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Originally published:

September 2021

**Inorganic Chemistry** 60(2021)19, 14550-14556

DOI: <https://doi.org/10.1021/acs.inorgchem.1c01071>

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# Charge distribution in $U_{1-x}Ce_xO_{2+y}$ nanoparticles

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## **ABSTRACT**

In view of a safe management of the nuclear wastes, a sound knowledge of the atomic-scale properties of  $U_{1-x}M_xO_{2+y}$  nanoparticles is essential. In particular, their cation valences and oxygen stoichiometries are of great interest as these properties drive their diffusion and migration behaviour into the environment. Here, we present an in-depth study of  $U_{1-x}Ce_xO_{2+y}$ , over the full compositional domain, by combining XRD and HERFD-XANES. We show on one hand the co-existence of  $U^{IV}$ ,  $U^V$  and  $U^{VI}$  and on the other hand that the fluorite structure is maintained despite this charge distribution.

**KEYWORDS:** Uranium, UO<sub>2</sub>, CeO<sub>2</sub>, HERFD-XANES

## **INTRODUCTION**

The safety assessment of nuclear waste management requires a sound understanding of the corrosion behaviour of the spent nuclear fuel (SNF). Considering that Ce is among the major fission products present in the SNF, which can be incorporated into the UO<sub>2</sub> structure, the crystallography of the present chemical phases and the oxidation states of both U and Ce have to be studied as they drive the concomitant release and migration of U<sub>1-x</sub>Ce<sub>x</sub>O<sub>2+y</sub> nanoparticles (NPs) in the environment<sup>1,2</sup>.

Due to their structural similarity, Uranium and cerium dioxide form solid solution covering the full compositional range of Ce content<sup>3-5</sup>. Several articles have been published on the U<sub>1-x</sub>Ce<sub>x</sub>O<sub>2+y</sub> properties (electrical conductivity, magnetic properties, oxygen potential, lattice parameter, heat capacity, thermal expansion, phase diagram and)<sup>6-8,3,9,10</sup>. Some interesting results have also been reported on both U and Ce valences. Contrary to other substituted-UO<sub>2</sub> compounds<sup>11-13</sup>, no charge transfer reaction between U<sup>IV</sup> and Ce<sup>IV</sup> leading to the formation Ce<sup>III</sup> and U<sup>V</sup> has been reported. Indeed, when the mixed oxide are prepared in the right oxygen potential condition to obtain stoichiometric compounds U<sub>1-x</sub>Ce<sub>x</sub>O<sub>2.00</sub>, their lattice parameters follow closely the Vegard's law<sup>8,14</sup>, suggesting the progressive substitution of U<sup>IV</sup> by Ce<sup>IV</sup> cation as a function of the composition. Even though there have been several investigation on the redox behaviour of Ce doped-UO<sub>2</sub> mainly on thin films using extreme surface sensitive technics<sup>6,7,15</sup>, there is none for NP materials. However, in those latter compounds, the quantum mechanical size effects, combined with a considerable increase of the surface to bulk ratio, may affect the local structure and the charge

distribution within the compounds<sup>16-18</sup>. Additionally, NPs are highly sensitive to room temperature oxidation as they show a considerable surface to bulk ratio<sup>19</sup>.

In this context, the present study aims at studying both U and Ce valences in room temperature oxidized  $U_{1-x}Ce_xO_{2+y}$  NPs. The crystal structure of both as-synthesized and room temperature oxidized  $U_{1-x}Ce_xO_{2+y}$  NPs was characterized using x-ray diffraction (XRD), giving access to their size and lattice parameter. Furthermore, we probed the electronic structure of the  $U_{1-x}Ce_xO_{2+y}$  NPs using high-energy resolution fluorescence-detection hard X-ray absorption near-edge structure (HERFD-XANES) spectroscopy at both U  $M_{IV}$  and Ce  $L_{III}$  edges.

## EXPERIMENTAL METHODS

Please note that a careful attention should be made for the characterization of these nanocrystalline materials to avoid any energy-induced transformations (such as reduction under beam for instance). It has to be mentioned that these materials are radioactive and hence should be manipulated adequately.

### Synthesis

The  $U_{1-x}Ce_xO_{2+y}$  nanopowders were produced by the decomposition of mixed hydroxides under hot compressed water.  $U_{1-x}Ce_x(OH)_4$  ( $x=0-1$ ) amorphous precipitates were prepared as followings:  $2-2x$  ml  $U^{IV}$  solution (0.5 M) and  $2x$  ml  $Ce^{IV}$  solution (0.5 M) were mixed in test tubes of 50 ml and diluted with 8 ml of distilled water. The coprecipitation was induced with excess (10 ml) of ammonia solution 25% (pH=14). The precipitates were separated from the alkaline solution and washed repeatedly with distilled water till neuter pH. After washing, the hydroxides precipitates were inserted in Teflon lined hydrothermal synthesis autoclave reactors together with 10 ml

distilled water and reacted for 4 h at 200 °C and 15 bar without stirring. The final product consists (usually) in nanocrystalline  $U_{1-x}Ce_xO_{2+y}$  solid solutions which could be easily separated from solution. The nanocrystals were repeatedly washed with ethanol and acetone in order to remove the water potentially absorbed at the surface. Finally, they were dried under air atmosphere.

The hydroxide decomposition method under hot compressed water proved to be straightforward in the case of  $CeO_2$ ,  $ThO_2$  and  $U_{1-x}Th_xO_2$  solid solutions<sup>20,21,16,22</sup>. However, the preparation of  $U_{1-x}Ce_xO_{2+y}$  solid solutions through this synthetic route is not always successful and the method still needs optimisation. Thus, we have observed (meta)schoepite-like impurities in more than half of the experimental trials, independent on the targeted composition. Potentially different reaction intermediates are formed in this specific case, but the mechanistic study is out of our scope.

The U:Ce ratio (i.e. the stoichiometry) was measured by a NuPlasma™ (NU Instruments, Oxford, United Kingdom) double-focusing multi-collector inductively coupled plasma mass spectrometer (MC-ICP-MS). U and Ce monoelemental solutions were used for the calibration of the instrument. For the dissolution, a small amount of the sample was dissolved in 8 M  $HNO_3$ , then successively diluted before the MC-ICP-MS measurement. All dilutions were performed gravimetrically. The results have +/-5% relative uncertainty.

