J|A|C|S
COMMUNICATIONS

$Cs_2K(UO)_2Si_4O_{12}$: A Mixed-Valence Uranium(IV,V) Silicate

Cheng-Shiuan Lee,[†] Sue-Lein Wang,*,[†] and Kwang-Hwa Lii*,[‡,§]

Department of Chemistry, National Tsing Hua University, Hsinchu, Taiwan 300, Department of Chemistry, National Central University, Jhongli, Taiwan 320, and Institute of Chemistry, Academia Sinica, Taipei, Taiwan 115, R.O.C.

Received August 25, 2009; E-mail: liikh@cc.ncu.edu.tw

Most uranium minerals can be classified as oxidized species, in which U is fully oxidized to U^{6+}, and reduced species, in which U occurs primarily as U^{4+}. Uranyl silicates are an important group of uranium(VI) minerals in the altered zones of many uranium deposits.[1] Uranyl silicates have also received attention because they form when spent nuclear fuel interacts with water containing silicon under oxidizing conditions.[2] One naturally occurring uranium(IV) silicate exists, namely coffinite ($USiO_4$),[3] which is the most important ore mineral for uranium after uraninite (UO_{2+x}). Numerous synthetic uranium(VI) silicates and germanates containing organic amines or alkali metals as countercations have also been reported.[4,5] In contrast to the uranium(VI) compounds, the chemistry of materials containing uranium(V) is considerably less developed owing to the tendency of U^{5+} to either oxidize to U^{6+} or disproportionate to U^{4+} and U^{6+}. Apart from its fundamental interest, species containing U^{5+} have environmental implications.[6]

We previously reported the first uranium(V) silicates, $K(UO)Si_2O_6$[7] and $K_3(U_3O_6)(Si_2O_7)$,[8] a uranium(V) germanate, $Rb_3(U_3O_6)(Ge_2O_7)$,[8] and mixed-valence uranium(V,VI) germanates, $A_3(U_2O_4)(Ge_2O_7)$ (A = Rb, Cs).[9] Mixed-valence uranium oxide materials are very rare. The minerals ianthinite ($[U^{4+}{}_2(U^{6+}O_2)_4O_6(OH)_4(H_2O)_4]\cdot 5H_2O$)[10] and wyartite ($Ca[U^{5+}(U^{6+}O_2)_2(CO_3)O_4(OH)]\cdot 7H_2O$)[11] and the synthetic compounds $[U^{5+}(H_2O)_2(U^{6+}O_2)_2O_4(OH)]\cdot 4H_2O$ and $U^{5+}(U^{4+}Y_5)O_{12}$ are the only other examples in literature.[12,13] Herein, we report the first mixed-valence uranium(IV,V) silicate, $Cs_2K(UO)_2Si_4O_{12}$ (**1**), which was synthesized by a high-temperature, high-pressure hydrothermal method.

A reaction mixture of 269 μL of CsOH(aq) (50 wt %), 153 μL of 5 M KF(aq), 22 mg of UO_3 (Cerac, 99.8%), and 55 mg of SiO_2 (Alfa Aesar, 99.995%) in the molar ratio Cs/K/U/Si = 10:5:0.5:6 was sealed in a 5.4 cm long gold ampule (i.d. = 4.85 mm), which was contained in an autoclave and counterpressured with water at a fill level of 55%. The autoclave was heated at 600 °C for 48 h, cooled to 350 °C at 5 $°C\cdot h^{-1}$, and then rapidly cooled to room temperature by turning off the power of the tube furnace. The pressure at 600 °C was estimated to be 170 MPa according to the pressure−temperature diagram for pure water. The reaction yielded dark red column crystals of **1** as the major product, along with some yellow crystals of $K_6(UO_2)_3Si_8O_{22}$.[14] Compound **1** could be manually separated from the side product, giving a pure sample, as indicated by powder X-ray diffraction (Supporting Information, Figure S1). Energy dispersive X-ray analysis of several dark red crystals showed the presence of Cs, K, U, and Si for **1**. The yield was 51.7% based on uranium. A suitable dark red crystal was selected for single-crystal X-ray diffraction analysis,[15] from which the chemical formula was determined to be $Cs_2K(UO)_2Si_4O_{12}$. To maintain charge neutrality, the average valence of the U cation must be 4.5+.

