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High-Temperature, High-Pressure Hydrothermal Synthesis and Characterization of an Open-Framework Uranyl Silicate with Nine-Ring Channels: $Cs_2UO_2Si_{10}O_{22}$

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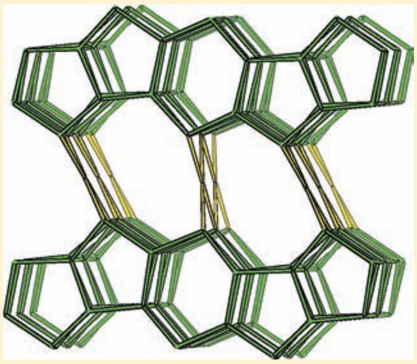
Ⓢ *Supporting Information*

ABSTRACT: A new uranium(VI) silicate, $Cs_2UO_2Si_{10}O_{22}$, has been synthesized by a high-temperature, high-pressure hydrothermal method and characterized by single-crystal X-ray diffraction, luminescence, and solid state NMR spectroscopy. It crystallizes in the monoclinic space group $P2_1/c$ (No. 14) with $a = 12.2506(4)$ Å, $b = 8.0518(3)$ Å, $c = 23.3796(8)$ Å, $\beta = 90.011(2)°$, and $Z = 4$. Its structure consists of silicate double layers in the *ab* plane which are connected by UO_6 tetragonal bipyramids via four equatorial oxygen atoms to form a 3D framework with nine-ring channels parallel to the *b* axis where the Cs^+ cations are located. The photoluminescence emission spectrum at room temperature consists of one broad structured band which is typical of uranyl. The ^{29}Si MAS NMR spectrum is consistent with the crystal structure as determined from X-ray diffraction, and the resonances in the spectrum are assigned. A comparison of related uranyl silicate structures is made.



INTRODUCTION

Most uranium minerals can be put into two groups: oxidized species that contain U as U^{6+} and reduced species that contain most U as U^{4+}. The U^{6+} cation is almost always present as part of a uranyl ion, UO_2^{2+}, that is linear or nearly so.[1] Several recent studies showed that U^{6+} could adopt a tetraoxide core rather than the uranyl ion.[2] Uranyl silicates are the most abundant group of uranyl minerals in many occurrences.[3] Only two naturally occurring U(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] Recently, we reported the first synthetic U(IV) silicate, $Cs_2USi_6O_{15}$.[6] It is noted that all members in the family of uranium silicates or germanates with the oxidation states of uranium from +4 to +6 including U(IV,V), U(IV,VI), U(V,VI), and U(IV,V,VI) have been observed.[7]

Uranyl silicates have received attention because they form when spent nuclear fuel interacts with water containing silicon under oxidizing conditions,[8] and the structural chemistry of uranyl minerals has been extensively studied by Burns et al.[9] Jacobson and co-workers reported a series of uranyl silicates including an organically templated compound (denoted as USH-n).[10] An interesting uranyl silicate was produced by vapor hydration experiments on a U-doped borosilicate glass at 200 °C. A structural study reveals the potential of this compound to incorporate radionuclides from nuclear-waste glasses.[11] We have also reported several uranyl silicates which were synthesized under high-temperature, high-pressure hydrothermal conditions or at a high temperature using mixtures of alkali metal fluorides as fluxes.[12] During our continued exploratory synthesis, we synthesized a new open-framework uranyl silicate, $Cs_2UO_2Si_{10}O_{22}$, using a high-temperature, high-pressure hydrothermal method. The structure contains silicate double layers with lateral five and six-ring channels, which are connected by UO_6 tetragonal bipyramids to form a 3D framework with nine-ring channels where the Cs^+ cations are located. The synthesis, crystal structure, photoluminescence, and solid-state NMR spectroscopy are reported.

EXPERIMENTAL SECTION

Synthesis. High-temperature, high-pressure hydrothermal synthesis was performed in gold ampules contained in a Leco Tem-Pres autoclave where pressure was provided by water. The apparatus is an externally heated cold-seal pressure vessel for use to 10 000 bar and 750 °C. The degree of filling of the autoclave by water at room temperature was 55%. A reaction mixture of 0.238 mL of 10 M CsF(aq) (CsF, STREM Chemicals, 99+%), 44.7 mg of UO_3 (NOAH, 99.9%), and 96.3 mg of SiO_2 (quartz, Alfa Aesar, 99.995%; molar ratio Cs/U/Si = 15:1:10) in a 4.1-cm-long gold ampule (inside diameter = 0.48 cm) was heated at 580 °C for 2 days. The pressure was estimated to be 1600 bar at the reaction temperature according to the pressure−temperature diagram for pure water. The autoclave was then cooled to 350 at 5 °C/h and quenched in the air 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

