# Neodymium uranyl peroxides synthesis by ion exchange on ammonium uranyl peroxide nanoclusters.

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#### SI1. Instrumentations

Powder X-ray diffraction (PXRD) data were collected from 5 to 40° with a step of 0.03° and the time for data collection was 0.5 s on a Bruker D8 Advance diffractometer with Cu K $\alpha$  radiation ( $\lambda$ =1.54056 Å) and a Lynxeye one-dimensional detector.

X-ray thermodiffractometry (HTPXRD) was performed in an Anton Paar HTK1200N of a D8 Advance Bruker diffractometer ( $\theta$ – $\theta$  mode, Cu K $\alpha$  radiation) equipped with a Vantec1 linear position sensitive detector (PSD). Each powder pattern was recorded in the range 16–60° (2 $\theta$ ) for U32R-NH4 and 16-80° (2 $\theta$ ) for U32R-Nd, at intervals of 20 or 25°C, with a 0.5 s/step scan, corresponding to an approximate duration of 30 min. The temperature ramp between two patterns was 0.08 °C.s<sup>-1</sup> in both cases. Gas flow was 5L.h<sup>-1</sup> under air atmosphere or N<sub>2</sub>/H<sub>2</sub> (3%) (reductive atmosphere).

The U32R-Nd compound was also placed in a platinum crucible and heated in a furnace in air atmosphere at 1400 °C or in reductive atmosphere at 800°C.

Thermogravimetric analysis was carried out on a SETARAM SETSYS instrument in the range of 30-1100°C under air or N<sub>2</sub>/H<sub>2</sub> flow at a heating rate of 5°C/min. The solid-state UV-vis spectra were recorded on a PerkinElmer Lambda 650 spectrophotometer. Infrared spectra were measured on PerkinElmer Spectrum Two spectrometer equipped with a diamond attenuated total reflectance (ATR) accessory. Raman spectra were acquired using a Horiba HR 800 UV spectrometer using  $\lambda$ =488nm, P=0.02mW (U32-NH4 and U32-Nd) and  $\lambda$ =633nm, P=3.6mW (U32-Nd). Scanning electron microscopy / energy-dispersive spectroscopy (SEM/EDS) images and data were collected using Hitachi S400. Electron microprobe maps were conducted on a CAMECA SX100. Inductively coupled plasma atomic emission spectroscopy (ICP-AES) analysis of U, Nd, Th and Sr was conducted using a VARIAN Vista-Pro instrument.

#### SI2. Syntheses

#### U32R-NH4

A solution 1 of uranyl ions (0,166 mol./L) was prepared by dissolving 0.500g (0,996 mmol) of uranyl nitrate hexahydrate  $UO_2(NO_3)_2.6H_2O$  in 6 mL of water.

A solution 2 was prepared by addition of 3mL of hydrogen peroxide  $H_2O_2$  30% (29,37mmol of  $H_2O_2$ ) to 4mL of ammonium hydroxide NH<sub>4</sub>OH 4 mol/L (16mmol of NH<sub>4</sub>OH).

The solution 1 is added drop by drop to the solution 2 maintained in an ice batch under stirring. Then stirring is cut off allowing rapid crystallization and the batch transferred in a fridge at 4°C. After 10 hrs the yield is higher than 80% and the solid is filtered under vacuum and washed with 5mL of methanol. The solid is constituted of a powder accompanied of single crystals. The PXRD shows only one phase (Figure S1) with a pattern corresponding to the one calculated from the results of the single crystal structure. After one hour the solid became essentially amorphous.



**Figure S1**. PXRD of U32R-NH4 realized just after the filtration (middle) compared with the pattern calculated from the results of the single crystal structure determination (bottom), and realized 1 hr after the filtration (top)

#### U32R-Nd

0,218g of neodymium nitrate Nd(NO<sub>3</sub>)<sub>3</sub>.6H<sub>2</sub>O are dissolved in 10 mL of water. This solution of Nd<sup>3+</sup> ions (0.0497mol/L) is added to the solid U32R-NH4. After 30 min, the solid is filtered under vacuum. The solid is constituted of a powder accompanied with

single crystals. The PXRD show only one phase (Figure S2) with a pattern similar to the one calculated from the results of the single crystal structure.