The synthetic procedure was performed under an air atmosphere in a fumehood. The products were stored in a desiccator under vacuum, after flushing with argon.

## **X-ray diffraction**

Due to the fast oxidation of the resulting powders, preliminary XRD analyses were performed with a Rigaku Miniflex 600 diffractometer at the same day of the synthesis. The diffractometer is calibrated with silicon, use  $Cu K_\alpha$  radiation (both  $K_{\alpha 1}$  and  $K_{\alpha 2}$ ) and is operated under air. The

crystallite size of the nanopowders was estimated from the XRD pattern using the Scherrer equation and averaging the results of 8 selected peaks in the  $2\theta$  range between  $25^\circ$  and  $80^\circ$ .

The other measurements (done 2 weeks and 3 months after synthesis) used for Rietveld refinement were performed using room temperature XRD analyses performed on about 10 mg of powder with a Bruker D8 Advance diffractometer (Cu  $K_\alpha$  radiation, 40 kV, 40 mA) mounted in a Bragg-Brentano configuration. The diffractometer was equipped with a curved Ge (111)  $K\alpha_1$  monochromator, a ceramic copper tube and a LinxEye position sensitive detector. It is calibrated with LaB6 reference material (NIST SMR 660b). The diffractometer is installed in a Nitrogen atmosphere glovebox, designed to handle highly radiotoxic materials.

With both diffractometers, the XRD patterns were recorded using a step size of  $0.02^\circ$  across the  $10^\circ \leq 2\theta \leq 120^\circ$  angular range. Structural analysis was performed by the Rietveld method using the Jana2006 software<sup>23</sup>.

## **Transmission Electron Microscopy**

Transmission electron microscopy (TEM) studies were performed using an aberration (image) corrected FEI™ Titan 80-300 operated at 300 kV. This provides a nominal information limit of  $0.8 \text{ \AA}$  in TEM mode and a resolution of  $1.4 \text{ \AA}$  in STEM mode. TEM micrographs have been recorded using a Gatan US1000 slowscan CCD camera. STEM images have been recorded using a Fischione high-angle annular dark-field (HAADF) detector with a camera length of 195 mm. The samples for analysis have been prepared by dropping coating with a suspension of the nanoparticles in ultrapure water on carbon coated copper grids.

## High-Energy Resolution Fluorescence-Detected X-ray Absorption Near Edge Structure

Inner-shell spectroscopy with the use of an X-ray emission spectrometer provides an element-selective probe of the electronic state and allows observing spectral features with significantly enhanced energy resolution compared to usual data limited by the core-hole life-time broadening<sup>16,24</sup>.

HERFD-XANES measurements were conducted at the CAT-ACT beamline (ACT station) of the KIT synchrotron light source (Karlsruhe Institute of Technology, Karlsruhe, Germany)<sup>25,26</sup>. The storage ring conditions were 2.5 GeV and 160 mA. Note that those were carried out 3 months after the synthesis. The incident energy was selected using the [111] reflection of a double Si crystal monochromator. The X-ray beam was focused to 1×1 mm onto the sample. A slit with a size of 500×500 μm was used in front of the sample, in order to further confine the size of the X-ray beam on the sample, leading to a slight improvement of the energy resolution. XANES spectra were measured in high-energy-resolution fluorescence detected (HERFD) mode using an X-ray emission spectrometer<sup>24,27</sup>. The sample, analyzer crystal, and a single diode VITUS Silicon Drift Detector (KETEK, Germany) were arranged in a vertical Rowland geometry.

The Ce L<sub>III</sub> HERFD-XANES spectra were obtained by recording the maximum intensity of the Ce L<sub>3</sub>-M<sub>5</sub> emission line (4839 eV) as a function of the incident energy. The emission energy was selected using the ⟨331⟩ reflection of four spherically bent Ge crystal analyser (with a bending radius R = 1 m) aligned at 80.7° Bragg angle. The molar fractions of Ce<sup>III</sup> and Ce<sup>IV</sup> were derived from the linear combination of CeO<sub>2</sub> and Ce<sup>III</sup> oxalate references<sup>16</sup>.

The U M<sub>IV</sub> HERFD-XANES were acquired by recording the intensities of the U M<sub>4</sub>-N<sub>6</sub> (~3337 eV) as a function of the incident energy. The emission energy was selected using the (220) reflection of four spherically bent Si crystal analyzers (with 1 m bending radius) aligned at 75.4° Bragg angle. The molar fractions of U<sup>IV</sup>, U<sup>V</sup> and U<sup>VI</sup> were derived from the linear combination of UO<sub>2</sub>, U<sub>4</sub>O<sub>9</sub>, U<sub>3</sub>O<sub>8</sub>, UO<sub>3</sub> and U<sub>0.50</sub>Am<sub>0.50</sub>O<sub>2-y</sub> references<sup>28,29</sup>.

The experimental energy resolutions were 1.15 eV and 0.85 eV for Ce L<sub>III</sub> and U M<sub>IV</sub>, respectively. Those were obtained by measuring the FWHM of the elastically scattered incident beam.

The sample, crystals and detector were set in a box filled with He. A constant He flow was maintained in order to minimize the loss of intensity due to absorption and scattering of the X-rays. The data were not corrected for self-absorption effects. The sample exposure to the beam was minimized to account for possible beam damage and checked by first collecting short XANES scans (~10 seconds) to look for irradiation effect.

## RESULTS AND DISCUSSION

### Lattice parameter and size of the as-synthesized NPs

XRD measurements were carried out a few hours after the synthesis.

Our XRD data show that the as-synthesized U<sub>1-x</sub>Ce<sub>x</sub>O<sub>2+y</sub> crystallize in the Fm-3m fluorite structure (space group 225). Depending on the Ce content, the average crystallite diameters vary from 5 to 13 nm. These XRD-refined parameters are gathered in the Table 3.



Table 1: Lattice parameter, space group and crystallite size derived from the Rietveld refinement.