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temperature. The reaction produced a greenish yellow tablet crystals of **1** as a major product along with some colorless crystals of leftover quartz and a small amount of colorless side product of Cs_2SiF_6 (JCPDS 7−6) powder. The greenish yellow crystals could be manually separated from the impurities giving a pure sample as indicated by powder X-ray diffraction using a powder diffractometer with Cu Kα radiation equipped with a scintillation detector. Data were collected in the range $5° \leq 2\theta \leq 50°$ using a transmission mode. The differences between the observed and calculated intensities are due to the effect of preferred orientation, although the sample was carefully prepared and the diffraction pattern was measured by using transmission. A qualitative EDX analysis of several greenish yellow crystals did not reveal any F and confirmed the presence of Cs, U, and Si. The yield was 52% (95 mg) based on uranium. The sample was used for photoluminescence and solid-state NMR measurements.

Single-Crystal X-Ray Diffraction. A suitable greenish yellow crystal of **1** having dimensions 0.187 × 0.055 × 0.045 mm was selected for indexing and intensity data collection on a Bruker Kappa Apex II CCD diffractometer equipped with a normal focus, 3-kW sealed tube X-ray source. Intensity data were collected at 296 K over 9689 frames with ω scans (width 0.5°/frame). The program SADABS was used for absorption correction ($T_{min/max}$ = 0.4561/0.7457).[13] The symmetry of the crystal revealed by intensity is monoclinic, even though the metric symmetry of the unit cell looks orthorhombic. On the basis of reflection conditions and successful solution and refinement of the structure, the space group was determined to be $P2_1/c$ (no. 14). The structure was solved by direct methods and successive difference Fourier syntheses. Two Cs atom sites were located and refined with full occupancy. The bond-valence parameters R_{ij} = 2.074 Å and b = 0.554 Å for $^{[6]}U^{6+}$ polyhedra were used to calculate the bond-valence sum at each uranium site,[9a] and the values for U(1) and U(2) were 6.15 and 6.03 valence units, respectively, indicating that both uranium atoms are hexavalent, consistent with the color of the crystals. The final cycles of least-squares refinement include atomic coordinates; anisotropic thermal parameters for all atoms converged at R_1 = 0.0381 and wR_2 = 0.0959. The largest residual electron densities in the final difference Fourier maps were near uranium atoms (2.51 e Å^{-3} at 0.89 Å from U(2); 2.37 e Å^{-3} at 0.87 Å from U(1)). All calculations were performed using the *SHELXTL* version 5.1 software package.[14] The software Platon has not found extra symmetry and suggests that the monoclinic $P2_1/c$ is the correct space group for this structure. The crystal data and structure refinement parameters are given in Table 1 and selected bond lengths in Table 2.

Table 1. Crystallographic Data for $Cs_2UO_2Si_{10}O_{22}$

chemical formula	$Cs_2O_{24}Si_{10}U$
a/Å	12.2506(4)
b/Å	8.0518(3)
c/Å	23.3796(8)
β	90.011(2)°
V/Å^3	2306.15(14)
Z	4
formula weight	1168.75
space group	$P2_1/c$ (No. 14)
T, °C	23
λ(Mo Kα), Å	0.71073
D_{calcd}, g cm^{-3}	3.366
μ(Mo Kα), cm^{-1}	107.78
$R_1{}^a$	0.0381
$wR_2{}^b$	0.0959

[a] $R_1 = \sum||F_o| - |F_c||/\sum|F_o|$. [b] $wR_2 = [\sum w(F_o{}^2 - F_c{}^2)^2/\sum w(F_o{}^2)^2]^{1/2}$, $w = 1/[\sigma^2(F_o{}^2) + (aP)^2 + bP]$, $P = [\mathrm{Max}(F_o{}^2,0) + 2(F_c)^2]/3$, where a = 0.0214 and b = 34.46.

Luminescence Spectroscopy. Photoluminescence data were measured on a powder sample of **1** at room temperature using a Hitachi F-4500 Fluorescence Spectrophotometer. Excitation was achieved using 365 nm light from a Xenon lamp.

