I: Density Functional-Theory Calculations

I.1 Basic Methods

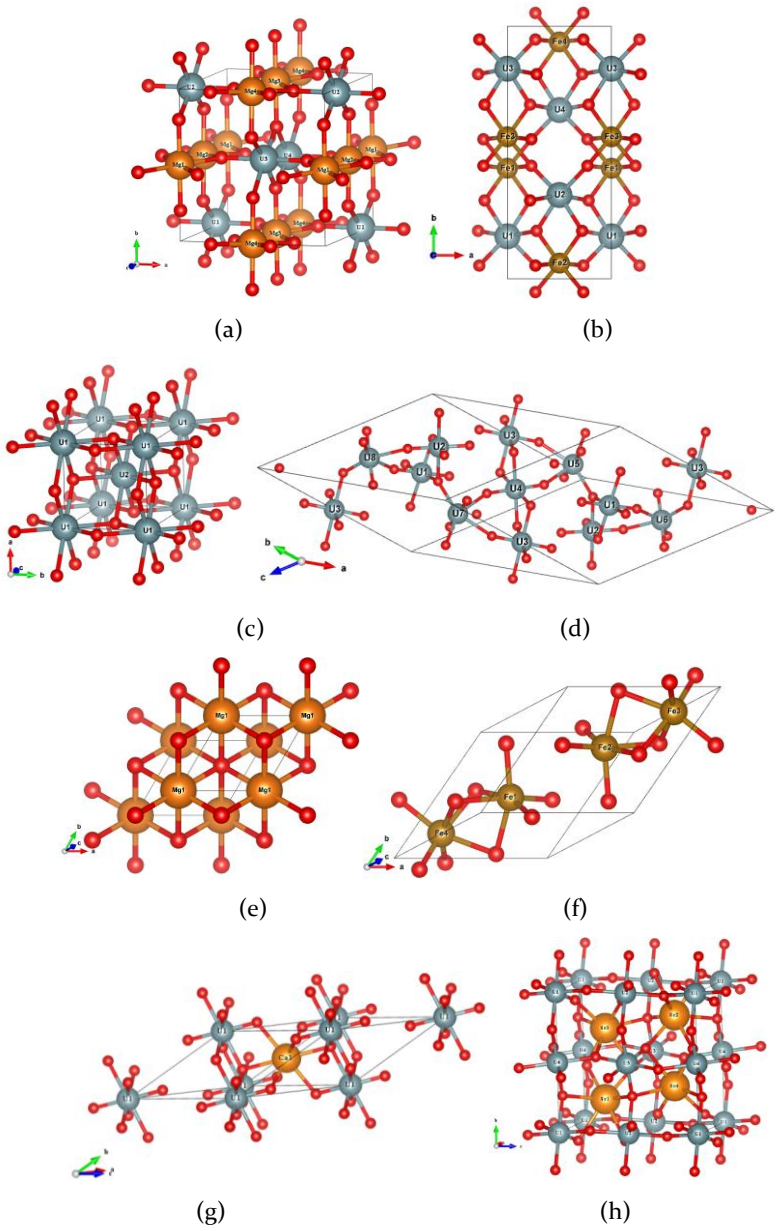

Figure S1 Atomic structures of uranates, uranium oxides and other (transition) metal oxides in supercells used for first-principles calculations. All cations are labeled according to the symmetry inequivalent sites. All O^{2-} are labeled in red color. (a): $Mg_4U_4O_{16}$ supercell with space group Iman. (b) $Fe_4U_4O_{16}$ supercell with space group *Pbcn*. The same structure is applied to $Cr_4U_4O_{16}$. (c): U_2O_4 supercell with CaF_2 structure (space group *Fm-3m*). (d): γ phase U_8O_{24} supercell with space group *I4₁/amd*. (e): MgO supercell with NaCl rocksalt (B1) structure (space group *Fm-3m*). The same structure is applied to CaO, SrO, and BaO. (f) Fe_4O_6 with corundum rhombohedral structure (space group *R-3c*). The same structure is applied to Cr_4O_6. (g) $CaUO_4$ supercell with space group *R-3m*. (h) $Sr_4U_4O_{16}$ supercell with space group *Pbcm*. The same structure is applied to $Ba_4U_4O_{16}$.

