Single Crystal Growth and Structural Characterization of Ternary Transition-Metal Uranium Oxides: MnUO_4 , FeUO_4 , and NiU_2O_6 .

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Abstract

Single crystals of MnUO_4 , FeUO_4 , and NiU_2O_6 were grown for the first time. The use of chloride fluxes facilitated the crystal growth. MnUO_4 , a hexavalent uranium compound, crystallizes in the orthorhombic space group, *Imma*, with $a = 6.6421(19)$ Å, $b = 6.978(2)$ Å, and $c = 6.748(2)$ Å, and exhibits typical uranyl, UO_2^{2+} , coordination. FeUO_4 and NiU_2O_6 contain pentavalent uranium and are structurally related, exhibiting three-dimensional connectivity. FeUO_4 crystallizes in the orthorhombic space group, *Pbcn*, with $a = 4.8844(2)$ Å, $b = 11.9328(5)$ Å, $c = 5.1070(2)$ Å. NiU_2O_6 crystallizes in the trigonal space group, *P321*, with $a = 9.0148(3)$ Å, $c = 5.0144(3)$ Å.

Keywords: Crystal growth; Single crystals; Transition-metal uranium oxides; Pentavalent uranium oxides; Chloride flux

1. Introduction

Many complex uranium oxides have been synthesized, with the majority of the publications stemming from work done in the 1960's and 1970's. More recently, there has been renewed interest in developing this class of materials to address the issues of long-term nuclear waste storage and improvement of fuel rod technologies. Much of the early work on complex uranium oxides focused on synthesis and characterization of polycrystalline powders. With the advancement of diffraction techniques and new crystal growth approaches, it is of interest to pursue the growth of single crystals and to re-investigate these materials to obtain more accurate structure determinations.

The single crystal growth of complex uranium-containing oxides has garnered recent attention, due to a strong desire to understand better existing structure-property relationships. Complex uranium-containing oxides have been grown as single crystals using a variety of methods, including chemical vapor transport[1-5], hydrothermal synthesis[6-12], traditional solid-state processing[8, 13-33], and flux crystal growth[15, 34-50]. Much of the reported crystal growth utilized the solid-state approach, however, there are some limitations with this method. The second most published crystal growth method for complex uranium-containing oxides is flux growth. We have explored the use of hydroxide[43, 44] and carbonate fluxes[42, 45, 46] for the crystal growth of complex oxides, and have found that the oxidizing nature of these melts limits these fluxes to compounds containing metals in high oxidation states, such as hexavalent uranium. We have recently begun using halide fluxes to explore the crystal growth of uranium containing oxides and related materials in a redox neutral environment,[51] targeting the crystal growth of complex oxides containing uranium in reduced oxidation states.

Ternary transition-metal uranium oxides have been the focus of several studies that centered on investigation of the physical properties of these oxides, particularly in the case of reduced uranium (U^{4+} or U^{5+}) containing oxides, as such studies are thought to improve our understanding of the role of $5f$ electrons in magnetic interactions. The crystal structures of U(VI) containing $MnUO_4$, [52] and of U(V) containing $FeUO_4$, [53] and NiU_2O_6 , [54, 55] solved by means of powder diffraction, have been reported together with their magnetic susceptibilities. [52, 54, 56-60] To date, several oxides containing both uranium and a transition-metal have been grown as single crystals, however, there have been only a few reports of single crystals grown using a flux growth approach. Some vanadates, molybdates, tungstates, and niobates have been grown from reactive alkali-metal carbonate, [40, 61, 62] alkali-metal halide, [15, 39] and low-melting oxide fluxes. [63-65] Regarding first-row transition-metal uranium oxides, the double perovskites, Ba_2MUO_6 ($M = Cu, Ni, Zn$), have been grown from alkali-metal carbonates, [46] and $UTiNb_2O_{10}$ was grown from a boric acid flux at 1200 °C. [66]

In this paper we report the first growth of $MnUO_4$, $FeUO_4$, and NiU_2O_6 single crystals along with their single crystal structure determinations. The latter two compounds contain pentavalent uranium, and represent a rare example of a flux grown complex uranium oxide containing uranium in an oxidation state lower than +6.

