

  ROBL-CRG	Experiment title: Investigation of solid state characteristics in the $\text{UO}_2 - \text{Nd}_2\text{O}_3$ solid solution system	Experiment number: 20-01-767
Beamline: BM 20	Date of experiment: from: 03.12.2015 to: 06.12.2015	Date of report:
Shifts: 12	Local contact(s): Marisol-Janeth Lozano-Rodriguez	<i>Received at ROBL:</i>
Names and affiliations of applicants (* indicates experimentalists): Christian Schreinemachers^{1*}, Stefan Neumeier¹, Marisol-Janeth Lozano-Rodriguez^{2*}, Andreas C. Scheinost² ¹ Forschungszentrum Jülich GmbH, Institute of Energy and Climate Research, IEK-6: Nuclear Waste Management and Reactor Safety, 52425 Jülich, Germany ² Helmholtz-Zentrum Dresden-Rossendorf, Institute of Resource Ecology, Bautzner Landstraße 400, 01328 Dresden, Germany		

Report:

The investigation of $\text{Nd}_y\text{U}_{1-y}\text{O}_2$ compounds is of interest for several reasons. On the one hand Nd is one of the most occurring fission products generated in spent nuclear fuel. On the other hand Nd serves as a surrogate simulating Am in advanced nuclear fuels for reactor systems with a fast neutron spectrum.

Pure UO_2 microspheres and compositions doped with different amounts of Nd were prepared by the sol-gel method via internal gelation [1].

The spherical shape was proven by scanning electron microscopy (SEM). Furthermore, the chemical composition, morphology and homogeneity was studied by SEM coupled with an energy dispersive X-ray spectroscope (EDX). Additionally inductively coupled plasma mass spectrometry (ICP-MS) measurements were performed on dissolved particles as second measure.

X-ray powder diffraction (long- range order) investigations revealed the samples to be single phase materials. The results were confirmed by (short-range order) XAS investigations at Rossendorf Beamline (ROBL), ESRF, Grenoble, France. Further data analyses have to be performed to determine the U-Nd and U-O bond lengths.

A plot containing the absorption data recorded at the U L_{III} edge $\mu(E_{inc})$ as well as their derivatives $(\frac{d\mu(E_{inc})}{\mu(E_{inc})})$ is shown as Figure 1.

With an increasing Nd content a shift to higher energies is observed (compare closeup in Figure 1). Besides a shift in energy the intensity of the main absorption signal decreases with increasing Nd content.

The spectra for UO₂ was used as a reference to emphasize this effect. Each spectrum belonging to the Nd_yU_{1-y}O₂ samples has been subtracted from the one of UO₂, the results are plotted in Figure 2. The plot reveals besides the decrease of the main absorption signal (at an incident energy of 17173.9 eV) an increase at an incident energy of 17182.4 eV. The decrease at $E_{inc} = 17173.9$ eV corresponds to a decrease of U(IV) in the composition, while the increase at an incident energy of $E_{inc} = 17182.4$ eV corresponds to a build up of U(V). Which proves that the charge non-equilibrium in the lattice due to the replacement of the U(IV) with Nd(III) is partially compensated via the oxidation of U(IV) to U(V). A clear dependence on the neodymium content can be seen. The composition containing 8.41 % Nd seems to be an outlier and is not taken into account for further analyses.

