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$K_2Ca_4[(UO_2)(Si_2O_7)_2]$: A Uranyl Silicate with a One-Dimensional Chain Structure

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Supporting Information

ABSTRACT: A new uranyl silicate, $K_2Ca_4[(UO_2)(Si_2O_7)_2]$, with a 1D chain structure has been synthesized from a solution of mixed alkali- and alkaline-earth-metal cations under hydrothermal conditions at 550 °C and 1400 bar and characterized by single-crystal X-ray diffraction and photoluminescence spectroscopy. It crystallizes in the triclinic space group $P\overline{1}$ (No. 2) with a = 6.6354(2) Å, b = 6.6791(2) Å, c = 9.6987(3) Å, α = 98.324(2)°, β = 93.624(2)°, γ = 112.310(2)°, and Z = 1. Its crystal structure consists of a 1D chain of uranyl disilicate formed of corner-sharing UO_6 tetragonal bipyramids and Si_2O_7 double groups. The adjacent chains are separated by K^+ and Ca^{2+} cations. It is the first example of uranyl silicate with a 1D chain structure.

Uranyl silicates are important uranium minerals in the altered zones of many uranium deposits.[1] They also form when spent nuclear fuel interacts with water-containing silicon in oxidizing conditions.[2] The crystal chemistry of uranyl silicates has been extensively studied by Burns et al.[3] A large number of synthetic uranyl silicates including an organically templated compound have also been reported.[4] A better understanding of their structural chemistry is important to understand the genesis of uranium deposits and the long-term performance of a geological repository for nuclear waste.

We have been interested in exploratory synthesis of new uranium compounds with novel structures and unusual oxidation states using a high-temperature, high-pressure hydrothermal method. A large number of uranyl, uranium(V), uranium(IV), and mixed-valence uranium silicates and germanates have been synthesized.[4c,d,5] All of these compounds that were synthesized by us contain alkali-metal cations in the structural channels or between the layers. This is in marked contrast to only a few uranyl silicates that contain alkaline-earth metals. The most common uranyl mineral, uranophane, has two polymorphs with the formula $Ca[(UO_2)_2(SiO_3OH)_2](H_2O)_5$.[6] Sklodowskite, $Mg(UO_2)_2(HSiO_4)_2\cdot 5H_2O$, is a uranyl mineral that contains magnesium.[7] Haiweeite, $Ca[(UO_2)_2Si_5O_{12}(OH)_2](H_2O)_6$, is another calcium-containing uranyl silicate.[8] All of the above minerals contain uranyl silicate sheets that are connected through alkaline-earth-metal cations and hydrogen bonds from H_2O groups in the interlayer. A barium uranyl disilicate with a layer structure, $BaUO_2Si_2O_6$, was synthesized by solid-state reaction at high temperature and structurally characterized by powder neutron diffraction.[9] Very recently, a calcium-containing uranyl silicate, $K_4Ca[(UO_2)Si_4O_{12}]$, was synthesized from a eutectic CaF_2−KF flux at high temperature.[10] Its 3D framework structure is related to that of the mineral fresnoite, $Ba_2TiSi_2O_8$.[11]

Most of the uranium silicates exhibit 3D framework structures composed of U−O polyhedra and SiO_4 tetrahedra. Uranium silicates with 2D layer structures are much less common. As noted above, several uranyl silicate minerals that contain alkaline-earth-metal cations adopt 2D layer structures. The synthetic mixed-valence uranium(IV,V,VI) silicate $Na_7U^{IV}O_2(U^{V}O)_2(U^{V/VI}O_2)_2Si_4O_{16}$ and the salt-inclusion mixed-valence uranium(V,VI) silicate $[Na_9F_2][(U^{V}O_2)(U^{VI}O_2)_2(Si_2O_7)_2]$ also have layer structures.[5d,f] To the best of our knowledge, uranium silicate with a 1D chain structure is hitherto unknown. Herein, we report high-temperature, high-pressure hydrothermal synthesis of a new pentanary uranyl silicate, $K_2Ca_4[(UO_2)(Si_2O_7)_2]$ (denoted as **1**), which adopts a 1D chain structure.

Caution! *Although depleted uranium was used in these experiments, it is radioactive and toxic and should only be handled by qualified personnel in appropriate facilities.* High-temperature, high-pressure hydrothermal synthesis was performed in gold ampules contained in a Tem-Pres high-pressure vessel, where the pressure was provided by water. A reaction mixture of 2.8 mg of $Ca(OH)_2$ (Merck, reagent grade), 11.0 mg of UO_3 (Cerac, 99.9%), 9.2 mg of SiO_2 (quartz, Alfa Aesar, 99.995%), 290 μL of 10 M KOH(aq) (Merck, reagent grade), and 279 μL of H_2O (molar ratio K/Ca/U/Si = 75/1/1/4) was welded completely closed in a 6.9-cm-long gold ampule (inside diameter = 0.48 cm) and heated at 550 °C for 4 days. The degree of filling of the pressure vessel by water at room temperature was 55%, and the pressure was estimated to be 1400 bar at the reaction temperature according to the P−T diagram for pure water. The vessel was then cooled to 350 °C at 5 °C/h and quenched in air at room temperature by removing it from the tube furnace. The product was filtered off, washed with water, rinsed with ethyl alcohol, and dried in a desiccator at room temperature. The product contained greenish-yellow foliated crystals of **1** as a major phase along with some orange plate crystals. The greenish-yellow crystals were manually separated from the orange side product under a microscope, giving a pure sample, as indicated by powder X-ray diffraction using a Bruker D2 PHASER powder X-ray diffractometer with Cu Kα radiation (Figure S1). A qualitative X-ray fluorescence (XRF) analysis of several greenish-yellow crystals using a Bruker S2 RANGER energy-dispersive

