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1 **Charge compensation mechanisms in Nd-doped UO<sub>2</sub> samples for stoichiometric and hypo-**  
2 **stoichiometric conditions: lack of miscibility gap.**

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10 **Highlights**

- 11 • Description of the solubility of the U<sub>1-y</sub>Nd<sub>y</sub>O<sub>2±x</sub> system at room temperature.
- 12 • Characterisation of the charge compensation mechanisms and local disorder for the U<sub>1-y</sub>Nd<sub>y</sub>O<sub>2±x</sub>  
13 system.
- 14 • Analysis of the crystal lattice of the U-Nd-O system assessed complementary by XRD and XAS.

15 **Abstract**

16 The evolution of the crystal lattice of samples made of UO<sub>2</sub> doped with different concentrations of  
17 Nd in stoichiometric and hypo-stoichiometric conditions has been systematically studied by X-ray  
18 diffraction (XRD) and X-ray absorption spectroscopy (XAS). The substitution of a trivalent cation for  
19 the U<sup>4+</sup> initial position is responsible for creating local structural disorder and changes in the  
20 oxidation states. In this scenario, the lattice parameter is affected and the concentration of U<sup>5+</sup> and  
21 formation of oxygen vacancies as well, since these are the mechanisms necessary to maintain the  
22 charge neutrality. The systematic oxidation of U<sup>4+</sup> as predominant charge compensation mechanism  
23 over the formation of vacancies can be reduced by performing a thermal treatment under reducing  
24 conditions. This paper presents an experimental characterization of the uranium oxidation state

25 mixture and local structure using XAS techniques in samples with chemical formula  $(U_{1-y}Nd_y)O_{2-x}$ , with  
26  $y=0.04, 0.17$  and  $0.25$  ( $0 < x < 0.038$ ). In all cases, the deviation from the ideal oxygen stoichiometry of a  
27 perfect fluorite is small and the average long-range structure is not affected because also the cation  
28 substitution occurs randomly onto the metal sites of the ideal fluorite. However, the local distances  
29 of the first atomic shell depend on the actual local chemical composition. The atomic arrangement of  
30 the Nd neighbours differs from those of U, which is also sensitive to the overall concentration of Nd  
31 and the amount of vacancies.

## 32 **Keywords**

33 Uranium dioxide, hypo-stoichiometry, local structural disorder, XAS, thermal annealing, Neodymium.

## 34 **1. Introduction**

35 Today,  $UO_2$  is the most widely used nuclear fuel. During in-pile irradiation, a large variety of fission  
36 products (FP) can be formed under the form of gas (Xe) [1-2], metallic precipitates (Mo, Tc, Ru...) [3-  
37 5] or dissolved on the crystal lattice [5-9]. The speciation of all these FP is of major importance since  
38 they can affect directly the global negative reactivity during operational conditions by acting as a  
39 neutronic poison ( $^{149}Sm$ ,  $^{157}Gd$ ) [11], or even increasing considerably the source term during the  
40 course of a severe accident ( $^{137}Cs$ ,  $^{131}I$ ) [12,13]. In particular, lanthanides (Nd, Ce or La) and some  
41 actinides (Pu, Np, Cm) represent an important part of the nuclear inventory, where Nd is the most  
42 abundant lanthanide of all [14]. Being  $Nd^{3+}$  a trivalent cation, its insertion into the  $UO_2$  face centered  
43 cubic (FCC) structure can cause changes on the interatomic distances, oxidation of the initial  $U^{4+}$ ,  
44 formation of vacancies or increasing on the structural disorder. In addition, the insertion of  $Nd^{3+}$   
45 drives the formation of  $U^{5+}$ ,  $U^{6+}$  and oxygen vacancies as charge compensation mechanisms,  
46 significantly affecting the oxygen chemical potential [15] and subsequently the global oxygen to  
47 metal ratio (O/M).

48 In this context, this work aims to study a set of stoichiometric and hypo-stoichiometric samples  
49 based on  $UO_2$  doped with Nd at different concentrations, produced after a thermal annealing. All

50 samples were characterised by X-ray diffraction (XRD) and X-ray absorption spectroscopy (XAS). XRD  
51 analysis is conveniently advantageous since it allows to directly relate the concentration of Nd and  
52 the formation of vacancies with the lattice parameter to a long-range extent. On the other hand, the  
53 XAS techniques are particularly sensitive to measure the presence of the different uranium oxidation  
54 states by X-ray absorption near edge spectroscopy (XANES) at the U  $M_4$ -edge and the local  
55 environment of a selected atom at the U and Nd  $L_3$ -edge by Extended X-ray absorption fine structure  
56 (EXAFS).

57 Concerning XANES acquisition, U  $M_4$ -edge spectra can be conveniently extracted by using high energy  
58 resolution fluorescence detected-XANES (HERFD-XANES). The use of this technique virtually reduce  
59 the core-hole broadening effect and evaluate directly metallic mixtures with different valence states  
60 [16,17].

61 The results obtained after the U  $M_4$ -edge spectra extraction for  $UO_2$ -based samples doped with Nd  
62 under the form of  $Nd^{3+}$ , along with the results from similar studies for other trivalent dopants, allow  
63 to have a better understanding of the charge compensation mechanisms for a general U-Ln-O system  
64 (where Ln is a trivalent dopant).

