Inorganic Chemistry
COMMUNICATION
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$Cs_4UGe_8O_{20}$: A Tetravalent Uranium Germanate Containing Four- and Five-Coordinate Germanium

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S Supporting Information

ABSTRACT: A very rare tetravalent uranium germanate has been synthesized under hydrothermal conditions at 585 °C and 160 MPa. Its structure contains layers of single-ring $Ge_3O_9^{6-}$ germanate anions that are connected by UO_6 octahedra and dimers of edge-sharing GeO_5 trigonal bipyramids to form a three-dimensional framework with intersecting 6- and 7-ring channels. UV–visible, photoluminescence, and U 4f X-ray photoelectron spectroscopy were used to confirm the valence state of uranium.

Compounds of uranium can be isolated in all oxidation states from 3+ to 6+, although uranium(VI) is the most common.[1] Uranyl silicates are an important group of uranium(VI) minerals found in the altered zones of many uranium deposits. Uranyl silicates have also attracted considerable interest because they are formed when spent nuclear fuel reacts with silicon-containing water under oxidizing conditions.[2] In the past 10 years, a large number of uranyl silicates and germanates that contain alkali metals as countercations have been synthesized,[3] and an organically templated uranyl silicate has also been reported.[4] The U^{3+} ion is a powerful reducing agent. No uranium(III) silicate or germanate has been reported. The pentavalent uranium is metastable and exists as the UO_2^+ species in a narrow pH range. Recently, we isolated several uranium(V) and mixed-valence uranium(IV,V), -(V,VI), -(IV,VI), and -(IV,V,VI) silicates and germanates.[5,6] Although uranium(IV) is more common, few uranium(IV) silicates and germanates have been reported. Two uranium(IV) silicate minerals, namely, coffinite, $USiO_4$, and arapovite, $U^{4+}(Ca,Na)_2(K_{1-x}\square_x)[Si_8O_{20}]$ (□ denotes vacancy), were discovered,[7] whereas uranium(IV) germanate, $UGeO_4$, was synthesized by a solid-state reaction.[8] Recently, we reported the first synthetic uranium(IV) silicate, $Cs_2USi_6O_{15}$,[9] whose structure is closely related to that of $Cs_2ThSi_6O_{15}$ and several neodymium and zirconium silicates.[10] Herein, we report a tetravalent uranium germanate, $Cs_4UGe_8O_{20}$ (denoted as **1**), which adopts a new structure and contains four- and five-coordinate germanium.

High-temperature, high-pressure hydrothermal synthesis was performed in gold ampules contained in a Tem-Pres autoclave where the pressure was provided by water. Typically, a reaction mixture of 236 μL of 10 M CsF(aq), 295 mg of CsI, 22.5 mg of UO_3, 2.1 mg of Al, and 117 mg of GeO_2 (molar ratio Cs:U:Al:Ge = 44:1:1:14) in a 3.6-cm-long gold ampule (inside diameter = 0.48 cm) was placed in an autoclave and counterpressured with water at a fill level of 55%. Aluminum metal was included in the reaction mixture as a reducing agent. The autoclave was heated at 585 °C for 2 days, cooled to 350 °C at 2 °C/h, and then quenched to room temperature by removal from the furnace. The pressure at 585 °C was estimated to be 160 MPa according to the $P-T$ diagram of pure water. 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 the major phase together with some colorless crystals of unidentified materials. A qualitative energy-dispersive X-ray analysis of several light-green crystals did not show any aluminum or fluorine and confirmed the presence of cesium, uranium, and germanium. A suitable crystal was selected for single-crystal X-ray diffraction, from which the chemical formula was determined.[11] The light-green crystals were manually separated from the others, giving a pure sample as indicated by powder X-ray diffraction (PXRD; Figure S1 in the Supporting Information). The yield of **1** was 68% based on uranium.

The absorption spectrum of **1** in the UV–visible range is shown in Figure 1a. The shoulder at about 450 nm and three absorption bands at 483–522, 560, and 584–686 nm correspond to the multiplets of $^3P_2$, $^1I_6$, $^3P_1$, and a mixture of several levels of $^1G_4$, $^1D_2$, and $^3P_0$. All of these absorption values are in agreement with those of U^{4+} in the literature.[12] The photoluminescence spectrum of **1** (Figure 1b) consists of two broad bands centered at 511 and 534 nm, which correspond to the transition of $^1I_6 \rightarrow {}^3H_4$ in the U^{4+} ions.[13]

The valence state of uranium in **1** was analyzed by X-ray photoelectron spectroscopy (XPS). The U 4f XPS spectrum is shown in Figure 2, which is fitted with one component of U^{4+} together with its satellites. The fitting data are given in Table S1 in the Supporting Information. The binding energies (BEs) of all of the peaks were referenced to the adventitious C 1s at 285.0 eV. The BEs of the primary peaks were at 379.96 eV (U $4f_{7/2}$) and 390.80 eV (U $4f_{5/2}$), which are comparable to those of U^{4+} in UO_2 and $Cs_2USi_6O_{15}$.[14,9] 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+}.[15] The separations between the satellites and primary peaks for **1** are 6.91 and 6.95 eV, which are in good agreement with the values for U^{4+}. Therefore, the XPS spectrum confirms the presence of U^{4+} in **1**.