	Lattice parameter (Å)	Space group	Crystallite size (nm)
$U_{0.90}Ce_{0.10}O_{2+y}$	5.460(2)	Fm-3m	13(1.2)
$U_{0.60}Ce_{0.40}O_{2+y}$	5.446(2)	Fm-3m	7.1(0.9)
$U_{0.50}Ce_{0.50}O_{2+y}$	5.441(2)	Fm-3m	7.3(1.0)
$U_{0.40}Ce_{0.60}O_{2+y}$	5.428(2)	Fm-3m	7.1(1.0)
$U_{0.17}Ce_{0.83}O_{2+y}$	5.417(2)	Fm-3m	7.0(0.9)
$U_{0.10}Ce_{0.90}O_{2+y}$	5.413(2)	Fm-3m	5.1(0.6)

The TEM measurements confirm the XRD data with respect of both phase purity and particle size. As a representative example, the Figure 1 shows the morphology of the nanometric  $U_{0.50}Ce_{0.50}O_{2+y}$  sample, which is clearly formed by one single family of particles with an average size of 7.3 (1.8) nm. Moreover, EDX analysis on independent particles has confirmed the homogeneity of all the samples as well as their U:Ce ratio.

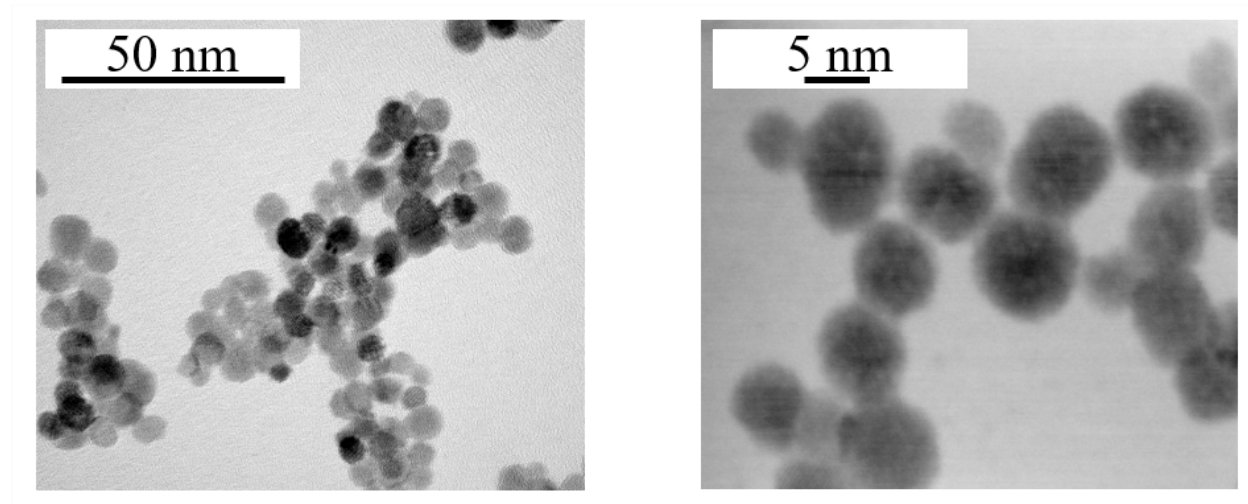


Figure 1: TEM images of the as-synthesized  $U_{0.50}Ce_{0.50}O_{2+y}$ .

As it can be expected from the literature data<sup>7,30-33</sup>, the Figure 7 shows that the lattice parameters of the as-synthesized compounds follow the  $\text{UO}_2\text{-CeO}_2$  Vegard law. Although the charge distribution has not been measured for these NPs, one can expect that the oxygen stoichiometry or O/M (with  $M=\text{U}+\text{Ce}$ ) ratio is equal to 2.00 or very close to these value. The principle of electroneutrality implies that either Ce and U are both tetravalent or that  $\text{Ce}^{\text{III}}$  and  $\text{U}^{\text{V}}$  co-exist in equimolar proportions, as it has been demonstrated in other doped  $\text{UO}_2$  compounds<sup>11-13</sup>. It is very interesting to notice that, despite the formation of nanoparticles having a very high surface area, and the use of water in the synthesis method, the conditions are obviously reductive enough to obtain close to stoichiometric materials. However, as presented in the next section, these particles stay very sensitive to the oxidation, and their oxidation actually take place in the following days despite the storage of the sample in nitrogen glove boxes.

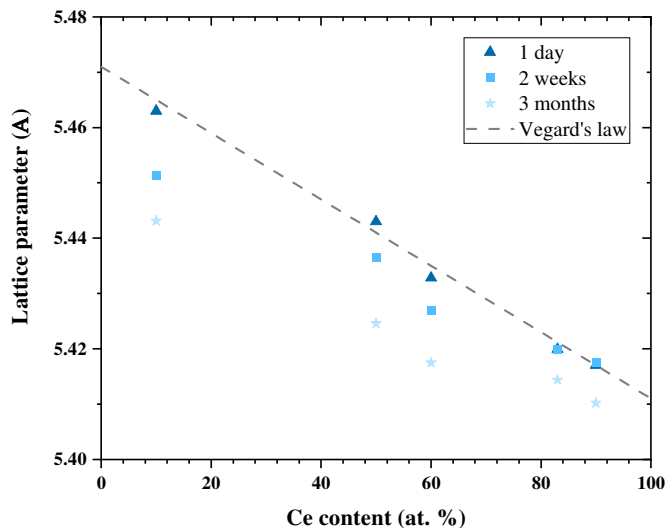


Figure 2: Lattice parameters as a function of Ce content. The lattice parameters of the as-synthesized compounds follows the Vegard's law law (drawn from pure  $\text{UO}_{2.00}$  and  $\text{CeO}_{2.00}$  values)

while an evolution in time is observed for those collected 1 day, 2 weeks, 3 months after the synthesis

### **Evolution of the NPs lattice parameter**

The  $U_{1-x}Ce_xO_{2+y}$  NPs were stored in a desiccator under vacuum, after flushing with argon during 3 months before the HERFD-XANES measurement. During this period, XRD measurements were regularly performed to assess the evolution of their lattice parameters.

