the 2LO band intensity; (D) and (E) Raman mapping of the  $T_{2g}$  band intensity. The color scale corresponds to the intensity scale, from the lowest (black) to the highest (red) value. For clarity, grain boundaries visible on the optical picture are represented by white lines on the mapping.

2B,C, respectively. For both samples, we observe black areas of micrometric size where the 2LO band intensity is very weak. Raman spectra extracted from one of these regions are presented in Figure 3A for both samples, corresponding to  $U_4O_9$  species. The 2LO band is visible, although its intensity is weak, probably because the zone probed by the laser also detected a  $UO_{2+x}$  phase. In these  $U_4O_9$  areas, the  $T_{2g}$  band position and width values (Table 3) are intermediate between those of  $UO_2$  and  $U_4O_9$ .

Outside the  $U_4O_9$  zones, the 2LO band intensity mapping is quite homogeneous at the surface of the samples. Raman spectra extracted from this region, on the same grain for the two samples (*UO2\_ox1\_A* and *UO2\_ox1\_B*), are presented in Figure 3B and are identical. For comparison, a spectrum of stoichiometric  $UO_2$  is also shown in Figure 3B. We did not observe significant changes on the  $T_{2g}$  band (same position and width, see Table 3) compared to  $UO_2$ .

However, the defect band intensity is noticeably higher than the stoichiometric  $UO_2$  spectrum.

On both samples, the  $U_4O_9$  phase forms aggregates inside grains, located heterogeneously. Note that no  $U_4O_9$  aggregates are present in grain boundaries. Comparing the first and second oxidation,  $U_4O_9$  aggregates have similar shapes, sizes, and locations on samples. This indicates that during the second oxidation,  $U_4O_9$  clusters formed in the same zones than during the first oxidation. This is noticeable considering the experiment that was performed; during the second oxidation process at 1600 °C, the  $U_4O_9$  phases formed in sample *UO2\_ox1\_A* dissolved and then re-crystallized during the sample cooling. Thus,  $U_4O_9$  crystallization inside grains is not a random process but is a reversible process that occurs in defined locations inside  $UO_2$  grains. In addition, the  $U_4O_9$  aggregate size is comparable for both oxidations, probably because the final

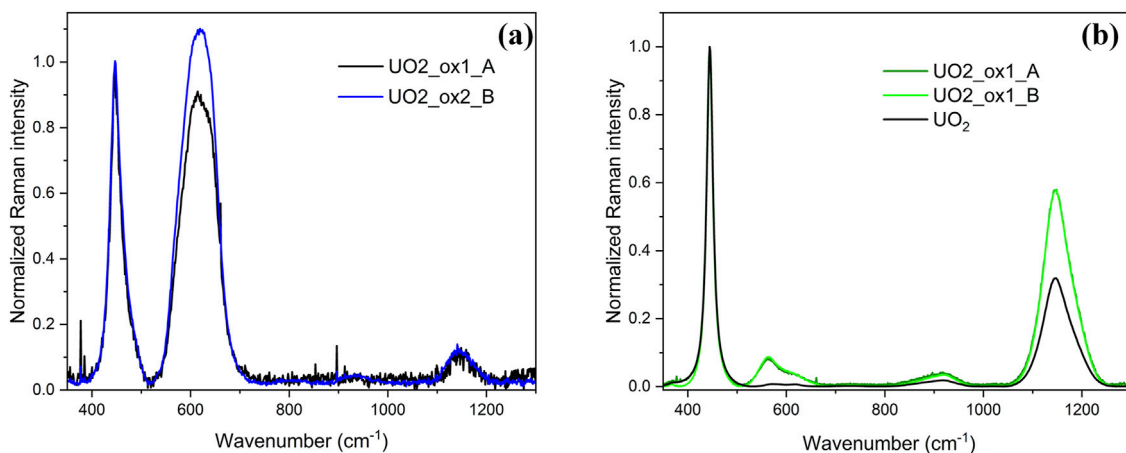


FIGURE 3

Raman spectra extracted from *UO2\_ox1\_A* and *UO2\_ox1\_B* sample mappings (cf. Figure 2). (A) Individual Raman spectra extracted in  $U_4O_9$  area (back pixels on the mapping); (B) individual Raman spectra extracted in  $UO_{2+x}$  area (green pixels on the mapping). Spectra were normalized on the  $T_{2g}$  band intensity for comparison.