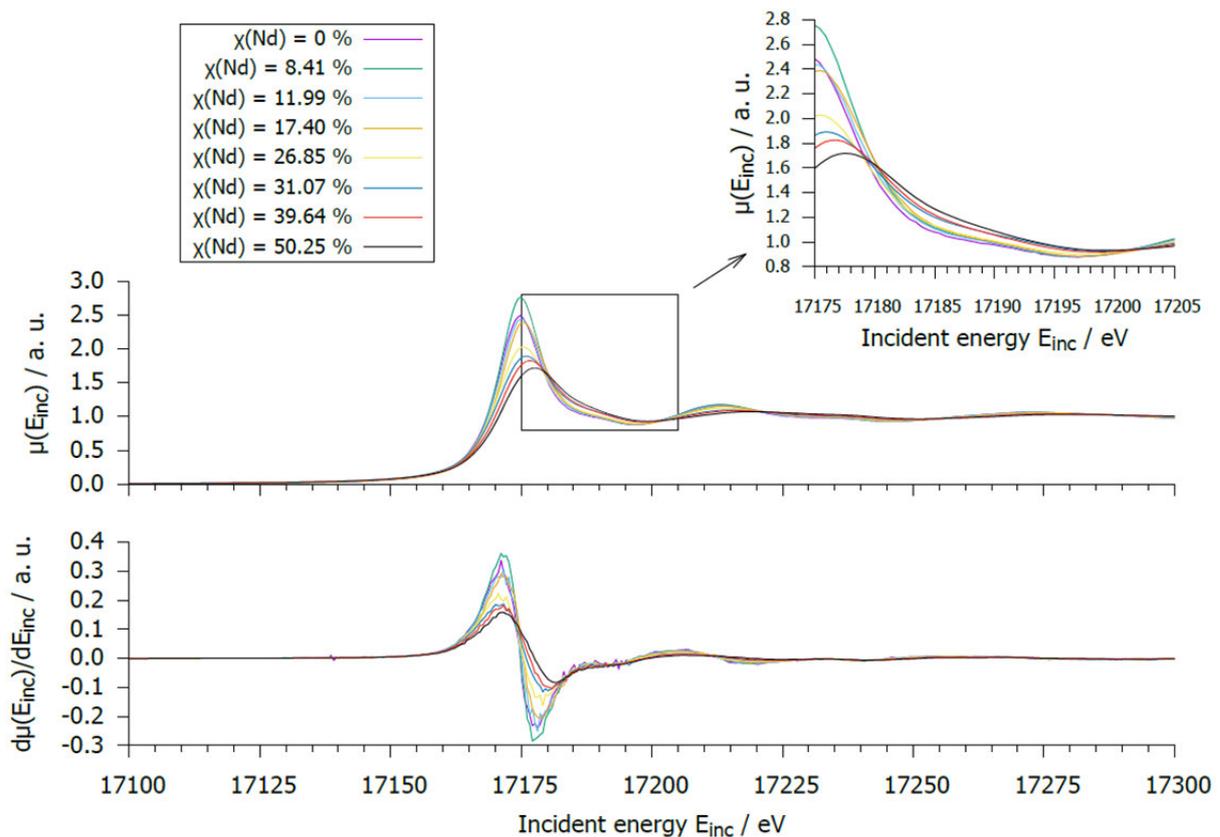


Figure 1.: XANES spectra of the UO₂ and Nd_yU_{1-y}O₂ solid solution samples (U L_{III} edge).