As a general trend, we can see on the Figure 7 that the lattice parameter decreases with time for each composition. This evolution of the unit cell is characteristic of an oxidation process<sup>34</sup>, which is besides in perfect agreement with the very high specific area of the studied NPs. Considering the oxidation mechanism in  $UO_2$ <sup>35,36</sup>, one can assume here that  $U^{IV}$  have been oxidized into higher valence states in agreement with O/M ratio greater than 2.00. The charge distribution of these 3 months – stored NPs have been assessed using HERFD-XANES.

### **Charge distribution of the room temperature oxidized NPs**

#### **Ce oxidations state**

The Ce  $L_{III}$  HERFD-XANES spectra of all the investigated  $U_{1-x}Ce_xO_{2+y}$  NPs, as well as  $Ce^{III}$  and  $Ce^{IV}$  references, are given in Figure 8 and compared with  $CeO_2$  and  $Ce^{III}$  references.

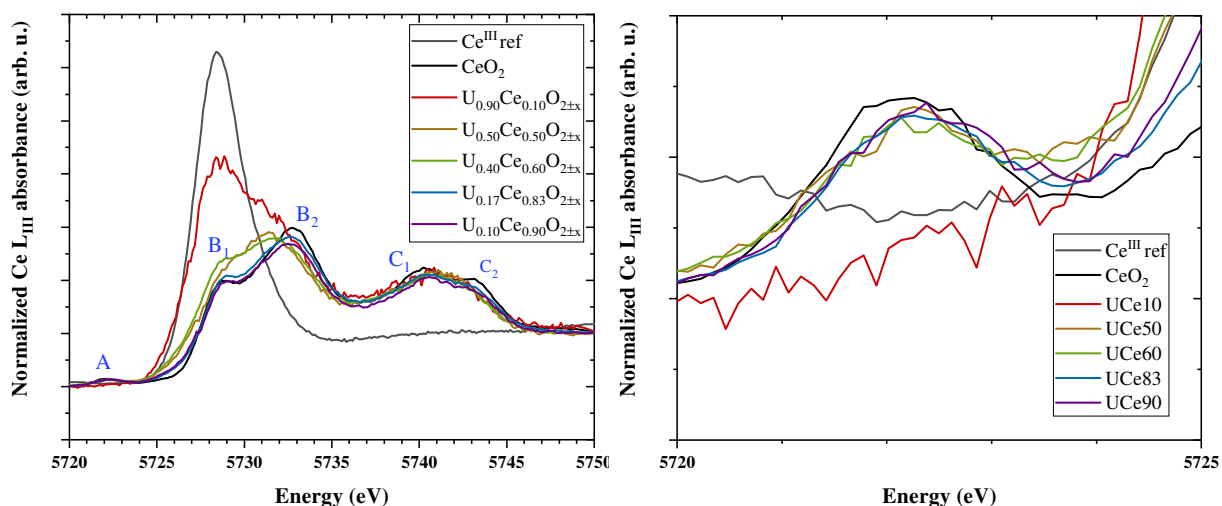


Figure 3: (Left) Ce L<sub>III</sub> HERFD-XANES spectra of U<sub>1-x</sub>Ce<sub>x</sub>O<sub>2+y</sub> NPs compared to CeO<sub>2</sub> reference. (Right) Pre-edge region of the Ce L<sub>III</sub> HERFD-XANES spectra.

Three characteristic features (A, B and C) are observed on the HERFD-XANES spectrum of bulk CeO<sub>2</sub>. The pre-edge peak (noted A) originates from the 2p transition to a mixed 5d-4f band/orbital/state. A doublet structure, due to the crystal field splitting of 5d states<sup>37</sup>, is observed for screened B (B<sub>1</sub>+B<sub>2</sub>) and unscreened C (C<sub>1</sub>+C<sub>2</sub>) excited states.<sup>38,39</sup>. These arises from transitions from 2p<sub>3/2</sub> → 5d<sub>5/2</sub> transitions.

In contrast, the HERFD-XANES spectrum of the bulk Ce<sup>III</sup> reference shows only one single feature.

Regarding the HERFD-XANES spectra of the U<sub>1-x</sub>Ce<sub>x</sub>O<sub>2+y</sub> NPs, one can observe that the spectra are quite similar in the 5735 eV – 5750 eV region, corresponding to the C (C<sub>1</sub>+C<sub>2</sub>) feature of the CeO<sub>2</sub> reference. One can then argue that this C doublet is not affected by the Ce oxidation state but mostly by the local structure (as the crystallographic structure remains the same for all compounds). However, strong differences can be observed in the 5720 eV – 5735 eV range,

corresponding to the A and B feature of the CeO<sub>2</sub> reference. In the case of U<sub>0.90</sub>Ce<sub>0.10</sub>O<sub>2±x</sub>, the Ce L<sub>III</sub> threshold is strongly shifted toward lower energy, and one maximum is observed at the same energy as the Ce<sup>III</sup> reference. For both U<sub>0.50</sub>Ce<sub>0.50</sub>O<sub>2+y</sub> and U<sub>0.40</sub>Ce<sub>0.60</sub>O<sub>2+y</sub> samples, the spectra look quite similar and can be compare to the shape of the CeO<sub>2</sub> reference, although the B<sub>1</sub> and B<sub>2</sub> positions are shifted toward lower energy. For the U<sub>0.17</sub>Ce<sub>0.83</sub>O<sub>2+y</sub> and U<sub>0.10</sub>Ce<sub>0.90</sub>O<sub>2+y</sub>, the spectra exhibit the same shape as the CeO<sub>2</sub> reference.

The Ce<sup>III</sup> and Ce<sup>IV</sup> molar fractions deduced from Ce L<sub>III</sub> HERFD-XANES are provided in **Error!**  
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Table 2: U and Ce valences, molar fractions and O/M ratios derived from the fitting of the U M<sub>IV</sub> and Ce L<sub>III</sub> HERFD-XANES spectra. \* U<sub>surf</sub> corresponds to the fraction of U atoms at the surface of the NPs. This fraction was derived taking into account the lattice parameter and the NP size.