O/M ratios after the two oxidation treatments are close (2.007 and 2.010).

Figures 2D,E map the  $T_{2g}$  band intensity for both oxidized samples. Outside the  $U_4O_9$  clusters, we observe that this  $T_{2g}$  intensity depends on grains. This effect is well-known and is due to the dependence of the  $T_{2g}$  intensity on the different crystalline orientations of  $UO_2$  grains (Morgan et al., 2021; Maslova et al., 2019). Thus, the precipitation of  $U_4O_9$  clusters inside grains does not affect global crystallography within the grain.

We performed AFM mapping on sample *UO2\_ox1\_B*. Particular interest was given to regions containing the  $U_4O_9$  phase. Supplementary Figure S3A displays the Raman 2LO band intensity mapping which locates  $U_4O_9$  zones on the pellet surface. This mapping was used to select two areas, indicated by white squares on Supplementary Figure S3A, where surface mapping was done by AFM. Supplementary Figures S3B–E show the 2D and 3D topography images. The color scale, from dark to light brown, indicates the roughness contrast at the surface.  $U_4O_9$  zones are clearly visible as darker zones, which means that they correspond to lower planes (up to ~50 nm) than  $UO_2$  zones. So we evidence that  $U_4O_9$  formation entails a measurable local contraction of the lattice inside  $UO_2$  grains, even if the lattice parameter of both oxides only differ slightly: 5.44 Å for  $U_4O_9$  (Gronvold, 1955; Allen and Holmes, 1995; Cooper and Willis, 2004) and 5.47 Å for  $UO_2$  (Gronvold, 1955; Desgranges et al., 2009; Leinders et al., 2015).

In conclusion, we detected the coexistence of  $UO_2$  and  $U_4O_9$  phases for low hyper-stoichiometric  $UO_2$ . The latter oxide crystallizes inside  $UO_2$  grains as micrometric clusters entail a local lattice contraction without altering the overall crystallography of the grains.

### 3.2.2 Effect of quenching on $U_4O_9$ formation

Quenching is a rapid cooling process which strongly limits atomic displacements and phase transformation. It permits obtaining at room temperature crystallographic phases formed at high temperature. Therefore, quenching, instead of a slow decrease in temperature, is an effective process for overcoming the

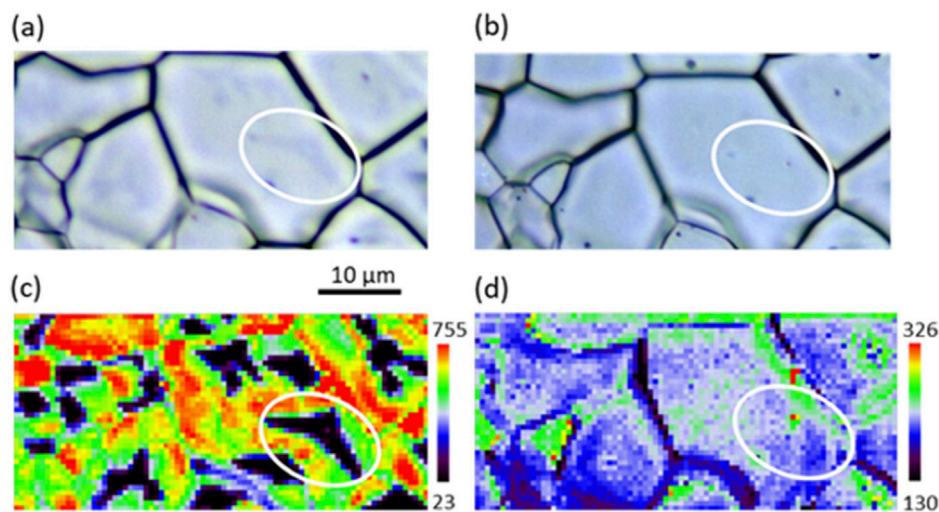
precipitation of  $U_4O_9$  formed during heating treatment (Gronvold, 1955; Schaner, 1960; Yao et al., 2018). Sample *UO2\_ox2* was first submitted to an oxidative annealing in order to obtain an O/U = 2.010. Then, it was submitted to a second thermal treatment at a temperature that entails the dissolution of the  $U_4O_9$  phase (900°C) followed by quenching. No weight evolution of the pellet was measured before and after the quenching, indicating that the O/U ratio did not change during the experiment.