2. Experimental Details

Caution: U_3O_8 contains depleted uranium, but standard precautions for handling radioactive and highly toxic substances should be followed.

2.1. Crystal Growth

U_3O_8 (International Bioanalytic Laboratories, Inc.), $\text{MnCl}_2 \cdot 4\text{H}_2\text{O}$ (Alfa Aesar, 99%), $\text{FeCl}_2 \cdot 4\text{H}_2\text{O}$ (Alfa Aesar, 99%), $\text{NiCl}_2 \cdot 4\text{H}_2\text{O}$ (Alfa Aesar, 99%), CsCl (Alfa Aesar, 99%), and KCl (Mallinckrodt, ACS grade) were used as received. $\text{BaCl}_2 \cdot 2\text{H}_2\text{O}$ (Alfa Aesar, 98%) was dried overnight at 150 °C to prepare the anhydrous flux.

Single crystals of MnUO_4 were grown from a molten cesium chloride flux. 0.33 mmol of U_3O_8 , 2 mmol of $\text{MnCl}_2 \cdot 4\text{H}_2\text{O}$, and 10 mmol of CsCl were loaded into an alumina crucible covered with an alumina disc. The reaction was heated at a rate of 10 °C/min to 900 °C. The furnace was held at this temperature for 12 h, after which time it was cooled at a rate of 0.1 °C/min to 550 °C, and subsequently cooled to room temperature by switching off the furnace.

Single crystals of FeUO_4 were grown from a molten barium chloride flux. 0.33 mmol of U_3O_8 , 1 mmol of $\text{FeCl}_2 \cdot 4\text{H}_2\text{O}$, and 10 mmol of BaCl_2 were loaded into an alumina crucible covered with an alumina disc. The reaction was heated at a rate of 10 °C/min to 1050 °C. The furnace was held at this temperature for 24 h, after which time it was cooled at a rate of 0.05 °C/min to 850 °C, and subsequently cooled to room temperature by switching off the furnace.

Single crystals of NiU_2O_6 were grown from a molten potassium chloride flux. 0.33 mmol of U_3O_8 , 1 mmol of $\text{NiCl}_2 \cdot 4\text{H}_2\text{O}$, and 20 mmol of KCl were loaded into an alumina crucible covered with an alumina disc. The reaction was heated at a rate of 10 °C/min to 900 °C. The furnace was held at this temperature for 12 h, after which time it was cooled at a rate of 0.1 °C/min to 700 °C, and subsequently cooled to room temperature by switching off the furnace.

The lustrous black polyhedral crystals of MnUO_4 and FeUO_4 and needle/rod

crystals of NiU_2O_6 were isolated from the solidified fluxes by dissolving the fluxes with water, assisted by sonication, and collected by vacuum filtration. Optical images of the as grown crystals are shown in Fig. 1a and 1b.

2.2. Single Crystal X-Ray Diffraction

X-ray intensity data from an irregular black blocky crystal of MnUO_4 , a lustrous black polyhedral crystal of FeUO_4 , and a lustrous black needle crystal of NiU_2O_6 , were collected at 296(2) K using a Bruker SMART APEX diffractometer (Mo $\text{K}\alpha$ radiation, $\lambda = 0.71073 \text{ \AA}$). [67] The data collection covered 100% of reciprocal space to $2\theta_{\text{max}} = 65.3\text{--}77.7^\circ$, with an average reflection redundancy of 8.8-16.0 and $R_{\text{int}} = 0.0338\text{--}0.0439$ after absorption correction. The raw area detector data frames were reduced and corrected for absorption effects with the SAINT+ and SADABS programs. [67] Final unit cell parameters were determined by least-squares refinement of 984-3526 reflections from the data set. Direct methods structure solution, difference Fourier calculations, and full-matrix least-squares refinement against F^2 were performed with SHELXS/L [68] using the ShelXle interface. [69] Relevant crystallographic data are presented in Table 1 and 2, and selected interatomic distances are in Table 3.

