Supporting Information for

Targeting Complex Plutonium Oxides by Combining Crystal Chemical Reasoning with Density-Functional Theory Calculations: The Quaternary Plutonium Oxide Cs$_2$PuSi$_6$O$_{15}$

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Description of Synthesis of $Cs_2PuSi_6O_{15}$:

Caution! Serious health risks are associated with handling plutonium, which is an α and γ emitter. Proper precautions must be taken. All studies were conducted in a laboratory designated for transuranics research. A 0.2 mL aliquot of a stock solution of weapons-grade plutonium (94% ^{239}Pu, 6% ^{240}Pu) in hydrochloric acid (0.097M in 8M HCl) was heated to dryness on a hot plate. The solid residue was then redissolved in 0.2 mL of 1M HCl to ensure complete conversion to the chloride form. To reduce to Pu(III), an excess of ascorbic acid (~10 mg) was added to the solution.

SiO$_2$ (99.9%, Alfa Aesar), CsCl (99%, Alfa Aesar), and CsF (99%, Alfa Aesar) were used as received. 43 μL of the plutonium chloride solution (4.17 μmol Pu) was dispensed into an 85 μL Pt/Rh DSC pan containing a mixture of 1.0 mg SiO$_2$ and 33.5 mg of a CsCl/CsF eutectic (19.3 mg CsCl, 14.2 mg CsF). The reaction mixture contained a 1 : 4 : 27.5 : 22.5 molar ratio of Pu : Si : Cl : F. The crucible was placed in a programmable furnace fitted with a nitrogen gas inlet to allow for a continuous nitrogen gas flow (~1 liter per minute) during heating. The reaction was first heated at 80°C for approximately two hours to dry the contents of the crucible. The crucible was then capped with a loosely fitting lid and the temperature was ramped to 800°C at a rate of 10°C per minute, followed by a dwell period of two hours at 800°C. The reaction was then slow-cooled to 400°C at a rate of 3°C per hour, at which point the furnace was shut off and allowed to cool to room temperature. Upon washing out residual salts from the flux with deionized water, the reaction product contained a mixture of amorphous material and pale blue hexagonal plates of $Cs_2PuSi_6O_{15}$.

Description of Synthesis of $Cs_2CeSi_6O_{15}$:

CeF$_3$ (99.9%, Alfa Aesar), SiO$_2$ (99.9%, Alfa Aesar), Al$_2$O$_3$ (99.98%, Alfa Aesar), CsCl (99%, Alfa Aesar), and CsF (99%, Alfa Aesar) were used as received. A mixture of 1.8 mg CeF$_3$, 235.3 mg SiO$_2$, 100.0 mg Al$_2$O$_3$, and 1.0 g of a CsCl/CsF eutectic (0.5 g CsCl, 0.5 g CsF) was added to a silver tube fused on one end and the tube was then crimped shut. The silver tube containing the reaction mixture was placed in a programmable furnace and heated to 900°C. The reaction dwelled at 900°C for 20 hours followed by a period of slow-cooling at 25°C per hour to 400°C, at which point the furnace was shut off and allowed to return to room temperature. Colorless blocks of $Cs_2CeSi_6O_{15}$ were obtained upon washing out residual salts from the flux with deionized water.

Description of Computational Details:

DFT calculations were carried out using the projector augmented plane-wave method[1] as implemented in the Vienna Ab Initio Simulation Package (VASP)[2–6] with calculation parameters equal to those used in the Open Quantum Materials Database (OQMD).[7, 8] This was done in order to ensure consistency when using their fitted atomic chemical potentials to calculate formation enthalpies. Each spin-polarized calculation used the Perdew-Burke-Ernzerhof generalized gradient approximation[9] with a Hubbard U correction[10] of 4.0 eV for the f-orbitals. The energy cut-off for the plane-wave basis was 600 eV with energy and force convergence criteria set to 10^{-6} eV and 10^{-3} eV/Å. Cold smearing[11] was used with a sigma value of 0.2 eV. A Monkhorst-Pack k-point mesh[12] was used with mesh sizes 8×8×5 and 7×5×4 for $A_2M\mathrm{Si}_3\mathrm{O}_9$ ($P6_3/m$ and $P2_1/n$, respectively) and 7×3×4 and 7×4×3 for $A_2M\mathrm{Si}_6\mathrm{O}_{15}$ ($Cmc2_1$ and $P1$, respectively).

