# Charge compensation mechanisms in Nd-doped UO2 samples for stoichiometric and hypo-stoichiometric conditions: Lack of miscibility gap

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## Highlights

- Description of the solubility of the $U_{1-y}Nd_yO_{2\pm x}$ system at room temperature.
- Characterisation of the charge compensation mechanisms and local disorder for the $U_{1-y}Nd_yO_{2\pm x}$ system.
- Analysis of the crystal lattice of the U-Nd-O system assessed complementary by XRD and XAS.

## Abstract

The evolution of the crystal lattice of samples made of $UO_2$ doped with different concentrations of Nd in stoichiometric and hypo-stoichiometric conditions has been systematically studied by X-ray diffraction (XRD) and X-ray absorption spectroscopy (XAS). The substitution of a trivalent cation for the $U^{4+}$ initial position is responsible for creating local structural disorder and changes in the oxidation states. In this scenario, the lattice parameter is affected and the concentration of $U^{5+}$ and formation of oxygen vacancies as well, since these are the mechanisms necessary to maintain the charge neutrality. The systematic oxidation of $U^{4+}$ as predominant charge compensation mechanism over the formation of vacancies can be reduced by performing a thermal treatment under reducing conditions. This paper presents an experimental characterization of the uranium oxidation state

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

**Keywords**

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

## 1. Introduction

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

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

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

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

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

## 2. Experimental procedure

### 2.1. Sample preparation

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

Oxalates samples were converted into the final oxides after calcination at 1273K for 60 h under an atmosphere of Ar + 4% $H_2$. Afterwards, each sample was pressed into a pellet with an applied pressure of 450 MPa and sintered at 1823K for 5 h under the same atmosphere.

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

### 2.2. Thermal treatment

The thermal annealing under controlled atmosphere was performed at CEA, Cadarache. It intended to produce hypo-stoichiometric samples to compare them with as-produced samples. In the following, the as synthesized samples are referred as T0, and the annealed samples (under different controlled atmospheres) as TT. To carry on this thermal treatment, an induction furnace with a molybdenum sample holder was used allowing a heating and cooling ramp of $1K.s^{-1}$. The oxygen partial pressure ($PO_2$) was monitored using the oxygen pump gauge Gen'Air from SETNAG, set to work using the principle of ionic conduction of zirconia on a flowing gas current of Ar+4% $H_2$. The thermal treatment was carried on in two stages: the first stage consisted of a dwell for 2 h at 1473K to generate the reducing conditions to achieve hypo-stoichiometry. The second stage was defined to stabilize a second crystallographic phase that would appear as the result of a phase separation caused by a miscibility gap at low temperature (T<745K for 25%Nd) [18]. Thus, in order to favour phase separation, this stage consisted of a dwell for 6 h at 673K.

For the first stage, the measured $PO_2$ at 923K (which is the working temperature of the oxygen control device) was $10^{-27}$ bar, which equals to an oxygen chemical potential ($\mu O_2$) of -732.32 $kJ.mol^{-1}$. According to calculations employing the Thermo-Calc software, this stated value allows the reduction

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

### 2.3. Characterization

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

X-ray absorption spectra (XAS) were measured at the MARS beamline at the SOLEIL synchrotron (Saint-Aubin, France) [21,22]. The storage ring was operating in top up mode at an electron current of 450 mA, 2.5 GeV. The beam size on sample was 250µm × 150µm FWHM (Full Width at Half Maximum) (HxV). HERFD-XANES was measured at the U $M_4$-edge (3.7 keV) using the DCM (Double Crystal Monochromator) with a pair of Si(111) crystals. Higher harmonics rejection and vertical focusing were achieved using the Si strip of each mirror inserted before and after the DCM with a 4 mrad incidence angle. The incident energy was calibrated using the absorption K-edge of potassium in a KBr pellet (3.6 keV). The incident X-ray flux on the sample position was 1.9 · 109 ph/s at 3.5 keV. HERFD-XANES were acquired at the U $M_\beta$ emission line (3.339 keV) using the emission spectrometer equipped with a Si(220) spherically bent diced crystal with curvature radius of 1 m, a KETEK single element silicon solid state (SDD) detector, along a Rowland type geometry. Samples were oriented at 45° from the incident beam, and the emission spectrometer was positioned at 90° from the incident beam to minimize self-absorption effects. A He-chamber was used to reduce the scattering of the X-rays by air. The overall energy resolution of the emission spectrometer was 1.1 eV as determined from the FWHM of the elastic scattering peak at the double energy.