The valence state of uranium in **1** and three reference compounds (UO_2, KUO_3, and UO_3) were studied using X-ray photoelectron spectroscopy (XPS). Their U 4f XPS spectra are shown in Figure S2, Supporting Information. Binding energies (BEs) of all of the peaks were referenced to adventitious C 1s at 285.0 eV. Because UO_2 is easily oxidized in the atmosphere,[16] its U4f XPS spectrum was measured after 45 s of Ar^+ etching. The U $4f_{7/2}$ peak in **1** is located at 381.0 eV (fwhm = 1.83 eV), which can be compared with the BE values of U $4f_{7/2}$ in UO_2, KUO_3, and UO_3 at 381.0 eV (fwhm = 2.60 eV), 381.7 eV (fwhm = 1.79 eV), and 382.4 eV (fwhm = 1.69 eV), respectively.

To further establish the valence state of the uranium in **1**, X-ray absorption near-edge structure (XANES) spectra were recorded at a wiggler BL17C beamline of the National Synchrotron Radiation Research Center, Taiwan, in transmission mode at 293 K. The U L_3-edge XANES spectra of compound **1** and three reference materials, $U^{IV}O_2$, $K_3(U^V{}_3O_6)(Si_2O_7)$[8] and $U^{VI}O_3$, are shown in Figure 1. The U^{VI} edge, measured at the position of the half-edge step marked by a horizontal dotted line in the figure, is at 17 169.4 eV, which is 0.7 eV above the U^V edge at 17 168.7 eV and 3.2 eV above the U^{IV} edge at 17 166.2 eV. The edge of **1** is at 17 167.1 eV, a value which is consistent with the presence of U^{IV}/U^V in this material.

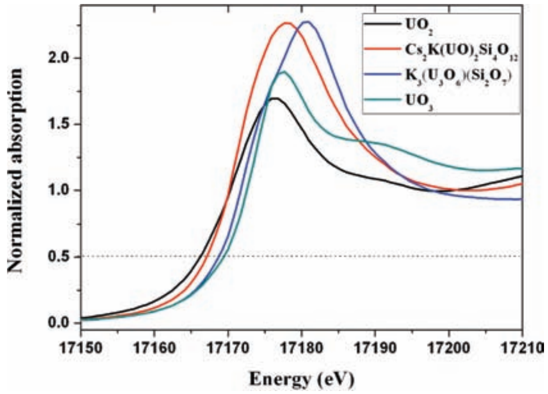

Figure 1. U L_3-edge XANES spectra of **1**, along with three standards, $U^{IV}O_2$, $K_3(U^V{}_3O_6)(Si_2O_7)$, and $U^{VI}O_3$. The dotted line at the absorption coefficient value of 0.5 is included to elucidate the chemical shift.

The structure of **1** is constructed by the following structural elements: one cesium site, one potassium site, one UO_6 octahedron, and one SiO_4 tetrahedron. All metal atoms are in special positions: K(1) and U(1) are at inversion centers, Si(1) lies in a mirror plane, and Cs(1) has a local symmetry of D_{2h}. In contrast to the uranium(VI) compounds, which contain two strongly bonded two uranyl oxygen 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) = 2.1232(2) Å (2×) and 2.234(3) Å (4×). Therefore, **1** is not a uranyl compound. The mean U−O bond length of 2.197(4) Å is somewhat

---

[†] National Tsing Hua University.
[‡] National Central University.
[§] Academia Sinica.

10.1021/ja9071805 CCC: $40.75 © 2009 American Chemical Society

longer than expected for an octahedron that contains only U^{5+}. The U^{5+} ions in $K(UO)Si_2O_6$ and $K_3(U_3O_6)(Si_2O_7)$ occur in regular octahedral coordination environments with a mean U−O bond length of 2.131 Å for the former and of 2.132 Å for the latter. U^{4+} ions generally accommodate more than six ligands in their coordination sphere. Ianthinite is a mixed-valence uranyl oxide hydrate mineral that contains U^{4+} and U^{6+}. The U^{4+} cations are coordinated by O^{2-}, OH^-, and H_2O in a distorted octahedral arrangement with a mean U−O bond length of 2.29 Å. The bond-valence parameters $R_{ij} = 2.051$ Å and $b = 0.519$ Å of Burns et al. can discriminate between U valence states.[17] The bond-valence sum is 5.16 v.u. for $K(U^{V}O)Si_2O_6$, 5.15 v.u. for $K_3(U^{V}{}_3O_6)(Si_2O_7)$, and 3.98 v.u. for the U^{4+} site in the ianthinite structure, in accord with the presence of U^{5+} and U^{4+} ions in these sites. The bond-valence sum at the U(1) site in the structure of **1**, calculated by using the same bond-valence parameters, is 4.56 v.u., indicating the occurrence of U^{4+}/U^{5+} ions. Therefore, the electroneutrality principle, polyhedral geometry, bond-valence sum, XPS, and XANES spectroscopy indicate that **1** is a mixed-valence uranium(IV,V) oxide material.

