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Applications of alkali metal hydroxide hydrofluxes to the synthesis of single crystal ternary actinide oxides.

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Abstract: Hydrofluxes are hydrated salts with melting points well below that of the dehydrated salt and boiling points well above that of water, affording a reaction medium where mild temperatures and pressures can be accessed for the synthesis of materials. Herein we describe the use of alkali metal hydroxide hydrofluxes for the synthesis of single crystal α - Na_2NpO_4 , and report the single crystal X-ray structure of α - Na_2NpO_4 , along with its X-ray absorption spectra and vibrational spectra. The ability to synthesize complex oxides of the actinides, in particular, transuranium materials, under mild conditions will serve to advance our ability to explore the structure-property relationships of the f-elements.

The synthesis of crystalline binary and complex metal oxides is often achieved using high-temperature syntheses involving flux growth techniques in molten salts or vapor transport techniques.^[1] The ability to synthesize materials as single crystals enables the study of their structure, as well as their physical and fundamental electronic properties for their technological and scientific applications. Recently, the use of alkali metal hydrofluxes has been demonstrated for the growth of single crystals of transition metal and rare earth hydroxides.^[2] Hydroflux reactions allow for lower temperature routes to the production of single crystal materials without the generation of the high pressures encountered in hydrothermal syntheses or the high temperatures often required for flux growth methods.^[2d]

Inspired by these reported successes, we have investigated the synthesis of transuranium oxides from alkali metal hydroxide solutions, hydrofluxes, and melts. Oxides of the actinide elements are technologically important materials as nuclear fuels^[3] and waste forms,^[4] as well as excellent systems for the study of the electronic properties of the f-elements,^[5] the periodic structural properties of the binary oxides having been central to Seaborg's actinide concept.^[6] Moreover, the chemical environments in these concentrated alkali metal fluxes and solutions are reminiscent of those present in the high-level waste storage tanks at the Hanford site, and similar to the environments that may be encountered in molten salt reactors, providing insight into the chemistry and speciation of the actinide elements in these extreme environments.^[7] Herein we present a mild hydroflux synthesis for the growth of single crystals of α - Na_2NpO_4 , a ternary actinide oxide, its single crystal X-ray structure, X-ray absorption near edge structure (XANES) spectrum and vibrational spectra.

Single crystals of α - Na_2NpO_4 were synthesized at 155°C from a 60% w/w NaOH hydroflux over a time period of 18 hours and the structure was determined using single crystal X-ray diffraction. As shown in Figure 1, α - Na_2NpO_4 crystallizes as bundled hair-like needles that appear golden brown in color. The needles are typically 10 to 20 μm wide and up to 100-200 μm in length. Liquid scintillation counting of the flux after the reaction and removal with methanol indicated that more than 99% of the neptunium was associated with the solid phase and not in the flux

supernatant. Powder X-ray diffraction measurements, shown in the supplemental information, of the methanol-washed solid demonstrate that the synthesized material is a principally pure phase of α - Na_2NpO_4 with minor amorphous components likely from the hydrolysis of the material during purification. Previous reports of the synthesis of this compound employed traditional solid state methods combining NpO_2 and Na_2O in a stream of oxygen at 400°C , producing a crystalline powder.^[8]

Single crystal X-ray diffraction measurements were carried out on a single needle of α - Na_2NpO_4 . α - Na_2NpO_4 crystallizes in the orthorhombic space group *Pbam*, which is in agreement with prior powder diffraction studies and is isostructural with α - Na_2UO_4 .^[8b, 9] The details of the crystallographic refinement are provided in the experimental details. In α - Na_2NpO_4 the neptunium and oxygen atoms form an axially compressed octahedron with two short neptunium-oxygen bonds, Np-O(I) of 1.895(2) Å, and four longer Np-O(II) bonds at 2.180(1) Å, Figure 2a, Table 1. The refined bond distances are somewhat longer than those bond distances for the two short, 1.762(5) Å, and four long, 2.086(5) Å, Np-O bonds previously reported from Rietveld refinements of α - Na_2NpO_4 .^[8, 10] The Np-O(I) bond is on the longer range of those typically observed in Np(VI) complexes of 1.73 to 1.80 Å^[11], and consistent with the elongation of the axial actinyl bond from electron donation from the coordinated equatorial oxygen atoms, Np-O(II).^[11d, 12] The Np-O octahedra form edge shared infinite chains that propagate along the *c*-axis of the crystals (Figure 2b). The sodium sites are seven coordinate, with the bonds to oxygen atoms spanning distances of 2.338(2) Å to 2.694(2) Å.