MnUO_4 crystallizes in the orthorhombic system. The space groups $Ima2$ and $Imma$ were consistent with the pattern of systematic absences in the intensity data. The centrosymmetric group $Imma$ (No. 74) was confirmed by structure solution. There are four atomic positions in the asymmetric unit: one uranium atom, one manganese atom and two unique oxygen atoms. Uranium U(1) is located on site $4e$ with $mm2$ site symmetry; manganese Mn(1) on site $4a$ with $2/m..$ site symmetry. Both unique oxygen

atoms O(1) and O(2) are located on mirror planes; O(1) on site $8i$ ($.m$ site symmetry) and O(2) on site $8h$ ($.m$ site symmetry). All atoms were refined with anisotropic displacement parameters. No deviation from full occupancy was observed for either of the metal atoms. The largest residual electron density peak and hole in the final difference map are $+4.0$ and $-1.6 \text{ e}^-/\text{\AA}^3$, located 0.68 and $1.39 \text{ \AA}$ from U(1) and O(1), respectively. Final atomic coordinates were standardized with Structure Tidy.[70]

FeUO_4 crystallizes in the orthorhombic system. The pattern of systematic absences in the intensity data was uniquely consistent with the space group $Pbcn$ (No. 60). The asymmetric unit consists of one uranium atom, one iron atom and two oxygen atoms. The uranium and iron atoms are both located on a two-fold rotational axis (site symmetry $.2$., Wyckoff position $4c$). The oxygen atoms are located on general positions ($8d$). All atoms were refined with anisotropic displacement parameters. Trial refinements of the site occupancy factors of the metal atoms showed no significant deviations from full occupancy. The largest residual electron density peak and hole in the final difference map are $+3.07$ and $-2.95 \text{ e}^-/\text{\AA}^3$, located 0.67 and $1.41 \text{ \AA}$ from U1 and Fe1, respectively. The reported atomic coordinates were standardized with Structure Tidy program.[70]

For NiU_2O_6 , the pattern of systematic absences in the intensity data showed many weak violations of the 6_3 symmetry element, and positively ruled out $6_1/6_5$ and c -glide elements, still leaving many space group choices. Based on published structure solutions from X-ray and neutron powder diffraction studies,[54, 55] the space group $P321$ (No. 150) was selected, and a reasonable solution and refinement were achieved. The ADDSYM program in PLATON[71] showed no missed symmetry when the 'EXACT' option was used. Further analysis suggested the structure is pseudosymmetric, with a

non-crystallographic 6_3 pseudo-element along [001]. This was also indicated by examination of the systematic absences. The mean $I/\sigma(I)$ for violations of the type $00l$, $l \neq 2n$ was 2.6, compared to typical $I/\sigma(I)$ values of 10.5 and 16.6 for c -glide operations. The false 6_3 axis nearly relates the two independent uranium atoms, with a deviation from symmetry-equivalence by the 6_3 axis of 0.207 Å between U(1) and U(2). Trial solutions in space group $P6_3$ were unsuccessful. The asymmetric unit in $P321$ consists of two uranium atom positions, two nickel atom positions, and three oxygen atom positions. Both uranium atoms are located on two-fold axes, with U(1) on site $3f$ and U(2) on site $3e$. Ni(1) is located on a three-fold axis (site $2d$) and Ni(2) is located on site $1a$ with (32.) site symmetry. The oxygen atoms are located on general positions. All atoms were refined with anisotropic displacement parameters (ADP), except for oxygen O(3) which was refined isotropically. The O(3) ADP refined to a physically senseless value (non-positive definite) when anisotropic. After all atoms were located, a pattern of $F_{\text{obs}} \gg F_{\text{calc}}$ was observed, suggesting twinning. The TwinRotMat algorithm implemented in PLATON was used to derive the twin law, which is (-100 / 110 / 00-1), corresponding to a two-fold rotation about the [120] direction. The twinning is not related to the pseudosymmetry. The major twin domain fraction refined to 0.61(1). The largest residual electron density peak and hole of +3.42 and -3.58 e⁻/Å³ in the final difference map are located 0.71 Å and 2.13 Å from U(2) and O(3), respectively. The instability of the anisotropic displacement parameters for oxygen atom O(3) is likely caused by the combined effects of twinning and the pseudosymmetry. The reported atomic coordinates were standardized using StructureTidy.[70]

