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Targeting Complex Plutonium Oxides by Combining Crystal Chemical Reasoning with Density-Functional Theory Calculations: The Quaternary Plutonium Oxide $Cs_2PuSi_6O_{15}$

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The stability of the novel Pu(IV) silicate, $Cs_2PuSi_6O_{15}$, was predicted from a combination of crystal chemical reasoning and DFT calculations and confirmed by its synthesis via flux crystal growth. Formation enthalpies of the $A_2M\mathrm{Si}_6\mathrm{O}_{15}$ (A = Na-Cs; M = Ce, Th, U-Pu) compositional family were calculated and indicated the Cs-containing phases should preferentially form in the $Cmc2_1$ structure type, consistent with previous experimental findings and the novel phases produced in this work, $Cs_2PuSi_6O_{15}$ and $Cs_2CeSi_6O_{15}$. The formation enthalpies of a second set of compositions, $A_2M\mathrm{Si}_3\mathrm{O}_9$, were also calculated and a comparison between the two compositional families correctly predicted $A_2M\mathrm{Si}_6\mathrm{O}_{15}$ to be on average more stable than $A_2M\mathrm{Si}_3\mathrm{O}_9$.

The chemistry of the actinides, especially the transuranic (TRU) actinides such as plutonium, has not been extensively explored and, hence, developing viable approaches for their synthesis is desirable. The development of new complex TRU containing hierarchical structures is of interest for nuclear waste form applications, which prompted us to choose candidate compositions that have framework structures.[1] Thus, for this investigation of Pu containing materials, systems with silicate framework-forming anions were selected based on their structural versatility.[2] One approach to the synthesis of complex oxides with new compositions is via isovalent chemical substitution, where a cation in a given oxidation state is replaced by a different cation in the same oxidation state. For this synthesis to succeed, the two cations should have similar ionic radii and coordination preferences.[3] This type of approach utilizes *crystal chemical reasoning* where an understanding of ionic radius and charge allows the prediction of structures based on charge balance and minimal lattice strain. The technique is routinely applied to estimate the chances of successfully synthesizing a target composition with a specific structure. While often successful, subtle differences in size or coordination preferences can influence overall phase stability;[4, 5] especially in the case of *f*-elements,[6–9] where substitutional predictions are not as reliable as for other compound classes, such as *d*-element systems. We addressed this issue by performing density-functional theory (DFT) calculations, which together with our crystal chemical reasoning narrowed the choices of prospective plutonium containing oxide phases/structures.

Only a relatively small number of plutonium oxides are known, with most existing as binary and ternary compounds [10] along with a few complex quaternary phases.[6, 11–15] The challenges of working with radiological materials, however, impede extensive exploration of phase space, encouraging the combination of crystal chemical prediction with DFT calculations to guide selection of target phases suitable for the isovalent chemical substitution needed to prepare desired phase compositions. In this report, we highlight the synthesis of a novel plutonium silicate phase, $Cs_2PuSi_6O_{15}$, and describe the use of DFT calculations to correctly predict an observed trend in the structure types adopted by a series of analogous $A_2M\mathrm{Si}_6\mathrm{O}_{15}$ (A = Na–Cs, M = Ce, Th, U, Np, Pu) compositions.

Considering that silicates are among the most abundant and stable minerals, we selected the U(IV)-containing $A_2\mathrm{USi}_6\mathrm{O}_{15}$ (A = Alkali metals) system as a model to evaluate the theory-guided approach. Calculations for each possible combination of alkali and tetravalent metal in different structure types were carried out for the two most abundant compositions containing both silicate and alkali metal cations, $A_2M\mathrm{Si}_6\mathrm{O}_{15}$ and $A_2M\mathrm{Si}_3\mathrm{O}_9$ (A = Na–Cs, M = Ce, Th, U, Np, Pu). Orthorhombic $Cs_2PuSi_6O_{15}$ was calculated to be the most stable Pu-containing structure and was synthesized for the first time using a flux crystal growth method.