Table 2. Selected Bond Lengths (Å) for $Cs_2UO_2Si_{10}O_{22}$[a]

U(1)−O(23)	1.793(5) (2×)	U(1)−O(19)	2.259(5) (2×)
U(1)−O(22)	2.264(5) (2×)	U(2)−O(24)	1.802(5) (2×)
U(2)−O(6)	2.269(5) (2×)	U(2)−O(8)	2.284(6) (2×)
Si(1)−O(1)	1.588(6)	Si(1)−O(2)	1.574(6)
Si(1)−O(3)	1.605(6)	Si(1)−O(4)	1.615(6)
Si(2)−O(2)	1.622(6)	Si(2)−O(5)	1.622(5)
Si(2)−O(6)	1.590(6)	Si(2)−O(7)	1.624(6)
Si(3)−O(3)	1.604(6)	Si(3)−O(8)	1.601(6)
Si(3)−O(9)	1.588(6)	Si(3)−O(10)	1.595(6)
Si(4)−O(4)	1.595(6)	Si(4)−O(11)	1.598(6)
Si(4)−O(12)	1.598(6)	Si(4)−O(13)	1.601(6)
Si(5)−O(5)	1.604(6)	Si(5)−O(8)	1.606(6)
Si(5)−O(14)	1.595(6)	Si(5)−O(15)	1.605(6)
Si(6)−O(16)	1.618(6)	Si(6)−O(17)	1.607(6)
Si(6)−O(18)	1.612(6)	Si(6)−O(19)	1.580(6)
Si(7)−O(7)	1.620(6)	Si(7)−O(10)	1.595(6)
Si(7)−O(20)	1.586(6)	Si(7)−O(21)	1.616(6)
Si(8)−O(13)	1.634(5)	Si(8)−O(14)	1.614(6)
Si(8)−O(16)	1.619(6)	Si(8)−O(22)	1.576(6)
Si(9)−O(1)	1.604(6)	Si(9)−O(15)	1.595(6)
Si(9)−O(18)	1.608(6)	Si(9)−O(21)	1.586(6)
Si(10)−O(9)	1.596(9)	Si(10)−O(11)	1.593(6)
Si(10)−O(12)	1.593(6)	Si(10)−O(17)	1.609(6)

[a] Cs−O distances are available from the Supporting Information.

Solid-State NMR Measurements. Solid-state ^{29}Si NMR experiments were performed on a Varian Infinityplus-500 spectrometer, equipped with a Chemagnetics 7.5 mm magic angle spinning (MAS) probe, with a resonance frequency of 99.03 MHz for the ^{29}Si nucleus. A pulse length of 9.25 μs (π/4 pulse) and a repetition time of 100 s were used to obtain the ^{29}Si MAS NMR spectrum. The ^{29}Si chemical shift was externally referenced to Q8M8 at −66.08 ppm.

■ RESULTS AND DISCUSSION

Structure. As shown in Figure 1, the structure of **1** is constructed from the following distinct structural elements: 10 SiO_4 tetrahedra, two UO_6 tetragonal bipyramids, and two Cs atom sites. All Cs, Si, and O atoms are in general positions. U(1) and U(2) are located at inversion centers. The observed Si−O bond lengths (1.574−1.634 Å) and O−Si−O bond angles (105.7−113.6°) are typical values and are within the normal range.[15] Both UO_6 tetragonal bipyramids have two short U−O bonds (U(1)═O, 1.793 Å; U(2)═O, 1.802 Å), forming the linear uranyl unit $[O{=}U{=}O]^{2+}$, as is typical for U^{6+} in crystal structures, and four longer U−O bonds (2.259−2.284 Å) in the plane normal to this UO_2 axis. Uranyl ions occur in three coordination polyhedra in crystal structures: tetragonal bipyramidal, pentagonal bipyramidal, and hexagonal bipyramidal, with uranyl pentagonal bipyramids being the most common.[1] Both Cs sites are fully occupied. 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 a coordination number of 10 for both Cs(1) and Cs(2) cations.

The structure of **1** contains silicate double layers of the composition $[Si_{10}O_{22}]$ in the *ab* plane which are connected by UO_6 tetragonal bipyramids via four equatorial oxygen atoms to form a 3D framework with nine-ring channels parallel to the *b* axis where the Cs^+ cations are located (Figure 2). Each silicate double layer can be regarded as a product of condensation of

