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Identification of NpO_{2+x} in the Binary Np-O System

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Supporting information:

EXAFS were extracted from the spectra by the standard procedure. After calibrating by defining the inflection points of the absorption edges as 17614.8 eV, the spectra were normalized by setting the value of a second order polynomial fit through the pre-edge region to zero at 17625 eV and then multiplying the spectra so that the value of a third order polynomial through the EXAFS region was unity at this same energy. After reducing the white line amplitude by subtracting an arctangent plus a Gaussian function fit to the edge region, the smooth atomic background was approximated by a polynomial spline function whose knots were set to minimize the integrated modulus of the Fourier transform of the EXAFS from R=0-1.1 Å. The EXAFS was obtained by subtracting this total background function from the spectra, then normalized by the absorption falloff from the MacMaster tables. Metrical parameters were obtained via non-linear least squares curve-fits over the region k= 2.6-12 $Å^{-1}$ for samples a and ppt and 2.6-10 $Å^{-1}$ for sample b, using amplitudes and phases calculated using Feff 9.6.4. The least squares error was minimized by floating the Np-O/Np distances, R, the numbers of neighbor atoms, N, ΔE_0 for the first shell which was constrained to be within a narrow range for the other shells, and σ for the shells in table 1 where it is listed with a "±". Best fits were obtained with ΔE_0=±2 eV for the nearest neighbor O, allowing this to vary by only 1.5 eV for the other O shells and for the Np shell.

Table S1. EXAFS fitting results for ref. and ppt. samples. Parameters without error bars are kept constant. Here R, N and σ are bond distance, number of atoms and Debye-Waller factor, respectively.

Sample		Np-O					Np-Np	Np-O
NpO_2 crystal structure	R(Å)	2.35					3.84	4.50
	N	8					12	24
calcined a	R(Å)	1.91±0.02		2.33±0.01	2.46±0.02	3.48±0.03	3.84±0.01	4.54±0.02
	N	0.12±0.08		7.02±1.1	0.7±0.4	0.7±0.3	3.5±1	6.14±0.9
	σ	0.04		0.03±0.02	0.06	0.1	0.06±0.01	0.09±0.02
ppt	R(Å)	1.87±0.02	2.19±0.02	2.35±0.02	2.99±0.03	3.27±0.02	3.85±0.01	4.46±0.02
	N	0.2±0.07	2.3±0.9	7.2±2.1	1.4±0.3	1.2±0.2	5.9±1.6	8.8±4.6
	σ	0.04	0.05	0.04±0.03	0.1	0.06	0.07±0.01	0.04±0.02
calcined b	R(Å)	1.81±0.02		2.35±0.02	3.00±0.02	3.33±0.02	3.85±0.01	4.45±0.02
	N	0.07±0.03		7.3±1.9	0.6±0.2	0.8±0.2	10.8±2.4	9.4±2.8
	σ	0.01±0.03		0.04±0.03	0.01±0.05	0.01	0.03±0.02	0.07±0.02

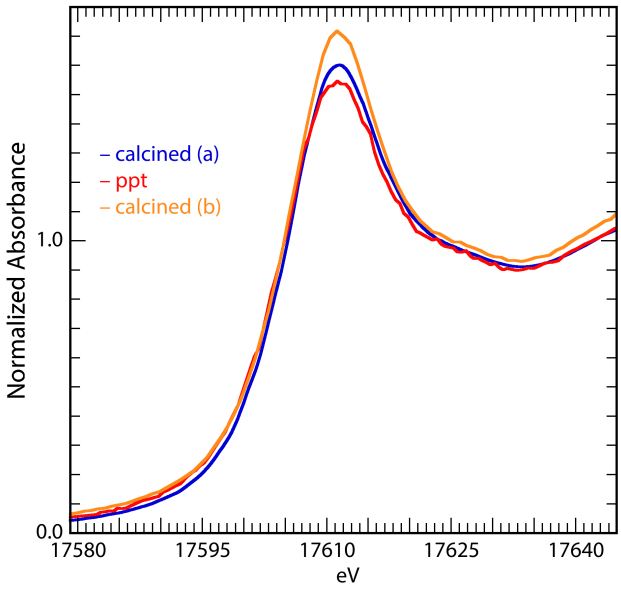

Figure SI1. XANES of NpO_{2+x} samples. Analous to UO_{2+x}, the amplitude of the principal absorbance peak at 17611 eV decreases with increasing x. In PuO_{2+x} materials that had been heated had lower amplitudes for this feature than ones that had only been precipitated, the opposite of the trend observed here.