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† Electronic Supplementary Information (ESI) available: Synthesis descriptions for $Cs_2PuSi_6O_{15}$ and $Cs_2CeSi_6O_{15}$, computational details, formation enthalpies of $A_2M\mathrm{Si}_3\mathrm{O}_9$ versus $A_2M\mathrm{Si}_6\mathrm{O}_{15}$, image of $Cs_2PuSi_6O_{15}$ crystal. CCDC 1993971 and 2011479. For ESI and crystallographic data in CIF or another electronic format, see DOI: 10.1039/x0xx00000x

To accommodate Pu^{4+} cations, the systems needed to include a tetravalent element of similar size, such as Ce^{4+}, Th^{4+}, U^{4+}, and Np^{4+}. Additionally, the selected systems should contain alkali metal cations to allow the unit cell sizes to be optimized using alkali cations with appropriate ionic radii. Furthermore, given that silicate crystal growth requires either highly alkaline media or the presence of fluorine anions, inclusion of an alkali metal was considered necessary. With the aforementioned search criteria, two compositions were identified in the Inorganic Crystal Structure Database, $A_2MSi_6O_{15}$ and $A_2MSi_3O_9$, which were selected as our model systems.

The $A_2MSi_6O_{15}$ family comprises several compositions with two distinct structure types. The main difference between them is the topology of the silicate sheets, which can be clearly seen in Fig. 1. In $Cs_2USi_6O_{15}$ (sp. gr. $Cmc2_1$),[16] the silicate tetrahedra form a topology with 8-, 6-, and 4-membered rings, whereas in $A_2USi_6O_{15}$ (A = K and Rb, sp. gr. $C2/c$, and $Rb_2ThSi_6O_{15}$, sp. gr. $P\overline{1}$),[17] every second row of 4- and 6-membered rings has changed into a row of only 5-membered rings. This difference in topology likely affects the calculated formation enthalpy, so both were used as parent structures for our calculations. The $A_2MSi_3O_9$ phases adopt the Wadeite structure type, sometimes with slight symmetry distortions.[18] A high symmetry $P6_3/m$ model was used as a basis for calculations.

Our DFT calculations showed that $A_2MSi_6O_{15}$ is energetically favored over $A_2MSi_3O_9$ (Table S1, ESI†) by an average of 7 kJ/mol per atom. The thorium compounds, however, were nearly equal, i.e., the difference between A = K–Cs for the two compositional types does not exceed 0.25 kJ/mol per atom. Since DFT calculations provide only 0 K formation enthalpies, the stability must be influenced as well by the entropic contribution at the finite laboratory synthesis temperatures. This is supported by the fact that multiple $A_2ThSi_6O_{15}$ and $A_2ThSi_3O_9$ compositions have been reported, including $A_2ThSi_6O_{15}$ (A = Cs and Rb)[19, 20] and $A_2ThSi_3O_9$ (A = Cs, Rb, and K).[21, 22]

In order to probe the relative stability of the $A_2MSi_6O_{15}$ compositional family (A = Na, K, Rb, Cs; M = Ce, Th, U, Np, Pu), DFT was also used to calculate the formation enthalpies of the $P1$ and $Cmc2_1$ structure types. A comparison of the experimentally determined versus the DFT-optimized structure is shown in Fig. 2. Overall, the $Cmc2_1$ structure type was calculated to be more stable for Cs-containing $A_2MSi_6O_{15}$ compositions, while those containing lighter alkali cations were found to be more stable in $P1$, as shown in Fig. 3 and Table 1. The calculated formation enthalpies indicate a general trend in stability that is consistent with what has been experimentally observed. The previously known phases $Cs_2MSi_6O_{15}$ (M = Th and U) and $Rb_2ThSi_6O_{15}$/$A_2USi_6O_{15}$ (A = K and Rb) were correctly computed to crystallize in the $Cmc2_1$ and $C2/c$ structure types, respectively. We successfully synthesized the previously unknown phase $Cs_2CeSi_6O_{15}$, (see supporting information for experimental details, ESI†) which was also found to crystallize in the correctly predicted $Cmc2_1$ structure type. We argue that this trend occurs as a consequence of the different sized channels between the two structure types, and indeed, unit cell volumes for the $Cmc2_1$ structures are overall larger than those for the $C2/c$ structures, ranging from ~1580 – 1700 Å^3 for $Cmc2_1$ in comparison to ~1400 – 1650 Å^3 for $C2/c$.

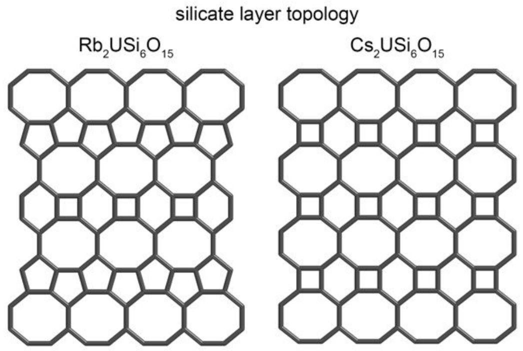

Fig. 1 Silicate sheet topologies in the two structure types of $A_2MSi_6O_{15}$.