Raman spectroscopy was used to analyze the sample before and after quenching (Figure 4). Before quenching (Figures 4A,C), Raman mapping of the 2LO band intensity (Figure 4C) evidenced in black the presence of  $U_4O_9$  clusters, as characterized previously. Interestingly, it is possible to see the shape of the  $U_4O_9$  region on the optical picture with a weak contrast of color between  $U_4O_9$  and  $UO_2$  (see white circles). Figures 4B and D present the optical picture and the corresponding 2LO band intensity mapping performed in the same zone after quenching from 900 °C. We observed the disappearance of the  $U_4O_9$  aggregates. Thus, the sample is solely composed of a  $UO_{2.01}$  phase.

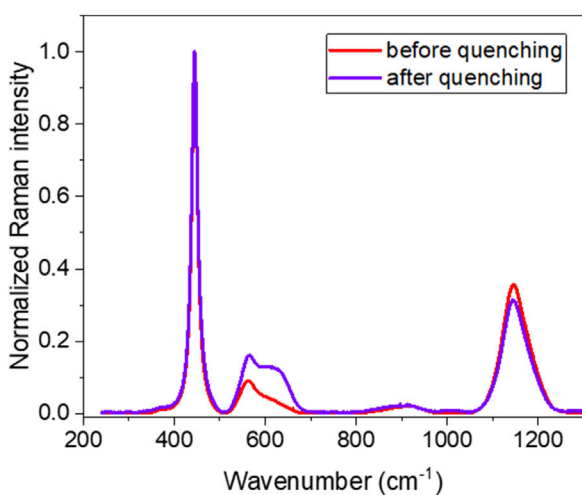
As observed previously for sample *UO2\_ox1*, the Raman mapping exhibited two vibrational signatures,  $U_4O_9$  and  $UO_{2+x}$ , before quenching. After quenching, only the  $UO_{2+x}$  vibrational signature is present. Figure 5 presents the average spectra of  $UO_{2+x}$  zones on the Raman mapping before (mapping without  $U_4O_9$  areas) and after (whole mapping) quenching. Their shapes are identical except for a strong increase of defect band intensity after quenching. This can be explained by the dissolution of  $U_4O_9$  aggregates at 900 °C and the incorporation of oxygen atoms in the  $UO_{2+x}$  lattice which increases defect concentration. This phenomenon is also visible by the slight widening of the  $T_{2g}$  band from 15.8 to 16.2 cm<sup>-1</sup> and a slight but significant shift in the  $T_{2g}$  band position (cf. Table 3).

### 3.2.3 Oxidized $UO_2$ microstructure for O/U = 2.050

Raman mapping of the sample *UO2\_ox3* is presented in Figure 6. According to mass gain measurements, this sample has an average hyper-stoichiometry of 2.05, while HERFD-XANES



**FIGURE 4**  
Effect of quenching on the 2LO band intensity Raman mapping of sample  $UO_{2+ox2}$ . (A) Optical picture of the analyzed zone before and (B) after quenching; (C) and (D) Raman mapping of the 2LO intensity before (C) and after quenching (D).



**FIGURE 5**  
Effect of quenching on the Raman spectra of sample  $UO_{2+ox2}$ . Average spectra of  $UO_{2+ox}$  zones on the Raman mapping before quenching (red); average spectrum of the mapping after quenching (blue). For comparison, spectra are normalized to the  $T_{2g}$  band intensity.

analysis shows that its hyper-stoichiometry in the first micrometer is slightly higher at 2.08. This corresponds to the presence of approximately 30% of  $U_4O_9$  in the sample, confirmed by the Raman analysis. Indeed, the 2LO band mapping intensity (Figure 6B) highlights numerous dark spots distributed over the sample surface, which correspond mainly to  $U_4O_9$ , as is shown on the Raman spectrum extracted from one of the black pixels (Supplementary Figure S4). In this sample,  $U_4O_9$  does not form big clusters inside grains, as shown previously for lower stoichiometric samples, but is present in a rather homogeneous distribution as very small clusters inside grains (cf. Figure 6B).