## 65 **2. Experimental procedure**

### 66 **2.1. Sample preparation**

67 The samples were produced by precipitation of oxalate precursors. This process is used to prepare  
68 the initially homogeneous solid solutions  $(U_{1-y}Nd_y)O_2$  ( $y$  is expressed hereafter in atomic percentage  
69 of the cations as  $y=4\%$ ,  $17\%$  and  $25\%$ ). Oxalic acid (0.5 M) is used to react with the cations  $U^{4+}$  ( $4.07$   
70  $10^{-4}$  mol.g $^{-1}$ ) and  $Nd^{3+}$  ( $4.721 \cdot 10^{-4}$  mol.g $^{-1}$ ) and precipitate in the form of mixed oxalates. The mixture  
71 of the starting reagents was made by pouring dropwise the solutions into a large excess of oxalic acid  
72 (0.5 M) to insure the precipitation of all cations at room temperature under stirring conditions. After  
73 few minutes, the precipitation was complete and the solution centrifuged, washed with water and  
74 ethanol, and finally dried at  $90^\circ C$ .

75 Oxalates samples were converted into the final oxides after calcination at 1273K for 60 h under an  
76 atmosphere of Ar + 4% H<sub>2</sub>. Afterwards, each sample was pressed into a pellet with an applied  
77 pressure of 450 MPa and sintered at 1823K for 5 h under the same atmosphere.

78 The verification of the expected final composition of the oxides was made through Energy Dispersive  
79 Spectroscopy (EDS) analysis. X-ray mapping was performed to obtain up to four 30x40 μm images on  
80 each sample. Complementary, line scans were also taken on each micrography. These results  
81 presented a good agreement with the theoretical values (4, 17 and 25 %Nd), confirming the full  
82 precipitation of the U<sup>4+</sup> and Nd<sup>3+</sup> initial cations, as well as the homogeneity throughout the whole  
83 pellet.

## 84 2.2. Thermal treatment

85 The thermal annealing under controlled atmosphere was performed at CEA, Cadarache. It intended  
86 to produce hypo-stoichiometric samples to compare them with as-produced samples. In the  
87 following, the as synthesized samples are referred as T0, and the annealed samples (under different  
88 controlled atmospheres) as TT. To carry on this thermal treatment, an induction furnace with a  
89 molybdenum sample holder was used allowing a heating and cooling ramp of 1K.s<sup>-1</sup>. The oxygen  
90 partial pressure (PO<sub>2</sub>) was monitored using the oxygen pump gauge Gen'Air from SETNAG, set to  
91 work using the principle of ionic conduction of zirconia on a flowing gas current of Ar+4% H<sub>2</sub>. The  
92 thermal treatment was carried on in two stages: the first stage consisted of a dwell for 2 h at 1473K  
93 to generate the reducing conditions to achieve hypo-stoichiometry. The second stage was defined to  
94 stabilize a second crystallographic phase that would appear as the result of a phase separation  
95 caused by a miscibility gap at low temperature (T<745K for 25%Nd) [18]. Thus, in order to favour  
96 phase separation, this stage consisted of a dwell for 6 h at 673K.

97 For the first stage, the measured PO<sub>2</sub> at 923K (which is the working temperature of the oxygen  
98 control device) was 10<sup>-27</sup> bar, which equals to an oxygen chemical potential (μO<sub>2</sub>) of -732.32 kJ.mol<sup>-1</sup>.  
99 According to calculations employing the Thermo-Calc software, this stated value allows the reduction

100 of the sample at 1473K. Similar analysis showing the evolution of the oxygen chemical potential for  
101 increasing temperatures on ternary systems can be seen in [15-16]. For the second stage, the oxygen  
102 atmosphere was set to the lowest achievable value of the equipment, reaching an oxygen partial  
103 pressure as low as  $10^{-29}$  bar.

### 104 2.3. Characterization

105 XRD patterns were measured before and after the thermal treatments using a Bruker D8 Advanced X-  
106 Ray diffractometer (Cu  $K\alpha_{1,2}$  radiation,  $\lambda=1.5418$  Å) equipped with a linear Lynx-Eye detector, and  
107 located at the CEA, Cadarache. The step used on the collection of the diffraction pattern was  $0.01^\circ$   
108 and a counting time of 0.5s/step within the  $2\theta$  range of  $20$ - $145^\circ$ . All XRD patterns and lattice  
109 parameter were analysed using the Jana 2006 software [21].

110 X-ray absorption spectra (XAS) were measured at the MARS beamline at the SOLEIL synchrotron  
111 (Saint-Aubin, France) [21,22]. The storage ring was operating in top up mode at an electron current  
112 of 450 mA, 2.5 GeV. The beam size on sample was  $250\mu\text{m} \times 150\mu\text{m}$  FWHM (Full Width at Half  
113 Maximum) (HxV). HERFD-XANES was measured at the U  $M_4$ -edge (3.7 keV) using the DCM (Double  
114 Crystal Monochromator) with a pair of Si(111) crystals. Higher harmonics rejection and vertical  
115 focusing were achieved using the Si strip of each mirror inserted before and after the DCM with a 4  
116 mrad incidence angle. The incident energy was calibrated using the absorption K-edge of potassium  
117 in a KBr pellet (3.6 keV). The incident X-ray flux on the sample position was  $1.9 \cdot 10^9$  ph/s at 3.5 keV.  
118 HERFD-XANES were acquired at the U  $M_\beta$  emission line (3.339 keV) using the emission spectrometer  
119 equipped with a Si(220) spherically bent diced crystal with curvature radius of 1 m, a KETEK single  
120 element silicon solid state (SDD) detector, along a Rowland type geometry. Samples were oriented at  
121  $45^\circ$  from the incident beam, and the emission spectrometer was positioned at  $90^\circ$  from the incident  
122 beam to minimize self-absorption effects. A He-chamber was used to reduce the scattering of the X-  
123 rays by air. The overall energy resolution of the emission spectrometer was 1.1 eV as determined  
124 from the FWHM of the elastic scattering peak at the double energy.