**Figure S2.** PXRD of U32R-Nd (top) compared with the pattern calculated from the results of the single crystal structure (down).

#### U32R-Th and U32R-Sr

The same procedure is used by changing the 10mL of  $Nd^{3+}$  solution by a  $Th^{4+}$  solution realized by dissolution of 0.285g of thorium nitrate  $Th(NO_3)_4.5H_2O$  in 10 mL of water or a  $Sr^{2+}$  solution realized by dissolution of 0.212g of strontium nitrate  $Sr(NO_3)_2$  solution in 20 mL of water.

#### U28-Nd

A solution of uranyl ions (0.067 mol/L) was prepared by dissolving 0.625g of uranyl nitrate hexahydrate UO<sub>2</sub>(NO<sub>3</sub>)<sub>2</sub>.6H<sub>2</sub>O in 18.75 mL of water. 0.250g of oxalate ammonium monohydrate (NH<sub>4</sub>)<sub>2</sub>C<sub>2</sub>O<sub>4</sub>.H<sub>2</sub>O is added to the previous solution (0.093 mol/L). A solution of hydrogen peroxide 1mol/L is prepared by diluting 638µL of 30% H<sub>2</sub>O<sub>2</sub> in 6.25mL of water.

These two solutions are mixed together under stirring. 7.9mL of ammonia NH₄OH 1M is added under stirring and drop by drop, leading to pH 8. A solid, constituted of a

powder accompanied of single crystals, is obtained after two weeks by vapor diffusion technique using methanol (33mL).

The PXRD shows only one phase (Figure S3) with a pattern corresponding to the one calculated from the results of the single crystal structure.

0.218g of neodymium nitrate Nd(NO<sub>3</sub>)<sub>3</sub>.6H<sub>2</sub>O are dissolved in 10 mL of water. This solution of Nd<sup>3+</sup> ions (0.0497mol/L) is added to the solid U28-NH<sub>4</sub>. After 30 min, the solid is filtered under vacuum. The solid is constituted of a powder accompanied of single crystals. The PXRD shows a non-crystalline phase (Figure S3).



**Figure S3.** PXRD of U28-NH4 realized just after the filtration (b) compared with the pattern calculated from the results of the single crystal structure (a), and PXRD of U28-Nd (c) (stars reflections ( $\star$ ) are sample holder contribution to the powder pattern, due to the use of Teflon sample holder).

#### SI3. Single crystal X-ray crystallography

Data collection for U32R-Nd, U32R-Th and U32R-Sr crystals was performed at room temperature on a Bruker X8 CCD 4K diffractometer using a MoKα radiation

(0.71073Å) with an optical fiber as collimator. The intensities were extracted from the collected frames and corrected for absorption effects using the program SAINT V7.53a<sup>1</sup>. The structure resolutions and refinements were performed with the SHELX software<sup>2</sup> with the WINGX interface<sup>3</sup>. An initial model consisting of uranium atoms is obtained with direct methods, while the remaining atoms were found from successive Fourier map analyses. As already pointed out by various authors, structure refinements for crystals containing such clusters are difficult due to several factors. However diffraction allows to determine unambiguously the position of the atoms (U, O) constituting the cluster, and so to determine its composition and its geometry. In the three structures, the position of the counter cations (Nd, Th and Sr) and their surrounding oxygen atoms were also determined. As already pointed out in Burns's supporting information for its U32R article, structure refinements for these crystals are difficult due to : strong scattering contrast between Nd, Th or U atoms and lighter atoms (namely oxygen), presence of significant void spaces that reduces diffraction intensities and disorder that may occur in these exchanged nano-cluster. Therefore, data collection and refinements parameters are a bit higher than IUCr standards but X-ray diffraction furnish essential and reliable information concerning clusters' connectivity and composition. The Squeeze procedure, as implemented in Platon, performs calculations on disordered cations and solvent contributions to the calculated structure factors<sup>4</sup>. In order to get better agreements indices (such as R, wR and Goof values), this technique was applied. Crystallographic data are reported in Table S1. Atomic coordinates for counter cations sites are reported in Tables S2 for U32R-Nd, U32R-Th and U32R-Sr. Solvent accessible volume and electrons count in void space are reported in Table S3.