Supplementary Figure S3 also presents a spectrum extracted from a green pixel of the mapping; it is typical of a  $UO_{2+ox}$  phase and exhibits a shift of the  $T_{2g}$  band to  $445.1\text{ cm}^{-1}$ . It is interesting to note that these  $UO_{2+ox}$  zones correspond mainly to grain boundaries, where little  $U_4O_9$  is detected. Grains are slightly visible on the Raman mapping of the  $T_{2g}$  band intensity (Figure 6C). So, despite the presence of about 30% of  $U_4O_9$ , the grain crystalline orientation is somehow maintained, and the fluorite structure remains present.

### 3.2.4 Oxidized $UO_2$ microstructure for $O/U = 2.10$

Sample  $UO_{2+ox4}$  was prepared with a final hyper-stoichiometry of 2.10, following the protocol explained in experimental Section (2.2). HERFD-XANES analysis shows that it contains approximately 65%  $U_4O_9$  on the first micrometer, resulting in a hyper-stoichiometry of 2.16. Its Raman mapping is presented in Figure 7. The 2LO band intensity mapping displays dark areas distributed as a zebra pattern on the sample surface. We did not observe any difference between grain and grain boundaries. As shown in Figure 8, these dark areas correspond to pure  $U_4O_9$ . Elsewhere on the pellet, Raman spectra show the presence of  $UO_{2+ox}$ . A spectrum extracted on a green pixel of the mapping is shown in Figure 8. A noticeable shift of the  $T_{2g}$  band position in the  $UO_{2+ox}$  area measures  $445.7\text{ cm}^{-1}$ , larger than that measured at  $x = 2.05$ . Thus, as global hyper-stoichiometry increases, the proportion of  $U_4O_9$  and the hyper-stoichiometry of the  $UO_{2+ox}$  phase increase. The  $T_{2g}$  band intensity mapping is displayed in Figure 8C. Despite the large  $U_4O_9$  concentration, it is still possible to distinguish the contrast between grains in the  $UO_{2+ox}$  phase. So, as observed at lower hyper-stoichiometries, the  $UO_2$  lattice is maintained despite the growth of the  $U_4O_9$  phase.

### 3.2.5 $UO_{2+ox}$ phase composition as a function of the sample hyper-stoichiometry

Table 3 summarizes the  $T_{2g}$  band position measured in  $UO_{2+ox}$  phase of oxidized samples, and we observe that this position shifts



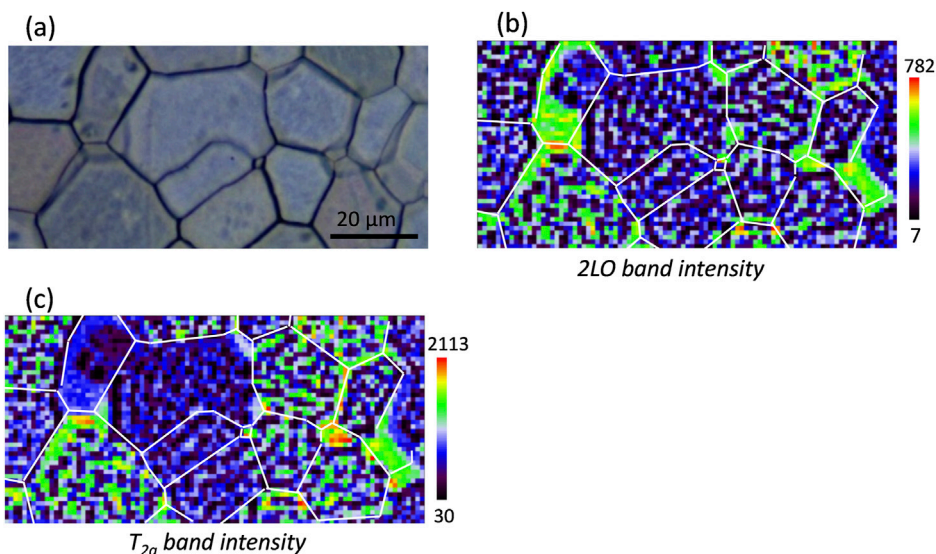


FIGURE 6 Raman mapping of sample  $UO_{2-ox3}$ . (A) Optical picture of the analyzed zone; (B) 2LO band intensity mapping; (C)  $T_{2g}$  band intensity mapping.