2.3. Energy-Dispersive Spectroscopy (EDS)

Elemental analysis was performed on the flux-grown crystals using a TESCAN Vega-3 SBU scanning electron microscope (SEM) with EDS capabilities. The crystals were mounted on carbon tape and analyzed using a 30 kV accelerating voltage and an accumulation time of 20 s. As a qualitative measure, the EDS confirmed the presence of each reported element in the title compounds. SEM images of the flux grown crystals can be seen in Fig. 1c and 1d.

3. Results and Discussion

3.1 Synthesis

Single crystals of uranium containing oxides have been grown by a variety of methods, including solid-state reactions[8, 13-33], hydrothermal[6-12], chemical vapor transport[1-5], and flux methods[15, 34-50]. Most of the crystals reported to date were obtained from solid-state reactions, which require very high temperatures and which work best for congruently melting solids. These requirements place significant limitations on the use of the traditional solid-state method for exploratory crystal growth. Hydrothermal crystal growth methods require high-pressure vessels and can result in the formation of non-oxide products. Flux crystal growth remains one of the most useful methods for the discovery of new materials,[72] and although the majority of crystals of complex oxides containing reduced uranium have been obtained from hydrothermal and CVT syntheses,[1-5, 7, 9] the flux technique can be adapted to promote the formation of this variety of materials as well. To date, there have been only a few reports of flux crystal growth of complex oxides containing reduced uranium in the literature, including that of

UMo₅O₁₆,[65] (Cu,Mn)UMo₃O₁₂,[64] and UNb₃O₁₀.[73] The chloride fluxes, used herein, provide a very useful redox neutral environment, which can be used for the crystallization of compounds containing reduced uranium. These fluxes also have moderate melting temperatures, and crystals grown within these fluxes are readily isolated by dissolving the flux in water.

One can rationalize why some compositions form over others by this synthetic approach. For example, FeCl₂, used in the synthesis of FeUO₄, decomposes and oxidizes into Fe₂O₃ around 400 °C in air, while U₃O₈ (U(V)/U(VI) mixed valent) is thermally stable up to the operating temperature of 1050 °C. This allows for the formation of Fe^{III}U^VO₄. Likewise, NiU₂O₆ can be formed in the flux, as the uranium(V) containing starting material remains stable while nickel will not readily oxidize to Ni(III), explaining why Ni^{II}U^V₂O₆ rather than Ni^{III}U^VO₄ forms by this method.

3.2 Structure Description

MnUO₄ crystallizes in the orthorhombic space group, *Imma*. The compound exhibits a three-dimensional (3D) structure of the MgUO₄, rutile structure type. There is one uranium site and one manganese site. The UO₂²⁺, uranyl, environment is present in this structure, as expected. The uranium coordination environment consists of a distorted octahedron with two short axial U-O bonds (1.938(7) Å) and four long equatorial U-O bonds (2.162(5)-2.181(5) Å). The UO₆ polyhedra share edges in the equatorial plane along *b*, creating infinite chains. The equatorial oxygen atoms are also corner-sharing with one Mn atom each, and the axial oxygen atoms are corner-sharing with two Mn atoms each. Since the axial oxygen atoms do not bond with other uranium centers, this can be classified as a Type 0 uranyl interaction, according to Read *et al.*[51] Similar to

the uranium, the manganese coordination environment consists of a distorted octahedron with two short axial Mn-O bonds (2.090(7) Å) and four long equatorial Mn-O bonds (2.229(4) Å). The extended connectivities of the MnO₆ octahedra are the same as those of the UO₆ octahedra (see Fig. 3b), such that the MnO₆ polyhedra share edges in the equatorial plane, and the axial oxygen atoms in MnO₆ occupy the equatorial position of the adjacent UO₆ and vice versa. Along the manganese chains, the Mn-Mn distance is 3.489 Å.