Compound **1** is constructed from the following distinct structural units: one UO_6 octahedron, one GeO_5 trigonal bipyramid, three GeO_4 tetrahedra, and two Cs sites. U(1) is at

Received: August 17, 2011
Published: September 22, 2011

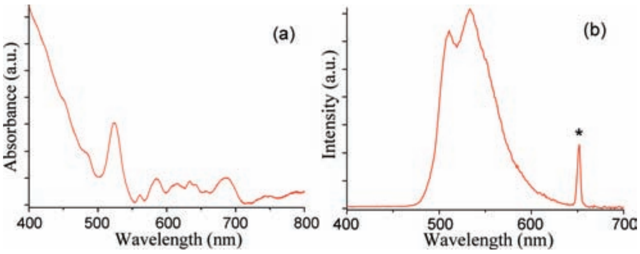

Figure 1. UV−visible absorption spectrum (a) and room-temperature photoluminescence spectrum excited at 325 nm (b) of **1**. The asterisk denotes the overtone at 650 nm.

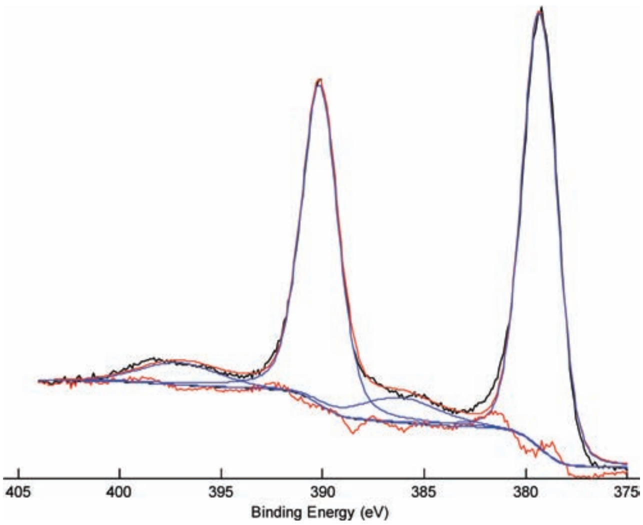

Figure 2. U 4f spectrum of **1**. The black, red, and blue curves are the data, fit envelope, and main peaks accompanied with the satellites, respectively. The red dotted curve is the deviation.

an inversion center, and the other atoms are in general positions. The U(1)O_6 octahedron is rather regular, with the U−O bond lengths ranging from 2.197(3) to 2.277(3) Å with an average value of 2.237 Å, which is close to the predicted value of 2.24 Å for the U^{4+}−O bond according to the effective ionic radius for a six-coordinate U^{4+} ion.[16] The bond valence sum at the U(1) site, calculated using the bond parameters R_{ij} = 2.051 Å and b = 0.519 Å, gives 4.20 valence unit (vu) which is consistent with the presence of the U^{4+} ion in this site.[17a] Therefore, the electroneutrality principle, polyhedral geometry, bond valence sum, and spectroscopy measurements confirmed that **1** is a tetravalent uranium compound. The bond valence sums at all Ge sites are in the range of 3.98−4.07 vu, which are in accordance with the valence state of the Ge atoms.[17b]

The Ge(1) atom is bonded to five O atoms in the geometry of a distorted trigonal bipyramid according to the calculated geometric parameter of 0.83, as defined by Addison et al.[18] The GeO_5 trigonal bipyramid contains two longer apical Ge−O bonds of 1.878(2) and 1.880(2) Å and three shorter equatorial Ge−O bonds of 1.777(2)−1.809(2) Å. Two trigonal bipyramids share a common edge to form a Ge_2O_8 dimer. The GeO_4 tetrahedra are regular. The observed Ge−O bond lengths and O−Ge−O bond angles are typical values and are within the normal range. Ge can exhibit GeO_4 tetrahedra, GeO_5 trigonal bipyramids, and GeO_6 octahedra owing to its larger atomic radius. For example, chains of corner-sharing GeO_5 trigonal bipyramids are observed in the uranyl germanate $Ag_2(UO_2)_3(GeO_4)_2(H_2O)_2$.[3d] To our knowledge, **1** is the first uranium germanate that contains both four- and five-coordinate germanium.