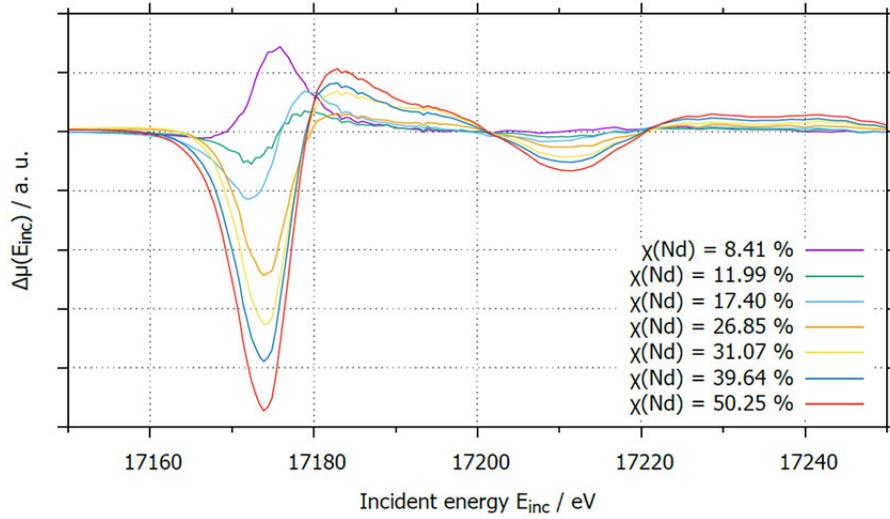


Figure 2.: Differences between the XANES spectra of UO_2 and the spectra of the $\text{Nd}_y\text{U}_{1-y}\text{O}_2$ compounds.

The program Athena, provided by the software package Demeter (Version 0.9.25), was used to apply a linear combination fitting (LCF) with UO_2 as standard for U(IV). The fitting has been performed using the derivative of $\mu(E_{inc})$ in the region $E_0 - 20$ eV to $E_0 + 30$ eV. In a later campaign U_4O_9 was measured and the result was used as U(V) standard. The achieved amount of U(V) was divided by 2 since U_4O_9 consist of a U(IV)/U(V) mixture with a ratio of 50:50. The results are listed in **Fehler! Verweisquelle konnte nicht gefunden werden.** and are visualized in Figure 3. Moreover, an expected value was calculated assuming that the charge non-equilibrium is fully compensated by the oxidation of U(IV) to U(V) according to equation 1 and 2, the results is implemented in Figure 3 as well.

$$\text{expected U(IV) content} = \frac{\chi(\text{Nd})}{1 - (2 \cdot \chi(\text{Nd})) + \chi(\text{Nd})} \quad 1$$

$$\text{expected U(V) content} = \frac{1 - (2 \cdot \chi(\text{Nd}))}{1 - (2 \cdot \chi(\text{Nd})) + \chi(\text{Nd})} \quad 2$$

Table 1.: Amount of U(IV) and U(V) determined via the LCF with UO_2 as standard for U(IV) and U_4O_9 as standards for U(V). The composition $\text{Nd}_{0.08}\text{U}_{0.92}\text{O}_2$ has not been taken into account.

Composition	U(IV) content	U(V) content
$\text{Nd}_{0.12}\text{U}_{0.88}\text{O}_2$	0.9675 ± 0.0075	0.0325 ± 0.0075
$\text{Nd}_{0.17}\text{U}_{0.83}\text{O}_2$	0.9315 ± 0.0145	0.0685 ± 0.0145
$\text{Nd}_{0.27}\text{U}_{0.73}\text{O}_2$	0.7620 ± 0.0090	0.2380 ± 0.0090
$\text{Nd}_{0.31}\text{U}_{0.69}\text{O}_2$	0.6675 ± 0.0120	0.3325 ± 0.0120
$\text{Nd}_{0.40}\text{U}_{0.60}\text{O}_2$	0.6120 ± 0.0165	0.3880 ± 0.0165
$\text{Nd}_{0.50}\text{U}_{0.50}\text{O}_2$	0.5430 ± 0.0185	0.4570 ± 0.0185

