# Supporting Information: Structural investigation of $Na_3NpO_4$ and $Na_3PuO_4$ using X-ray diffraction and $^{237}Np$ Mössbauer spectroscopy

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## 1. High temperature X-ray diffraction study of $\alpha$-$Na_3NpO_4$

*Experimental section*

$\alpha$-$Na_3NpO_4$ was prepared by mixing neptunium dioxide with sodium carbonate in a (1:2) ratio, as was done for $\alpha$-$Na_3PuO_4$, and heating the mixture under a flow of argon in a tubular furnace at 1093 K. The compound was obtained with small admixtures of $Na_4NpO_5$ and unreacted $NpO_2$.

The thermal expansion and stability of the $\alpha$-$Na_3NpO_4$ phase was assessed by high temperature X-ray diffraction using a Bruker D8 X-ray diffractometer mounted with a curved Ge monochromator (111), a copper ceramic X-ray tube (40 kV, 40 mA), a Vantec position sensitive detector, and equipped with an Anton Paar HTK 2000 chamber. Measurements were conducted under helium at atmospheric pressure up to 973 K. The temperature, measured with a thermocouple, was previously calibrated using the thermal expansion data of MgO [1]. The uncertainty on the temperature is estimated to be 20 K at 1473 K.

*Study of the compounds' thermal expansion*

As the $Na_3AnO_4$ (An=Np,Pu) phase could form in Sodium-cooled Fast Reactors following the interaction between the sodium metallic coolant and the (U,Np,Pu)$O_2$ nuclear fuel, it is essential from the point of view of safety to assess its thermal expansion behaviour.

No change was detected in the X-ray diffraction patterns recorded up to 973 K except for a shift to lower $2\theta$ values following the thermal expansion of the unit cell in all three directions. The evolution of the lattice parameters with temperature are shown in Figure 1. The corresponding thermal expansion coefficients were fitted by linear regression using the following expressions (1):

$$\alpha_a = \frac{1}{a_{298}} \cdot \frac{\partial a}{\partial T};\ \alpha_b = \frac{1}{b_{298}} \cdot \frac{\partial b}{\partial T};\ \alpha_c = \frac{1}{c_{298}} \cdot \frac{\partial c}{\partial T} \quad (1)$$

The corresponding coefficients of thermal expansion were estimated as $\alpha_a = 12.4 \cdot 10^{-6} K^{-1}$, $\alpha_b = 34.3 \cdot 10^{-6} K^{-1}$, $\alpha_c = 12.8 \cdot 10^{-6} K^{-1}$, and $\alpha_{vol} = 60.0 \cdot 10^{-6} K^{-1}$ in the temperature range 298-973 K. The expansion is more limited in the $a$ and $c$ directions compared to $b$, because of the corner- and edge-sharing of the $NpO_6$ octahedra in the $ac$ plane.

The latter values are larger than pure $UO_2$, reported as $\alpha_a = 10.8 \cdot 10^{-6} K^{-1}$ under vacuum in the temperature range 298-1600 K [2]. This confirms that

swelling could be significant in case of a clad breach, and needs to be accounted for in the design of SFRs.

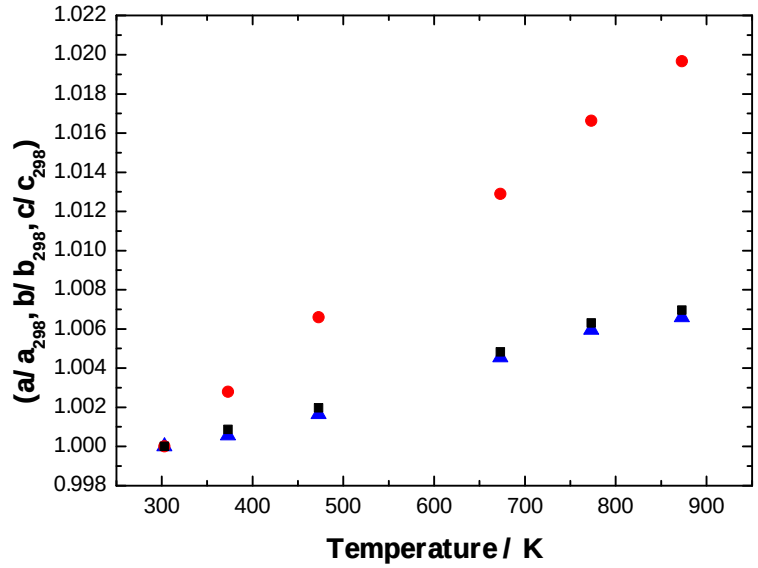



Figure 1: Evolution of the $a$ (■), $b$ (●), and $c$ (▲) cell parameters of $Na_3NpO_4$ as a function of temperature relative to the values recorded at 298 K.