	U <sup>IV</sup> (%)	U <sup>V</sup> (%)	U <sup>VI</sup> (%)	Valence of U	Ce <sup>III</sup> (%)	Ce <sup>IV</sup> (%)	Valence of Ce	O/M	U <sub>surf</sub> * (%)
U <sub>0.90</sub> Ce <sub>0.10</sub> O <sub>2+y</sub>	38 (5)	57 (5)	5 (5)	4.67	60 (5)	40 (5)	3.6	2.28 (1)	12
U <sub>0.50</sub> Ce <sub>0.50</sub> O <sub>2+y</sub>	9 (5)	50 (5)	41 (5)	5.33	14 (5)	86 (5)	3.86	2.25 (1)	22
U <sub>0.40</sub> Ce <sub>0.60</sub> O <sub>2+y</sub>	5 (5)	39 (5)	56 (5)	5.51	13 (5)	87 (5)	3.87	2.26 (1)	22
U <sub>0.17</sub> Ce <sub>0.83</sub> O <sub>2+y</sub>	3 (5)	31 (5)	66 (5)	5.64	0	100 (5)	4	2.13 (1)	22

$U_{0.10}Ce_{0.90}O_{2+y}$	3 (5)	31 (5)	66 (5)	5.62	0	100 (5)	4	2.08	(1)	29
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In addition, some papers<sup>40</sup> recommend using the Ce L<sub>III</sub> pre-edge to assess the molar fractions of Ce<sup>III</sup> and Ce<sup>IV</sup>. However, in our present work, the pre-edges of all of our NPs have both similar shape, amplitude and position while the features above the edge are clearly different. This shows that a proper determination of the Ce valence can only be achieved fitting the edge region.

### U oxidation state

The oxidation state and electronic structure of U was assessed using U M<sub>IV</sub> edge HERFD-XANES. The corresponding spectra of each NP sample compared to U<sup>IV</sup>O<sub>2.00</sub> and (U<sup>V</sup><sub>0.67</sub>U<sup>VI</sup><sub>0.33</sub>)<sub>3</sub>O<sub>8</sub> references<sup>28</sup> are provided in the Figure 9.

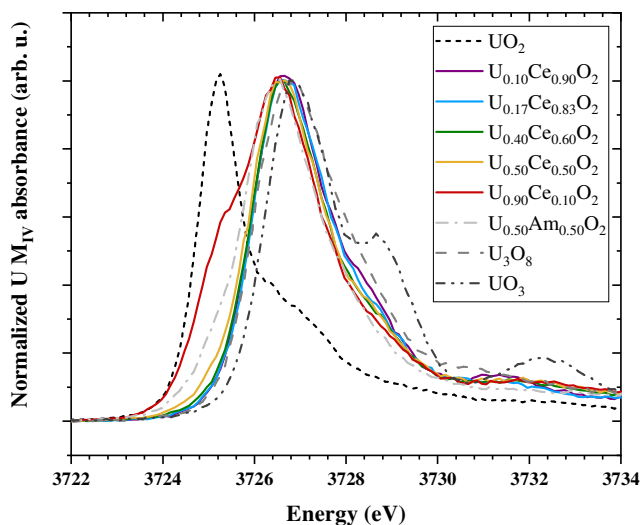


Figure 4: U M<sub>4</sub> HERFD-XANES spectra of U<sub>1-x</sub>Ce<sub>x</sub>O<sub>2+y</sub> NPs compared to UO<sub>2</sub>, U<sub>3</sub>O<sub>8</sub>, UO<sub>3</sub> and U<sub>0.50</sub>Am<sub>0.50</sub>O<sub>2</sub> references.

As previously reported <sup>41,28,42–45,11,36,46,35</sup>, the various oxidation states of U are perfectly identifiable at M<sub>IV</sub> edges. The HERFD-XANES spectrum of U<sup>IV</sup>O<sub>2</sub> shows a sharp peak at 3725.2 (2) eV, resulting from the transition from the 3d<sub>5/2</sub> core level to the unoccupied 5f<sub>5/2</sub> levels. The (U<sup>IV</sup><sub>0.5</sub>U<sup>V</sup><sub>0.5</sub>)<sub>4</sub>O<sub>9</sub> HERFD-XANES spectrum presents this U<sup>IV</sup> characteristic feature as well as a peak at 3726.2 (2) eV corresponding to U<sup>V</sup>. In the case of (U<sup>V</sup><sub>0.67</sub>U<sup>VI</sup><sub>0.33</sub>)<sub>3</sub>O<sub>8</sub>, the HERFD-XANES spectrum exhibits a white line at 3726.9 (2) eV attributed to U<sup>VI</sup>. At the lower energy side, a shoulder is observed, which energy matches the same position as the characteristic feature of U<sup>V</sup> in (U<sup>IV</sup><sub>0.5</sub>U<sup>V</sup><sub>0.5</sub>)<sub>4</sub>O<sub>9</sub> <sup>28</sup>.

Except the U<sub>0.90</sub>Ce<sub>0.10</sub>O<sub>2+y</sub> U M<sub>IV</sub> HERFD-XANES spectrum, all the other spectra are ranging between the U<sub>4</sub>O<sub>9</sub> and U<sub>3</sub>O<sub>8</sub> reference spectra. Their white line shapes are close to U<sub>3</sub>O<sub>8</sub> although various intensities of the U<sup>V</sup> and U<sup>VI</sup> features are observed, suggesting varying fractions of this species. Also, one should note that the presence of U<sup>IV</sup> is also clearly evidenced by its 3725.2 (2) eV feature. For U<sub>0.90</sub>Ce<sub>0.10</sub>O<sub>2+y</sub> NP, one can clearly observe a shoulder at the left side which is at the same position as the peak characteristic of U<sup>IV</sup> in U<sup>IV</sup>O<sub>2</sub>, which confirms the presence of U<sup>IV</sup>.

### **Charge distribution**

From the assessed molar fractions of Ce and U provided in the Table 2, it is clear that the U and Ce valences are proportional. Those oxidation states increase with the Ce content. For the higher content of Ce, the main valence states are U<sup>V</sup>, U<sup>VI</sup> and Ce<sup>IV</sup>. For all NPs, hyper-stoichiometric materials are achieved. This is in good agreement with the strong decrease of the lattice parameter compared to the values measured on the as-synthesized compounds and with the values of ionic radius <sup>47</sup>. We can then assume that after the synthesis the NPs were nearly stoichiometric (as the

lattice parameter are matching the Vegard's law) and then oxidize during the next 3 months with the oxidation of  $U^{IV}$  into  $U^V$  and  $U^{VI}$ .