Although some of the $A_2M\mathrm{Si}_6\mathrm{O}_{15}$ phases exhibit the $C2/c$ structure type, it is crystallographically very similar to $P\bar{1}$, where a slight distortion of the monoclinic structure results in a lowering of the symmetry. The $C2/c$ structure type is marginally different from the lowest symmetry $P1$ cell but contains twice as many atoms in the unit cell, and although entropy differences between the two unit cells may not be negligible, calculations were performed in $P1$ to reduce computational time.

Table S1. Formation enthalpies of $A_2M\mathrm{Si}_6\mathrm{O}_{15}$ versus $A_2M\mathrm{Si}_3\mathrm{O}_9$ (eV/atom)

$A_2M\mathrm{Si}_6\mathrm{O}_{15}$	$Cmc2_1$					$P1$				
	Ce	Th	U	Np	Pu	Ce	Th	U	Np	Pu
Na	-2.932	-3.069	-2.994	-2.886	-2.938	-2.937	-3.075	-2.964	-2.936	-2.940
K	-2.968	-3.113	-3.010	-2.977	-2.983	-2.980	-3.120	-3.011	-2.983	-2.988
Rb	-2.974	-3.120	-3.011	-2.983	-2.990	-2.983	-3.121	-3.014	-2.986	-2.991
Cs	-2.993	-3.135	-3.031	-2.999	-3.006	-2.991	-3.134	-3.024	-2.997	-3.002

$A_2M\mathrm{Si}_3\mathrm{O}_9$	$P6_3/m$					$P2_1/n$				
	Ce	Th	U	Np	Pu	Ce	Th	U	Np	Pu
Na	-2.859	-3.063	-2.895	-2.850	-2.856	-2.855	-3.060	-2.892	-2.847	-2.858
K	-2.910	-3.123	-2.959	-2.913	-2.923	-2.908	-3.121	-2.956	-2.910	-2.920
Rb	-2.908	-3.123	-2.958	-2.912	-2.921	-2.907	-3.122	-2.956	-2.909	-2.918
Cs	-2.923	-3.137	-2.969	-2.921	-2.929	--*	-3.137	-2.967	-2.919	-2.927

*Calculations for $Cs_2CeSi_3O_9$ in space group $P2_1/n$ did not converge.
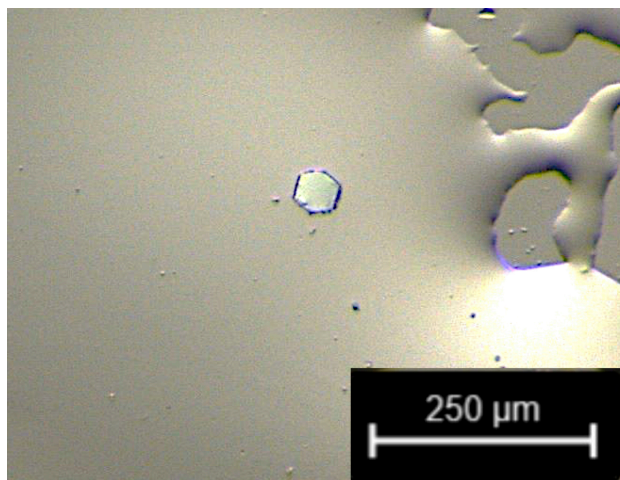
Fig. S1 A pale blue hexagonal plate of $Cs_2PuSi_6O_{15}$ in immersion oil.

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