FeUO₄ crystallizes in the orthorhombic space group, *Pbcn*. The compound exhibits a 3D structure (see Fig. 4) of the CrUO₄ structure type consisting of infinite chains of FeO₆ and UO₆ octahedra that are linked to one another. There is one iron environment, FeO₆, with Fe-O bond lengths ranging from 1.994(3) to 2.029(3) Å. The FeO₆ distorted octahedra share two edges with other FeO₆ octahedra, forming a zigzag rutile chain, with one edge of each FeO₆ shared with a UO₆ polyhedron, which alternates sides along the chain (see Fig. 5). The three oxygen atoms forming one face of the FeO₆ octahedron are corner-sharing with one uranium atom each above that face. The sole uranium environment has bond lengths ranging from 2.110(3) to 2.230(3) Å. This bonding motif is not like the typical uranyl coordination environment, as it is nearly holosymmetric. The UO₆ octahedron shares one edge with an FeO₆ octahedron, whose oxygen atoms both corner-share with another uranium atom in another chain, one above and one below (see Fig. 5b). The two oxygen atoms opposite the shared edge are each corner-sharing with two iron atoms in other chains above or below. The remaining two oxo ligands are corner-sharing with one U-atom and one Fe-atom each to different chains, further strengthening the 3D network. Along the Fe chains, the Fe-Fe distance is

2.968 Å, and the O-Fe-O angle is 84.265°.

NiU₂O₆ crystallizes in the trigonal space group, *P*321. The compound exhibits a 3D structure (see Fig. 6) of the Na₂SiF₆ structure type, and is isostructural with CoU₂O₆. There are two uranium and two nickel environments (see Fig. 7), all of which are octahedrally coordinated by oxygen. The UO₆ octahedra are slightly distorted, with U-O bond lengths of 2.118(11)-2.293(11) Å. These environments, as also observed in FeUO₄, are not representative of the typical uranyl motif. One of the NiO₆ octahedra is regular, with Ni-O distances of 2.048(13) Å, and one is slightly distorted, with Ni-O bond lengths of 2.059(10) and 2.102(11) Å. The structure is composed of two distinct layers (see Fig. 7). Layer **A** consists of alternating edge-shared NiO₆ and UO₆ octahedra, that arrange to create triangular voids in the layer. Layer **B** consists of tetramers of NiO₆ octahedra edge-sharing with three UO₆ octahedra, creating the exact triangular shape to bond above and below the void in layer **A**. Layer **A** is occupied by the U(2) and Ni(2) atoms, while layer **B** is occupied by the U(1) and Ni(1) atoms. The UO₆ and NiO₆ octahedra in the layers are corner-sharing with those above and below the layer, completing the 3D structure.

The existence of the rutile structure for MnUO₄ can be explained by the ionic radii. Table 4 lists the Shannon ionic radii ratios of the cations, r_M/r_U , [74] and the corresponding structures for all the reported ternary transition metal uranium oxides of the compositions, MUO₄ ($M = \text{Cr, Mn, Fe, Co, Cu, Cd}$) and MU₂O₆ ($M = \text{Co, Ni}$), along with the forms in which they were previously synthesized, that is single crystals or polycrystalline powders.[52-55, 57, 75-77] CaUO₄ [42] and MgUO₄, [78] although not containing a transition metal, were also included in the table, because the structures are relevant, providing additional points of reference. There is a notable trend that as the