Supercells of uranates, uranium oxides and other metal oxides employed in the first-principles calculations are plotted in Fig. S1. For $MgUO_4$ in Fig. S1(a), the supercell (space group *Iman*) contains 4 Mg^{2+} cations and 4 U^{6+}

cations. For $CrUO_4$/$FeUO_4$ in Fig. S1(b), the supercell (space group *Pbcn*) contains 4 Cr^{3+}/Fe^{3+} cations and 4 U^{5+} cations. The supercells of all binary uranium oxides and metal oxides are plotted in Figs. S1(c) to (f). For $CaUO_4$ in Fig. S1(g), the supercell (space group *R-3m*) contains 1 Ca^{2+} cation and 1 U^{6+} cation. For $SrUO_4$ and $BaUO_4$ in Fig. S1(h), the supercell (space group *Pbcm*) contains 4 Sr^{2+}/Ba^{2+} cation and 4 U^{6+} cations. The supercell volume and shape were allowed to change during ionic relaxations.

I.2 Methods to Investigate Multiple Charge States

To study the stability of $FeUO_4$ with different charge states, we investigated two types of charge transfer reactions:

$$U^{5+} + Fe^{3+} \rightarrow U^{6+} + Fe^{2+}.$$

$$2\ U^{5+} \rightarrow U^{6+} + U^{4+}.$$

In both reactions, the charge transfer always occurs between two cations in the same supercell. We induce these charge transfer reactions inside the $FeUO_4$ supercell by employing the following procedure, which was also applied in a recent publication[1]. Starting from a ground state calculation with normal GGA+*U* parameters as U_0 = 4.0 and 4.3 eV for uranium and iron, respectively, we chose one pair of cations as the candidates for charge transfer reaction, and changed their local U values to $U_0 - 2\ dU$ and $U_0 + dU$ for the cation that is supposed to contribute and obtain one electron, respectively. With large values of d*U* imposed (several eV), we observed changes in local magnetic moments and projected density of states (pDOS) consistent with the transfer of an electron from one U^{5+} to the nearby Fe^{3+} or U^{5+} cation, resulting in the formation of U^{6+} and Fe^{2+}/U^{4+}, as described in the above reaction equations. After stabilizing this charge-transfer state, we performed a series of calculations in which the value of d*U* is decreased sequentially to zero, seeding each subsequent calculation for the new value of d*U* with the relaxed geometry and charge density from the previous calculation. The U^{6+} and Fe^{2+}/U^{4+} states remain metastable when $dU \rightarrow 0$. The energy of this final state was compared to that for the supercells with all U^{5+} and Fe^{3+} states, to compute the energy stabilities of $FeUO_4$ uranates with multiple charge states. Detailed analyses of pDOS for the cations at these different states are discussed in the main text.

II: Electron Probe Microanalysis Results

Table S1 Compositions of the synthesized monouranates obtained by EPMA.

	$MgUO_4$	$CrUO_4$	$FeUO_4$
Mg	7.26 ± 0.06 (16.27)*	--	--
Cr	--	14.18 ± 0.15 (16.25)	--
Fe	--	--	15.91 ± 0.19 (16.67)
U	73.67 ± 0.80 (16.87)	67.67 ± 0.79 (16.96)	67.80 ± 0.33 (16.67)

* wt. % with at. % in parenthesis. Uncertainty is two standard deviations of the mean.

III: X-ray Photoelectron Spectroscopic Results

Table S2 U oxidation states obtained from fitting XPS spectra of uranate samples.

Sample	U(VI)1		U(VI)2		U(VI)	U(V)		U
	mol %	BE(eV)	mol %	BE(eV)	total	mol %	BE(eV)	(apfu)
$MgUO_4$	nd*	nd	100.0	381.4	100.0	nd	nd	--
$CrUO_4$	16.9	382.3	32.4	381.4	49.3	50.7	380.2	0.98
$FeUO_4$	11.2	382.3	22.4	381.5	33.6	66.4	380.4	1.08

* nd: not detected.

IV: Thermochemical cycles for $MgUO_4$, $CrUO_4$ and $FeUO_4$

Table S3 Thermochemical cycles for determination of the enthalpies of formation of $MgUO_4$ from binary oxides at 25 °C (based on drop solution calorimetry in molten $3Na_2O{\cdot}4MoO_3$ at 702 °C).