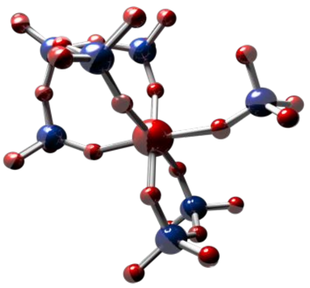

Fig. 2 The subtle differences between the experimental $Cs_2PuSi_6O_{15}$ structure (solid) versus the optimized structure (shadowed/semi-transparent) are shown.

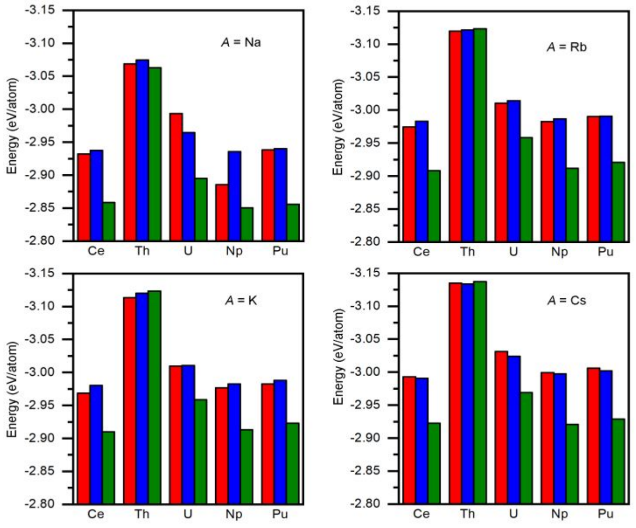

Fig. 3 Comparison of the DFT formation enthalpies where red, blue, and green represent energies of $A_2MSi_6O_{15}$ in $Cmc2_1$, $P1$, and Wadeite $A_2MSi_3O_9$, respectively.

Table 1 Comparison of DFT formation enthalpies for $A_2MSi_6O_{15}$ (A = Na-Cs; M = Ce, Th, U-Pu) in $Cmc2_1$ vs. $P1$

***Cmc*2₁**	Ce	Th	U	Np	Pu
Na	-27157	-28426	-27728	-26728	-27216
K	-27496	-28838	-27878	-27572	-27628
Rb	-27551	-28896	-27886	-27626	-27696
Cs	**-27722**	**-29038**	**-28077**	-27781	**-27843**
***P*1**					
Na	-27207	-28480	-27457	-27193	-27233
K	-27605	-28900	**-27886**	-27627	-27677
Rb	-27631	**-28912**	**-27919**	-27662	-27703
Cs	-27702	-29026	-28011	-27764	-27806

Formation enthalpies are expressed in kJ/mol. Dark green and bolded indicates polymorphs that are both experimentally observed and predicted to be stable from DFT, light green indicates polymorphs that have not yet been experimentally prepared but are predicted to be stable from DFT. No highlight indicates polymorphs predicted to be relatively less stable and are not known to exist (more stable polymorph predicted).

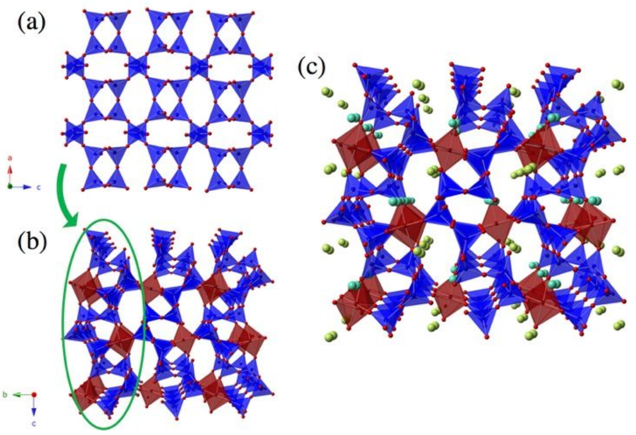

Fig. 4 (a) Silicate sheets compose (b) the framework of $Cs_2PuSi_6O_{15}$ which contains (c) disordered cesium cations, shown as light blue and green spheres, within the channels of the framework.