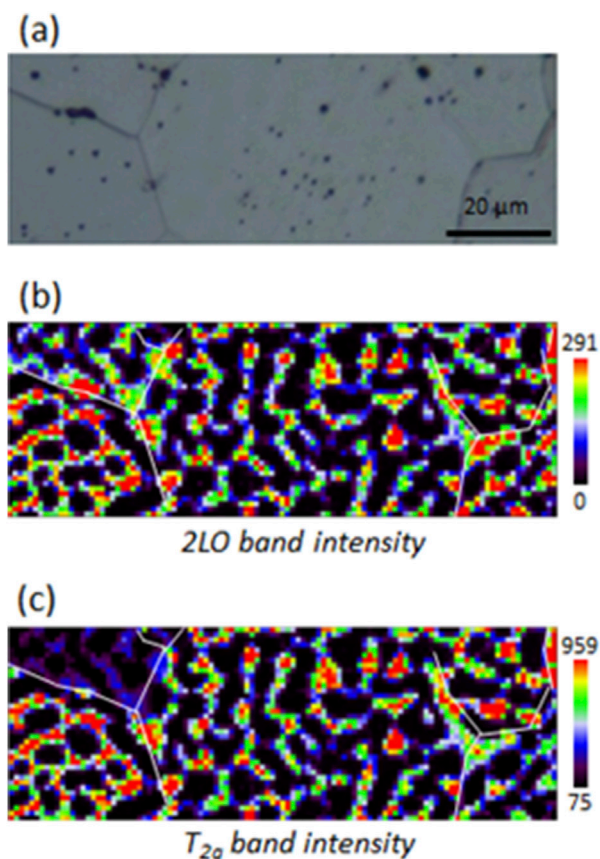


FIGURE 7 Raman mappings of sample  $UO_{2-ox4}$ . (A) Optical picture of the analyzed zone; (B) 2LO band intensity mapping; (C)  $T_{2g}$  band intensity mapping.

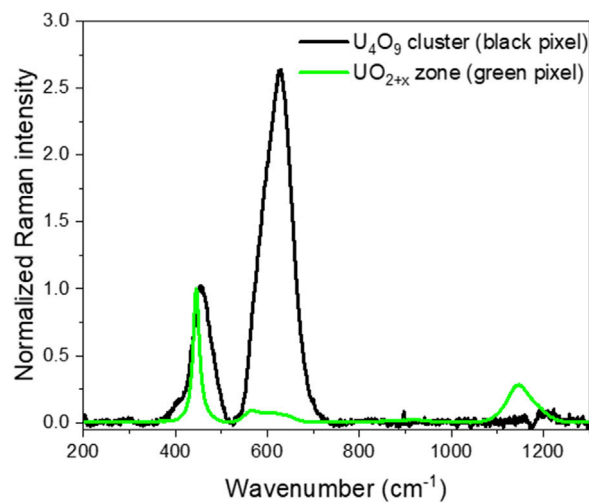


FIGURE 8 Raman spectra extracted on the mapping of sample  $UO_{2-ox4}$  in  $U_4O_9$  clusters (black pixel on the mapping) and in  $UO_{2+x}$  zone (green pixel on the mapping). Spectra are normalized to the  $T_{2g}$  band intensity.

with the global hyper-stoichiometry of samples. Thanks to these measurements, it is possible to evaluate the O/M ratio specifically in  $UO_{2+x}$  phases of our samples. Indeed, the increase of hyper-stoichiometry entails a contraction of the fluorite lattice parameter (Gronvold, 1955). This effect has a direct impact on the  $T_{2g}$  band position, which is expected to shift to higher frequencies according to the Equation 1 (McBride et al., 1994):

$$\Delta T_{2g} = -3\gamma\omega \frac{\Delta a}{a_0} \tag{1}$$

TABLE 4 Calculation of lattice parameters A and O/U ratio in the  $UO_{2+x}$  phase of analyzed samples, from the  $T_{2g}$  band shift  $\Delta T_{2g}$ . For comparison, O/U ratios obtained by mass gain are given.