Reaction	ΔH (kJ/mol)
(1) $MgUO_{4(s,\ 25\ °C)} \rightarrow UO_{3(sln,702\ °C)} + MgO_{(sln,702\ °C)}$	$\Delta H_1 = \Delta H_{ds}$ $= 37.92^{*} \pm 0.66^{\dagger}(9)^{\ddagger}$
(2) $\gamma\text{-}UO_{3(s,\ 25\ °C)} \rightarrow UO_{3(sln,\ 702\ °C)}$	$\Delta H_2 = 9.49 \pm 1.53(2)$ [2]
(3) $MgO_{(s,\ 25\ °C)} \rightarrow MgO_{(sln,\ 702\ °C)}$	$\Delta H_3 = -5.34 \pm 0.26(8)$ [3]
(4) $U_{(s,\ 25\ °C)} + 3/2O_{2(g,\ 25\ °C)} \rightarrow \gamma\text{-}UO_{3(s,\ 25\ °C)}$	$\Delta H_4 = -1223.8 \pm 0.8$ [4]
(5) $Mg_{(s,\ 25\ °C)} + 1/2O_{2(g,\ 25\ °C)} \rightarrow MgO_{(s,\ 702\ °C)}$	$\Delta H_5 = -601.6 \pm 0.3$ [5]
Thermochemical cycles	
(6) $\gamma\text{-}UO_{3(s,25\ °C)} + MgO_{(s,25\ °C)} \rightarrow MgUO_{4(s,\ 25\ °C)}$	
$\Delta H_{f,ox} = -\Delta H_1 + \Delta H_2 + \Delta H_3$	$\Delta H_6 = -33.8 \pm 1.7$
(7) $U_{(s,\ 25\ °C)} + Mg_{(s,\ 25\ °C)} + 2O_{2(g,\ 25\ °C)} \rightarrow MgUO_{4(s,\ 25\ °C)}$	
$\Delta H°_f = \Delta H_6 + \Delta H_4 + \Delta H_5$	$\Delta H_7 = -1859.2 \pm 1.9$

* Average; † Two standard deviations of the average value; ‡ Number of measurements.

Table S4 Thermochemical cycles for determination of the enthalpies of formation of $CrUO_4$ from binary oxides at 25 °C (based on drop solution calorimetry in molten $3Na_2O{\cdot}4MoO_3$ at 802 °C).

Reaction	ΔH (kJ/mol)
(1) $CrUO_{4\ (s,\ 25\ °C)} + 1/4O_{2(g,\ 802\ °C)} \rightarrow UO_{3(sln,\ 802\ °C)} + 1/2Cr_2O_{3(sln,\ 802\ °C)}$	$\Delta H_1 = \Delta H_{ds}$ $= -9.55 \pm 0.48(10)$
(2) $\gamma\text{-}UO_{3(s,\ 25\ °C)} \rightarrow UO_{3(sln,\ 802\ °C)}$	$\Delta H_2 = 26.11 \pm 1.47(5)$
(3) $UO_{2.06(s,\ 25\ °C)} + 0.47O_{2(g,802\ °C)} \rightarrow UO_{3(sln,\ 802\ °C)}$	$\Delta H_3 = -116.80 \pm 0.80(4)$
(4) $O_{2(g,\ 25\ °C)} \rightarrow O_{2(g,\ 802\ °C)}$	$\Delta H_4 = 25.4$ [6]
(5) $Cr_2O_{3(s,\ 25\ °C)} \rightarrow Cr_2O_{3(sln,\ 802\ °C)}$	$\Delta H_5 = 16.54 \pm 0.83(7)$
(6) $U_{(s,\ 25\ °C)} + O_{2(g,\ 25\ °C)} \rightarrow UO_{2(s,\ 25\ °C)}$	$\Delta H_6 = -1084.9 \pm 1.0$ [4]
(7) $U_{(s,\ 25\ °C)} + 3/2O_{2(g,\ 25\ °C)} \rightarrow \gamma\text{-}UO_{3(s,\ 25\ °C)}$	$\Delta H_7 = -1223.8 \pm 0.8$ [4]
(8) $2Cr_{(s,\ 25\ °C)} + 3/2O_{2(g,\ 25\ °C)} \rightarrow Cr_2O_{3(s,\ 25\ °C)}$	$\Delta H_8 = -1134.7 \pm 8.4$ [4]
Thermochemical cycles	
Cycle for calculating ΔH_{ds} of UO_2 correcting for oxidation	
(9) $UO_{2(s,\ 25\ °C)} + 1/2O_{2(g,\ 802\ °C)} \rightarrow UO_{3(sln,\ 802\ °C)}$	
$\Delta H_9 = \Delta H_{ds}(UO_2) = [\Delta H_3 - 0.06\Delta H_2]/0.94$	$\Delta H_9 = -128.64 \pm 1.61$
Cycle for calculating $\Delta H°_{oxidation}$ of UO_2	
(10) $UO_{2(s,\ 25\ °C)} + 1/2O_{2(g,\ 25\ °C)} \rightarrow \gamma\text{-}UO_{3(s,\ 25\ °C)}$	