radius ratio decreases from 1.37 for CaUO_4 to 1.30 for CdUO_4 , the structure goes from the layered CaUO_4 structure to the rutile structure, where Cd adopts both. For Mn, Co, and Mg, the rutile structure is reported exclusively, where the uranyl environment causes the MO_6 octahedron to distort in the typical fashion, with two short and four long $M\text{-O}$ bonds. Although $r_{\text{Co}} < r_{\text{Cu}} < r_{\text{Mg}}$, CuUO_4 adopts the rare dirutile structure, where the cations order within the rutile chains. The CuO_6 are distorted and have 4 short and 2 long Cu-O bonds, rather than the 2 short and 4 long bonds that are typical in the rutile phase. This is by far the most typical geometric distortion in Cu(II) oxides to accommodate the strong Jahn-Teller distortion. The radius ratio for the hypothetical NiUO_4 would be less than that of MgUO_4 , however, no such compound has been structurally characterized and reported, suggesting that Ni(II) is too small relative to the size of U(VI) to be accommodated into the rutile lattice. For FeUO_4 and CrUO_4 , the ratio of the metal radii is even smaller than that of Ni/U (0.85 and 0.81 compared to 0.95) and, as a result, Fe also is too small to fit into the uranium containing rutile structure. Instead, the iron forms zig-zag chains of edge-sharing FeO_6 octahedra similar to those seen in PbO_2 , [79] zig-zag rutile, which are also edge-sharing with one UO_6 octahedron each. The same is true for isostructural CrUO_4 .

When additional uranium is added to the composition, the MU_2O_6 phase forms. As seen in Table 4, the trirutile structure is not formed. The trend observed for the MUO_4 system cannot be simply extrapolated to include these compositions, because the stoichiometry is different. The rutile structure cannot accommodate such a density of large, highly charged cations, and consequently, the structure distorts to minimize the number of edge-sharing of uranium containing octahedra. This structural change creates

uranium octahedra that edge-share with two lower charged M^{2+} octahedra, where only corners are shared between uranium polyhedra and not edges.

Bond valence sums have been calculated for the title compounds, and are listed in Table 5. The optimized parameters provided by Burns,[80] $r_{U-O} = 2.051$ and $b = 0.519$, were used for calculating the U-O valences, and the parameters provided by Brown and Altermatt were used for calculating TM-O valences.[81] The BVS values of 5.66 for $MnUO_4$ is in reasonable agreement with uranium being in the +6 oxidation state, while the values of 4.81-4.95 for $FeUO_4$ and NiU_2O_6 are in excellent agreement with uranium being in the +5 oxidation state. The values of 2.11, 3.05, and 2.07-1.90 for Mn, Fe, and Ni, respectively, are also in good agreement with Mn^{2+} , Fe^{3+} , and Ni^{2+} , which corroborates the uranium oxidation state by charge balancing the respective compositions.

4. Conclusions

$MnUO_4$, $FeUO_4$, and NiU_2O_6 were grown as single crystals for the first time. The latter two compounds contain uranium(V), which is quite rare in complex uranium oxides. Many of the transition metal uranium oxides that have been reported with analogous compositions adopt rutile or rutile-like structures, where the adaptation of the rutile and other structures is highly dependent on the ionic radii of the cations present. All of the crystals reported herein were isolated from a redox-neutral chloride melt and were grown with no atmosphere control. The growth of these complex uranium-containing oxide crystals demonstrate that these fluxes can be used for stabilizing compounds with uranium in reduced oxidation states.

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Supporting Information

Further details of the crystal structure investigation can be obtained from the Fachinformationszentrum Karlsruhe, 76344 Eggenstein-Leopoldshafen, Germany (fax: +497247808666; e-mail: crystdata@fiz-karlsruhe.de) on quoting the depository numbers CSD-427978, CSD-427979, and CSD-427980.

