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$Cs_2USi_6O_{15}$: A Tetravalent Uranium Silicate

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S *Supporting Information*

ABSTRACT: A uranium(IV) silicate has been synthesized under high-temperature, high-pressure hydrothermal conditions. The structure consists of unbranched dreier single layers with the composition $[Si_2O_5]$ that are connected by UO_6 octahedra to form a 3D framework with 7-ring channels where the Cs^+ cations are located. Each UO_6 octahedron spans four neighboring dreier single chains and, therefore, introduces a high degree of corrugation in the silicate layers. The U 4f X-ray photoelectron spectroscopy spectrum was measured to confirm the valence state of the uranium. A comparison of related metal silicate structures is made. After the synthesis of this compound, all members in the family of uranium silicates and germanates with oxidation states of uranium from 4+ to 6+ have been observed.

Uranium exhibits oxidation states from 3+ to 6+, although uranium(IV) and -(VI) are more common.[1] The U^{3+} ion is a powerful reducing agent. Uranium(V) is somewhat unstable with respect to the disproportionation reaction. The U^{6+} cation is almost always present as part of a uranyl ion, UO_2^{2+}, which is linear or nearly so. Uranyl silicates are the most abundant group of uranyl minerals in many occurrences and, in addition, a large number of synthetic uranyl silicates have been reported.[2,3] In contrast, only two naturally occurring uranium(IV) silicates, namely, coffinite, $USiO_4$, and arapovite, $U^{4+}(Ca,Na)_2(K_{1-x}\square_x)[Si_8O_{22}]$ ($\square$ denotes vacancy), were discovered.[4,5] After uraninite (UO_{2+x}), coffinite is the most important ore mineral for uranium. The structure of coffinite was reported for a synthetic crystal to be a tetragonal orthosilicate isostructural with zircon, $ZrSiO_4$. To our knowledge, no other uranium(IV) silicate was reported, whereas a uranium(IV) germanate, $UGeO_4$, has been synthesized by a solid-state reaction.[6] Following our previous work on the synthesis of uranium(V) and mixed-valence uranium(IV,V), -(IV,VI), -(V,VI), and -(IV,V,VI) silicates and germanates under high-temperature, high-pressure hydrothermal conditions,[7] we report in this paper the first synthetic tetravalent uranium silicate, $Cs_2USi_6O_{15}$ (denoted as **1**). The synthesis, crystal structure, and X-ray photoelectron spectroscopy (XPS) are reported.

High-temperature, high-pressure hydrothermal synthesis was performed in gold ampules contained in a Leco Tem-Pres autoclave where the pressure was provided by water. The degree of filling of the autoclave by water at room temperature was 55%. A reaction mixture of 0.531 mL of 10 M CsF(aq), 30.7 mg of UO_3, 39.4 mg of SiO_2, and 1.9 mg of Al (molar ratio Cs:U:Si:Al = 50:1:6:0.6) in a 6.9-cm-long gold ampule (inside diameter = 0.48 cm) was heated at 600 °C for 2 days. Aluminum metal was included in the reaction mixture as a reducing agent. The pressure was estimated to be 165 MPa at the reaction temperature according to the pressure—temperature diagram of pure water. The autoclave was then cooled to 350 °C at 5 °C h^{-1} and quenched at room temperature by removing the autoclave from the furnace. The product was filtered off, washed with water, rinsed with ethanol, and dried at ambient temperature. The reaction produced light-green block crystals of **1** as a major product along with some colorless quartz crystals and yellow crystals of a new uranium(VI) silicate, $Cs_2UO_2Si_4O_{10}$.[8] A qualitative energy-dispersive X-ray (EDX) analysis of several light-green crystals did not reveal any fluorine or aluminum and confirmed the presence of cesium, uranium, and silicon. A suitable light-green crystal was selected for single-crystal X-ray diffraction analysis, from which the chemical formula was determined.[9] The light-green crystals were manually separated from the side products, giving a pure sample, as indicated by powder X-ray diffraction (PXRD; Figure S1 in the Supporting Information). The yield was 49% based on uranium. The thermal stability of **1** has been investigated by heating a powder sample in a platinum crucible in air for 1 h at certain temperatures, then cooling to room temperature, and measuring the PXRD patterns. The results (Figure S2 in the Supporting Information) indicate that the framework structure is retained at 700 °C and begins to decompose at about 800 °C.

The U 4f XPS spectrum of **1** is shown in Figure 1, which was fitted with one component and satellite peaks. The binding energies (BEs) of all peaks were referenced to the adventitious C 1s at 285 eV. The fitting parameters are given in Table S1 and Figure S3 in the Supporting Information. The primary peak positions were at 379.7 eV (U $4f_{7/2}$) and 390.5 eV (U $4f_{5/2}$), which are comparable with those for surface-bound U^{4+} and the U^{4+} in a mixed-valence uranium silicate[10,7d] but are a little lower than those for the U^{4+} in $U(C_2O_4)_2 \cdot 6H_2O$ and UO_2.[7e,11] For uranium, both U 4f peaks show satellites at higher BEs: 6—7 eV for U^{4+}, 7.8—8.5 eV for U^{5+}, and 4 and 10 eV for U^{6+}.[12] The separations between the satellites and primary peaks for **1** are 6.23 and 6.13 eV, which are in good agreement with the values for U^{4+}. The XPS spectrum confirms the presence of U^{4+} in **1**.