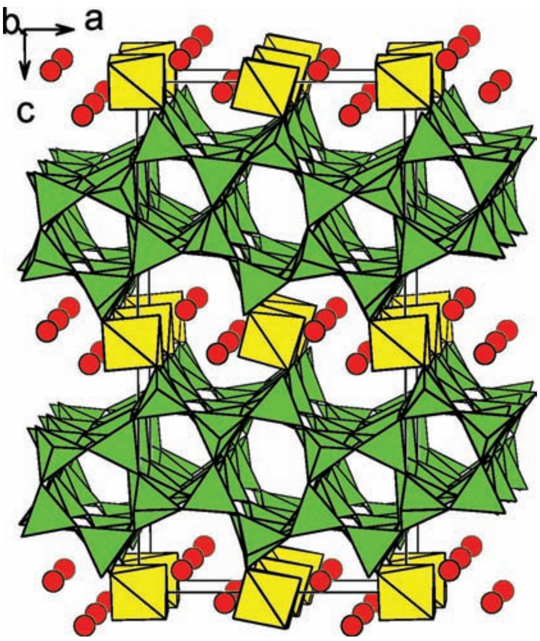

Figure 1. Structure of **1** viewed along the *b* axis. The yellow and green polyhedra are UO_6 tetragonal bipyramids and SiO_4 tetrahedra, respectively. Red circles are Cs atoms.

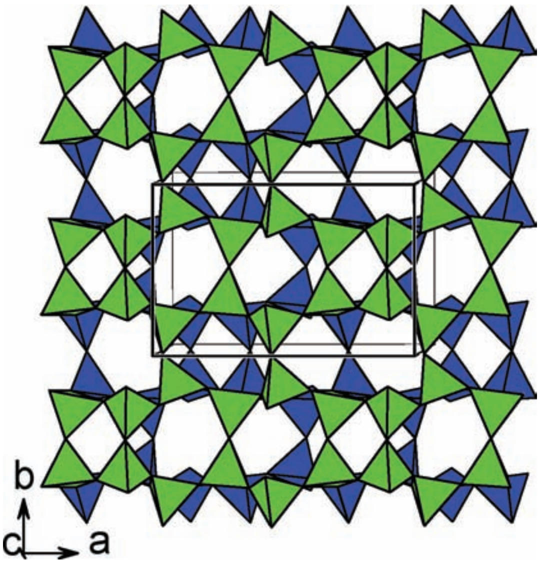

Figure 2. Section of a silicate double layer of **1**. The two silicate single layers of the double layer are shown in green and blue, respectively.

two single layers with the composition $[Si_2O_5]$ that are related by a 2_1 screw axis. The layer is an unbranched vier single layer because it can be generated by successive linking of fundamental chains parallel to the *b* axis with a periodicity of four. The Schläfli symbol of the three-connected plane net for this single layer is $(4,6,8)_2(6^3)_1(6^2,8)_2$. The two single layers are linked via only 3/5 of their apical oxygen atoms; then the Si/O ratio of the double layer is 10:22. Interconnection of the fundamental chains results in four-, six-, and eight-ring voids in the single layer, but the eight-ring voids are blocked by the other single layer. Each double layer has lateral five- and six-ring channels along the *b* axis. Two-fifths of the tetrahedra in the double layer are three-connected with their fourth terminal oxygen atoms being bonded to interlayer uranium atoms in the equatorial positions of the uranyl units. The 3D framework formed by connection of the uranyl units and the silicate double layers has nine-ring channels along the *b* axis which are occupied by 10-coordinate Cs^+ cations.

Among the known microporous framework structures of metal silicates and germanates, channels bound by odd-membered rings are rare, with the exception of more frequent five rings. Several zeotype materials such as LOV, RSN, and VSV structure types[17] and the vanadium silicate $Cs_2VOSi_4O_{10}\cdot xH_2O$ (VSH-12) possess nine-ring channels.[18] The nine-ring channels in the lanthanide silicate $Na_3TbSi_3O_9\cdot 3H_2O$ consist of four TbO_6 octahedra and five SiO_4 tetrahedra.[19] One uranyl silicate, $K_5(UO_2)_2[Si_4O_{12}(OH)]$,[20] and a mixed-valence U(IV,VI) germanate, $Cs_8U(UO_2)_3(Ge_3O_9)_3\cdot 3H_2O$,[7e] contain nine-ring channels. Compound **1** is the third example of nine-ring channels in the family of uranium silicates and germanates.

The structure of **1** bears some resemblances to that of USH-8, an organically templated open-framework uranyl silicate.[10a] The framework is characterized by silicate double layers, which have been found in the structure of the zeolite ferrierite,[21] and infinite chains of edge-sharing UO_3F_4 pentagonal bipyramids. Each of the two silicate single layers of the double layer contains large 10-ring windows, but the windows are blocked by the other single layer. The double layers are connected by uranate chains to form 12-ring channels which are occupied by ordered tetramethylammonium cations and disordered pyridinium and trimethylammonium cations. The double layers in USH-8 contain lateral five-ring channels only; by contrast, the double layers in **1** contain five- and six-ring channels.