The stoichiometry of the material, as suggested from the single crystal X-ray diffraction studies, indicates that the neptunium is hexavalent. However, the neptunium was originally added to the reaction as an aqueous pentavalent neptunium nitrate solution. Prior electrochemical studies of neptunium in alkaline solution show that the Np(VI/V) redox couple in highly concentrated sodium hydroxide solutions shifts significantly toward 0 volts, indicating an increasing thermodynamic stability toward the hexavalent oxidation state under alkaline conditions.^[13] In exploration of the phase space of this reaction using aqueous solutions of 1 to 5 M NaOH, the resultant reaction products were those of the previously reported pentavalent compound, $\text{Na}[\text{NpO}_2(\text{OH})_2]$, in which no oxidation was observed.^[14] Only at the higher concentrations of NaOH, 50 % w/w (ca. 13 M), do we observe oxidation, indicating that the 50% w/w and higher NaOH hydrofluxes are driving the redox chemistry in this system by the production of peroxide and superoxide within the hydroflux, a reaction known for higher temperature hydroxide fluxes in contact with oxygen and water vapor.^[15] As a secondary check to the valence state of the neptunium in this complex, X-ray absorption near edge spectra (XANES) were collected on the reaction products of Np(V) in 55 % w/w NaOH and are shown in Figure 3. The XANES spectra, with its characteristic broadened white line with a maximum at 17625.3(5) eV and an absorption edge energy of 17612.7(5) eV, are in close agreement to those previously reported for α - Na_2NpO_4 .^[8a] Taken together, these data indicate that the oxidation state is hexavalent and that the sodium and neptunium sites in the crystals are fully occupied.

FT-IR and Raman spectra were collected on α - Na_2NpO_4 and the full spectra are provided in the supplemental information. The shorter Np-O(I) bond has actinyl-like, multiple-bond character, as

indicated by the Np-O(I) symmetric stretching frequency observed in the Raman spectrum at 692 cm^{-1} . The asymmetric stretching frequency in the FT-IR is assigned at 720 cm^{-1} based on comparison with the isostructural disodium uranates.^[16] For comparison, the symmetric vibrational frequency reported for aqueous $\text{NpO}_2(\text{OH})_4^{2-}$ is 769 cm^{-1} indicating a strong destabilization and elongation of the axial Np-O(I) bond due to the interaction of the equatorial oxygen atoms with the neptunium cation.^[11d] Two lower frequency vibrations are observed around 200 cm^{-1} associated with the bending modes of the Np-O(I) bonds at 124 cm^{-1} and 199 cm^{-1} . These two frequencies are not observed in the off-diagonal configurations in the polarized Raman spectra shown in the supplemental information. The rough orientation of the crystals with respect to the optical axes and the observed Raman spectra indicates that the crystals are propagating along the *c*-axis. Vibrational modes associated with the Np-O(II) stretching modes are observed as weak bands around 500-550 cm^{-1} . Compared to Na_2UO_4 , where vibrations of 712 cm^{-1} and 809 cm^{-1} respectively are observed for the U-O(I) bond, the neptunium frequencies are slightly red shifted. This shift is typical when moving across the actinide(VI) series.^[11c, 11f] Several additional higher frequency peaks are present in the FT-IR spectrum, suggesting that the material may have begun to hydrolyze after sitting for several days. The instability of these types of materials with respect to hydrolysis and their hygroscopic behavior has been previously reported.^[16c]

This synthesis of $\alpha\text{-Na}_2\text{NpO}_4$ under relatively mild conditions highlights new opportunities for complex metal oxide synthesis and crystal growth. In particular, the high yield of the reactions and the mild reaction conditions lend themselves particularly well to the synthesis of transuranium materials, where quantities of available materials are often quite limited or expensive. The ability to synthesize complex oxides of the actinides as single crystals will advance our capabilities in understanding f-element structure-property relationships and inform our understanding of the complex electronic and magnetic properties of these materials. Understanding the fundamental structural, electronic, and thermochemical properties is necessary for the effective and safe application of nuclear energy in the development of advanced fuels and stable waste forms, and the managing existing high-level wastes.