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Table 1. Crystal structure and refinement data for MnUO₄, FeUO₄, and NiU₂O₆^a

Compound	MnUO ₄	FeUO ₄	NiU ₂ O ₆
Formula weight	356.97	357.88	630.77
Color and habit	black block	black block	black needle
Crystal system	Orthorhombic	Orthorhombic	Trigonal
Space group	<i>Imma</i>	<i>Pbcn</i>	<i>P321</i>
<i>Z</i>	4	4	3
<i>a</i> (Å)	6.6421(19)	4.8844(2)	9.0148(3)
<i>b</i> (Å)	6.978(2)	11.9328(5)	9.0148(3)
<i>c</i> (Å)	6.748(2)	5.1070(2)	5.0144(3)
γ (°)	90	90	120
<i>V</i> (Å ³)	312.75(16)	297.66(2)	352.91(3)
ρ_c (g cm ⁻³)	7.581	7.986	8.904
μ (mm ⁻¹)	55.572	59.021	72.567
<i>F</i> (000)	596	600	780
Crystal size (mm)	0.04 x 0.04 x 0.02	0.06 x 0.04 x 0.03	0.08 x 0.04 x 0.04
$\theta_{\max}$ (°)	4.201 to 32.637	3.41 to 38.87	2.609 to 34.955
Index ranges	-10 ≤ <i>h</i> ≤ 9; -10 ≤ <i>k</i> ≤ 10; -10 ≤ <i>l</i> ≤ 9	-8 ≤ <i>h</i> ≤ 8; -21 ≤ <i>k</i> ≤ 20; -7 ≤ <i>l</i> ≤ 9	-13 ≤ <i>h</i> ≤ 14; -14 ≤ <i>k</i> ≤ 13; -7 ≤ <i>l</i> ≤ 8
Reflections collected	3222	8148	9678
Independent reflections	330 [R(int) = 0.0361]	862 [R(int) = 0.0338]	1052 [R(int) = 0.0439]
Goodness-of-fit on <i>F</i> ²	1.144	1.071	1.146
<i>R</i> indices (all data)	<i>R</i> 1 = 0.0238, w <i>R</i> 2 = 0.0550	<i>R</i> 1 = 0.0281, w <i>R</i> 2 = 0.0463	<i>R</i> 1 = 0.0291, w <i>R</i> 2 = 0.0696
Largest difference peak/hole (e Å ⁻³)	4.035/-1.556	3.065/-2.951	3.418/-3.581

^a For all structures, T = 298(2) K and λ = 0.71073 Å.

Table 2. Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters ($\text{\AA}^2 \times 10^3$) for MnUO_4 , FeUO_4 , and NiU_2O_6 . $U(\text{eq})$ is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U_{eq}
<i>MnUO₄</i>				
Mn	0	0	0	11(1)
U	0	2500	4841(1)	13(1)
O(1)	2083(10)	2500	170(8)	17(1)
O(2)	0	5130(6)	3095(10)	15(1)
<i>FeUO₄</i>				
Fe	0	4366(1)	2500	6(1)
U	0	1674(1)	2500	5(1)
O(1)	2675(6)	520(3)	699(6)	8(1)
O(2)	2192(6)	3095(3)	901(6)	7(1)
<i>NiU₂O₆</i>				
Ni(1)	0	0	0	11(1)
Ni(2)	3333	6667	4899(12)	11(1)
U(1)	3591(1)	0	0	10(1)
U(2)	6939(1)	0	5000	10(1)
O(1)	928(16)	2190(17)	2230(20)	13(3)
O(2)	1128(13)	5698(16)	2660(17)	11(2)
O(3)	4461(13)	2195(16)	2699(18)	11(2)

Table 3. Selected interatomic distances ($\text{\AA}$) for MnUO_4 , FeUO_4 , and NiU_2O_6 .