### **Presence of $U^{VI}$ within the fluorite structure**

The presence of  $U^{VI}$  has already been reported in  $U_{1-x}Ce_xO_{2+y}$  thin films, but the nature of the  $U^{VI}$  phase is not discussed in this paper<sup>15</sup>. In  $Ln^{III}$ <sup>48-50</sup> and  $Am^{51}$  doped  $UO_2$  compounds,  $U^{VI}$  was also evidenced and attributed to the presence of  $(U,M)_3O_8$  phase. For  $U_{1-x}Bi_xO_{2+y}$  materials, no evidence of such  $(U,M)_3O_8$  phase was found and hence  $U^{VI}$  was assumed to crystallize in the fluorite structure<sup>43,52</sup>. In the present work, only fluorite solid solutions are derived from XRD and no  $(U,Ce)_3O_8$  is detected. Considering that we work in presence of NPs and with bulk+surface-sensitive techniques, we could assume that the molar fraction of  $U^{VI}$  in our NPs solely originates from the presence of surface species. However, except the  $U_{0.90}Ce_{0.10}O_{2+y}$ , the Table 2 shows that the number of U atoms at the surface is always lower than the  $U^{VI}$  molar fraction, which means that  $U^{VI}$  co-exist with  $U^{IV}$  and  $U^V$  within the fluorite-structured bulk.

### **Co-existence of $U^{IV}$ , $U^V$ and $U^{VI}$ within the fluorite structure**

The co-existence of several U oxidation states in the doped  $UO_2$  fluorite structure has already been evidenced. Indeed, it was shown that the incorporation of non-tetravalent cation in the  $UO_2$  structure is accommodated through the formation of  $U^V$  in  $U_{1-x}Am_xO_2$ ,  $U_{1-x}La_xO_2$ ,  $U_{1-x}Bi_xO_2$  and  $U_{1-x}Gd_xO_2$  in the range  $0 < x_M < 0.50$ <sup>11,12,43,52</sup>. Doping with a trivalent cation results hence in the oxidation of  $U^{IV}$  into  $U^V$ . Remarkably, equimolar fractions of  $M^{III}$  and  $U^V$  were often measured leading to oxygen stoichiometry very close equal to 2.00. However, for  $0.40 \leq x_{Am} \leq 0.70$ , this charge compensation mechanism is no longer sufficient as the molar fraction of  $U^V$  becomes higher



than that of  $\text{Am}^{\text{III}}$  and, for even higher Am content,  $\text{Am}^{\text{III}}$  starts oxidizing into  $\text{Am}^{\text{IV}}$ . These variations of the average oxidation state (AOS) of U and Am in  $\text{U}_{1-x}\text{Am}_x\text{O}_2$  are given in green in the Figure 10 as a function of the M content. On this plot, the AOS of Ce and U determined in this work are also presented in blue. Overall, the tendency between  $\text{U}_{1-x}\text{Am}_x\text{O}_2$  and  $\text{U}_{1-x}\text{Ce}_x\text{O}_2$  NPs is similar, meaning that both U and M AOS are proportional to the M content. Even if the two systems shows significant differences in term of valence ratio, probably due to the difference of  $\text{Am}^{\text{III}}$  and  $\text{Ce}^{\text{III}}$  stability in oxides, it is interesting to see the similarity between the two systems. Indeed, at high uranium content ( $0.50 \leq x_{\text{Am}}$ ),  $\text{Am}^{\text{III}}$  is fully stabilised in the  $\text{U}_{1-x}\text{Am}_x\text{O}_{2\pm x}$  system, and this even after air oxidation at high temperature<sup>53</sup>. Similarly here, the  $\text{Ce}^{\text{III}}$  is partially stabilised in the  $\text{U}_{1-x}\text{Ce}_x\text{O}_{2\pm x}$  system, especially for low cerium content, and this despite the room temperature oxidation of the nanoparticles over the time.

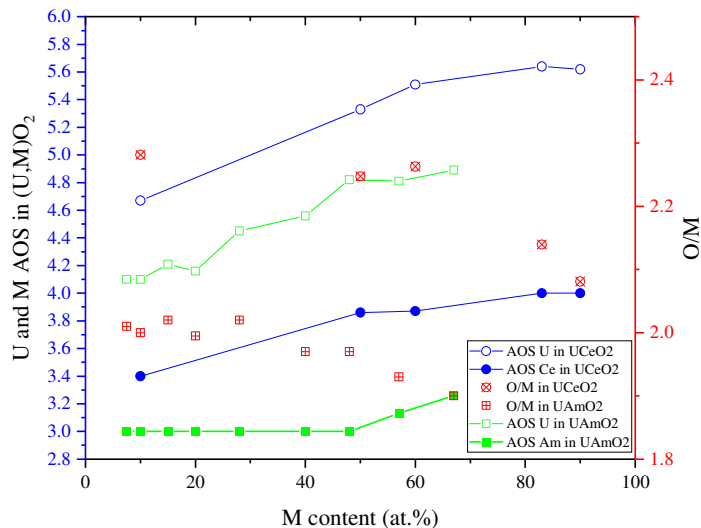


Figure 5: (Left axis) U and M average oxidation states and (Right axis) O/M as a function of the M content in  $\text{U}_{1-x}\text{Ce}_x\text{O}_{2+y}$  and  $(\text{U},\text{Am})\text{O}_{2+y}$ .