Measured $\Delta H_{10} = \Delta H_9 - \Delta H_2 + 1/2\Delta H_4$	ΔH_{10} = 142.1 ± 2.2
Reference = $-\Delta H_6 + \Delta H_7$	(138.8 ± 1.3)
(11) $1/2\gamma\text{-}UO_{3(s,\ 25\ °C)} + 1/2UO_{2(s,\ 25\ °C)} + 1/2Cr_2O_{3(s,\ 25\ °C)} \rightarrow CrUO_{4\ (s,\ 25\ °C)}$	
$\Delta H_{f,ox} = -\Delta H_1 + 1/2\Delta H_9 + 1/2\Delta H_2 + 1/2\Delta H_5$	ΔH_{11} = -33.4 ± 1.3
(12) $U_{(s,\ 25\ °C)} + Cr_{(s,\ 25\ °C)} + 2O_{2(g,\ 25\ °C)} \rightarrow CrUO_{4\ (s,\ 25\ °C)}$	
$\Delta H°_f = \Delta H_{11} + \Delta H_7 + 1/2\Delta H_8$	ΔH_{12} = -1824.6 ± 4.5

Table S5 Thermochemical cycles for determination of the enthalpies of formation of $FeUO_4$ from binary oxides at 25 °C (based on drop solution calorimetry in molten $2PbO{\cdot}B_2O_3$ at 802 °C).

Reaction	ΔH (kJ/mol)
(1) $FeUO_{4\ (s,\ 25\ °C)} + 1/4O_{2(g,\ 802\ °C)} \rightarrow UO_{3(sln,\ 802\ °C)} + 1/2Fe_2O_{3(sln,\ 802\ °C)}$	$\Delta H_1 = \Delta H_{ds}$ = 74.08 ± 0.67(4)
(2) $\gamma\text{-}UO_{3(s,\ 25\ °C)} \rightarrow UO_{3(sln,\ 802\ °C)}$	ΔH_2 = 26.67 ± 4.02(2)[7]
(3) $UO_{2(s,\ 25\ °C)} + 1/2O_{2(g,802\ °C)} \rightarrow UO_{3(sln,\ 802\ °C)}$	ΔH_3 = -125.21 ± 3.41(6)[7]
(4) $1/3U_3O_{8(s,\ 25\ °C)} + 1/6O_{2(g,\ 25\ °C)} \rightarrow UO_{3(s,\ 25\ °C)}$	ΔH_4 = -32.2 ± 1.1[4]
(5) $Fe_2O_{3(s,\ 25\ °C)} \rightarrow Fe_2O_{3\ (sln,\ 802\ °C)}$	ΔH_5 = 182.29 ± 1.34(8)[8]
(6) $Fe_3O_{4(s,\ 25\ °C)} + 1/4O_{2(g,\ 802\ °C)} \rightarrow 3/2Fe_2O_{3\ (sln,\ 802\ °C)}$	ΔH_6 = 147.58 ± 1.12(8)[8]
(7) $O_{2(g,\ 25\ °C)} \rightarrow O_{2(g,\ 802\ °C)}$	ΔH_7 = 25.3[6]
(8) $U_{(s,\ 25\ °C)} + O_{2(g,\ 25\ °C)} \rightarrow UO_{2(s,\ 25\ °C)}$	ΔH_8 = -1084.9 ± 1.0[4]
(9) $U_{(s,\ 25\ °C)} + 3/2O_{2(g,\ 25\ °C)} \rightarrow \gamma\text{-}UO_{3(s,\ 25\ °C)}$	ΔH_9 = -1223.8 ± 0.8[4]
(10) $2Fe_{(s,\ 25\ °C)} + 3/2O_{2(g,\ 25\ °C)} \rightarrow Fe_2O_{3(s,\ 25\ °C)}$	ΔH_{10} = -826.2 ± 1.3[4]
Thermochemical cycles	
(11) $1/2\gamma\text{-}UO_{3(s,\ 25\ °C)} + 1/2UO_{2(s,\ 25\ °C)} + 1/2Fe_2O_{3(s,\ 25\ °C)} \rightarrow FeUO_{4\ (s,\ 25\ °C)}$	
$\Delta H_{f,ox} = -\Delta H_1 + 1/2\Delta H_2 + 1/2\Delta H_3 + 1/2\Delta H_5$	ΔH_{11} = -32.2 ± 2.8
(12) $1/3U_3O_{8(s,\ 25\ °C)} + 1/3Fe_3O_{4\ (s,\ 25\ °C)} \rightarrow FeUO_{4\ (s,\ 25\ °C)}$	
$\Delta H'_{f,ox} = -\Delta H_1 + (\Delta H_4 + \Delta H_2 - 1/6\Delta H_7) + 1/3\Delta H_6$	ΔH_{12} = -34.6 ± 4.2
(13) $U_{(s,\ 25\ °C)} + Fe_{(s,\ 25\ °C)} + 2O_{2(g,\ 25\ °C)} \rightarrow FeUO_{4\ (s,\ 25\ °C)}$	
$\Delta H°_f = \Delta H_{f,ox} + (\Delta H_8 + \Delta H_9)/2 + 1/2\Delta H_{10}$	ΔH_{13} = -1599.7 ± 3.0

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