MnUO_4			FeUO_4			NiU_2O_6					
U1	O1	1.938(7)	U1	O1	2.110(3)	U1	O2	2.118(11)	U2	O3	2.126(11)
	O1	1.938(7)		O1	2.110(3)		O2	2.118(11)		O3	2.126(11)
	O2	2.162(5)		O2	2.165(3)		O1	2.145(12)		O1	2.176(12)
	O2	2.162(5)		O2	2.165(3)		O1	2.145(12)		O1	2.176(12)
	O2	2.181(5)		O2	2.230(3)		O3	2.293(11)		O2	2.191(12)
	O2	2.181(5)		O2	2.230(3)		O3	2.293(11)		O2	2.191(12)
Mn1	O2	2.090(7)	Fe1	O1	1.994(3)	Ni1	O1	2.048(13)	Ni2	O2	2.059(10)
	O2	2.090(7)		O1	1.994(3)		O1	2.048(13)		O2	2.059(10)
	O1	2.229(4)		O1	2.007(3)		O1	2.048(13)		O2	2.059(10)
	O1	2.229(4)		O1	2.007(3)		O1	2.048(13)		O3	2.102(11)
	O1	2.229(4)		O2	2.029(3)		O1	2.048(13)		O3	2.102(11)
	O1	2.229(4)		O2	2.029(3)		O1	2.048(13)		O3	2.102(11)

Table 4. Structures and the previously reported synthetic product forms of the known $M\text{UO}_4$ and $M\text{U}_2\text{O}_6$ ternary transition metal uranium oxides, comparing the Shannon ionic radii for the six-coordinate cations. CaUO_4 and MgUO_4 are included for reference.

Compound	r_M (Å)	r_U (Å)	r_M/r_U	Structure	Previous Synthesis	Ref.
CaUO_4	1.00	0.73	1.37	CaUO_4	Single Crystal	[42]
a- CdUO_4	0.95	0.73	1.30	CaUO_4	Powder	[76]
b- CdUO_4	0.95	0.73	1.30	Rutile	Powder	[76]
MnUO_4	0.83	0.73	1.14	Rutile	Powder	[52]
CoUO_4	0.74	0.73	1.01	Rutile	Powder	[57]
CuUO_4	0.73	0.73	1.00	Dirutile	Powder	[75]
MgUO_4	0.72	0.73	0.99	Rutile	Single Crystal	[78]
NiUO_4	0.69	0.73	0.95	not reported	-	-
FeUO_4	0.65	0.76	0.85	CrUO_4	Powder	[53]
CrUO_4	0.62	0.76	0.81	CrUO_4	Powder	[77]
<hr/>						
CoU_2O_6	0.74	0.76	0.97	Na_2SiF_6	Powder	[54]
NiU_2O_6	0.69	0.76	0.91	Na_2SiF_6	Powder	[55]

Table 5. Bond valence sums for MnUO_4 , FeUO_4 , and NiU_2O_6 .

MnUO_4		FeUO_4		NiU_2O_6			
U1	5.66	U1	4.81	U1	4.95	U2	4.83
Mn1	2.11	Fe1	3.05	Ni1	2.07	Ni2	1.90

Figure 1. Optical and SEM images of FeUO_4 (a) and (c) and NiU_2O_6 (b) and (d).

Figure 2. View of MnUO_4 along b . Uranium and manganese polyhedra are shown in green and brown, respectively. The oxygen atoms are omitted for clarity.

Figure 3. The UO_6 (a) and MnO_6 (b) environments in MnUO_4 . Uranium, manganese, and oxygen polyhedra/atoms are shown in green, brown, and red, respectively.

Figure 4. View of FeUO_4 along c . Uranium and iron polyhedra are shown in green and brown, respectively. The oxygen atoms are omitted for clarity.

Figure 5. Polyhedral representation of (a) an individual layer, (b) the uranium environment, and (c) the iron environment in FeUO_4 . Uranium, iron, and oxygen polyhedra/atoms are shown in green, brown, and red, respectively.

Figure 6. View of the 3D structure of NiU_2O_6 , distinct layers are denoted by “a” and “b”. Uranium and nickel polyhedra are shown in green and brown, respectively. The oxygen atoms are omitted for clarity.

Figure 7. View of the layers in NiU_2O_6 . (a) layer containing U2 and Ni2 octahedra, (b) layer containing U1 and Ni1 octahedra, and the local environments of (c) U2 , (d) U1 , (e) Ni2 , and (f) Ni1 . Uranium, nickel, and oxygen polyhedra/atoms are shown in green, brown, and red, respectively.