## FIGURES

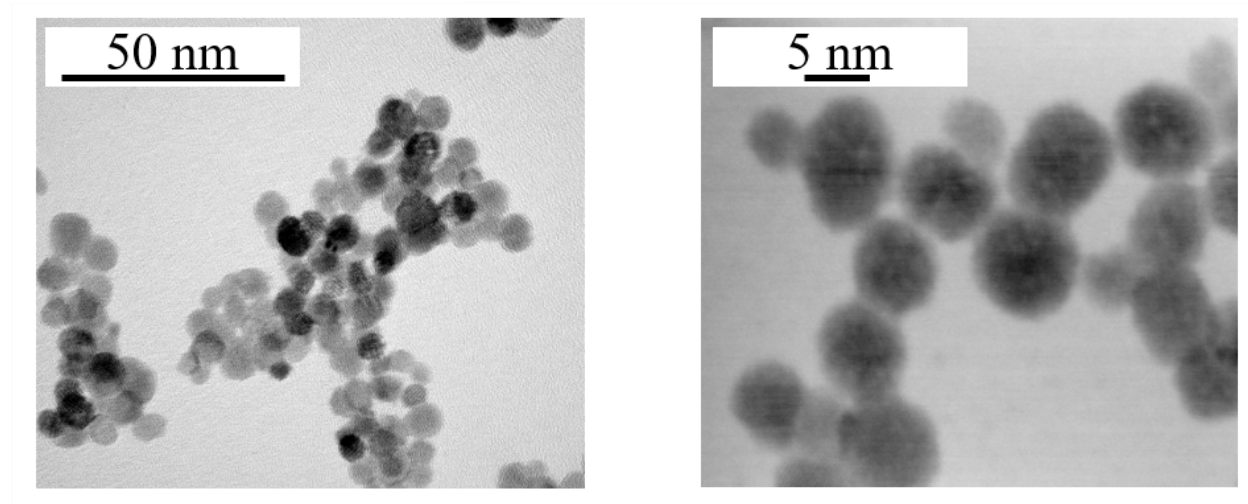


Figure 6: TEM images of the as-synthesized  $U_{0.50}Ce_{0.50}O_{2+y}$ .

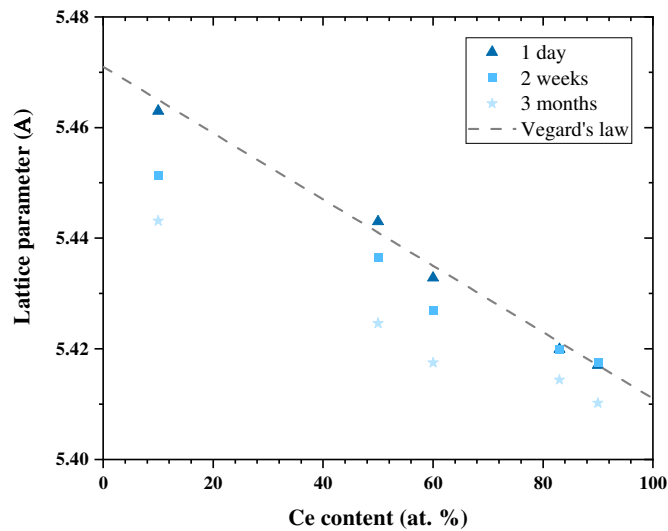


Figure 7: Lattice parameters as a function of Ce content. The lattice parameters of the as-synthesized compounds follows the Vegard's law law (drawn from pure  $UO_{2.00}$  and  $CeO_{2.00}$  values) while an evolution in time is observed for those collected 1 day, 2 weeks, 3 months after the synthesis

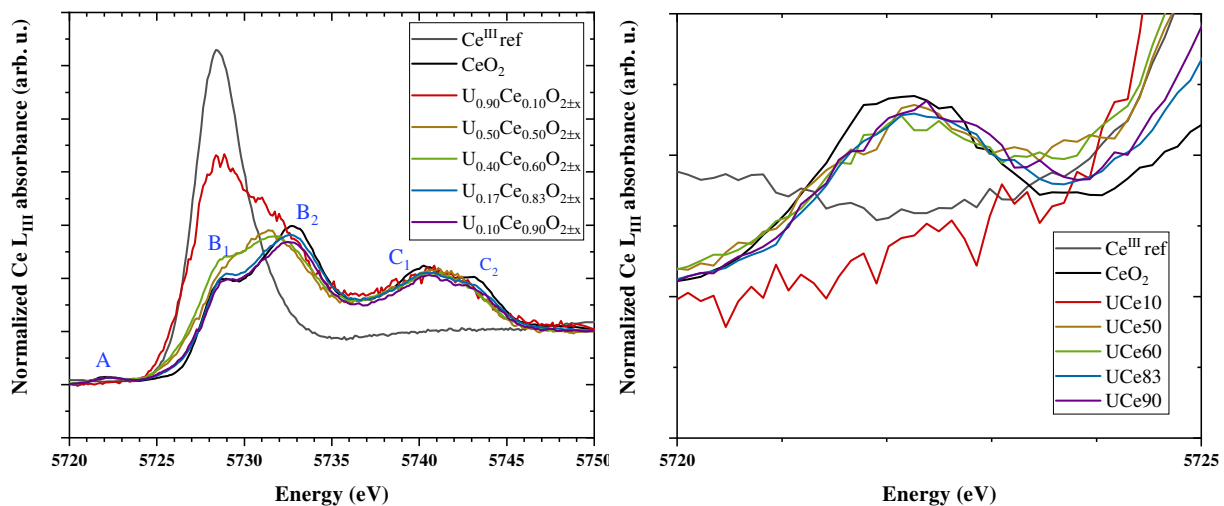


Figure 8: (Left) Ce L<sub>III</sub> HERFD-XANES spectra of U<sub>1-x</sub>Ce<sub>x</sub>O<sub>2+y</sub> NPs compared to CeO<sub>2</sub> reference. (Right) Pre-edge region of the Ce L<sub>III</sub> HERFD-XANES spectra.

