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1 **Charge compensation mechanisms in Nd-doped UO2 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 $U_{1-y}Nd_yO_{2\pm x}$ system at room temperature.

12 • Characterisation of the charge compensation mechanisms and local disorder for the $U_{1-y}Nd_yO_{2\pm x}$

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_2 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^{4+} 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^{5+} 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^{4+} 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 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°C.

75   Oxalates samples were converted <u>into</u> the final oxides after calcination at 1273K for 60 h under an

76   atmosphere of Ar + 4% H_2. 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^{4+} and Nd^{3+} initial cations, as well as the homogeneity throughout the whole

83   pellet.

84   2.2. <u>Thermal treatment</u>

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 $1K.s^{-1}$. The oxygen

90   partial pressure (PO_2) 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_2. 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_2 at 923K (which is the working temperature of the oxygen

98   control device) was 10^{-27} bar, which equals to an oxygen chemical potential (μO_2) of -732.32 $kJ.mol^{-1}$.

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, λ=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°

108   and a counting time of 0.5s/step within the 2θ range of 20-145°. 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 250µm × 150µm 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_β 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° from the incident beam, and the emission spectrometer was positioned at 90° 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_3-edge (17.166 keV) and Nd L_3-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_3-edge and a pair of Si(111)

128 crystals for the Nd L_3-edge. Energy calibration was performed by measuring Y K-edge (17.038 keV) of

129 a Y metallic foil for U L_3-edge and Fe K-edge (7.112keV) of a Fe metallic foil for Nd L_3-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_4-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_2 for U^{4+}, $NaUO_3$ for U^{5+} and β-

136 UO_3 for U^{6+}. The UO_2 spectrum was obtained during this experiment, however, the $NaUO_3$ and β-UO_3

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_3-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_2 and Nd_2O_3 at the

146 U and Nd L_3-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^{3+}, 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-}

163 $_y Nd_y)O_2$ [15], [27]–[30], [18]. Lee et al. interpreted the evolution as a function of the Nd atomic

164 concentration according to the following expression :

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

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^{4+}	1.001
U^{5+}	0.88
U^{6+}	0.86
Nd^{3+}	1.109
O^{2-}	1.368
V_O	1.09±0.05

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

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-y/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_2 and Nd_2O_3, 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. <u>XANES: charge compensation mechanisms</u>

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 E0 are detailed in **table 3**.

Sample	E_0 (eV)	White-line (eV)
UO_2	3725.3 (2)	3725.8 (2)
$NaUO_3$	3726.6 (2)	3727.2 (2)
β-UO_3	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 $$\text{Model 1: } (1 - 2y)U^{4+} + yU^{5+} + yNd^{3+} \qquad (2)$$

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

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

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^{4+} (%)	U^{5+} (%)	U^{6+} (%)
4%T0	96 (2)	4 (2)	0(1)
4%TT	99 (2)	1 (2)	0(2)
17%T0	86 (4)	14 (4)	0(2)
17%TT	89 (3)	11 (3)	0(3)
25%T0	75 (4)	25 (4)	0(1)
25%TT	77 (4)	23 (4)	0(2)

230
231   *Table 4. Calculated concentration of U^{4+}, U^{5+} and U^{6+} for each sample after the linear combination fitting of the HERFD-XANES data.*

232   The influence of the reducing thermal annealing is also seen on the concentration of U^{5+}. **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^{4+}, 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^{5+} and U^{6+} in comparison with Models 1, 2, and 3 [25]. Following the same

243   reasoning, **figure 8** displays the percentage of U^{5+} 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^{6+} is seen in our samples.