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XRF spectrometer confirmed the presence of K, Ca, U, and Si. A suitable crystal was used for single-crystal X-ray diffraction, from which the structure and chemical formula were determined.[12] The yield was 45% based on $Ca(OH)_2$ as a limiting reagent. Attempts to synthesize a monophasic product of **1** have been unsuccessful. The orange crystals contain K and U but no Si according to XRF analysis. A satisfactory orange crystal for structural analysis has not been obtained.

The photoluminescence spectrum of **1** at room temperature exhibits a broad structured band ranging from 490 to 630 nm (Figure S2). This spectrum is typical of uranyl and is interpreted as an electronic luminescence transition at about 520 nm, followed by a coupling of the O═U═O vibrations, resulting in the other peaks in the band.

The structure of **1** is formed of the following structural elements: one UO_6 tetragonal bipyramid, two SiO_4 tetrahedra, and one K and two Ca atom sites. The UO_6 tetragonal bipyramid sits on an inversion center and has two short $U═O_{Ur}$ bonds [1.840(2) Å], forming a linear uranyl unit $[O═U═O]^{2+}$, as is typical for U^{6+} in crystal structures, and four longer $U-O_{eq}$ bonds [2.200(2) and 2.209(2) Å] in the equatorial plane. The bond-valence parameters R_{ij} = 2.051 Å and b = 0.519 Å for U^{6+} polyhedra were used to calculate the bond-valence sum, and the value for U(1) was 5.98 valence units (vu),[3a,13] indicating that the U atom is hexavalent. Every SiO_4 tetrahedron shares a corner with another tetrahedron to form a Si_2O_7 unit, with the $Si-O_{br}-Si$ bond angle at the bridging O atom, O(4), being 153.3(2)°. The Si−O bond lengths and O−Si−O bond angles are within the normal ranges.[14] The $Si-O_{br}$ bonds are longer than the $Si-O_{term}$ bonds between Si and a terminal O atom. The sums of bond valences (bv) at the Si(1) and Si(2) sites are 4.06 and 4.09 vu, respectively. The values of the bv's for the O atoms range from 1.90 to 2.20. The coordination numbers and values of the bv's for K and Ca atoms are as follows: K(1), 6, 0.84; Ca(1), 8, 1.83; Ca(2), 6, 2.00.[15]

As shown in Figure 1, each UO_6 tetragonal bipyramid shares four equatorial corners with four different Si_2O_7 units and each Si_2O_7 unit links two UO_6 tetragonal bipyramids such that a 1D chain of uranyl disilicate along the [110] direction with the composition $[(UO_2)(Si_2O_7)_{4/2}]$ is formed. In the structure, adjacent chains are not cross-linked to form a sheet but rather occur as separate units. The adjacent chains are separated by K^+ cations in the *ab* plane and separated by Ca^{2+} cations along the *c* axis (Figure 2). K(1) is coordinated by O_{Ur}, O_{eq}, and O_{br} atoms, Ca(1) by O_{Ur}, O_{term}, and O_{br} atoms, and Ca(2) by O_{term} atoms only.

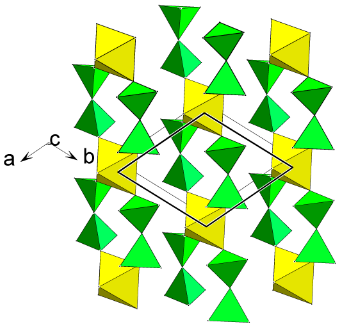

Figure 1. Uranyl silicate chains in the structure of **1**. The yellow and green polyhedra are UO_6 tetragonal bipyramids and SiO_4 tetrahedra, respectively.