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Experimental Section

Caution! ^{237}Np is an alpha- and gamma-emitting isotope. The described experiments were performed in specially designed laboratories with negative-pressure fume hoods and gloveboxes, using strict radiological controls.

Synthesis of $\alpha\text{-Na}_2\text{NpO}_4$ was carried out by first preparing a stock solution of neptunium(V) ($^{237}\text{Np}(\text{V})\text{O}_2^+$ (23 mg)) from ANL stocks in ~1 mL of 1M HNO_3 . This solution was brought to dryness over several hours under a stream of N_2 , then dissolved in 60 μL DI-water. A 5 μL (~2 mg ^{237}Np) aliquot of this solution was pipetted into a 3-mL Teflon screw cap vessel (Savillex),

containing a 60% NaOH/water solution (0.1207 g NaOH (Sigma-Aldrich, micropearls, 97%), 80 μ L DI-water). The vial was then closed and sealed inside a 45 mL Teflon-lined Parr general purpose acid digestion bomb and heated to 155 °C in a box furnace for 18 hours. After cooling to room temperature, the vessel was opened and gold/brown, thin, needle-like crystals were observed, as shown in Figure 1. To determine the yield of the reaction, radiometric liquid scintillation counting was done to establish the amount of ^{237}Np remaining in the supernatant after centrifugation of the material. Based on the Np mass balance, the Np associated with the solid phases was determined to be approximately 99 %. Similar reactions were conducted with 50 % wt NaOH also resulting in the formation of $\alpha\text{-Na}_2\text{NpO}_4$. As commented in the text, reactions conducted using 1-5 M NaOH resulted in the formation of $\text{Na}(\text{NpO}_2(\text{OH})_2)$.

Crystallographic Data Collection: Single crystal data were collected a Bruker APEX-II CCD X-ray diffractometer. Crystal Data: $\alpha\text{-Na}_2\text{NpO}_4$, $M_r = 346.98$, crystal size = 0.05 x 0.01 x 0.01 mm, orthorhombic *Pbam*, $a = 5.7171(6)$ Å, $b = 9.6754(11)$ Å, $c = 3.4584(4)$ Å, $\alpha = \beta = \gamma = 90.00^\circ$, $Z = 2$, $\rho_{\text{calcd}} = 6.024$, $\mu = 27.247$ mm $^{-1}$, $\text{MoK}\alpha$ 0.71073 Å, $T = 100$ K, $2\theta_{\text{max}} = 66.121^\circ$, measured reflections 3139, independent reflections 399, $R_{\text{int}} = 0.0152$, $R_1 = 0.0122$, $wR_2 = 0.0254$ ($I > 2\sigma I$), $\text{GOOF} = 1.031$, residual density (max/min) 1.362/-0.714. Data were collected on a Bruker APEX II diffractometer. Absorption corrections were applied using the program SADABS.^[17] The structure solution was solved using direct methods and subsequent full-matrix least-squares refinements on F^2 .^[18] Crystallographic data is available from the ICSD citing reference number 1954771.

X-ray Absorption Spectroscopy: X-ray absorption near edge spectra were collected at the Advanced Photon Source at Argonne National Laboratory on beamline 12-BM-B.^[19] The beamline is equipped with a water-cooled Si(111) double crystal monochromator. Beam collimation and higher-order harmonics filtering is achieved with a double mirror system (flat plus toroidal). A 13-element Ge solid state detector (Canberra) was used for data collection in fluorescence mode. Monochromator energy calibration was carried out at the zirconium K-edge (17.998 keV). All measurements were performed at room temperature with the samples prepared identically to those reported for the synthesis above and encapsulated in 2mm diameter Teflon tubes and further packaged in two layers of Kapton which were contained in a sealed motorized sample changing box. Data were collected at the Np LIII absorption edge (17.610 keV). The XANES data were processed using SIXPACK^[20], and the edge energy taken as the maxima of the first derivative of the XANES spectrum.