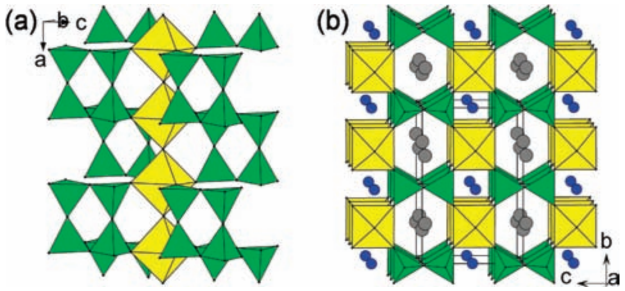

Figure 2. (a) Section of the structure of **1** showing the connection between the cyclotetrasilicates and a $UO_{4/1}O_{2/2}$ infinite chain. (b) Structure of **1** viewed along the *a*-axis. The yellow and green polyhedra represent UO_6 octahedra and SiO_4 tetrahedra, respectively. Grey circles, Cs^+ cations; blue circles, K^+ cations.

As shown in Figure 2a, every UO_6 octahedron in **1** has four equatorial silicate oxygen atoms and two axial oxygen atoms that act as common vertices to neighboring octahedra to form a 1-D chain along the *a* axis, corresponding to the Niggli formula $UO_{4/1}O_{2/2}$. The U(1)−O(4)−U(1) bond angle is 177.2(2)°. The observed Si−O bond lengths (1.601(3) (2×), 1.614(1), and 1.636(1) Å) and O−Si−O bond angles (106.9(2)°−112.8(2)°) are typical values and are within the normal range.[18] The structure consists of four-membered single rings of corner-sharing SiO_4 tetrahedra linked together via corner-sharing 1-D $UO_{4/1}O_{2/2}$ chains to form a 3-D framework that delimits six-ring and four-ring channels along the *a* axis, where the Cs and K atoms are located respectively (Figure 2b). The Cs atom is less tightly bound than the K atom in the channels, as indicated by larger thermal parameters ($U_{eq} = 0.0230(1)$ vs 0.0142(4) $Å^2$) and the unsaturated bond-valence sum (0.77 vs 1.25 v.u.).

Compound **1** is structurally related to the pentavalent-uranium silicate $K(UO)Si_2O_6$.[7] The latter, which crystallizes in the tetragonal space group *P*4/*mbm*, also contains infinite chains of corner-shared UO_6 octahedra, which are coupled together by Si_4O_{12} rings. The U atom sits on a 4-fold rotation axis such that each UO_6 shares corners with four symmetry related Si_4O_{12} rings which are at the same position relative to the U−O chain. This arrangement delimits one type of five-ring channels wherein the K^+ cations are situated. In the structure of **1** the U atom is at an inversion center and in addition to the six-ring channel for the large Cs^+ cation, there is a four-ring channel which can accommodate the smaller K^+ cation such that U^{5+} is further reduced to form a mixed-valence U^{4+}/U^{5+} compound.

In summary, we have successfully synthesized a new mixed-valence uranium silicate under high-temperature, high-pressure hydrothermal conditions. This is the first example of mixed-valence uranium(IV,V) silicate in literature. Previously, we reported two mixed-valence uranium(V,VI) germanates whose structures contain distinct $U^{V}O_6$ and $U^{VI}O_6$ polyhedra that share corners to give infinite $-U^{6+}-O-U^{5+}-O-U^{6+}-$ chains. In contrast, in the structure of **1** there is only one unique U site and the crystal structure analysis results do not reveal the presence of two distinct coordination environments. It is, therefore, of great interest to study the physical properties such as the electrical conductivity of **1**. We have also noted that all U^{5+} silicates which have been synthesized up to now are isostructural to the Nb^{5+} or Ta^{5+} analogues. The synthesis of **1** may indicate the presence of a mixed-valence Nb^{4+}/Nb^{5+} silicate. The physical properties of **1** and the synthesis of niobium silicate analogues are presently being investigated.

Acknowledgment. We thank the National Science Council for support and Dr. T.-S. Chan at NSRRC and Ms. S.-L. Cheah at NTHU for assistance in the XANES and XPS measurements.

Supporting Information Available: Crystal data in CIF format, X-ray powder pattern, and XPS spectra are available. This material is available free of charge via the Internet at http://pubs.acs.org.