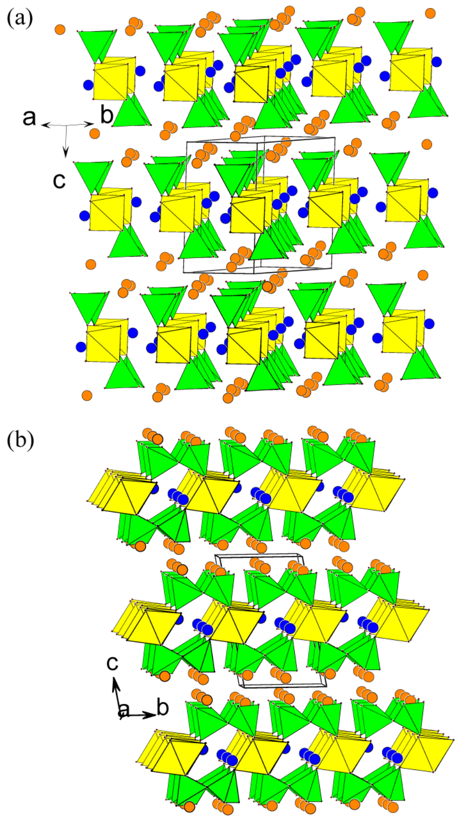

Figure 2. Structure of **1** viewed along the [110] direction (a) and along the *a* axis (b). Blue and orange circles are K and Ca atoms, respectively.

One of the observations made by Burns et al. by examining the nature of polyhedral polymerization in a large number of structures containing uranyl polyhedra is that cation polyhedra with lower cation charge (≤4) almost always share edges with Urϕ_5 or Urϕ_6, but never with Urϕ_4 polyhedra.[13] In the structure of **1**, each UO_6 tetragonal bipyramid (Urϕ_4) shares its equatorial corners with TO_4 tetrahedra. For uranyl compounds containing hexavalent cations and $UO_n/TO_4 = 1/2$, there are two types of c1/2a chains, as indicated by Krivovichev and Burns.[16] One chain consists of corner-sharing $UO_6(H_2O)$ pentagonal bipyramids and TO_4 tetrahedra (denoted as the c1/2a-1 type), as observed in $Mg[(UO_2)(SeO_4)_2(H_2O)](H_2O)_4$,[17] whereas the other one has UO_6 tetragonal bipyramids and TO_4 tetrahedra (denoted as the c1/2a-2 type), as observed in $Li_2[(UO_2)(MoO_4)_2]$.[18] Several chain structures have also been found in the uranyl compounds containing pentavalent cations such as P^{5+}. For example, in the structure of $Cu_2[(UO_2)(PO_4)_2]$, uranyl square bipyramids share equatorial corners with phosphate tetrahedra to form infinite chains.[19] The c1/2a-1 type chain in the structure of $[(UO_2)(H_2PO_4)_2(H_2O)](H_2O)$ consists of uranyl pentagonal bipyramids that share equatorial vertices with four H_2PO_4 groups.[20] The unshared equatorial vertex is a water ligand. The lanthanide/actinide phosphate $Cs_{11}Eu_4(UO_2)_2(P_2O_7)_6(PO_4)$ has a 3D framework structure, in which the connection between uranyl polyhedra and diphosphate groups is the same as that between uranyl polyhedra and disilicate groups in **1**.[21] However, a 1D chain structure in uranyl compounds containing tetravalent cations such as Si^{4+} has not been reported in the literature. Assuming a uranyl silicate containing the c1/2a-2-type chain, the composition of the chain would be $[(UO_2)(SiO_4)_2]^{6-}$. The structure needs six alkali-metal cations or three alkaline-earth-metal cations per formula unit to balance the charge. Compound **1** contains disilicate instead of monosilicate groups, and the composition of the chain is $[(UO_2)(Si_2O_7)_2]^{10-}$. There is not enough space to accommodate 6 or 10 alkali-metal countercations per formula unit in the structures containing $[(UO_2)(SiO_4)_2]^{6-}$ or $[(UO_2)(Si_2O_7)_2]^{10-}$ chains. It was envisaged that a mixture of monovalent and divalent cations can balance the charges of the uranyl silicate chains and stabilize the structures. Synthesis of **1**, the first example of a uranyl silicate with a 1D chain structure, has been achieved from a solution of mixed alkali- and alkaline-earth-metal cations under high-temperature, high-pressure hydrothermal conditions.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.inorgchem.5b01390.

Powder X-ray diffraction patterns and a photoluminescence spectrum (PDF)

Crystallographic data for **1** in CIF format (CIF)

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Notes

The authors declare no competing financial interest.

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(12) Crystal data of **1**: A total of 6552 reflections of a greenish-yellow crystal with dimensions 0.01 × 0.05 × 0.2 mm^3, triclinic, $P\bar{1}$ (No. 2), a = 6.6354(2) Å, b = 6.6791(2) Å, c = 9.6987(3) Å, α = 98.324(2)°, β = 93.624(2)°, γ = 112.310(2)°, V = 390.17(2) Å^3, Z = 1, D_{calc} = 3.596 g/cm^3, and λ(Mo Kα) = 12.64 mm^{-1} were measured on a Kappa Apex II diffractometer at 296 K, which gave 1916 independent reflections $[I_0 > 2\sigma(I_0)]$ with R(int) = 0.0272. An empirical absorption correction based on the symmetry equivalent was applied with T_{min}/T_{max} = 0.5654/0.7468. The final cycles of refinement converged at R1 = 0.0133, wR2 = 0.0314, and GOF = 1.087 with 125 parameters, $\rho_{max/min}$ = + 0.71/−0.61 e/Å^3.

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