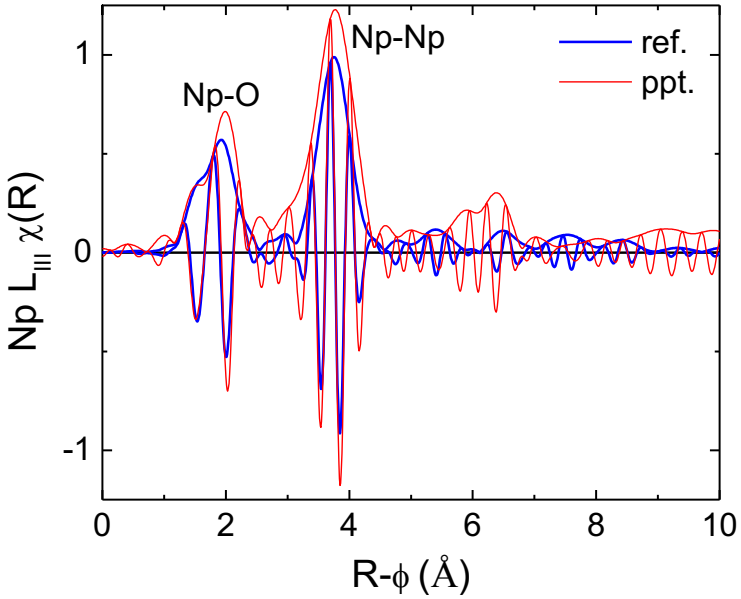

Figure SI2. |χ(R)| and Re[χ(R)] of the EXAFS of the two NpO_2 samples over full spectral range through k=14 $Å^{-1}$. "ref" = calcined (a) is blue, ppt is red.

Trigonal subgroup of 4x4x4 fluorite lattice:

The highest symmetry trigonal subgroup of $I\bar{4}3d$ is space group R3c, which is non-symmorphic and it consists of 18 symmetry operators (generated by the symmetry operators of the threefold axis, the *c* glide plane, and the R centering). The matrix S that describes the lattice transformation of the high temperature body centred cubic lattice into the trigonal one (hexagonal setting) is given by

$$S = \begin{bmatrix} -1 & 1 & 0 \\ 0 & -1 & 1 \\ \frac{1}{2} & \frac{1}{2} & \frac{1}{2} \end{bmatrix}$$

The ratio of the volumes of the two conventional cells is given by the determinant of this matrix. The Miller's indices of the reflections transform as covariant quantities while the reduced coordinates of the atomic positions transform as contravariant quantities. Applying the S matrix to the structural model of the β

phase of U_4O_9 and using as generators, one supplementary symmetry element from each of the other three cosets of R3c in $I\bar{4}3d$, it is then possible to obtain the complete set of the independent atoms for the model structure that consists of 71 independent atoms (22 Np atoms and 49 O atoms).

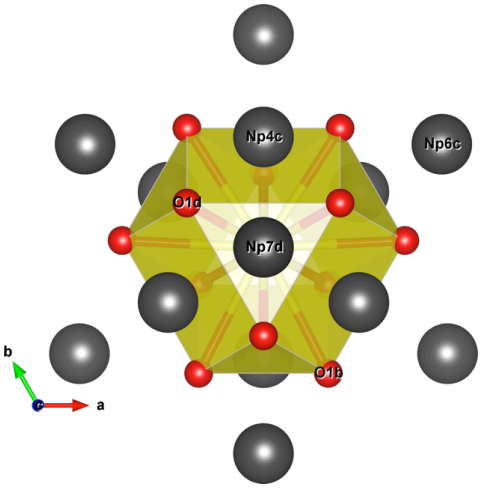

Figure SI3. Schematic description of the motif of Np_4O_9 that allows the accommodation of the supplementary O atoms in the fluorite structure. Three independent Np atoms are required when a -3 (C3i) local symmetry is enforced

Np environments from the constrained structural refinement:

Np4

This Np atom forms 8 bonds with the surrounding O atoms ranging from 2.09 to 2.33Å, for an average bond length of about 2.22 Å. Using Brown and Altermatt bond valence sums analysis (BVS), the estimated charge of this Np atom is close to +6.

Np6

This Np atom forms 10 bonds with the surrounding O atoms ranging from 2.26 to 2.94Å, for an average bond length of about 2.52 Å. Using BVS analysis, the estimated charge of this Np atom is slightly less than +4.

Np7

This Np atom also forms 10 bonds with the surrounding O atoms. Distances range from 2.26 to 2.70Å, for an average bond length of about 2.49 Å. Using BVS analysis, the estimated charge of this Np atom is also slightly less than +4.

The atomic coordinates of the remaining Np atoms were not refined. Therefore, those atoms are 8-fold coordinated like in the ideal fluorite structure and they form 8 identical bonds at 2.35Å. BVS analysis gives a formal charge of +4 for those Np atoms.