125 In addition, U L<sub>3</sub>-edge (17.166 keV) and Nd L<sub>3</sub>-edge (6.208 keV) EXAFS spectra were also collected in  
126 fluorescence mode using a 13-element HPGe detector from ORTEC. The beamline double-crystal  
127 monochromator (DCM) consists in a pair of Si(220) crystals for the U L<sub>3</sub>-edge and a pair of Si(111)  
128 crystals for the Nd L<sub>3</sub>-edge. Energy calibration was performed by measuring Y K-edge (17.038 keV) of  
129 a Y metallic foil for U L<sub>3</sub>-edge and Fe K-edge (7.112keV) of a Fe metallic foil for Nd L<sub>3</sub>-edge.

130 The treatment of the XAS data was performed with the software package Demeter. ATHENA  
131 software was used to remove the pre-edge data, as well as to normalize the post-edge using linear  
132 functions at the U M<sub>4</sub>-edge [24]. Finally, the energy threshold ( $E_0$ ) was defined as the maximum of  
133 the first derivative of the white-line relative to the incident energy.

134 Uranium valence state mixture was deduced from linear combination fitting within the range of  
135 3.720 to 3.731 keV. For this purpose, three references were used: UO<sub>2</sub> for U<sup>4+</sup>, NaUO<sub>3</sub> for U<sup>5+</sup> and  $\beta$ -  
136 UO<sub>3</sub> for U<sup>6+</sup>. The UO<sub>2</sub> spectrum was obtained during this experiment, however, the NaUO<sub>3</sub> and  $\beta$ -UO<sub>3</sub>  
137 references were obtained in a different analysis carried on at the ID26 beamline of the European  
138 Synchrotron Facility (ESRF) in Grenoble, France, and reported in [25]. Special attention was given on  
139 the possible effect on results arising from beamline energy resolution differences when dealing with  
140 such references.

141 The EXAFS data analysis was performed using the ARTEMIS software [24,26]. Hanning window was  
142 used to transform the EXAFS spectra into the Fourier transform over the k-range 3.2 to 12 and 2.8 to  
143 9.0, for U and Nd L<sub>3</sub>-edge, respectively. The first and second O coordinated shells, as well as the first  
144 intermetallic shell were determined assuming a fluorite structure with a random substitution of Nd  
145 into the metallic sublattice. The scattering factors  $S_0^2$  deduced from the fit for UO<sub>2</sub> and Nd<sub>2</sub>O<sub>3</sub> at the  
146 U and Nd L<sub>3</sub>-edge respectively were considered equal to 1.

147 Concerning the estimation of the O/M ratio, this is done through XAS determination of U valence  
148 state mixture, considering that Nd can only be found in solution as Nd<sup>3+</sup>, on the basis of sample  
149 composition. The study of the formation of vacancies is then indirect, by taking into account both the

150 lattice parameter changes (from XRD) and the deduced O/M (from XAS). This approach has  
151 demonstrated its reliability in the past, within limited accuracy, and remains accurate enough for  
152 properly analyze our sample composition. A more accurate analysis would involve the experimental  
153 characterization of the stoichiometry (using, for example, a thermogravimetric analysis) to establish  
154 a direct and more reliable comparison between the stoichiometries of the different samples, but  
155 such characterization was not possible during this work.

### 156 **3. Results and discussion**

#### 157 **3.1. XRD: Solubility studies**

158 XRD patterns at room temperature of all three T0 samples are shown in **figure 1 (a)**. It is clearly  
159 visible that the samples display a well crystallized single FCC structure with a small shift towards  
160 higher angles with increasing concentration of Nd, indicating a progressive lattice contraction but no  
161 symmetry change, see **figure 1 (b)**.

162 Numerous studies assessed the evolution of the lattice parameter,  $a$ , on stoichiometric samples ( $U_{1-y}Nd_y$ )O<sub>2</sub> [15], [27]-[30], [18]. Lee et al. interpreted the evolution as a function of the Nd atomic  
163 concentration according to the following expression :

$$165 \quad a = \frac{4}{\sqrt{3}} \left\{ (1 - 2y)r_{U4+} + yr_{U5+} + yr_{Nd3+} + r_{O2-} \right\} \left( 1 - \frac{y}{200} \right) \quad (\text{Eq. 1})$$

166 where  $y$  is the Nd concentration in atomic fraction and  $r$  is the atomic radius of the ion (see **table 1**)  
167 reported by Ohmichi et al. and Shannon [27], [28], [31]. This equation was first defined by Ohmichi et  
168 al. describing the lattice parameter only as a function of the atomic radii multiplied by the atomic  
169 fraction of each atom. However, later on Lee et al. added an empirical correction factor  $(1-y/200)$  to  
170 better describe the measured values of the lattice parameter up to a concentration of Nd as high as  
171 53%.



Ion	Radius (Å)
U <sup>4+</sup>	1.001
U <sup>5+</sup>	0.88
U <sup>6+</sup>	0.86
Nd <sup>3+</sup>	1.109
O <sup>2-</sup>	1.368
V <sub>o</sub>	1.09±0.05

Table 1. Ionic radius used in expression 1 taken from Ohmichi et al. and Shannon [27], [31].

172

173 **Figure 2** compares the values of the experimental lattice with the second order polynomial curve  
 174 defined by the equation (1). There is a general agreement concerning the evolution of the lattice  
 175 parameter for low concentrations of Nd. On the other hand, for concentrations of Nd higher than  
 176 50%, Barabash et al. reported a deviation of this behaviour, suggesting a possible underestimation of  
 177 the correction factor,  $(1-\gamma/200)$ , even for lower concentrations [32].