245   The evolution of all the samples shows a coherent behaviour. U^{5+} concentration increases with the

246   concentration of Nd^{3+}, indicating that the compensation mechanism as described by Model 1 is

247   observed. As no U^{6+} was observed (within the experimental uncertainties), we can exclude Model 2

248   from the main charge compensation mechanisms. However, U^{5+} 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 y=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^{4+}	U^{5+}	U^{4+}	U^{5+}	U^{6+}	
Bi	$(U_{0.85}Bi_{0.15.})O_2$	M_4	82.35	17.6	82 (5)	18 (5)	0	Popa et al [38]
	$(U_{0.68}Bi_{0.32})O_2$	M_4	52.9	47.0	44 (5)	56 (5)	0	
	$(U_{0.50}Bi_{0.50})O_2$	M_4	0	100	0	100 (5)	0	
	$(U_{0.40}Bi_{0.60.})O_{1.95}$	M_4	0	0	0	74 (5)	26(5)	
	$(U_{0.33}Bi_{0.67.})O_2$	M_4	0	0	0	0	100(5)	
	$(U_{0.21}Bi_{0.79})O_{1.81}$	M_4	0	0	0	10 (5)	90(5)	
La	$(U_{0.94}La_{0.06.})O_{2\pm x}$	L_3	93.6	6.3	94 (5)	6 (5)	0	Prieur et al [39]
	$(U_{0.89}La_{0.11.})O_{2\pm x}$	L_3	87.6	12.3	89 (5)	11 (5)	0	
	$(U_{0.78}La_{0.22.})O_{2\pm x}$	L_3	71.79	28.2	72 (5)	28 (5)	0	
	$(U_{0.94}La_{0.06})O_{2\pm x}$	M_4	93.6	6.3	90 (2)	8 (2)	3 (2)	
	$(U_{0.89}La_{0.11.})O_{2\pm x}$	M_4	87.6	12.3	86 (2)	11(2)	3 (2)	
	$(U_{0.78}La_{0.22.})O_{2\pm x}$	M_4	71.79	28.2	76 (2)	21 (2)	3 (2)	
Gd	$(U_{0.96}Gd_{0.04.})O_2$	M_4	95.8	4.1	100 (5)	0 (5)	0	Bès et al [40]
	$(U_{0.93}Gd_{0.07.})O_2$	M_4	92.4	7.5	92 (4)	8 (4)	0	
	$(U_{0.89}Gd_{0.11.})O_2$	M_4	87.6	12.3	88 (3)	12 (3)	0	
	$(U_{0.86}Gd_{0.14.})O_2$	M_4	83.7	16.2	83 (2)	17 (2)	0	
Nd	$(U_{0.91}Nd_{0.09})O_2$	M_4	90.1	9.8	93 (3)	7 (3)	0	Bès et al [25]
	$(U_{0.85}Nd_{0.15.})O_2$	M_4	82.35	17.6	83 (3)	17 (3)	0	
	$(U_{0.71}Nd_{0.29.})O_2$	M_4	59.1	40.8	73 (3)	22 (3)	0	
	$(U_{0.38}Nd_{0.62})O_2$	M_4	0	0	2 (3)	0	98 (3)	
Nd	$(U_{0.96}Nd_{0.04.})O_2$	M_4	95.8	4.1	96 (3)	4 (3)	0 (3)	This work
	$(U_{0.96}Nd_{0.04.})O_{2-x}$	M_4	95.8	4.1	99 (3)	1 (3)	0 (3)	
	$(U_{0.83}Nd_{0.17.})O_2$	M_4	79.5	20.4	86 (3)	14 (3)	0 (3)	
	$(U_{0.83}Nd_{0.17.})O_{2-x}$	M_4	79.5	20.4	89 (3)	11 (3)	0 (3)	
	$(U_{0.75}Nd_{0.25.})O_2$	M_4	66.6	33.3	75 (3)	25 (3)	0 (3)	
	$(U_{0.75}Nd_{0.25.})O_{2-x}$	M_4	66.6	33.3	72 (3)	25 (3)	0 (3)	

299   *Table 5. Concentration of U4+ and U5+ 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_3-edge and U L_3-edge for the thermally

302   treated (TT) samples, and the U L_3-edge for the non-thermally treated (T0) samples. An immediate