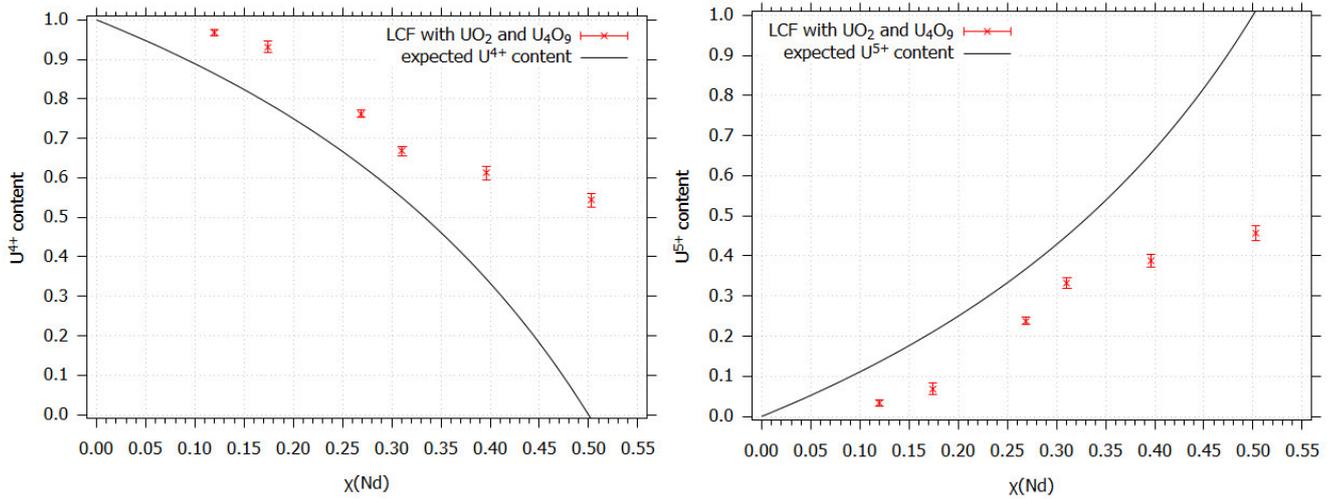


Figure 3.: Linear combination fitting (LCF) results with UO_2 as U(IV) standard and U_4O_9 as U(V) standard.

Ohmichi et al. [2] enunciated 3 models to describe the compensation of the charge non-equilibrium in the $\text{UO}_2/\text{Nd}_2\text{O}_3$ system:

1. formation of oxygen vacancies ov $(\text{Nd}_y^{3+}\text{U}_{1-y}^{4+}\text{O}_{2-ov_{0.5y}}^{2-})$,
2. oxidation of U(IV) to U(V) $(\text{Nd}_y^{3+}\text{U}_{1-2y}^{4+}\text{U}_y^{5+}\text{O}_2^{2-})$ and
3. oxidation of U(IV) to U(VI) $(\text{Nd}_y^{3+}\text{U}_{1-1.5y}^{4+}\text{U}_{0.5y}^{6+}\text{O}_2^{2-})$.

Since the expected U(IV) content (Figure 3, equation 1) differs from the U(IV) content found in the compositions it has been demonstrated that the compensation of the charge non-equilibrium takes place via the formation of oxygen vacancies (model 1) and the oxidation of U(IV) to U(V) (model 2). The portions have been calculated and are listed in Table 2.

Table 2.: Portion of charge compensation due to model 1 and model 2 in the $\text{Nd}_y\text{U}_{1-y}\text{O}_2$ compounds.

Composition	model 1	model 2
$\text{Nd}_{0.12}\text{U}_{0.88}\text{O}_2$	10.4 %	89.6 %
$\text{Nd}_{0.17}\text{U}_{0.83}\text{O}_2$	14.2 %	85.8 %
$\text{Nd}_{0.27}\text{U}_{0.73}\text{O}_2$	12.9 %	87.1 %
$\text{Nd}_{0.31}\text{U}_{0.69}\text{O}_2$	11.8 %	88.2 %
$\text{Nd}_{0.40}\text{U}_{0.60}\text{O}_2$	26.9 %	73.1 %
$\text{Nd}_{0.50}\text{U}_{0.50}\text{O}_2$	55.3 %	44.7 %

References:

1. Schreinemachers, C., et al., *Characterization of uranium neodymium oxide microspheres synthesized by internal gelation*. Progress in Nuclear Energy, 2014. **72**: p. 17-21.
2. Ohmichi, T., et al., *On the Relation between Lattice-Parameter and O/M Ratio for Uranium-Dioxide Trivalent Rare-Earth-Oxide Solid-Solution*. Journal of Nuclear Materials, 1981. **102**(1-2): p. 40-46.