178 The samples undergoing a controlled atmosphere annealing were also studied by XRD (**figure 3 (a)**).

179 It is possible to see a clear narrowing of the peak widths and the contraction of the crystal lattice  
 180 caused by the increasing concentration of Nd. This trend of the samples treated thermally as a  
 181 function of the Nd substitution is analogous to the one of the as-produced samples (**figure 3 (b)**).

182 The FCC structure is maintained in all cases.

183 At all compositions and annealing temperatures, the system shows only a single fluorite-like phase,  
 184 which agrees with what is proposed by several authors for hypo-stoichiometric conditions [8,29,32-  
 185 35]. Therefore, the results presented in this work differ from those published by Desgranges et al.  
 186 and Dottavio et al. [18], [30], [36] where a miscibility gap was identified: no peak splitting is observed  
 187 in the samples object of this study and therefore there is no evidence for a phase separation. This  
 188 discrepancy was addressed in [37] where it is found that the samples used in [18], [30], [36]  
 189 presented an incomplete reaction between the initial powders of UO<sub>2</sub> and Nd<sub>2</sub>O<sub>3</sub>, which produces  
 190 the formation of phases out of the thermodynamic equilibrium, instead of a miscibility gap.

191 The objective of the thermal treatment was to create oxygen vacancies, which are responsible for an  
 192 expansion of the lattice parameter. This particular behaviour is seen repeatedly on the U-Nd-O  
 193 system and can be extrapolated to other ternary U-Ln-O systems (being Ln= Gd, Ce, Eu or Y)

194 [5,7,18,19]. A Rietveld refinement on the 25% Nd-substituted samples before and after thermal  
 195 annealing allowed to evidence the effect of lattice expansion and microstrain reduction on the (111)  
 196 peak, see **figure 4**. The blue arrows point at the peak defined by the  $K\alpha_1$  wavelength to better  
 197 visualize the lattice expansion caused by the annealing process. This peak is directly visible on the  
 198 annealed sample along with the  $K\alpha_2$  (smaller red peak), and hidden on the as-produced sample due  
 199 to the enlarged broadening. The corresponding numerical values for all samples are reported in **table**  
 200 **2**.

Sample [Nd] (%)	a T0 (Å)	a TT (Å)
0	5.4715 (4)	-
4	5.4671 (8)	5.468 (1)
17	5.4594 (5)	5.4607(4)
25	5.4568 (3)	5.4582 (3)

201 *Table 2. Lattice parameter of all the samples before and after thermal annealing under reducing controlled atmosphere.*

### 202 3.2. XANES: charge compensation mechanisms

203 The U  $M_4$ -edge spectra of all the samples (black) and all the references (blue) are shown in **figure 5**.  
 204 As indicated in the Experimental section, the  $UO_2$ ,  $NaUO_3$  and  $UO_3$  references correspond to pure  $U^{4+}$ ,  
 205  $U^{5+}$  and  $U^{6+}$  valence state, respectively.

206 All the samples present a sharp peak at 3725.8 eV, which belongs to the absorption energy of the U  
 207  $M_4$ -edge of  $U^{4+}$ . In addition, they also present a shoulder at a higher energy than the  $U^{4+}$  white-line  
 208 that increases progressively with higher concentrations of Nd. This behaviour is then explained by  
 209 the partial oxidation of  $U^{4+}$  to  $U^{5+}$  or  $U^{6+}$  to compensate the charge imbalance when  $Nd^{3+}$  is  
 210 substituted for  $U^{4+}$ . Therefore, this shoulder does not seem particularly sensitive to the actual O shell

211 surrounding the U atoms that is modified when oxygen vacancies are formed. The precise positions  
 212 of the white-line, as well as the  $E_0$  are detailed in **table 3**.

Sample	$E_0$ (eV)	White-line (eV)
UO <sub>2</sub>	3725.3 (2)	3725.8 (2)
NaUO <sub>3</sub>	3726.6 (2)	3727.2 (2)
$\beta$ -UO <sub>3</sub>	3727.1 (2)	3727.6 (2)
4% T0	3725.4 (2)	3725.8 (2)
4% TT	3725.4 (2)	3725.9 (2)
17% T0	3725.6 (2)	3726.0 (2)
17% TT	3725.6 (2)	3725.9 (2)
25% T0	3725.4 (2)	3725.9 (2)
25% TT	3725.6 (2)	3726.1 (2)

213 *Table 3. Position of the  $E_0$  and the white-line for each sample at the U  $M_4$ -edge XANES spectra.*

214 From a strictly electrical-balance standpoint, three models, as already mentioned by Bès et al. [25],  
 215 can be defined to describe the charge compensation mechanisms. These models are as follows,

216 Model 1:  $(1 - 2y)U^{4+} + yU^{5+} + yNd^{3+}$  (2)

217 Model 2:  $\left(1 - \frac{3}{2}y\right)U^{4+} + \frac{1}{2}yU^{6+} + yNd^{3+}$  (3)

218 Model 3:  $(1 - y)U^{4+} + \frac{y}{2}V_O + yNd^{3+}$  (4)

219 These models describe different scenario for the sample composition following the introduction of a  
 220 trivalent atom. Model 1 indicates the formation of equal amounts of  $U^{5+}$  for the substituted  $Nd^{3+}$ .  
 221 Model 2 describes the formation of one  $U^{6+}$  when two atoms of  $Nd^{3+}$  are substituted, whereas the  
 222 Model 3 compensates the missing charge with a half oxygen vacancy for each substituted atom of  
 223  $Nd^{3+}$ . This latter model is directly related to the global O/M ratio, since it does not imply a change of  
 224 the oxidation state of the U atoms of the system.