The effect of entropic contributions may increase energetic differences or change the predicted polymorph stability for all or some TRU compounds. However, computing the entropic contribution for each member of the two polymorphs would require vibration calculations on the 2x2x2 crystal cell. The additional computational time required to calculate this for all compositions would have been substantial. Given this constraint, we still generally find that calculations of the 0 K formation enthalpies were in fairly good agreement with observed trends for the existing phases and has proved adequate for our purposes.

To further investigate the preferred structure trend predicted by DFT calculations, crystallochemical analysis was utilized to compute the Voronoi polyhedra [23] of the alkali cation for each composition. The alkali bonding environment in each structure type was analyzed by comparing the radius of the spherical domain R_{sd}, an indication of the size of an atom in the selected structure.[24] Consistent with the notion that larger alkali cations will prefer larger sized channels, Table 2 demonstrates that the $Cmc2_1$ structure type gives rise to larger R_{sd} values for the alkali cation of each composition, suggesting that larger alkali cations should occupy the channels.

The results from DFT and crystallochemical calculations help to explain the experimental results, specifically the formation of $Cs_2PuSi_6O_{15}$ in the space group $Cmc2_1$. Its synthesis employed a modified small-scale flux growth method based on conditions for the synthesis of $A_2USi_6O_{15}$ (A = Rb, K);[17] a detailed description of the synthesis method is presented in the supporting information (ESI†). The product was a phase consisting of pale blue hexagonal plates (Fig. S1, ESI†) of $Cs_2PuSi_6O_{15}$ with ~5-10% yield. While the blue color is unusual for Pu(IV), there are a couple other examples in the literature where Pu(IV) compounds have been obtained as blue crystals.[9, 25]

$Cs_2PuSi_6O_{15}$ was structurally characterized by single crystal X-ray diffraction and, as expected, was determined to be isostructural to $Cs_2USi_6O_{15}$, crystallizing in the orthorhombic space group $Cmc2_1$ with lattice parameters a = 7.2509(2), b = 16.1708(3) and c = 13.4124(2) Å. There are 19 atoms within the asymmetric unit, including one plutonium atom, four silicon atoms, ten oxygen atoms, and four cesium atoms. The structure consists of a framework of PuO_6 octahedra connected via corner sharing to silicate sheets (Fig. 4a). Within the silicate sheets, SiO_4 tetrahedra form six-membered rings that are connected by a central four-member ring; adjacent sets of four- and six-membered rings are in turn joined by an eight-member ring in the perpendicular direction (Fig. 4b). Disordered cesium cations reside within the channels of the framework (Fig. 4c). Although six is an unusually low coordination number for plutonium, there are a few examples of Pu^{4+} adopting an octahedral coordination environment.[9, 26] An analysis of the bond distances in the structure of $Cs_2PuSi_6O_{15}$ indicates that they are consistent with Pu^{4+}, with d(Pu-O) ranging from 2.175-2.228 Å. The bond-

Table 2 Average calculated R_{SD} values for alkali cations in $A_2MSi_6O_{15}$ (A = Na-Cs; M = Ce, Th, U-Pu)

		Ce		Th		U		Np		Pu	
		*Cmc*2₁	*P*1	*Cmc*2₁	*P*1	*Cmc*2₁	*P*1	*Cmc*2₁	*P*1	*Cmc*2₁	*P*1
Avg. R_{SD}	Na	1.86	1.75	1.84	1.77	2.02	1.75	1.98	1.77	1.84	1.77
	K	1.99	1.84	1.94	1.84	2.02	1.90	1.97	1.88	1.96	1.85
	Rb	2.02	1.90	1.98	1.89	2.01	1.88	2.00	1.90	1.99	1.90
	Cs	2.04	1.99	2.01	1.97	2.02	1.95	2.01	1.97	2.01	1.97

valence sum at the Pu1 site, calculated using the parameters R_0 = 2.09 and B = 0.35,[27] was determined to be 4.38.

In summary, we report on the synthesis of the novel complex plutonium oxide $Cs_2PuSi_6O_{15}$, by flux crystal growth methods. Relative phase stability was assessed through a comparison of the DFT-calculated formation enthalpies of alkali and lanthanide/actinide-containing analogs of the candidate structure types, $A_2MSi_6O_{15}$ and $A_2MSi_3O_9$. A general trend in the $A_2MSi_6O_{15}$ preferred structure type emerged wherein only the compositions containing larger Cs cations were favored to form in $Cmc2_1$ while those containing smaller alkali cations were favored to form in $P1$. This trend is consistent with previous reports and was further confirmed in this work through the synthesis of $Cs_2PuSi_6O_{15}$ and $Cs_2CeSi_6O_{15}$, which both crystallize in the expected $Cmc2_1$ structure type. Future investigations will focus on the targeted synthesis of other TRU element-containing members within this extensive structural family in an effort to expand the currently limited database of known complex actinide compounds.