In addition, U $L_3$-edge (17.166 keV) and Nd $L_3$-edge (6.208 keV) EXAFS spectra were also collected in fluorescence mode using a 13-element HPGe detector from ORTEC. The beamline double-crystal monochromator (DCM) consists in a pair of Si(220) crystals for the U $L_3$-edge and a pair of Si(111) crystals for the Nd $L_3$-edge. Energy calibration was performed by measuring Y K-edge (17.038 keV) of 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.

The treatment of the XAS data was performed with the software package Demeter. ATHENA software was used to remove the pre-edge data, as well as to normalize the post-edge using linear functions at the U $M_4$-edge [24]. Finally, the energy threshold ($E_0$) was defined as the maximum of the first derivative of the white-line relative to the incident energy.

Uranium valence state mixture was deduced from linear combination fitting within the range of 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-$UO_3$ for $U^{6+}$. The $UO_2$ spectrum was obtained during this experiment, however, the $NaUO_3$ and β-$UO_3$ references were obtained in a different analysis carried on at the ID26 beamline of the European Synchrotron Facility (ESRF) in Grenoble, France, and reported in [25]. Special attention was given on the possible effect on results arising from beamline energy resolution differences when dealing with such references.

The EXAFS data analysis was performed using the ARTEMIS software [24,26]. Hanning window was used to transform the EXAFS spectra into the Fourier transform over the k-range 3.2 to 12 and 2.8 to 9.0, for U and Nd $L_3$-edge, respectively. The first and second O coordinated shells, as well as the first intermetallic shell were determined assuming a fluorite structure with a random substitution of Nd into the metallic sublattice. The scattering factors $S_0^2$ deduced from the fit for $UO_2$ and $Nd_2O_3$ at the U and Nd $L_3$-edge respectively were considered equal to 1.

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

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

## 3. Results and discussion

### 3.1. XRD: Solubility studies

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

Numerous studies assessed the evolution of the lattice parameter, *a*, on stoichiometric samples $(U_{1-y}Nd_y)O_2$ [15], [27]–[30], [18]. Lee et al. interpreted the evolution as a function of the Nd atomic concentration according to the following expression :

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

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

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

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

The samples undergoing a controlled atmosphere annealing were also studied by XRD (**figure 3 (a)**). It is possible to see a clear narrowing of the peak widths and the contraction of the crystal lattice caused by the increasing concentration of Nd. This trend of the samples treated thermally as a function of the Nd substitution is analogous to the one of the as-produced samples (**figure 3 (b)**). The FCC structure is maintained in all cases.

At all compositions and annealing temperatures, the system shows only a single fluorite-like phase, which agrees with what is proposed by several authors for hypo-stoichiometric conditions [8,29,32-35]. Therefore, the results presented in this work differ from those published by Desgranges et al. and Dottavio et al. [18], [30], [36] where a miscibility gap was identified: no peak splitting is observed in the samples object of this study and therefore there is no evidence for a phase separation. This discrepancy was addressed in [37] where it is found that the samples used in [18], [30], [36] presented an incomplete reaction between the initial powders of $UO_2$ and $Nd_2O_3$, which produces the formation of phases out of the thermodynamic equilibrium, instead of a miscibility gap.

The objective of the thermal treatment was to create oxygen vacancies, which are responsible for an expansion of the lattice parameter. This particular behaviour is seen repeatedly on the U-Nd-O 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

surrounding the U atoms that is modified when oxygen vacancies are formed. The precise positions 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) |

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

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

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

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

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

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

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

to explain the actual chemical composition of each sample. **Figure 6** shows for illustrative purposes 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) |

*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.*

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

To visualize more clearly the dominant charge compensation mechanisms, Bès et al. schematized the concentration of $U^{5+}$ and $U^{6+}$ in comparison with Models 1, 2, and 3 [25]. Following the same reasoning, **figure 8** displays the percentage of $U^{5+}$ for each valence state in comparison to Model 1, the curve that expresses Model 2 was not introduced in the graphic as no $U^{6+}$ is seen in our samples.

The evolution of all the samples shows a coherent behaviour. $U^{5+}$ concentration increases with the concentration of $Nd^{3+}$, indicating that the compensation mechanism as described by Model 1 is observed. As no $U^{6+}$ was observed (within the experimental uncertainties), we can exclude Model 2 from the main charge compensation mechanisms. However, $U^{5+}$ concentration appears below the expected values as obtained using solely Model 1 for Nd concentrations higher than 4 %, indicating

that oxygen vacancies, i.e. Model 3, are also created, where x can adopt a value up to 0.038 on the sample 25%TT. In addition, the charge compensation mechanisms for all six samples are not the same since the contribution of Models 1 and 3 to electroneutrality varies between the samples.