225 The XANES features of the samples were adjusted to find the amounts of  $U^{4+}$ ,  $U^{5+}$ , and  $U^{6+}$ ,  
 226 summarized in **table 4**. No  $U^{6+}$  was found in any sample, in good agreement with already reported  
 227 values [17]. This means that only Models 1 and 3, or any linear combination of the two, can be used

228 to explain the actual chemical composition of each sample. **Figure 6** shows for illustrative purposes  
 229 the results of the linear combination fitting of the sample with 25% Nd thermally annealed.

Sample	U <sup>4+</sup> (%)	U <sup>5+</sup> (%)	U <sup>6+</sup> (%)
4%TO	96 (2)	4 (2)	0(1)
4%TT	99 (2)	1 (2)	0(2)
17%TO	86 (4)	14 (4)	0(2)
17%TT	89 (3)	11 (3)	0(3)
25%TO	75 (4)	25 (4)	0(1)
25%TT	77 (4)	23 (4)	0(2)

230 *Table 4. Calculated concentration of U<sup>4+</sup>, U<sup>5+</sup> and U<sup>6+</sup> for each sample after the linear combination fitting of the HERFD-*  
 231 *XANES data.*

232 The influence of the reducing thermal annealing is also seen on the concentration of U<sup>5+</sup>. **Figure 7**  
 233 presents the comparison between the spectra of as-produced and annealed samples having a 25%  
 234 Nd substitution. In good agreement with the XRD analysis, the samples treated thermally present a  
 235 lower intensity of the peak located at 3726 eV, which is proportional to the global concentration of  
 236 uranium valence state higher than U<sup>4+</sup>, establishing that the formation of vacancies in the annealed  
 237 samples is more important than in as-produced samples. Indeed, these differences between the as-  
 238 produced samples and the ones treated thermally are small and require a careful data treatment.  
 239 However, the behaviour is systematic and consistent in both characterisation techniques XRD and  
 240 XAS.

241 To visualize more clearly the dominant charge compensation mechanisms, Bès et al. schematized the  
 242 concentration of U<sup>5+</sup> and U<sup>6+</sup> in comparison with Models 1, 2, and 3 [25]. Following the same  
 243 reasoning, **figure 8** displays the percentage of U<sup>5+</sup> for each valence state in comparison to Model 1,  
 244 the curve that expresses Model 2 was not introduced in the graphic as no U<sup>6+</sup> is seen in our samples.  
 245 The evolution of all the samples shows a coherent behaviour. U<sup>5+</sup> concentration increases with the  
 246 concentration of Nd<sup>3+</sup>, indicating that the compensation mechanism as described by Model 1 is  
 247 observed. As no U<sup>6+</sup> was observed (within the experimental uncertainties), we can exclude Model 2  
 248 from the main charge compensation mechanisms. However, U<sup>5+</sup> concentration appears below the  
 249 expected values as obtained using solely Model 1 for Nd concentrations higher than 4 %, indicating

250 that oxygen vacancies, i.e. Model 3, are also created, where x can adopt a value up to 0.038 on the  
251 sample 25%TT. In addition, the charge compensation mechanisms for all six samples are not the  
252 same since the contribution of Models 1 and 3 to electroneutrality varies between the samples.  
253 Those findings are in good agreement with the results reported in [17] where the experimental value  
254 matches the theoretical curve for concentrations of Nd lower than 9%, and where a mixed charge  
255 compensation between Model 1 and Model 3 is observed for higher Nd concentration. According to  
256 the work reported by Bès [25], it is only for a greater value of  $\gamma=30\%$  that the system exhibits the  
257 presence of  $U^{6+}$ . This value deviates significantly from the Model 1, since it shows a mixed charge  
258 compensation mechanism combining all three models.

### 259 3.3. XANES: comparison with other ternary systems

260 Other ternary systems have been also studied through XANES to analyse the local structure  
261 surrounding uranium atoms by measuring the  $L_3$ -edge or the  $M_4$ -edge spectra. Popa et al. studied the  
262 U-Bi-O system also through HERFD-XANES by analysing the U  $M_4$ -edge [38]. The study used samples  
263 varying the concentration of Bi from 15% until 79%. They showed that despite the ability of Bi to  
264 change from trivalent to pentavalent it remained trivalent for all cases, which makes the reported  
265 values suitable for direct analysis. Their results show a complete absence of  $U^{6+}$  up to a Bi  
266 concentration of 60%, which is in perfect agreement with our results.

267 Concerning the study of trivalent lanthanides, Prieur et al. [39] compared both measures of U  $L_3$ -edge  
268 and U  $M_4$ -edge for the system U-La-O. They reported the valence state on stoichiometric samples  
269 with relatively low concentrations of La. Regardless the concentration of La, they found consistently  
270 some small fraction of  $U^{6+}$  on the U  $M_4$ -edge spectra. On homogenous samples, this kind of  
271 behaviour is highly unlikely if the number of trivalent dopants remains inferior to 30%. To explain  
272 these findings, they stated the superficial oxidation of the samples, which justifies why the same  
273 amount of  $U^{6+}$  is seen on all samples. Bès et al [40] focused their study on the system U-Gd-O with  
274 samples containing low concentration of Gd. As expected, they saw only the formation of  $U^{5+}$

275 predominantly as the main factor for charge compensation. Finally, Bès et al [25] calculated the  
276 concentration of  $U^{5+}$  and  $U^{6+}$  on the system U-Nd-O. These measurements showed the presence of  
277  $U^{6+}$  on the samples starting from 29% of Nd. However, the author named repeatedly that the  
278 samples were not completely homogeneous due to the nature of the manufacturing process.  
279 Therefore, these results have only a qualitative meaning.