The structure of **1** is constructed from the following structural elements: one UO_6 octahedron, four SiO_4 tetrahedra, and two Cs sites. Both Cs atoms, U(1), Si(1), and Si(4) lie on mirror planes. The observed Si—O bond lengths (1.564—1.619 Å) and O—Si—O bond angles (104.9—112.9°) are typical values and are within the normal range.[13] In contrast to the uranium(VI) compounds, which contain two strongly bonded uranyl O atoms with U—O bond lengths of ~1.8 Å, the $U(1)O_6$ octahedron in **1** is considerably more regular, with d(U—O) in the range from 2.209(6) to 2.256(4) Å. Therefore, **1** is not a uranyl compound.

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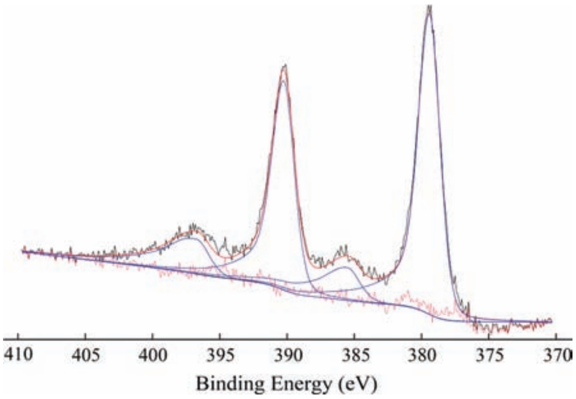

Figure 1. U 4f XPS spectrum of **1** (black —, data; red —, fit envelop; blue —, main peaks and satellites; red · · ·, deviation).

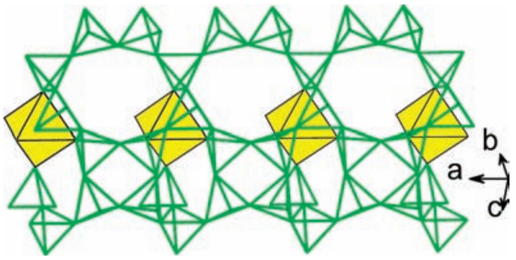

Figure 2. Section of a silicate layer in **1** showing the connectivity between the layer and UO_6 octahedra.

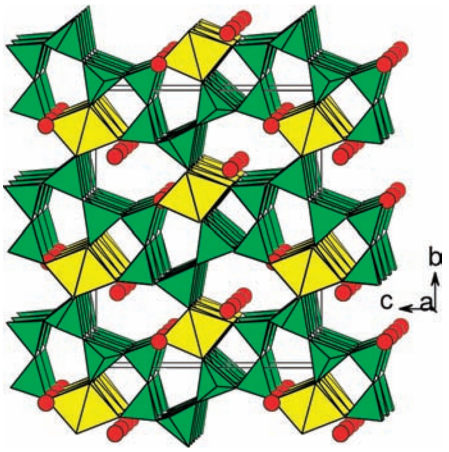

Figure 3. Structure of **1** viewed along the *a* axis. The yellow and green polyhedra are UO_6 octahedra and SiO_4 tetrahedra, respectively. Red circles are Cs atoms.

The mean U—O bond length of 2.242 Å is somewhat longer than that expected for an octahedron that contains only U^{5+}. The U^{4+} cation typically occurs in mineral structures in regular coordination polyhedra that contain from six to eight ligands. The predicted six-coordinate U^{4+}—O bond length is 2.25 Å according to the effective ionic radii provided by Shannon.[14] The bond-valence sum at the U(1) site in the structure of **1**, calculated by using the parameters R_{ij} = 2.051 Å and b = 0.519 Å,[15] is 4.16, consistent with the presence of a U^{4+} ion in this site. Therefore, the electroneutrality principle, polyhedral geometry, bond-valence sum, and XPS indicate that **1** is a uranium(IV) silicate. Both Cs sites are fully occupied and ordered. The coordination number of the Cs^+ cation was determined on the basis of the maximum cation—anion distance by Donnay and Allmann.[16] A limit of 3.70 Å was set for Cs—O interactions, which gives coordination numbers of 11 and 7 for Cs(1) and Cs(2), respectively. Cs(2) has an additional five neighboring O atoms at distances from 3.733 to 3.783 Å. The coordination environments of the Cs^+ cations are shown in Figure S4 in the Supporting Information.