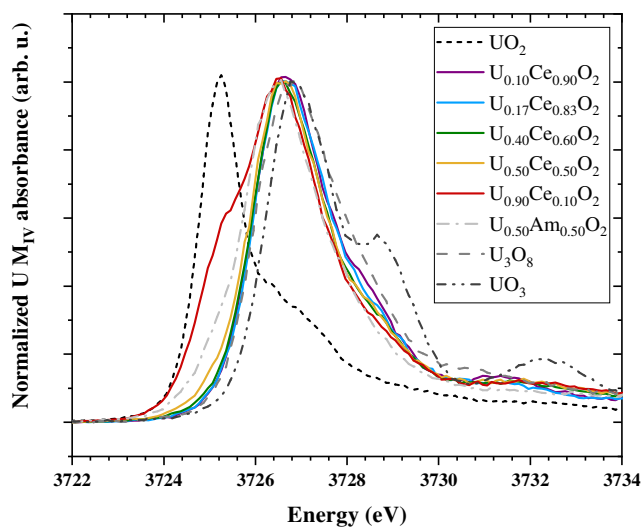


Figure 9: U M<sub>IV</sub> HERFD-XANES spectra of U<sub>1-x</sub>Ce<sub>x</sub>O<sub>2+y</sub> NPs compared to UO<sub>2</sub>, U<sub>3</sub>O<sub>8</sub>, UO<sub>3</sub> and U<sub>0.50</sub>Am<sub>0.50</sub>O<sub>2</sub> references.

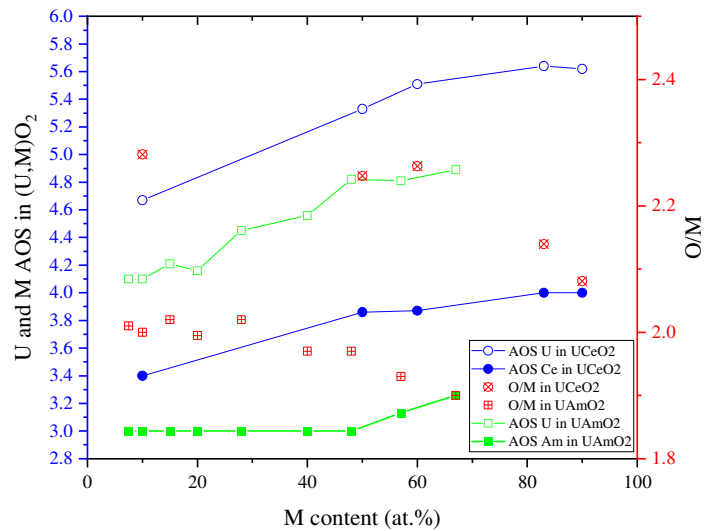


Figure 10: (Left axis) U and M average oxidation states and (Right axis) O/M as a function of the M content in  $U_{1-x}Ce_xO_{2+y}$  and  $(U,Am)O_{2+y}$ .

## TABLES

Table 3: Lattice parameter, space group and crystallite size derived from the Rietveld refinement.

	Lattice parameter (Å)	Space group	Crystallite size (nm)
$\text{U}_{0.90}\text{Ce}_{0.10}\text{O}_{2+y}$	5.460(2)	Fm-3m	13(1.2)
$\text{U}_{0.60}\text{Ce}_{0.40}\text{O}_{2+y}$	5.446(2)	Fm-3m	7.1(0.9)
$\text{U}_{0.50}\text{Ce}_{0.50}\text{O}_{2+y}$	5.441(2)	Fm-3m	7.3(1.0)
$\text{U}_{0.40}\text{Ce}_{0.60}\text{O}_{2+y}$	5.428(2)	Fm-3m	7.1(1.0)
$\text{U}_{0.17}\text{Ce}_{0.83}\text{O}_{2+y}$	5.417(2)	Fm-3m	7.0(0.9)
$\text{U}_{0.10}\text{Ce}_{0.90}\text{O}_{2+y}$	5.413(2)	Fm-3m	5.1(0.6)

Table 4: U and Ce valences, molar fractions and O/M ratios derived from the fitting of the U  $M_{IV}$  and Ce  $L_{III}$  HERFD-XANES spectra. \*  $U_{surf}$  corresponds to the fraction of U atoms at the surface of the NPs. This fraction was derived taking into account the lattice parameter and the NP size.

	$U^{IV}$ (%)	$U^V$ (%)	$U^{VI}$ (%)	Valence of U	$Ce^{III}$ (%)	$Ce^{IV}$ (%)	Valence of Ce	O/M	$U_{surf}$ *
$U_{0.90}Ce_{0.10}O_{2+y}$	38 (5)	57 (5)	5 (5)	4.67	60 (5)	40 (5)	3.6	2.28 (1)	12
$U_{0.50}Ce_{0.50}O_{2+y}$	9 (5)	50 (5)	41 (5)	5.33	14 (5)	86 (5)	3.86	2.25 (1)	22
$U_{0.40}Ce_{0.60}O_{2+y}$	5 (5)	39 (5)	56 (5)	5.51	13 (5)	87 (5)	3.87	2.26 (1)	22
$U_{0.17}Ce_{0.83}O_{2+y}$	3 (5)	31 (5)	66 (5)	5.64	0	100 (5)	4	2.13 (1)	22
$U_{0.10}Ce_{0.90}O_{2+y}$	3 (5)	31 (5)	66 (5)	5.62	0	100 (5)	4	2.08 (1)	29

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### **Author Contributions**

K.P. and O.W. carried out the NPs synthesis work. J-F.V, K.P., O.W., O.D.B. and Z.V. performed characterizations of the samples using in-house laboratory equipment. D.P. and P.M performed synchrotrons measurements and associated data treatment. K.D., J.R., A.B. and T.V. set up the spectrometer for U M<sub>IV</sub> and Ce L<sub>III</sub> measurements. D.P., J-F.V., K.P. and P.M. co-wrote the paper. D.P., K.P., P.M., O.W. and A.C.S. were involved in planning and supervision of the work. All authors discussed the results and contributed to the final manuscript.

### **Conflicts of interest**

**There are no conflicts to declare.**

## **ACKNOWLEDGMENT**

D. P., P.M., K.P. and O.W. acknowledge the KIT light source for provision of instruments at their beamlines and the Institute for Beam Physics and Technology (IBPT) for the operation of the storage ring, the Karlsruhe Research Accelerator (KARA). K.P., W.B. and O.W. acknowledge Daniel Bouëxière, Antony Guiot and Herwin Hein for the technical support.

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## TOC (For Table of Contents Only)

Uranium coexist in different valence states ( $U^{IV}$ ,  $U^V$  and  $U^{VI}$ ) in  $(U,Ce)O_2$  fluorite structure.