280 All those reported results are summarized in **table 5**. Throughout all systems, there are trends that  
281 repeat and that can be pointed out. First, it is evident that the concentration of  $U^{5+}$  increases with  
282 the number of trivalent dopants, meaning that the oxidation of uranium onto higher valence state is  
283 preferred than the formation of oxygen vacancies. Further, for very low concentrations of dopants  
284 ( $y < 0.1$ ), the only model for charge compensation that seems to predominate is the Model 1, as the  
285 experimental values are similar to the theoretical values within the margin of error. After that, the  
286 experimental values are slightly lower than the theoretical ones, indicating a compromise between  
287 Model 1 and Model 3 justified by the presence of vacancies.

288 For concentration of dopants lower than 30%, no formation of  $U^{6+}$  is detected. In contrast, its  
289 formation becomes predominant for concentration of trivalent dopants higher than 50%, which  
290 corresponds to the natural limit of Model 1, i.e. all  $U^{4+}$  are converted to  $U^{5+}$ . This statement can be  
291 explained by the atomic disposition on the cationic sub lattice. If a trivalent atom is surrounded only  
292 by uranium atoms and another trivalent atom is fairly distanced, the natural tendency is to increase  
293 the valence of uranium from  $U^{4+}$  to  $U^{5+}$ , which is the case on very low doped samples. While  
294 increasing the concentration of dopants, the probability for two trivalent atoms to be first  
295 neighbours is higher. Hence, the charge compensation through oxidation of uranium will compete  
296 with the formation of one vacancy. Finally, if the sample has over 50% of trivalent dopants, all the  
297 uranium has been oxidized from  $U^{4+}$  to  $U^{5+}$  and the system will have no option but to oxidize the  $U^{5+}$   
298 to  $U^{6+}$ .

Dopant	Concentration	Abs. U Edge	Theoretical (%) - Model 1		Experimental (%)			Author
			U <sup>4+</sup>	U <sup>5+</sup>	U <sup>4+</sup>	U <sup>5+</sup>	U <sup>6+</sup>	
Bi	(U <sub>0.85</sub> Bi <sub>0.15</sub> )O <sub>2</sub>	M <sub>4</sub>	82.35	17.6	82 (5)	18 (5)	0	Popa et al [38]
	(U <sub>0.68</sub> Bi <sub>0.32</sub> )O <sub>2</sub>	M <sub>4</sub>	52.9	47.0	44 (5)	56 (5)	0	
	(U <sub>0.50</sub> Bi <sub>0.50</sub> )O <sub>2</sub>	M <sub>4</sub>	0	100	0	100 (5)	0	
	(U <sub>0.40</sub> Bi <sub>0.60</sub> )O <sub>1.95</sub>	M <sub>4</sub>	0	0	0	74 (5)	26(5)	
	(U <sub>0.33</sub> Bi <sub>0.67</sub> )O <sub>2</sub>	M <sub>4</sub>	0	0	0	0	100(5)	
	(U <sub>0.21</sub> Bi <sub>0.79</sub> )O <sub>1.81</sub>	M <sub>4</sub>	0	0	0	10 (5)	90(5)	
La	(U <sub>0.94</sub> La <sub>0.06</sub> )O <sub>2±x</sub>	L <sub>3</sub>	93.6	6.3	94 (5)	6 (5)	0	Prieur et al [39]
	(U <sub>0.89</sub> La <sub>0.11</sub> )O <sub>2±x</sub>	L <sub>3</sub>	87.6	12.3	89 (5)	11 (5)	0	
	(U <sub>0.78</sub> La <sub>0.22</sub> )O <sub>2±x</sub>	L <sub>3</sub>	71.79	28.2	72 (5)	28 (5)	0	
	(U <sub>0.94</sub> La <sub>0.06</sub> )O <sub>2±x</sub>	M <sub>4</sub>	93.6	6.3	90 (2)	8 (2)	3 (2)	
	(U <sub>0.89</sub> La <sub>0.11</sub> )O <sub>2±x</sub>	M <sub>4</sub>	87.6	12.3	86 (2)	11(2)	3 (2)	
	(U <sub>0.78</sub> La <sub>0.22</sub> )O <sub>2±x</sub>	M <sub>4</sub>	71.79	28.2	76 (2)	21 (2)	3 (2)	
Gd	(U <sub>0.96</sub> Gd <sub>0.04</sub> )O <sub>2</sub>	M <sub>4</sub>	95.8	4.1	100 (5)	0 (5)	0	Bès et al [40]
	(U <sub>0.93</sub> Gd <sub>0.07</sub> )O <sub>2</sub>	M <sub>4</sub>	92.4	7.5	92 (4)	8 (4)	0	
	(U <sub>0.89</sub> Gd <sub>0.11</sub> )O <sub>2</sub>	M <sub>4</sub>	87.6	12.3	88 (3)	12 (3)	0	
	(U <sub>0.86</sub> Gd <sub>0.14</sub> )O <sub>2</sub>	M <sub>4</sub>	83.7	16.2	83 (2)	17 (2)	0	
Nd	(U <sub>0.91</sub> Nd <sub>0.09</sub> )O <sub>2</sub>	M <sub>4</sub>	90.1	9.8	93 (3)	7 (3)	0	Bès et al [25]
	(U <sub>0.85</sub> Nd <sub>0.15</sub> )O <sub>2</sub>	M <sub>4</sub>	82.35	17.6	83 (3)	17 (3)	0	
	(U <sub>0.71</sub> Nd <sub>0.29</sub> )O <sub>2</sub>	M <sub>4</sub>	59.1	40.8	73 (3)	22 (3)	0	
	(U <sub>0.38</sub> Nd <sub>0.62</sub> )O <sub>2</sub>	M <sub>4</sub>	0	0	2 (3)	0	98 (3)	
Nd	(U <sub>0.96</sub> Nd <sub>0.04</sub> )O <sub>2</sub>	M <sub>4</sub>	95.8	4.1	96 (3)	4 (3)	0 (3)	This work
	(U <sub>0.96</sub> Nd <sub>0.04</sub> )O <sub>2-x</sub>	M <sub>4</sub>	95.8	4.1	99 (3)	1 (3)	0 (3)	
	(U <sub>0.83</sub> Nd <sub>0.17</sub> )O <sub>2</sub>	M <sub>4</sub>	79.5	20.4	86 (3)	14 (3)	0 (3)	
	(U <sub>0.83</sub> Nd <sub>0.17</sub> )O <sub>2-x</sub>	M <sub>4</sub>	79.5	20.4	89 (3)	11 (3)	0 (3)	
	(U <sub>0.75</sub> Nd <sub>0.25</sub> )O <sub>2</sub>	M <sub>4</sub>	66.6	33.3	75 (3)	25 (3)	0 (3)	
	(U <sub>0.75</sub> Nd <sub>0.25</sub> )O <sub>2-x</sub>	M <sub>4</sub>	66.6	33.3	72 (3)	25 (3)	0 (3)	