**Table S1.** Crystal data, intensity collection and structure refinement parameters for U32R-Nd, U32R-Th and U32R-Sr.

	U32R-Nd	U32R-Th	U32R-Sr	
CCDC number	1421676	1421678	1421678 1421677	
Formula	$O_{225,76}Nd_{11,54}U_{32}$	$O_{224}Th_{8.61}U_{32}$	$O_{236}Sr_{14.2}U_{32}$	
Formula weight	12894.23	13198.36	12637.17	
Temperature/K	293	293	293 293	
Crystal color	yellow	yellow	v yellow	
Crystal size/mm	0.031 x 0.015 x 0.011	0.030 x 0.016 x 0.013	30 x 0.016 x 0.013 0.036 x 0.014 x 0.011	
Crystal system	Orthorhombic	Orthorhombic Orthorhombic		
Space group	Immm	Immm	Immm Immm	
a/Å	18.3228(8)	18.067(2) 18.327(2)		
b/Å	20.827(2)	20.770(2)	20.750(3)	
c/Å	35.402(2)	35. 180(4)	35.815(4)	
Volume/Å <sup>3</sup>	13510(1)	13201(2)	13620(3)	
Z, $\rho_{calculated}/g.cm^{-3}$	2, 3.170	2, 3.320	2, 3.082	
µ/mm <sup>-1</sup>	21.370	24.409	21.802	
Θ range/°	1.13 – 23.73	1.14 – 22.46	1.13 – 20.99	
Limiting indices	-19 ≤ h ≤ 20 -23 ≤ k ≤ 20 -39 ≤ l ≤ 39	-19 ≤ h ≤ 19 -22 ≤ k ≤ 22 -37 ≤ l ≤ 37	-18 ≤ h ≤ 17 -18 ≤ k ≤ 20 -35 ≤ l ≤ 35	
Collected reflections	38985	81388 15791		
Unique reflections	5568	4701	4701 3913	
R(int)	0.1155	0.2188 0.1060		
Parameters	204	199	199 207	
Goodness-of-fit on F <sup>2</sup>	1.018	1.284	1.031	
Final R indices [I>2σ(I)]	$R1^2 = 0.0633$ w $R2^3 = 0.1701$	R1 = 0.1216 wR2 = 0.3356	R1 = 0.0650 wR2 = 0.1604	
R indices (all data)	R1 = 0.1062 wR2 = 0.2015	R1 = 0.1618 wR2 = 0.3708	R1 = 0.1134 wR2 = 0.1840	
Largest diff. peak and hole/e.Å <sup>-3</sup>	4.562 and -2.928	7.417 and -3.584	3.139 and -2.167	

 $\frac{1}{R(int)} = \sum \langle |c|_{obs} \rangle - |c|_{obs}| / \sum |c|_{obs} \rangle |c|_{R1} = \sum ||F_{obs} - F_{calc}|| / \sum |F_{obs}|, {}^{3}wR2 = \sum (\omega(Fobs^{2} - Fcalc^{2})^{2} / \sum (\omega F_{obs}^{4}))^{1/2} \text{ and } w = 1 / [\sigma^{2}(F_{obs}^{2}) + (aP)^{2} + bP].$ 

**Table S2.** Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters ( $Å^2$ ) for U32R-Nd (first line), U32R-Th (second line), U32R-Sr (third line).