303   inspection at the Fourier transform of the k space for the samples U L_3-edge TT and T0 (**figure 9 (a)**

304   and **(b))** show a gradual decrease of the intensities when the concentration of Nd increases. This

305   behaviour was evidenced in other UO_2 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_3-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_3-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_2-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 1st, 2nd or 3rd 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 (A)	$\sigma^2(10^{-3}\ \text{Å}^2)$	N	N_{exp}	R-factor
4% T0		U-O$_1$	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$_2$	4.491(11)	10.0(1.5)	24	27(4)	
17% T0		U-O$_1$	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$_2$	4.484(16)	10.5(2.2)	24	25(5)	
25% T0		U-O$_1$	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 L$_3$-edge	U-O$_2$	4.480(12)	12.5(1.7)	24	26(4)	
4% TT		U-O$_1$	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$_2$	4.488(17)	11.0(2)	24	27(6)	
17% TT		U-O$_1$	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$_2$	4.480(16)	11.48(1.9)	25	25(5)	
25% TT		U-O$_1$	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$_2$	4.481(13)	12.7(1.8)	24	25(4)	
17% TT		Nd-O$_1$	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$_2$	4.436(11)	11.7(2.2)	24	23(4)	
25% TT	Nd L$_3$-edge	Nd-O$_1$	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$_2$	4.430(11)	10.2(1.7)	24	23(3)	

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

Another remark can be made concerning the Nd-O distances calculated from the Nd L$_3$-edge EXAFS

spectra. In contrast with the U-O distances calculated from the U L$_3$-edge EXAFS analysis, the Nd-O

distances are much larger and equal in value for the two analysed samples (figure 11). This means

that the local distances of the first shell will vary depending if it is U or Nd, which is consistent with

the observation of the variation of the k space mentioned earlier in the document. Similar

conclusions were seen in [27,35]. Barabash et al. argued that the atoms of Nd, which are inserted

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 Nd^{3+}, U^{4+} and U^{5+} cations. This behaviour can also be justified by looking at

345   the Debye-Waller factor (σ^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 UO_2 doped with Nd is reported. This work indicates that Nd is completely

353   miscible in 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 (U^{4+}) by a trivalent cation (Nd^{3+}) is compensated by the formation

358   of 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 U^{5+} needed to maintain the

360   electroneutrality of the system. It was also stated that no 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 UO_2 was doped

365   with other trivalent cations, such as Gd^{3+}, La^{3+} or 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.

6. <u>Bibliography</u>

[1]   J. Noirot, L. Desgranges, and J. Lamontagne, 'Detailed characterisations of high burn-up

structures in oxide fuels', J. Nucl. Mater., vol. 372, no. 2–3, pp. 318–339, Jan. 2008, doi:

10.1016/j.jnucmat.2007.04.037.

[2]   C. T. Walker, 'Assessment of the radial extent and completion of recrystallisation in high burn-

up UO_2 nuclear fuel by EPMA', J. Nucl. Mater., vol. 275, no. 1, pp. 56–62, Oct. 1999, doi:

10.1016/S0022-3115(99)00108-7.

[3]   E. Geiger, 'Study of Fission Products (Cs, Ba, Mo, Ru) behaviour in irradiated and simulated

Nuclear Fuels during Severe Accidents using X-ray Absorption Spectroscopy, SIMS and EPMA',

PhD thesis, Université Paris Saclay 2016.

[4]   C. Le Gall et al., 'Fission products and nuclear fuel behaviour under severe accident conditions

part 3: Speciation of fission products in the VERDON-1 sample', J. Nucl. Mater., vol. 495, pp.

291–298, Nov. 2017, doi: 10.1016/j.jnucmat.2017.08.001.

[5]   H. Kleykamp, 'THE CHEMICAL STATE OF THE FISSION PRODUCTS IN OXIDE FUELS', p. 26, 1985.