299

Table 5. Concentration of U<sup>4+</sup> and U<sup>5+</sup> obtained after the LCF in comparison with theoretical values.

## 300 3.4. EXAFS: local environment analysis

301 The EXAFS spectra have also been measured on the Nd L<sub>3</sub>-edge and U L<sub>3</sub>-edge for the thermally302 treated (TT) samples, and the U L<sub>3</sub>-edge for the non-thermally treated (T0) samples. An immediate303 inspection at the Fourier transform of the k space for the samples U L<sub>3</sub>-edge TT and T0 (**figure 9 (a)**304 and **(b)**) show a gradual decrease of the intensities when the concentration of Nd increases. This305 behaviour was evidenced in other UO<sub>2</sub> doped systems [37-39] and it is explained by the destructive

306 interferences due to opposites phases and similar intensities for the U-U and U-Nd paths [35]. In

307 contrast, no relevant differences can be observed between the intensities of the samples T0 and TT

308 with equal concentration of Nd.

309 The k space with its respective Fourier transform and the EXAFS fit for each sample are shown in  
310 **figure 10**. The Nd L<sub>3</sub>-edge for the sample at 4% Nd was also acquired but the concentration of Nd was  
311 so little that achieving such measurement with good statistics was not possible within the granted  
312 beamtime. It is then not included in this document.

313 The small evolution of the k space on each set of samples indicates little differences on the local  
314 distances but no major changes on the local surroundings of the U or Nd atoms as the FCC structure  
315 remains in all cases as such. Subfigures b, d and f in **figure 10** represent the Fourier transform of the k  
316 space for each set of samples. The two larger peaks reveal qualitative information about the U-O, U-  
317 Nd and U-U distances. The first peak around 1.8 Å is mainly the consequence of the single scattering  
318 path of the nearest oxygen atom. The second peak around 3.8 Å is composed of the single and  
319 multiple scattering paths of the first and second shells (M-O and M-M shells).

320 The results of the refinements for all samples are shown in **table 6**. It is possible to see that in all  
321 cases the R-factor obtained from the analysis of the experimental data and the EXAFS fit varies from  
322 0.0124 to 0.0182, allowing to extract general trends concerning the atomic distances and local  
323 disordering. Some differences can be found on the EXAFS fit respecting the presence of a peak on the  
324 Fourier transform graphs at around 4.5 Å, particularly on the Nd L<sub>3</sub>-edge EXAFS spectra. This peak  
325 does not seem to vary with the Nd concentration and could be explained by a multi-scattering effect.  
326 The enhanced intensity displayed in the **figures 10 (d)** and **10 (f)** might be due to the reduced  
327 intensity of the Nd/M as a consequence of the destructive interference of the EXAFS signals. Similar  
328 observations were seen on UO<sub>2</sub>-based samples doped with Gd in [40].

329 Respecting the interatomic distances (R), all samples display a coherent decreasing evolution with  
330 increasing concentration of Nd regardless if it is the 1<sup>st</sup>, 2<sup>nd</sup> or 3<sup>rd</sup> shell, that is  $R_{04} > R_{17} > R_{25}$ . As for the  
331 samples treated thermally, the distances remain slightly greater than those of the samples non-  
332 treated thermally, that is  $R_{T0} < R_{TT}$ . However, the difference is very small and in all cases is lower than  
333 the uncertainty.