Luminescence. Figure 3 shows the photoluminescence spectrum of **1** at room temperature. It exhibits several characteristic peaks at 512, 534, 558, 582, and 610 nm. This broad structured band is typical of uranyl and is interpreted as a pure electronic luminescence transition at 512 nm followed by a coupling of the $O{=}U{=}O$ vibrations resulting in the other peaks in the spectrum. Compared to the spectrum of the uranyl silicate $BaUO_2Si_2O_6$,[22] **1** displays a blue shift about 6 nm.

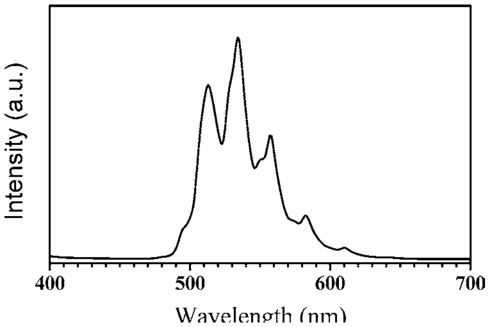

Figure 3. Room-temperature emission spectrum of **1** excited at 365 nm.

^{29}Si NMR. ^{29}Si solid-state NMR is used to provide information on the local environments of silicon atoms in the framework. The local environment of the SiO_4 unit is sensitively reflected in the chemical shift of the central Si atom. In aluminosilicates, the replacement of one or more Si atoms by Al atoms results in significant low-field shifts.[23] There are 10 unique Si sites in the structure of **1** which can be classified into two groups, according to the coordination environment of SiO_4. Si(2), Si(6), Si(7), and Si(8) are Q^4(1U) units because their SiO_4 tetrahedra are bonded to three SiO_4 tetrahedra and one UO_6 tetragonal bipyramid, whereas the other six SiO_4 tetrahedra are bonded to Si atoms only, Q^4(0U). The one-pulse ^{29}Si MAS NMR spectrum is shown in Figure 4.

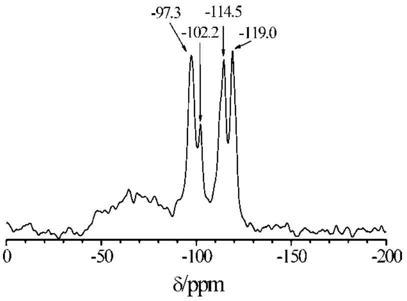

Figure 4. ^{29}Si one-pulse MAS NMR spectrum of **1** acquired at a spinning speed of 5 kHz.

Four resonances, which can be divided into two subgroups at (−97.3, −102.2) and (−114.5, −119.0) ppm, are observed. The resonances of the former group are assigned to Q^4(1U) units and those of the latter to Q^4(0U) units. It has been reported that the ^{29}Si chemical shift depends on the average value of the four Si−O−T bond angles and shifts upfield with increasing Si−O−T bond angle.[23] The average bond angles are 145.4, 147.4, 154.4, and 143.6° for Si(2), Si(6), Si(7), and Si(8), respectively. The resonance at −97.3 ppm is assigned to Si(2), Si(6), and Si(8) and the other resonance (−102.2 ppm) to Si(7). The average bond angles for the Q^4(0U) units are as follows: Si(1), 151.1°; Si(3), 158.6°; Si(4), 148.4°; Si(5), 150.0°; Si(9), 159.6°; Si(10), 158.4°. Therefore, the resonances at −114.5 and −119.0 ppm are assigned to (Si(1), Si(4), Si(5)) and (Si(3), Si(9), Si(10)), respectively. The weak broad band from about 50 to 80 ppm is ascribed to an impurity.

In summary, we have synthesized a new uranyl silicate using a high-temperature, high-pressure hydrothermal method and characterized its structure using single-crystal X-ray diffraction, photoluminescence, and solid-state NMR spectroscopy. The luminescence spectrum is typical of uranyl. The ^{29}Si NMR spectrum is consistent with the crystal structure as determined from X-ray diffraction, and the four resonances in the spectrum are assigned. Its structure consists of silicate double layers which are connected by UO_6 tetragonal bipyramids to form a 3D framework with nine-ring channels where the Cs^+ cations are located. The structure is related to that of the organically templated uranyl silicate USH-8. The uranium silicate system has a rich crystal chemistry and contains a large number of new structural types. 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. The hydrothermal method has been successfully used in the uranium silicate system, and therefore, further research to synthesize new compounds with novel frameworks and unusual oxidation states is in progress.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Crystallographic data for $Cs_2UO_2Si_{10}O_{22}$ in CIF format and X-ray powder patterns. This material is available free of charge via the Internet at http://pubs.acs.org.

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