[6]   T. L. Markin, R. S. Street, and E. C. Crouch, 'The uranium-cerium-oxygen ternary phase diagram',

J. Inorg. Nucl. Chem., vol. 32, no. 1, pp. 59–75, Jan. 1970, doi: 10.1016/0022-1902(70)80449-3.

[7]   T. L. Markin and R. S. Street, 'The uranium-plutonium-oxygen ternary phase diagram', J. Inorg.

Nucl. Chem., vol. 29, no. 9, pp. 2265–2280, Sep. 1967, doi: 10.1016/0022-1902(67)80281-1.

[8]   R. Venkata Krishnan et al., 'Solubility studies and thermophysical properties of uranium–

neodymium mixed oxides system', Ceram. Int., vol. 40, no. 3, pp. 4395–4405, Apr. 2014, doi:

10.1016/j.ceramint.2013.08.111.

392 [9] R. Venkata Krishnan, G. Panneerselvam, M. P. Antony, and K. Nagarajan, 'Solubility studies and

393   thermal expansion coefficient of uranium–lanthanum mixed oxide system', *J. Nucl. Mater.*, vol.

394   403, no. 1, pp. 25–31, Aug. 2010, doi: 10.1016/j.jnucmat.2010.05.026.

395 [10] T. B. Lindemer and A. L. Sutton, 'Study of Nonstoichiometry of $\langle U_{1-z}Gd_zO_{2\pm x}\rangle$ ', *J. Am. Ceram.*

396   *Soc.*, vol. 71, no. 7, pp. 553–561, 1988, doi: 10.1111/j.1151-2916.1988.tb05919.x.

397 [11] D. T. Goldman, *Neutron cross sections and technology: proceedings of a conference*. U.S.

398   National Bureau of Standards; for sale by the Supt. of Docs., U.S. Govt. Print. Off., 1968.

399 [12] V. Winiarek, M. Bocquet, N. Duhanyan, Y. Roustan, O. Saunier, and A. Mathieu, 'Estimation of

400   the caesium-137 source term from the Fukushima Daiichi nuclear power plant using a

401   consistent joint assimilation of air concentration and deposition observations', *Atmos. Environ.*,

402   vol. 82, pp. 268–279, Jan. 2014, doi: 10.1016/j.atmosenv.2013.10.017.

403 [13] Internationale Atomenergie-Organisation, Ed., *The Fukushima Daiichi accident*. Vienna:

404   International Atomic Energy Agency, 2015.

405 [14] B. J. Lewis, W. T. Thompson, and F. C. Iglesias, 'Fission Product Chemistry in Oxide Fuels', in

406   *Comprehensive Nuclear Materials*, Elsevier, 2012, pp. 515–546.

407 [15] K. Une and M. Oguma, 'Oxygen potentials of $(U,Nd)O_{2\pm x}$ solid solutions in the temperature

408   range 1000–1500°C', *J. Nucl. Mater.*, vol. 118, no. 2, pp. 189–194, Sep. 1983, doi:

409   10.1016/0022-3115(83)90224-6.

410 [16] K. O. Kvashnina, S. M. Butorin, P. Martin, and P. Glatzel, 'Chemical State of Complex Uranium

411   Oxides', *Phys. Rev. Lett.*, vol. 111, no. 25, p. 253002, Dec. 2013, doi:

412   10.1103/PhysRevLett.111.253002.

413 [17] O. Proux *et al.*, 'High-Energy Resolution Fluorescence Detected X-Ray Absorption Spectroscopy:

414   A Powerful New Structural Tool in Environmental Biogeochemistry Sciences', *J. Environ. Qual.*,

415   vol. 46, no. 6, pp. 1146–1157, 2017, doi: 10.2134/jeq2017.01.0023.

416   [18] G. Dottavio *et al.*, 'Existence of a miscibility gap in uranium neodymium oxide materials used as

417   nuclear fuels simulants', *Prog. Nucl. Energy*, vol. 72, pp. 22–26, Apr. 2014, doi:

418   10.1016/j.pnucene.2013.09.008.