References

(1) (a) Burns, P. C. *Rev. Mineral.* **1999**, *38*, 23–90. (b) Finch, R. J.; Murakami, T. *Rev. Mineral.* **1999**, *38*, 24–179, and references therein.
(2) Finch, R. J.; Buck, E. C.; Finn, P. A.; Bates, J. K. *Mater. Res. Soc. Symp. Proc.* **1999**, *556*, 431–438.
(3) Stieff, L. R.; Stern, T. W.; Sherwood, A. M. *Science* **1955**, *121*, 608.
(4) (a) Wang, X.; Huang, J.; Jacobson, A. J. *J. Am. Chem. Soc.* **2002**, *124*, 15190–15191. (b) Wang, X.; Huang, J.; Liu, L.; Jacobson, A. J. *J. Mater. Chem.* **2002**, *12*, 406–410. (c) Huang, J.; Wang, X.; Jacobson, A. J. *J. Mater. Chem.* **2003**, *13*, 191–196.
(5) (a) Chen, C.-S.; Kao, H.-M.; Lii, K.-H. *Inorg. Chem.* **2005**, *44*, 935–940. (b) Chen, C.-S.; Chiang, R.-K.; Kao, H.-M. *Inorg. Chem.* **2005**, *44*, 3914–3918. (c) Lin, C.-H.; Chiang, R.-K.; Lii, K.-H. *J. Am. Chem. Soc.* **2009**, *131*, 2068–2069.
(6) Renshaw, J. C.; Butchins, L. J. C.; Lvens, F. R.; May, I.; Charnock, J. M.; Lloyd, J. R. *Environ. Sci. Technol.* **2005**, *39*, 5657–5660.
(7) Chen, C.-S.; Lee, S.-F.; Lii, K.-H. *J. Am. Chem. Soc.* **2005**, *127*, 12208–12209.
(8) Lin, C.-H.; Chen, C.-S.; Shiryaev, A. A.; Zubavichus, Ya. V.; Lii, K.-H. *Inorg. Chem.* **2008**, *47*, 4445–4447.
(9) Lin, C.-H.; Lii, K.-H. *Angew. Chem., Int. Ed.* **2008**, *47*, 8711–8713.
(10) (a) Finch, R. J.; Ewing, R. C. *Mater. Res. Soc. Symp. Proc.* **1994**, *333*, 625–630. (b) Burns, P. C.; Finch, R. J.; Hawthorne, F. C.; Miller, M. L.; Ewing, R. C. *J. Nucl. Mater.* **1997**, *249*, 199–206.
(11) Burns, P. C.; Finch, R. J. *Am. Mineral.* **1999**, *84*, 1456–1460.
(12) Belai, N.; Frisch, M.; Ilton, E. S.; Ravel, B.; Cahill, C. L. *Inorg. Chem.* **2008**, *47*, 10135–10140.
(13) Bartram, S. F. *Inorg. Chem.* **1966**, *5*, 749–754.
(14) It is a uranyl silicate with a new structure formed of discrete $Ur\phi_4$ tetragonal bipyramids and unusual $Si_8O_{22}{}^{12-}$ oligosilicate anions. Crystal data: monoclinic, *C*2/*m*, $a = 12.4062(9)$ Å, $b = 14.5678(8)$ Å, $c = 8.1199(5)$ Å, $\beta = 103.992(4)°$, $V = 1423.98(16)$ $Å^3$, $Z = 2$, and $R1 = 0.0329$.
(15) Crystal data for **1**: dark red column crystal of dimensions 0.050 × 0.037 × 0.025 mm^3, orthorhombic, space group *Cmmm* (No. 65), $M_r = 1117.34$, $a = 8.4902(5)$ Å, $b = 11.6888(9)$ Å, $c = 7.6132(5)$ Å, $V = 755.54(9)$ $Å^3$, $Z = 2$, $d_{cal} = 4.911$ g cm^{-3}, μ(Mo Kα) = 268.17 cm^{-1}. 2119 reflections were measured on a CCD diffractometer at 293 K, which gave 562 independent reflections with $R_{int} = 0.0188$. An empirical absorption correction was made ($T_{min/max} = 0.5766/0.7457$). Final refinement converged at $R1 = 0.0138$ and $wR2 = 0.0345$ for 546 reflections with $I > 2\sigma(I)$ and 40 parameters.
(16) Tempest, P. A.; Tucker, P. M.; Tyler, J. W. *J. Nucl. Mater.* **1988**, *151*, 269–274.
(17) Burns, P. C.; Ewing, R. C.; Hawthorne, F. C. *Can. Mineral.* **1997**, *35*, 1551–1570.
(18) Liebau, F. *Structural Chemistry of Silicates: Structure, Bonding and Classification*; Springer-Verlag: Berlin, 1985.

JA9071805