## 2. $Na_3NpO_4$ structure solution

After determination of the symmetry (orthorhombic) and space group ($Fmmm$) of the $Na_3NpO_4$ structure, and refinement of the unit cell parameters, the position of the heaviest atom (neptunium) was firstly assigned to the Wyckoff position ($8g$), i.e. ($x$, 0, 0). One neptunium atom could reproduce reasonably well the experimental X-ray diffraction pattern with an arbitrary value for the fractional coordinate $x$=0.1. The calculated intensities after refinement of the neptunium atomic position are shown in Figure 2 hereafter.

The positions of the lightest atoms - Na and O - were subsequently assessed by calculating 3D Fourier differences using the program GFourier (Version 04.06) of the Fullprof2k suite [3]. This procedure allows the visualization

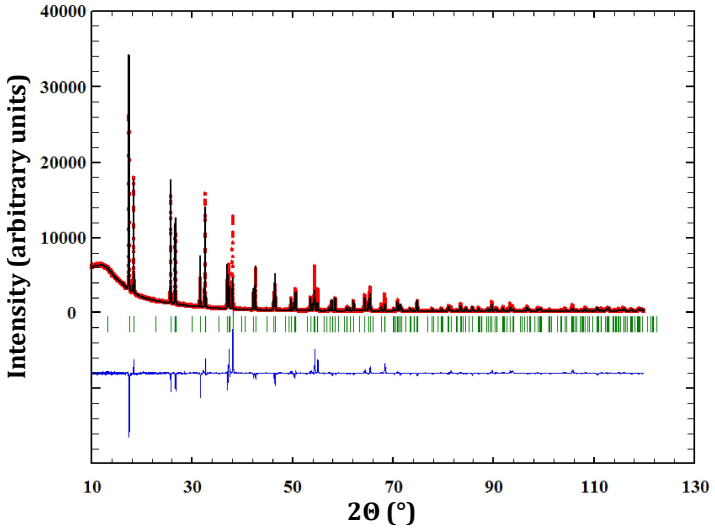
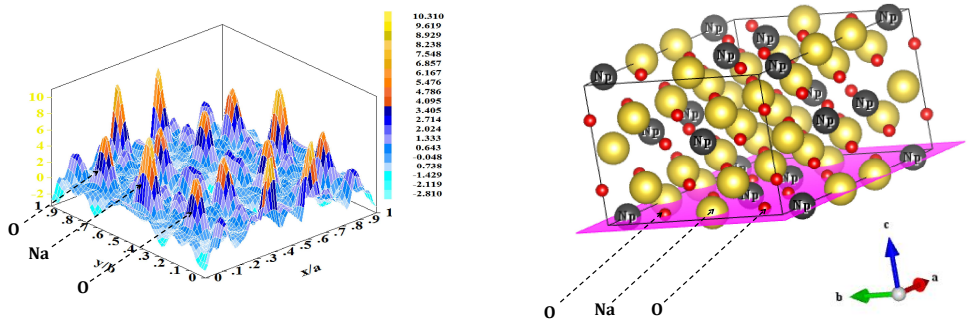



Figure 2: Comparison between the observed ($Y_{obs}$, in red) and calculated ($Y_{calc}$, in black) X-ray diffraction pattern of $\alpha$-$Na_3NpO_4$ considering the neptunium atomic positions only. $Y_{obs}$-$Y_{calc}$, in blue is the difference between the experimental and calculated intensities. The refinement yields $R_{wp}$ = 36.8, $R_{exp}$ = 7.82, $\chi^2$ = 22.2. The Bragg reflections are marked in green. Measurement at $\lambda$ = Cu-K$\alpha$1.