Compound name	Atom	x	У	Z	U(eq)	Occupancy factor
U32R-Nd	Nd1	0.0000	0.25850(11)	0.32199(7)	0.0452(6)	1
	Nd2A	0.0000	0.3614(4)	0.42228(18)	0.032(3)	0.343(13)
	Nd2B	0.0000	0.397(2)	0.4136(9)	0.064(13)	0.107(14)
	Nd3	0.0000	0.2064(2)	0.04467(13)	0.0401(11)	0.5
	Nd4	0.0000	0.0770(2)	0.11846(12)	0.0353(10)	0.5
	Nd5A	0.0911(13)	0.5000	0.1836(8)	0.027(8)	0.14(2)
	Nd5B	0.0698(15)	0.5000	0.1960(8)	0.042(7)	0.16(2)
	Nd6	0.2933(12)	0.0724(11)	0.0422(6)	0.037(9)	0.068(6)
U32R-Th	Th1	0.0000	0.25648(19)	0.31952(12)	0.0608(18)	0.644(10)
	Th2A	0.0000	0.3651(7)	0.4204(4)	0.045(8)	0.152(13)
	Th2B	0.0000	0.407(2)	0.4399(13)	0.35(3)	0.34(2)
	Th3	0.0000	0.2073(5)	0.0425(3)	0.054(5)	0.228(9)
	Th4	0.0000	0.0755(4)	0.1155(2)	0.051(3)	0.314(9)
	Th5A	0.0839(15)	0.5000	0.1869(11)	0.032(10)	0.13(2)
	Th5B	0.0665(18)	0.5000	0.2004(12)	0.058(9)	0.16(3)
	Th6	0.3509(10)	0.5000	0.0575(5)	0.087(8)	0.184(10)
U32R-Sr	Sr1	0.0000	0.2568(3)	0.31946(17)	0.0807(18)	1
	Sr2A	0.0000	0.364(2)	0.4203(8)	0.076(14)	0.27(4)
	Sr2B	0.0000	0.3987(11)	0.4109(4)	0.063(8)	0.44(4)
	Sr3	0.0000	0.2070(6)	0.0397(3)	0.070(3)	0.5
	Sr4	0.0000	0.0688(5)	0.1175(3)	0.055(3)	0.5
	Sr5A	0.095(3)	0.5000	0.1839(10)	0.052(16)	0.19(3)
	Sr5B	0.0591(18)	0.5000	0.1967(7)	0.071(11)	0.31(3)
	Sr6	-0.0200(13)	0.5000	0.5000	0.080(11)	0.35(2)
	Sr7	0.1801(10)	0.5000	0.0000	0.039(9)	0.33(2)

**Table S3.** Solvent accessible volume  $(Å^3)$  and electrons count in void space for U32R-Nd, U32R-Th, U32R-Sr.

Compound name	Solvent accessible volume (Å <sup>3</sup> )	Electrons count	
U32R-Nd	3058.1	1573.6	
U32R-Th	3166.5	1762.0	
U32R-Sr	3472.2	1728.8	



**Figure S4**. UV-Vis absorbance spectra of  $Nd(NO_3)_3 \cdot 6H_2O$  (black), U32R-NH4 (blue) and U32R-Nd (red).



Figure S5. Infrared spectra of U32R-NH4 (blue) and U32R-Nd (red)



**Figure S6**. Raman spectra of U32R-NH4 sample  $\lambda$ =488 nm, P=0.02mW (a) and U32R-Nd  $\lambda$ =488 nm, P=0.02mW (bottom) and  $\lambda$ =633 nm, P=3.6mW (top) (b)



**Figure S7**. UV-Vis absorbance spectra of  $Nd(NO_3)_3 \cdot 6H_2O$  (black), U28-NH4 (blue) and U28-Nd (red).

### SI5. Electron microprobe maps



**Figure S8.** Electron microprobe maps of U32R-Nd showing the homogeneous repartition of U (left) and Nd (right) in U32R-Nd powder.



## SI6. Thermal behavior

Figure S9. HTPXRD of U32R-NH4 in air from 50 to 800°C (25°C step between diagrams).



Figure S10. HTPXRD of U32R-NH4 in  $N_2/H_2$  (3%) from 25 to 800°C (25°C step between diagrams).



**Figure S11.** HTPXRD of U32R-Nd in air from 50 to 1100°C. Top diagram is PXRD of the product obtained after calcination in air at 1400°C (20°C step between diagrams).



Figure S12. HTPXRD of U32R-Nd in  $N_2/H_2$  (3%) from 50 to 800°C (25°C step between diagrams).



**Figure S13.** SEM images showing that the rod-like morphology of U32R-Nd is kept during the thermal decomposition until the formation of the fluorite phase both in air at 1400°C and in  $N_2/H_2$  (3%) at 800°C

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<sup>1</sup> SAINT Plus Version 7.53a, Bruker Analytical X-Ray Systems, Madison, WI (2008).

<sup>2</sup> G. M. Sheldrick, Acta Cryst., 2008, A64, 112–122.