Vibrational Spectroscopy: Raman spectra were collected on single crystals pulled directly from the reaction vessel. Raman spectra were collected using a Renishaw in-Via confocal Raman microscope with an excitation line of 532 nm. Spectra were collected using both circularly polarized radiation as well as linearly polarized. FT-IR spectra were collected on crystals removed from the reaction vessel and washed repeatedly with methanol in air. The crystals were then ground with Teflon powder (~2 % wt Np) and pressed into a pellet. FT-IR data were collected on a Nicolet Nexus 870 FT-IR system.

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Table 1. Selected bond lengths (Å) and bond angles (deg.) for α -Na₂NpO₄.

Bond	Distance (Å)	Bond Angle (deg.)
Np – O(I)	1.8947(19)	
Np – O(II)	2.1796(11)	
Np – Np	3.4584(4)	
Na – O	2.338(2) - 2.694(2) Å	
Na – Np	3.5241(12)	
O(I) – Np – O(I)		180.0°
O(I) – Np – O(II)		89.15°

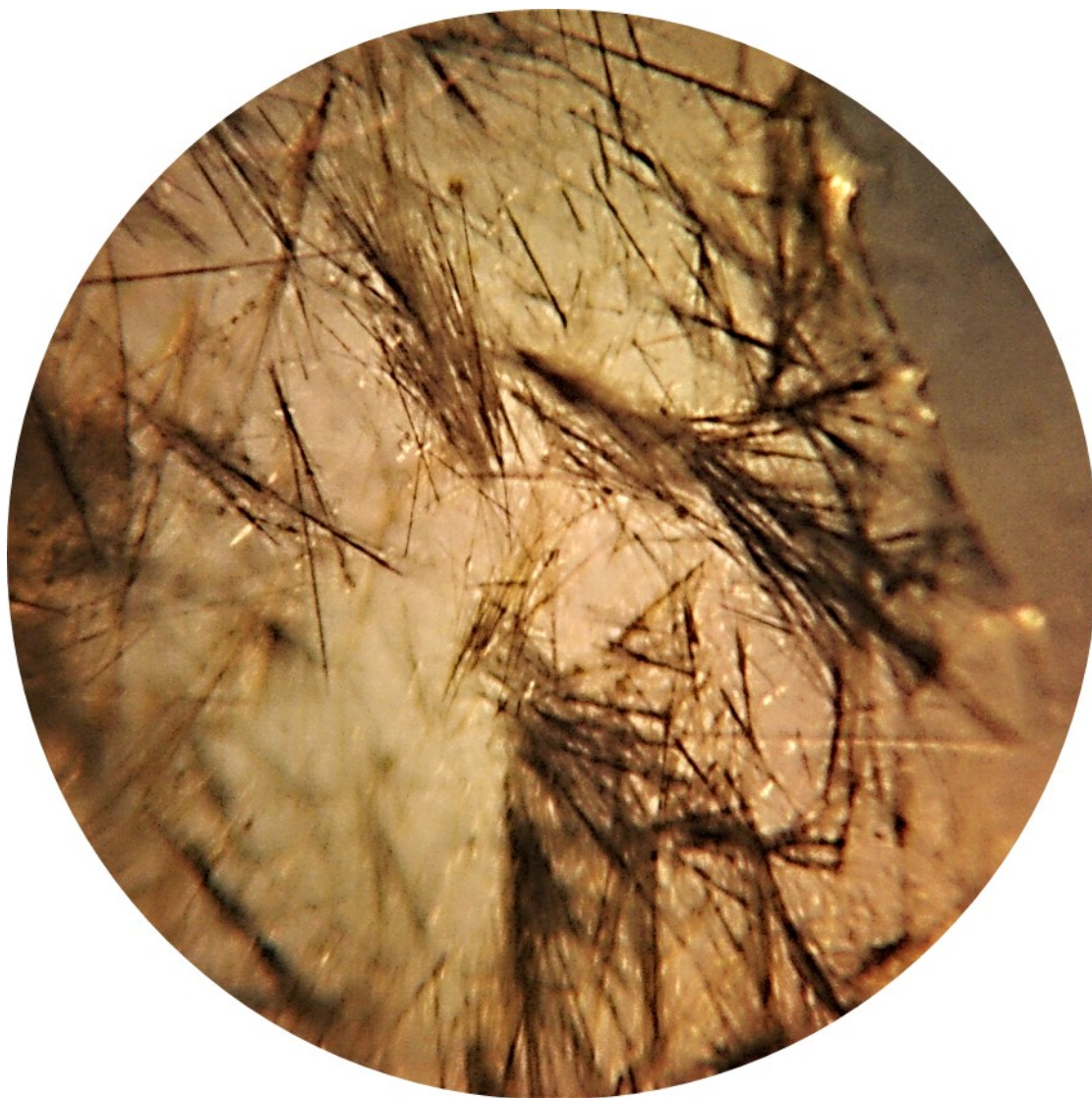


Figure 1. Photograph of the reaction vessel showing the bundles of hair-like single crystals of α - Na_2NpO_4 . The crystals are typically 10-20 μm wide and 100-200 μm in length.