Sample ID	$\Delta T_{2g}$ ( $cm^{-1}$ )	$UO_{2+x}$ phase		Average in the sample
		Calculated A ( $\text{\AA}$ )	Calculated O/U	O/U from mass gain
UO2	0	5.4703	2.000	2.00
UO2_ox1_A	0.1	5.4701	2.002	2.007
UO2_ox1_B	0.1	5.4701	2.002	2.01
UO2_ox2 BQ	0.2	5.4699	2.004	2.01
UO2_ox2 AQ	0.3	5.4697	2.007	2.01
UO2_ox3	0.5	5.4693	2.010	2.05
UO2_ox4	1.1	5.4682	2.023	2.10

where  $\gamma$  is the Gruneisen parameter (2.17 for  $UO_2$ ),  $\omega$  is the  $T_{2g}$  position for stoichiometric  $UO_2$ , and  $\Delta a$  is the variation of the lattice parameter compared to the  $UO_2$  one ( $a_0$ ).

Therefore, knowing the  $T_{2g}$  band position shift from pristine  $UO_2$  ( $\Delta T_{2g}$ ), it is possible to determine the corresponding variation of the lattice parameter ( $\Delta a$ ) (Medyk et al., 2020), and thus to evaluate the O/M ratio in the  $UO_{2+x}$  phase. Indeed, the variation of the  $UO_{2+x}$  lattice parameter as a function of  $x$  has been widely reported in the literature (Spino and Peerani, 2008). Results are given in Table 4, where they are compared with the O/U ratio calculated for the whole pellet from mass gain after oxidative treatments. For low oxidized samples  $UO2_{ox1}$  and  $UO2_{ox2\_BQ}$ , the  $T_{2g}$  band shift measured in the  $UO_{2+x}$  phase inside grains is uncertain; the corresponding O/U is actually close to 2. This means that in these samples, most additional oxygen atoms have formed the  $U_4O_9$  phase while the  $UO_{2+x}$  phase is stoichiometric or nearly so. In sample  $UO2_{ox2\_AQ}$  formed by a sole  $UO_{2+x}$  phase, the O/U value obtained by Raman measurement is in line with that obtained by mass gain measurement:  $\sim 2.01$ . For samples  $UO2_{ox3}$  and  $UO2_{ox4}$ , O/U ratios of the  $UO_{2+x}$  phase increase with the global hyper-stoichiometry of the samples (respectively 2.010 and 2.023) and correspond roughly to 20% of the global O/U ratio.

## 4 Discussion

Our study consisted of oxidizing  $UO_2$  pellets, initially stoichiometric, to hyper-stoichiometries up to 2.1. As expected from the U–O phase diagram, we characterized two crystallographic phases,  $UO_{2+x}$  and  $U_4O_9$ , by coupling HERFD-XANES and Raman spectroscopy measurements at room temperature. A significant discrepancy is observed between the calculated O/U ratios from XANES measurements and that obtained from the mass gain of samples for the most oxidized sample at 2.1. Indeed, the hyper-stoichiometry is higher at the extreme surface of the sample (XANES probes the first micrometer) than expected. Contrary to other samples, its thermal treatment was performed at 850 °C, not at 1600 °C. At the latter, the oxygen diffusion coefficient ( $D$ ) in stoichiometric polycrystalline  $UO_2$  pellets is in the order of  $10^{-6}$   $cm^2/s$  (Sabioni