Those findings are in good agreement with the results reported in [17] where the experimental value matches the theoretical curve for concentrations of Nd lower than 9%, and where a mixed charge compensation between Model 1 and Model 3 is observed for higher Nd concentration. According to the work reported by Bès [25], it is only for a greater value of y=30% that the system exhibits the presence of $U^{6+}$. This value deviates significantly from the Model 1, since it shows a mixed charge compensation mechanism combining all three models.

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

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

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

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

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

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

| | | | Theoretical (%)-Model 1 | | Experimental (%) | | | |
|---|---|---|---|---|---|---|---|---|
| **Dopant** | **Concentration** | **Abs. U Edge** | **$U^{4+}$** | **$U^{5+}$** | **$U^{4+}$** | **$U^{5+}$** | **$U^{6+}$** | **Author** |
| **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) | |

*Table 5. Concentration of U4+ and U5+ obtained after the LCF in comparison with theoretical values.*

### 3.4. EXAFS: local environment analysis

The EXAFS spectra have also been measured on the Nd $L_3$-edge and U $L_3$-edge for the thermally treated (TT) samples, and the U $L_3$-edge for the non-thermally treated (T0) samples. An immediate inspection at the Fourier transform of the k space for the samples U $L_3$-edge TT and T0 (**figure 9 (a)** and **(b))** show a gradual decrease of the intensities when the concentration of Nd increases. This behaviour was evidenced in other $UO_2$ doped systems [37-39] and it is explained by the destructive interferences due to opposites phases and similar intensities for the U-U and U-Nd paths [35]. In contrast, no relevant differences can be observed between the intensities of the samples T0 and TT with equal concentration of Nd.

The k space with its respective Fourier transform and the EXAFS fit for each sample are shown in **figure 10.** The Nd $L_3$-edge for the sample at 4% Nd was also acquired but the concentration of Nd was so little that achieving such measurement with good statistics was not possible within the granted beamtime. It is then not included in this document.

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

The results of the refinements for all samples are shown in **table 6**. It is possible to see that in all cases the R-factor obtained from the analysis of the experimental data and the EXAFS fit varies from 0.0124 to 0.0182, allowing to extract general trends concerning the atomic distances and local disordering. Some differences can be found on the EXAFS fit respecting the presence of a peak on the Fourier transform graphs at around 4.5 Å, particularly on the Nd $L_3$-edge EXAFS spectra. This peak does not seem to vary with the Nd concentration and could be explained by a multi-scattering effect. The enhanced intensity displayed in the **figures 10 (d)** and **10 (f)** might be due to the reduced intensity of the Nd/M as a consequence of the destructive interference of the EXAFS signals. Similar observations were seen on $UO_2$-based samples doped with Gd in [40].

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

| Sample | Edge | Shell | R (A) | $\sigma^2(10^{-3}$ Å$^2)$ | N | $N_{exp}$ | R-factor |
|---|---|---|---|---|---|---|---|
| 4% T0 | U $L_3$-edge | 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-$O_2$ | 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 $L_3$-edge | 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-$O_1$ | 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

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

## 4. Conclusion

Based on analysis through X-ray diffraction, U $M_4$-edge HERFD-XANES, U $L_3$-edge and Nd $L_3$-edge EXAFS analysis, an assessment of the crystal lattice, charge compensation mechanisms and local atomic environment on $UO_2$ doped with Nd is reported. This work indicates that Nd is completely miscible in $UO_2$ for all assessed concentrations (4, 17 and 25%Nd), even after the samples were thermally treated under reducing conditions, indicating the lack of a miscibility gap. In addition, it was seen that random insertion of Nd atoms into the fluorite structure generates distortions on the crystal lattice by changing the atomic distances and increasing the structural disorder. The replacement of a tetravalent cation ($U^{4+}$) by a trivalent cation ($Nd^{3+}$) is compensated by the formation of $U^{5+}$ cations and anion vacancies. In addition, thermal treatment under reducing conditions increases the amount of vacancies and, therefore, reduces the amount of $U^{5+}$ needed to maintain the electroneutrality of the system. It was also stated that no $U^{6+}$ is formed when the addition of Nd is lower than 25%. Finally, it was seen that the local distances on the surroundings of the atoms of U are different from those of the atoms of Nd since the latter has a different ionic radius and charge, and are capable to displace the oxygen atoms of the first shell out of their initial position.

These results are in good agreement with similar studies made on systems where $UO_2$ was doped with other trivalent cations, such as $Gd^{3+}$, $La^{3+}$ or $Bi^{3+}$, which proves that charge compensation mechanisms do not depend on the element used as dopant, on the contrary, it is mostly defined by its valence.

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