419   [19] R. C. Belin, P. M. Martin, J. Lechelle, M. Reynaud, and A. C. Scheinost, 'Role of Cation

420   Interactions in the Reduction Process in Plutonium–Americium Mixed Oxides', *Inorg. Chem.*,

421   vol. 52, no. 6, pp. 2966–2972, Mar. 2013, doi: 10.1021/ic3023776.

422   [20] R. Vauchy, R. C. Belin, A.-C. Robisson, and F. Hodaj, 'High temperature X-ray diffraction study of

423   the kinetics of phase separation in hypostoichiometric uranium–plutonium mixed oxides', *J.*

424   *Eur. Ceram. Soc.*, vol. 34, no. 10, pp. 2543–2551, Sep. 2014, doi:

425   10.1016/j.jeurceramsoc.2014.02.028.

426   [21] M. Dusek, V. Petricek, and L. Palatinus, 'Introduction to JANA2006', *Acta Crystallogr. A*, vol. 62,

427   no. a1, pp. s46–s46, Aug. 2006, doi: 10.1107/S0108767306099089.

428   [22] B. Sitaud, P. L. Solari, S. Schlutig, I. Llorens, and H. Hermange, 'Characterization of radioactive

429   materials using the MARS beamline at the synchrotron SOLEIL', *J. Nucl. Mater.*, vol. 425, no. 1–

430   3, pp. 238–243, Jun. 2012, doi: 10.1016/j.jnucmat.2011.08.017.

431   [23] I. LLorens *et al.*, 'X-ray absorption spectroscopy investigations on radioactive matter using

432   MARS beamline at SOLEIL synchrotron', *Radiochim. Acta*, vol. 0, no. 0, Jan. 2014, doi:

433   10.1515/ract-2013-2241.

434   [24] B. Ravel and M. Newville, 'ATHENA, ARTEMIS, HEPHAESTUS: data analysis for X-ray absorption

435   spectroscopy using IFEFFIT', *J. Synchrotron Radiat.*, vol. 12, no. Pt 4, pp. 537–541, Jul. 2005, doi:

436   10.1107/S0909049505012719.

437   [25] R. Bès *et al.*, 'New insight in the uranium valence state determination in $U_yNd_{1-y}O_{2\pm x}$', *J. Nucl.*

438   *Mater.*, vol. 507, pp. 145–150, Aug. 2018, doi: 10.1016/j.jnucmat.2018.04.046.

439   [26] M. Newville and IUCr, 'IFEFFIT : interactive XAFS analysis and FEFF fitting', *Journal of*

440   *Synchrotron Radiation*, Mar. 01, 2001. http://scripts.iucr.org/cgi-

441   bin/paper?S0909049500016964 (accessed Jan. 09, 2020).

442   [27]   T. Ohmichi, S. Fukushima, A. Maeda, and H. Watanabe, 'On the relation between lattice

443   parameter and O/M ratio for uranium dioxide-trivalent rare earth oxide solid solution', *J. Nucl.*

444   *Mater.*, vol. 102, no. 1, pp. 40–46, Nov. 1981, doi: 10.1016/0022-3115(81)90544-4.

445   [28]   S. M. Lee, T. W. Knight, S. L. Voit, and R. I. Barabash, 'Lattice Parameter Behavior with Different

446   Nd and O Concentrations in $(U_{1-y}Nd_y)O_{2\pm x}$ Solid Solution', *Nucl. Technol.*, vol. 193, no. 2, pp.

447   287–296, Feb. 2016, doi: 10.13182/NT14-136.

448   [29]   J.-F. Wadier, 'Phase diagrams and thermodynamic properties of the uranium-neodymium-

449   oxygen system', Rapport CEA-R-4507, 1973. Accessed: Apr. 17, 2019. [Online]. Available:

450   http://inis.iaea.org/Search/search.aspx?orig_q=RN:5112178.