(a) Residual density at $z$=0

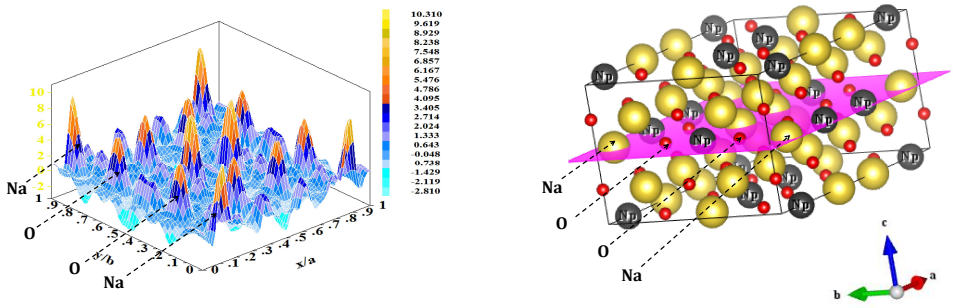
(b) Unit cell

Figure 3: (a) Residual electronic density ($F^{obs}$ - $F^{calc}$) calculated using the program GFourier at $z$=0 after refinement of the X-ray diffraction data of $Na_3NpO_4$ considering the neptunium atomic positions only.(b) Sketch of the $Na_3NpO_4$ structure (Np atoms represented in grey, Na atoms in yellow, O atoms in red).

of the residual electronic density in the unit cell. Figure 3a shows the residual electronic density at the height $z$=0. One can clearly identify the oxygen and sodium atoms in the plane (0,0,1) and determine their approximate fractional positions along the $x$ and $y$ axes. Figure 3b shows the atoms in the unit cell, stressing the correspondence between the electronic density and the atomic positions of the light atoms at the height $z$=0.

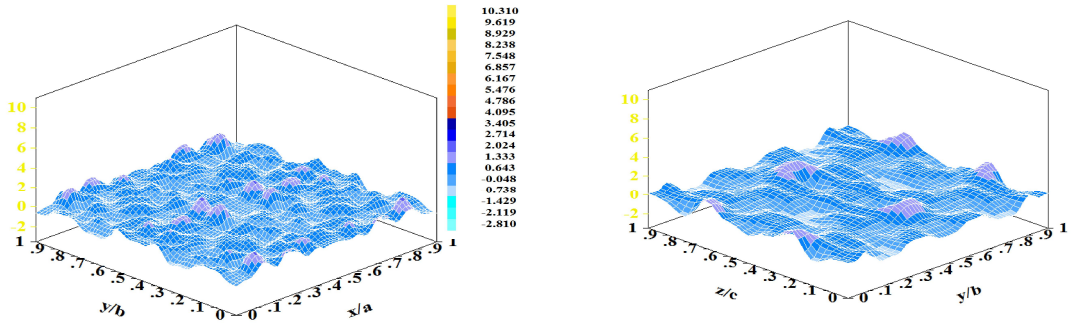
In the same manner, the residual electronic density was calculated at different heights until all atoms were localized. Figure 4a is the calculation at the height $z$=0.5, showing the position of the oxygen and sodium atoms within this plane.

The final atomic positions were finally refined by the Rietveld method. Figures 5a and 5b show that there is no more residual electronic density after refinement of the $Na_3NpO_4$ structure considering all atomic positions, i.e. Np site in Wyckoff position ($8g$), Na sites in ($8g$), ($8c$) and ($8f$), O sites in ($8i$), ($8d$) and ($16o$).




(a) Residual density at $z$=0.5 (b) Unit cell

Figure 4: (a) Residual electronic density ($F^{obs}$ - $F^{calc}$) calculated using the program GFourier at $z$=0.5 after refinement of the X-ray diffraction data of $Na_3NpO_4$ considering the neptunium atomic positions only.(b) Sketch of the $Na_3NpO_4$ structure (Np atoms represented in grey, Na atoms in yellow, O atoms in red).




(a) $z$=0 (b) $z$=0.5

Figure 5: Residual electronic density ($F^{obs}$ - $F^{calc}$) calculated using the program GFourier at (a) $z$=0 and (b) $z$=0.5 after final refinement of the X-ray diffraction data of $Na_3NpO_4$ considering all atomic positions (Np, Na and O sites).

[1] D. Taylor, Thermal expansion data. I:Binary oxides with the sodium chloride and wurtzite structures, MO, Brit. Ceram. Trans. J. 83 (1) (1984) 5–9.

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[3] J. Rodriguez-Carvajal, Recent advances in magnetic structure determination by neutron powder diffraction, Physica B 192 (1993) 55–69.