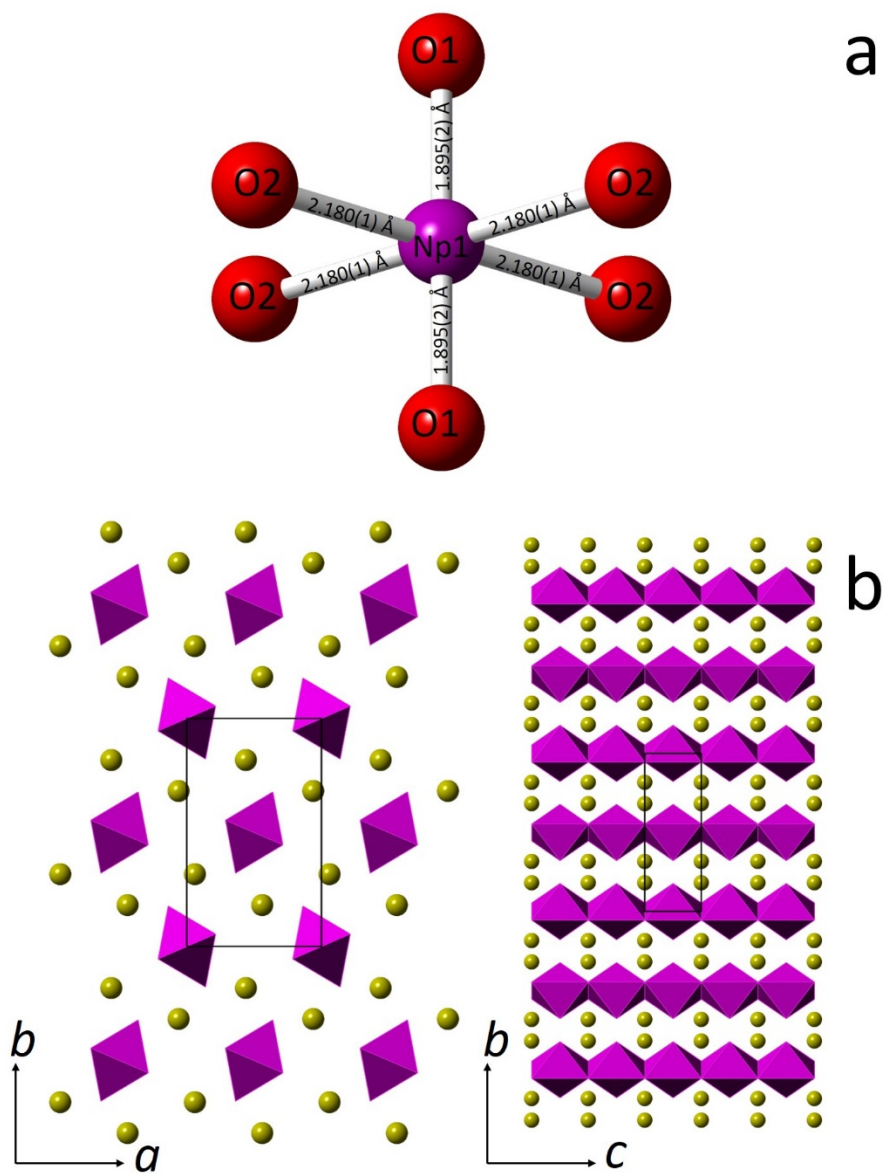


Figure 2. (a) Ball and stick representation of the axially compressed Np(VI)O_6 octahedra, Np in magenta, oxygen in red. (b) Projections of the crystal packing showing the propagation of the edge-shared Np(VI)O_6 octahedra along the c -axis. The NpO_6 octahedra are magenta, while the sodium atoms are represented by the gold spheres.

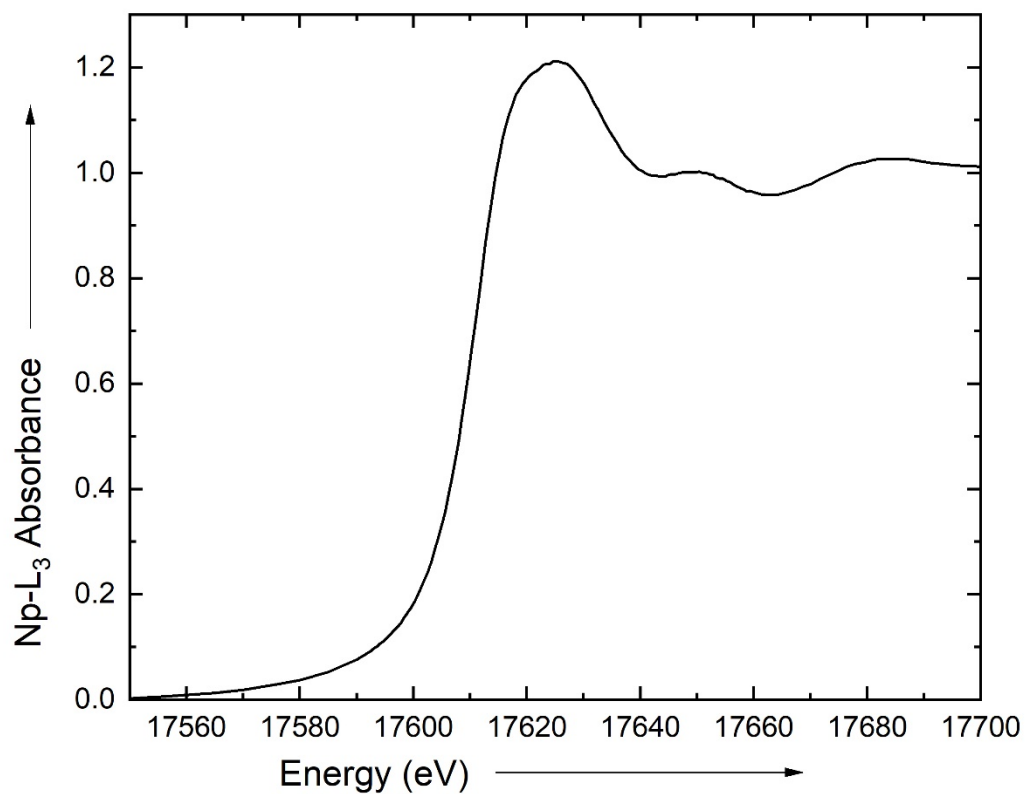


Figure 3. Np L₃-edge X-ray absorption near edge spectrum of α -Na₂NpO₄. The absorption edge energy was determined from the peak of the first derivative at 17,612.7(5) eV. The maximum of the white line is observed at 16625.3(5) eV. The monochromator was calibrated using the Zr K-edge.



Single crystals of α - NaNpO_4 were synthesized from a sodium hydroxide hydroflux at 155°C and its single crystal structure determined. The mild reaction conditions used are in contrast to traditional high-temperature solid state syntheses and highlight a rich chemistry of the actinide elements in alkaline conditions.