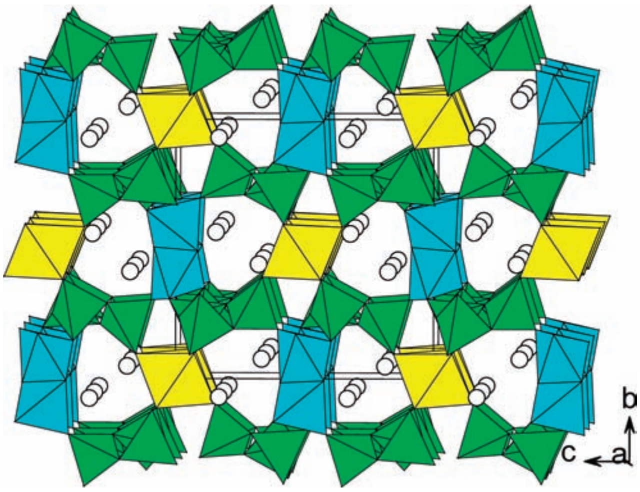

Figure 3. Structure of **1** viewed along the *a* axis. The yellow, cyan, and green polyhedra are UO_6 octahedra, GeO_5 trigonal bipyramids, and GeO_4 tetrahedra, respectively. The open circles are Cs atoms.

Each GeO_4 tetrahedron shares two O atoms with two others to form discrete three-membered single-ring $Ge_3O_9{}^{6-}$ germanate anions in the *ac* plane. Adjacent layers of $Ge_3O_9{}^{6-}$ rings are connected by UO_6 octahedra and Ge_2O_8 dimers to form a three-dimensional framework with 7-ring channels along the *a* axis (Figure 3). The octahedra around U^{4+} cations derive three of their O atoms from a germanate layer and the remaining three from the neighboring layer. The manner in which the Ge_2O_8 dimers are linked to the germanate layers is similar to that for the UO_6 octahedra. Six-membered ring channels are also formed along the [101] direction. Both of the Cs sites are fully occupied, ordered, and located at the intersections of the six- and seven-membered ring channels. On the basis of the maximum cation−anion distance given by Donnay and Allmann,[19] a limit of 3.70 Å was set for Cs−O interactions, which gives a coordination number of 8 for both $Cs(1)^+$ and $Cs(2)^+$ cations. Cs(1) has two additional neighboring O atoms at distances of 3.752(3) and 3.785(3) Å, whereas Cs(2) has one at 3.711(3) Å. Bond valence sums at the Cs(1) and Cs(2) sites are 0.83 and 0.91 vu, respectively.[17b]

In summary, we have synthesized and structurally characterized a very rare tetravalent uranium germanate. Its structure contains layers of single-ring $Ge_3O_9{}^{6-}$ germanate anions that are connected by UO_6 octahedra and dimers of edge-sharing GeO_5 trigonal bipyramids to form a three-dimensional framework with intersecting 6- and 7-ring channels. The high-temperature, high-pressure hydrothermal method facilitates crystal growth and the formation of compounds with elements in oxidation states that are difficult to attain and has been successfully used in the uranium silicate and germanate systems. Further research to synthesize new uranium compounds with novel frameworks and unusual oxidation states is in progress.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information. X-ray crystallographic data in CIF format, PXRD patterns, and the U 4f XPS fitting parameters.

This material is available free of charge via the Internet at http://pubs.acs.org.

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ACKNOWLEDGMENT

We thank the National Science Council of Taiwan for support and S.-L. Cheah and Pei-Ci Jhang at NTHU for assistance in the XPS and photoluminescence measurements.

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(11) Crystal data of $Cs_4UGe_8O_{20}$: A total of 9344 reflections of a light-green block crystal with dimensions of 0.15 × 0.12 × 0.12 mm^3, monoclinic, $P2_1/n$ (No. 14), a = 7.4320(4) Å, b = 12.3777(6) Å, c = 12.2351(6) Å, β = 90.134(2)°, V = 1125.52(10) $Å^3$, Z = 2, ρ_{calc} = 4.929 $g \cdot cm^{-3}$, and μ(Mo Kα) = 24.151 mm^{-1} were measured on a Kappa Apex II diffractometer at 296 K, which gave 2823 independent reflections with R(int) = 0.0313. An empirical absorption correction based on the symmetry equivalent was applied with T_{min}/T_{max} = 0.6063/0.7457. The final cycles of refinement converged at R1 = 0.0166, wR2 = 0.0430, and GOF = 1.013 with 152 parameters, $\rho_{max,min}$ = +1.079/−1.469 $e \cdot Å^{-3}$.

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