et al., 2000). Therefore, a constant repartition of oxygen over the whole pellet depth is obtained after a 4-h annealing, and the hyper-stoichiometry can be considered as constant inside the sample. This may not be the case at 850 °C for a 3.5 h annealing. The oxygen diffusion coefficient is significantly lower at this temperature, in the order of  $10^{-11}$ – $10^{-12}$   $cm^2/s$  (Sabioni et al., 2000; Dorado et al., 2011; Berthinier et al., 2013). This corresponds to a diffusion of oxygen over the first  $\sim 20$   $\mu m$  in sample  $UO2_{ox4}$ . However, it is known that the increase of  $UO_2$  stoichiometry entails a significant increase of oxygen diffusion. Large discrepancies exist in the literature concerning oxygen diffusion coefficients in  $UO_{2+x}$ , probably because of the different experimental protocols used to make D measurements (Bittel et al., 1969; Bayoglu and Loreznelli, 1984; Lay, 1970; Ruello et al., 2004). According to those data, the oxygen diffusion coefficient may range from  $10^{-8}$  to  $10^{-13}$   $cm^2/s$  at 850 °C. Therefore, it is difficult to precisely evaluate the diffusion depth of oxygen in sample  $UO2_{ox4}$ . It is expected to be above 20  $\mu m$  but may not be large enough to assure a constant repartition of oxygen over the whole depth. This question will be addressed in further research by the characterization of pellet cross-sections.

Some have noticed preferential oxidation as a function of the grain orientation, based on work on  $UO_2$  single-crystals (Allen et al., 1988a; Allen et al., 1988b). We did not observe this phenomenon, as the amount of  $U_4O_9$  was homogeneous at the pellet surface whatever the O/U. However, the experimental conditions used by Allen (300 °C, 1 torr of  $O_2$ ) significantly differ from ours and led to the formation of upper oxides ( $U_3O_7$  and  $U_3O_8$ ) not observed in our work. This also highlights the effect of the oxidative conditions on the nature of the oxides formed. In our study, oxidative annealing treatments were performed at 1600 °C or 850 °C—temperatures where the sole existing phase is  $UO_{2+x}$ . The crystallographic phases we further characterized at room temperature are those “allowed” to form during the sample cooling— $UO_{2+x}$  and  $U_4O_9$  according to the U–O phase diagram. When oxidation treatments are performed at lower temperature and under stronger oxidative conditions such as air, a prompt conversion of  $U_4O_9$  into  $U_3O_7$  and eventually  $U_3O_8$  is observed (De Bona et al., 2022; Milena-Perez et al., 2023; Teixeira and Imakuma, 1991).

Thanks to the analysis of Raman mapping, we could evaluate the composition of the  $\text{UO}_{2+x}$  phases as a function of the global O/U ratio of samples, while XANES could help evaluate the proportion of  $\text{U}_4\text{O}_9$  inside samples. At low O/U ( $\sim 0.01$ ), the  $\text{UO}_{2+x}$  phase can be considered stoichiometric, which means that samples are composed of  $\text{UO}_2$  and  $\sim 10\%$  of  $\text{U}_4\text{O}_9$ . For  $\text{O/U} \geq 2.05$ , samples are composed of  $\text{U}_4\text{O}_9$  and of a  $\text{UO}_{2+x}$  phase whose hyper-stoichiometry increases with the global O/U ratio. For  $\text{O/U} = 2.05$ , samples are composed of  $\sim 70\%$  of  $\text{UO}_{2.01}$  and  $\sim 30\%$  of  $\text{U}_4\text{O}_9$ , while at  $\text{O/U} = 2.1$ , they are composed of  $\sim 65\%$   $\text{U}_4\text{O}_9$  and  $35\%$   $\text{UO}_{2.02}$ . We thus observe that  $\text{UO}_{2+x}$  phases display quite low O/M ratios, even for high global hyper-stoichiometries.