The SiO_4 tetrahedra share three of their four O corners with a corner of a neighboring SiO_4 group to form corrugated silicate single layers with the composition [Si_2O_5] in the *ac* plane containing four-, six-, and eight-membered rings (Figure 2). The fourth corner is unshared, being bonded to uranium cations. According to the definition of the layer types based on the periodicity of the fundamental chain from which the layer can be generated by successive linking of these chains,[13] the [Si_2O_5] layer in **1** is an unbranched dreier single layer. Condensation of two dreier single chains produces a dreier double chain with eight-membered rings. Further condensation of the dreier double chains forms the unbranched dreier single layer.

Similar single layers were found in the minerals armstrongite, $CaZrSi_6O_{15}$,[17] and dalyite, $K_2ZrSi_6O_{15}$,[18] the synthetic neodymium silicates, α-$K_3NdSi_6O_{15}\cdot 2H_2O$ and β-$K_3NdSi_6O_{15}$,[19] the thorium silicate, $Cs_2ThSi_6O_{15}$,[20] and the indium germanate incorporating an organic amine ligand, γ-$In_2Ge_6O_{15}(NH_2CH_2CH_2NH_2)_2$,[21] disregarding the directedness of the silicate or germanate tetrahedra. The layers in dalyite and indium germanate are significantly distorted from the idealized rectangular nets that are characteristic of the other four structures. In the structure of **1**, the UO_6 octahedra link two neighboring unbranched dreier single layers to form a 3D framework with 4-, 5-, and 7-ring channels parallel to the *a* axis (Figure 3). The Cs^+ cations are located near the edge of the 7-ring channels. The octahedra around U^{4+} cations derive four of their O atoms from a silicate layer and the remaining two from the neighboring layer. In contrast, in all of the above-mentioned silicate minerals and the synthetic neodymium silicates, three of the six O atoms in MO_6 (M = Zr, Nd) derive from a silicate layer and the remaining three from the other layer. The manner in which the UO_6 octahedra are linked to the silicate layers in **1** is the same as those in the thorium silicate, $Cs_2ThSi_6O_{15}$, and the beryllium silicate, $K_2Be_2Si_6O_{15}$,[22] where the two BeO_4 tetrahedra share an edge in such a way that six O atoms effectively form a distorted octahedron about each pair of Be atoms. In the structure of **1**, each UO_6 octahedron spans four neighboring dreier single chains and, therefore, introduces a high degree of corrugation in the silicate layers.

In summary, we have synthesized a uranium(IV) silicate by a high-temperature, high-pressure hydrothermal method and characterized its structure by single-crystal X-ray diffraction and XPS. The compound consists of corrugated unbranched dreier single layers with the composition [Si_2O_5] that are connected by UO_6 octahedra to form a 3D framework, whose structure is related to those of zirconium silicate minerals, armstrongite and dalyite, and several synthetic neodymium and thorium silicates. It is the first known synthetic uranium(IV) silicate, whereas two naturally occurring uranium(IV) silicates, namely, coffinite and arapovite, exist. Previously, we have synthesized a good number of uranyl silicates, several uranium(V) silicates, and mixed-valence uranium(IV,V), -(IV,VI), -(V,VI), and -(IV,V,VI) silicates and germanates. After the synthesis of **1**, all members in the family of uranium silicates or germanates with oxidation states of uranium from 4+ to 6+ have been observed.

ASSOCIATED CONTENT

Supporting Information. Crystallographic data for $Cs_2USi_6O_{15}$ in CIF format, PXRD patterns, and fitting parameters of XPS data. This material is available free of charge via the Internet at http://pubs.acs.org.

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(8) Crystallographic data for $Cs_2UO_2Si_4O_{10}$: orthorhombic, space group *Cmca* (No. 64), $Z = 12$, $M_r = 808.21$, $a = 7.7156(3)$ Å, $b = 19.8719(8)$ Å, $c = 24.016(1)$ Å, $V = 3682.2(3)$ Å^3, $D_{calc} = 4.374$ g cm^{-3}, $\lambda = 0.710\,73$ Å, $\mu = 19.52$ mm^{-1}, 2134 unique reflections with $I > 2\sigma(I)$ ($2\theta_{max} = 56.71°$; $R_{int} = 0.0345$), $\Delta\rho_{max,min} = +2.85, -2.43$ e Å^{-3}, R1 = 0.0276, wR2 = 0.0637, and GOF = 1.048. The 3D framework structure of this uranyl silicate contains 4-, 8-, and 12-ring channels.

(9) Crystallographic data for $Cs_2USi_6O_{15}$: orthorhombic, space group $Cmc2_1$ (No. 36), $Z = 4$, $M_r = 912.39$, $a = 7.2717(3)$ Å, $b = 16.3061(7)$ Å, $c = 13.4983(6)$ Å, $V = 1600.5(1)$ Å^3, $D_{calc} = 3.786$ g cm^{-3}, $\lambda = 0.710\,73$ Å, $\mu = 15.15$ mm^{-1}, 1784 unique reflections with $I > 2\sigma(I)$ ($2\theta_{max} = 56.61°$; $R_{int} = 0.0373$), $\Delta\rho_{max,min} = +1.88, -1.80$ e Å^{-3}, R1 = 0.0225, wR2 = 0.0447, and GOF = 1.073.

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