451   [30]   L. Desgranges *et al.*, 'Miscibility Gap in the U–Nd–O Phase Diagram: a New Approach of Nuclear

452   Oxides in the Environment?', *Inorg. Chem.*, vol. 51, no. 17, pp. 9147–9149, Sep. 2012, doi:

453   10.1021/ic301100c.

454   [31]   R. D. Shannon, 'Revised effective ionic radii and systematic studies of interatomic distances in

455   halides and chalcogenides', *Acta Crystallogr. A*, vol. 32, no. 5, pp. 751–767, Sep. 1976, doi:

456   10.1107/S0567739476001551.

457   [32]   R. I. Barabash *et al.*, 'Cation and vacancy disorder in $U_{1-y}Nd_yO_{2.00-x}$ alloys', *J. Mater. Res.*, vol. 30,

458   no. 20, pp. 3026–3040, Oct. 2015, doi: 10.1557/jmr.2015.261.

459   [33]   W. A. Lambertson and M. H. Mueller, 'Uranium oxide phase equilibrium systems: V, UO_2-Nd_2O_3;

460   VI, U_3O_8-MgO; VII, U_3O_8-TiO_2'. Sep. 14, 1954.

461   [34]   C. Keller and A. Boroujerdi, 'Phasengleichgewichte in den systemen UO_2-UO_3-$NdO_{1,5}$ und

462   NpO_{2+x}-$NdO_{1,5}$', *J. Inorg. Nucl. Chem.*, vol. 34, no. 4, pp. 1187–1193, Apr. 1972, doi:

463   10.1016/0022-1902(72)80318-X.

464   [35]   S. M. Lee, T. W. Knight, J. W. McMurray, and T. M. Besmann, 'Measurement of the oxygen

465   partial pressure and thermodynamic modeling of the U–Nd–O system', *J. Nucl. Mater.*, vol. 473,

466   pp. 272–282, May 2016, doi: 10.1016/j.jnucmat.2016.02.024.

467   [36] G. Dottavio, Y. Pontillon, L. Desgranges, C. Guéneau, and R. C. Belin, 'Characterising the U–Nd–

468   O miscibility gap by an experimental and a theoretical approach', *J. Nucl. Mater.*, vol. 458, pp.

469   394–405, Mar. 2015, doi: 10.1016/j.jnucmat.2014.12.061.

470   [37] B. Herrero, 'Assessment of the ternary phase diagram on the stoichiometric and hypo-

471   stoichiometric U-Nd-O system', *PhD thesis, Université de Paris-Saclay, 2020.*

472   *[38] K. Popa et al., 'Further insights into the ch*emistry of the Bi–U–O system', *Dalton Trans.*, vol. 45,

473   no. 18, pp. 7847–7855, May 2016, doi: 10.1039/C6DT00735J.

474   [39] D. Prieur *et al.*, 'Aliovalent Cation Substitution in UO_2: Electronic and Local Structures of $U_{1-y}La_yO_{2\pm x}$ Solid Solutions', *Inorg. Chem.*, vol. 57, no. 3, pp. 1535–1544, Feb. 2018, doi:

476   10.1021/acs.inorgchem.7b02839.

477   [40] R. Bès, J. Pakarinen, A. Baena, S. Conradson, M. Verwerft, and F. Tuomisto, 'Charge

478   compensation mechanisms in $U_{1-x}Gd_xO_2$ and $Th_{1-x}Gd_xO_{2-x/2}$ studied by X-ray Absorption

479   Spectroscopy', *J. Nucl. Mater.*, vol. 489, pp. 9–21, Jun. 2017, doi:

480   10.1016/j.jnucmat.2017.03.042.

481   [41] H. Cao *et al.*, 'Differential interplay between Ce and U on local structures of $U_{1-x}Ce_xO_2$ solid

482   solutions probed by X-ray absorption spectroscopy', *J. Nucl. Mater.*, vol. 515, pp. 238–244, Mar.

483   2019, doi: 10.1016/j.jnucmat.2018.12.042.

484