We could detect the  $\text{U}_4\text{O}_9$  growth mechanism inside grains. At low hyper-stoichiometry (2.01),  $\text{U}_4\text{O}_9$  is present as micrometric clusters inside stoichiometric  $\text{UO}_2$  grains. These clusters were formed during the slow cooling of our sample from a homogeneous  $\text{UO}_{2+x}$  phase. Such clusters were evidenced by Allen et al. (1983) but for highly oxidized  $\text{UO}_2$  pellets at  $\text{O/U} = 2.24$ . As the hyper-stoichiometry increases to  $\text{O/U} = 2.1$ , these clusters coalesce to form a  $\text{U}_4\text{O}_9$  network at the surface of the material. This kind of microstructure can be compared to those reported by previous research, showing that the precipitation of  $\text{U}_4\text{O}_9$  in  $\text{UO}_{2+x}$  leads to a Widmanstätten needle structure or the formation of platelets (Tuxworth and Evans, 1959) (Lierde et al., 1970; Whillock and Pearce, 1990; Schaner, 1960). The formation of  $\text{U}_4\text{O}_9$  entails a local lattice contraction inside grains, evidenced by AFM, but without affecting the surrounding  $\text{UO}_2$  matrix. Even for high hyper-stoichiometry ( $x > 2.1$ ) where  $\text{U}_4\text{O}_9$  is the main crystallographic phase, the  $\text{UO}_2$  lattice is preserved and, consequently, we always observe a joint presence of two crystallographic phases. This is comparable with observations made by Allen et al. (1983) on  $\text{UO}_2$  pellets and Leinders et al. (2016) on  $\text{UO}_2$  nanopowders. We also show by twice oxidizing a  $\text{UO}_2$  sample at high temperature (1600 °C) that  $\text{U}_4\text{O}_9$  clustering inside  $\text{UO}_2$  grains is not a random process and that it occurs in defined zones inside grains. One may link this fact with the presence of defects in grains that may constitute nucleation sites. The precipitation of  $\text{U}_4\text{O}_9$  in  $\text{UO}_{2+x}$  occurs by the agglomeration of oxygen atoms that produces defects. For this reason, some authors consider that the interface between  $\text{UO}_{2+x}$  and  $\text{U}_4\text{O}_9$  is equivalent to dislocations (Chevrel, 1992). One may envision that after the re-dissolution of  $\text{U}_4\text{O}_9$ , dislocations remain and, during the second oxidation annealing, favor the recrystallization of  $\text{U}_4\text{O}_9$  in the same zone of grains. We have also observed that the formation of  $\text{U}_4\text{O}_9$  occurs only inside grains, not in grain boundaries. The latter contain a high concentration of defects like dislocations that entail a lower crystallinity and, probably, tensile strains that may entail the clustering of  $\text{U}_4\text{O}_9$ .

## 5 Conclusion

We studied the  $\text{UO}_{2+x}/\text{U}_4\text{O}_9$  phase equilibrium in  $\text{UO}_2$  in the hyper-stoichiometry range  $0.01 < x < 0.1$  after thermal oxidation treatments performed under dry conditions at 850 °C or 1600 °C. By coupling HERFD-XANES at the uranium  $M_4$ -edge and micro-

Raman spectroscopy mapping, we could determine the proportion between each phase and their composition.

At low O/U,  $\text{U}_4\text{O}_9$  is present as small clusters inside  $\text{UO}_2$  grains. Their formation, occurring during the slow cooling of our samples, does not occur in a random area of grains. Indeed, we show by twice repeating the annealing/cooling process that the  $\text{U}_4\text{O}_9$  cluster size and location are identical. The presence of  $\text{U}_4\text{O}_9$  entails a local contraction of the lattice, measurable by AFM, which does not affect the global structure of grains, even at a high  $\text{U}_4\text{O}_9$  concentration.

As the O/U increases, the proportion of  $\text{U}_4\text{O}_9$  and the  $\text{UO}_{2+x}$  phase hyper-stoichiometry increase, leading to the formation of a network of  $\text{U}_4\text{O}_9$  crystallized inside  $\text{UO}_{2+x}$  grains. However, even for highly oxidized samples, we observed that the  $\text{UO}_{2+x}$  phases exhibit only a slight O/M, meaning that during the slow cooling process, most of the additional oxygen atoms are incorporated as  $\text{U}_4\text{O}_9$  in the samples.

## Data availability statement

The raw data supporting the conclusions of this article will be made available by the authors, without undue reservation.

## Author contributions

CG: conceptualization, formal analysis, funding acquisition, investigation, project administration, supervision, and writing—original draft. HL: formal analysis, investigation, and writing—original draft. LS: formal analysis, investigation, and writing—original draft. YP: funding acquisition and writing—review and editing. RD: funding acquisition and writing—review and editing. NM: funding acquisition and writing—review and editing.

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## Conflict of interest

The authors declare that the research was conducted in the absence of any commercial or financial relationships that could be construed as a potential conflict of interest.

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## Supplementary material

The Supplementary Material for this article can be found online at: <https://www.frontiersin.org/articles/10.3389/fnuen.2024.1465080/full#supplementary-material>

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