Sample	Edge	Shell	R (Å)	$\sigma^2(10^{-3} \text{ \AA}^2)$	N	$N_{\text{exp}}$	R-factor
4% T0	U L <sub>3</sub> -edge	U-O <sub>1</sub>	2.351(3)	5.8(4)	8	8.5(3)	0.0128
		U-U	3.875(2)	2.9(2)	11.5	11.5(2)	
		U-Nd	3.875(2)	2.9(2)	0.5	0.5(2)	
		U-O <sub>2</sub>	4.491(11)	10.0(1.5)	24	27(4)	
17% T0		U-O <sub>1</sub>	2.337(4)	7.4(6)	8	8.4(4)	0.0139
		U-U	3.869(3)	3.6(3)	10	10(3)	
		U-Nd	3.869(3)	3.6(3)	2	2(3)	
		U-O <sub>2</sub>	4.484(16)	10.5(2.2)	24	25(5)	
25% T0		U-O <sub>1</sub>	2.332(3)	9.0(4)	8	8.5(4)	0.01315
		U-U	3.870(2)	4.2(2)	9.3	9.3(2)	
		U-Nd	3.870(2)	4.2(2)	2.7	2.7(2)	
		U-O <sub>2</sub>	4.480(12)	12.5(1.7)	24	26(4)	
4% TT		U-O <sub>1</sub>	2.353(4)	5.5(5)	8	8.6(5)	0.0182
		U-U	3.876(2)	2.5(2)	11.5	0.5(2)	
		U-Nd	3.876(2)	2.5(2)	0.5	11.5(2)	
		U-O <sub>2</sub>	4.488(17)	11.0(2)	24	27(6)	
17% TT	U-O <sub>1</sub>	2.339(4)	7.79(5)	8	8.3(4)	0.0124	
	U-U	3.872(2)	3.72(2)	10	9.9(2)		
	U-Nd	3.872(2)	3.72(2)	2	2.1(2)		
	U-O <sub>2</sub>	4.480(16)	11.48(1.9)	25	25(5)		
25% TT	U-O <sub>1</sub>	2.334(3)	8.7(5)	8	8.3(4)	0.0143	
	U-U	3.875(2)	4.0(2)	9.3	9.0(2)		
	U-Nd	3.875(2)	4.0(2)	2.7	3(2)		
	U-O <sub>2</sub>	4.481(13)	12.7(1.8)	24	25(4)		
17% TT	Nd L <sub>3</sub> -edge	Nd-O <sub>1</sub>	2.441(4)	6.5(6)	8	8.2(4)	0.01709
		Nd-U	3.866(4)	4.1(5)	10	9.6(5)	
		Nd-Nd	3.866(4)	4.1(5)	2	2.4(5)	
		Nd-O <sub>2</sub>	4.436(11)	11.7(2.2)	24	23(4)	
25% TT		Nd-O <sub>1</sub>	2.440(4)	6.9(6)	8	8.1(4)	0.01502
		Nd-U	3.864(4)	3.2(5)	9.3	8.8(4)	
		Nd-Nd	3.864(4)	3.2(5)	2.7	3.2(4)	
		Nd-O <sub>2</sub>	4.430(11)	10.2(1.7)	24	23(3)	

335

Table 6. Results of the EXAFS refinement of all measured samples

336 Another remark can be made concerning the Nd-O distances calculated from the Nd L<sub>3</sub>-edge EXAFS  
337 spectra. In contrast with the U-O distances calculated from the U L<sub>3</sub>-edge EXAFS analysis, the Nd-O  
338 distances are much larger and equal in value for the two analysed samples (figure 11). This means  
339 that the local distances of the first shell will vary depending if it is U or Nd, which is consistent with  
340 the observation of the variation of the k space mentioned earlier in the document. Similar  
341 conclusions were seen in [27,35]. Barabash et al. argued that the atoms of Nd, which are inserted  
342 randomly on the cationic sub lattice, are able to push the surrounding atoms of oxygen out of their

343 regular position, creating a local structural disorder along with the distortion created by the size  
344 mismatch between the  $\text{Nd}^{3+}$ ,  $\text{U}^{4+}$  and  $\text{U}^{5+}$  cations. This behaviour can also be justified by looking at  
345 the Debye-Waller factor ( $\sigma^2$ ). Indeed, the structural disorder on the surroundings of the uranium  
346 atoms increases with the concentration of Nd. Contrarily to what is seen on the surroundings of the  
347 Nd atoms, since they are randomly introduced and fairly distanced to each other, the Debye-Waller  
348 factor remains unaffected on a given shell on both assessed concentrations 17 and 25% Nd.

#### 349 **4. Conclusion**

350 Based on analysis through X-ray diffraction, U  $M_4$ -edge HERFD-XANES, U  $L_3$ -edge and Nd  $L_3$ -edge  
351 EXAFS analysis, an assessment of the crystal lattice, charge compensation mechanisms and local  
352 atomic environment on  $\text{UO}_2$  doped with Nd is reported. This work indicates that Nd is completely  
353 miscible in  $\text{UO}_2$  for all assessed concentrations (4, 17 and 25%Nd), even after the samples were  
354 thermally treated under reducing conditions, indicating the lack of a miscibility gap. In addition, it  
355 was seen that random insertion of Nd atoms into the fluorite structure generates distortions on the  
356 crystal lattice by changing the atomic distances and increasing the structural disorder. The  
357 replacement of a tetravalent cation ( $\text{U}^{4+}$ ) by a trivalent cation ( $\text{Nd}^{3+}$ ) is compensated by the formation  
358 of  $\text{U}^{5+}$  cations and anion vacancies. In addition, thermal treatment under reducing conditions  
359 increases the amount of vacancies and, therefore, reduces the amount of  $\text{U}^{5+}$  needed to maintain the  
360 electroneutrality of the system. It was also stated that no  $\text{U}^{6+}$  is formed when the addition of Nd is  
361 lower than 25%. Finally, it was seen that the local distances on the surroundings of the atoms of U  
362 are different from those of the atoms of Nd since the latter has a different ionic radius and charge,  
363 and are capable to displace the oxygen atoms of the first shell out of their initial position.

364 These results are in good agreement with similar studies made on systems where  $\text{UO}_2$  was doped  
365 with other trivalent cations, such as  $\text{Gd}^{3+}$ ,  $\text{La}^{3+}$  or  $\text{Bi}^{3+}$ , which proves that charge compensation  
366 mechanisms do not depend on the element used as dopant, on the contrary, it is mostly defined by  
367 its valence.

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371        **6. Bibliography**

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