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Conflicts of interest

There are no conflicts to declare.

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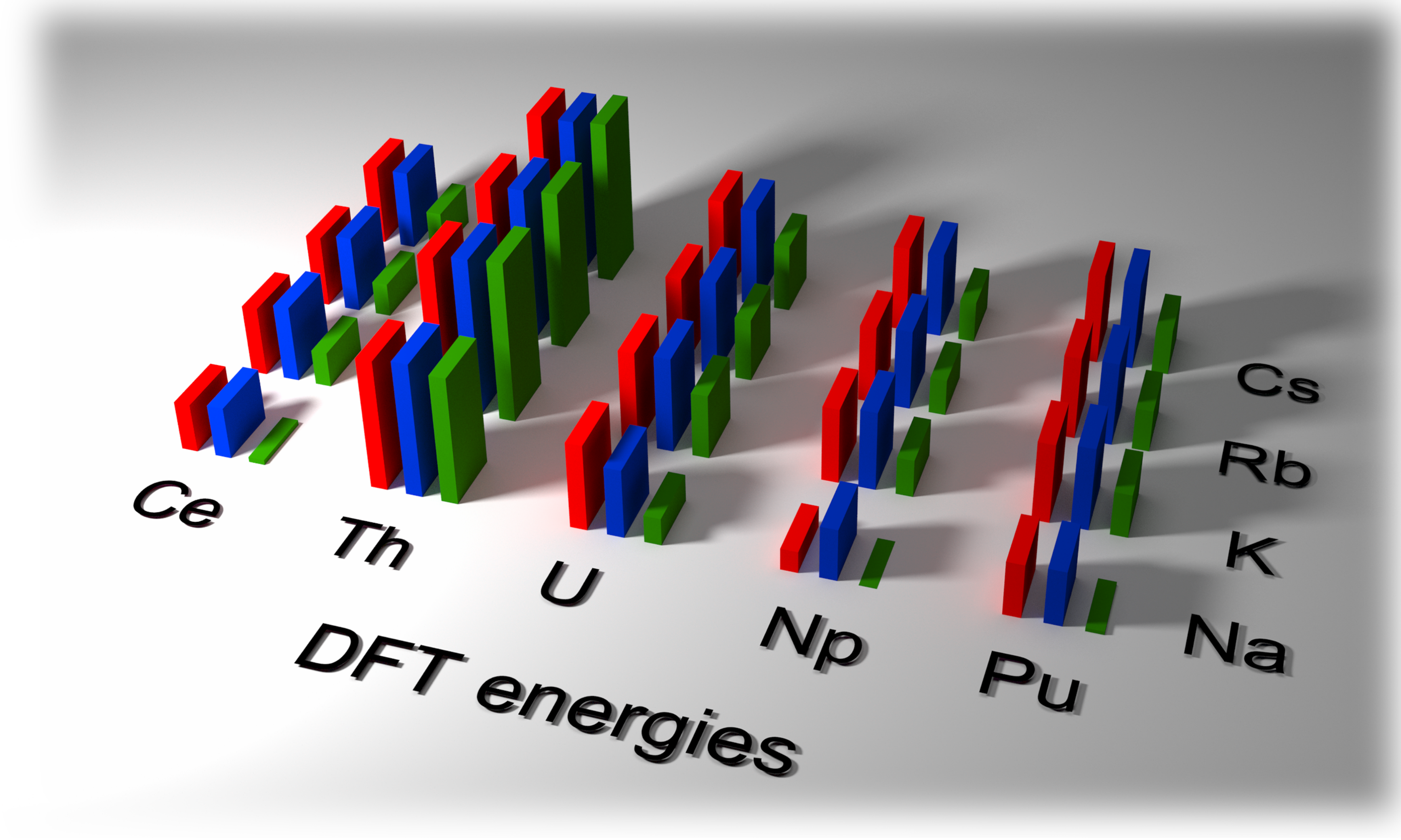
Ce
Th
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Cs
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DFT energies