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Synthesis of Thermally Stable Extra-Large Pore Crystalline Materials: A Uranyl Germanate with 12-Ring Channels

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Uranyl silicates are common constituents of the oxidized portions of uranium deposits and typically form as a result of the alteration of uraninite (UO_{2+x}).[1] The crystal chemistry of uranyl silicates has been extensively studied because an understanding of their structures may be a key to understanding the long-term performance of a geological repository for nuclear waste. Recently, a large number of synthetic uranyl silicates including an organically templated uranyl silicate have been reported.[2,3] They were synthesized under either mild hydrothermal conditions at 180−245 °C or high-temperature, high-pressure hydrothermal conditions at 550−600 °C. We previously reported two uranium(V) silicates, $K(UO)Si_2O_6$ and $K_3(U_3O_6)(Si_2O_7)$,[4,5] a uranium(V) germanate, $Rb_3(U_3O_6)(Ge_2O_7)$,[5] and two mixed-valence uranium(V,VI) germanates, $A_3(U_2O_4)(Ge_2O_7)$ (A = Rb, Cs).[6] Among the above-mentioned U silicates and germanates, USH-8,[2a] an organically templated open-framework uranyl silicate, is the only extra-large pore crystalline material, namely with a ring size $\geq$ 12. Extra-large pores are interesting because the pore size allows practical applications for which materials with smaller pores are not suitable.[7] The synthesis and structural characterization of new materials with extra-large pores is an extremely active area of research in solid state and materials chemistry. Here, we report high-temperature, high-pressure hydrothermal synthesis of a new open-framework uranyl germanate, $Cs_6[(UO_2)_3(Ge_2O_7)_2]\cdot 4H_2O$ (denoted as **1**), having a structure that contains 12-ring channels.

A reaction mixture of 418 μL of CsOH(aq) (Aldrich, 50 wt%), 68.6 mg of UO_3 (Cerac, 99.8%), and 100.4 mg of GeO_2 (Cerac, 99.999%) (molar ratio Cs/U/Ge = 10:1:4) was sealed in a 6.35 cm long gold ampule (inside diameter = 0.48 cm), which was contained in a Leco Tem-Pres autoclave and counterpressured with water at a fill level of 55%. The autoclave was heated at 585 °C for 2 d, cooled to 350 at 5 $°C\cdot h^{-1}$, and then quenched at room temperature by removing the autoclave from the tube furnace. The pressure at 585 °C was estimated to be 150 MPa according to the pressure−temperature diagram for pure water. The product contained yellow prismatic crystals of **1** as the major product in a yield of 59% along with some dark brown prismatic crystals of the mixed-valence uranium(V,VI) germanate $Cs_3(U_2O_4)(Ge_2O_7)$.[6] The yellow crystals could be easily manually separated from the dark brown crystals giving a pure sample as indicated by powder X-ray diffraction (Figure S1). A qualitative EDX analysis of several yellow crystals showed the presence of Cs, U, and Ge. A suitable crystal was selected for single-crystal X-ray diffraction analysis from which the chemical formula was determined to be $Cs_6[(UO_2)_3(Ge_2O_7)_2]\cdot 4H_2O$.[8] Attempts to synthesize the silicate analogue produced the uranyl silicate $Cs_2(UO_2)(Si_2O_6)$ with 8-ring pore openings as the major product.[3b]

The infrared spectrum of **1** shows strong, broad bands with maxima at 808 and 820 cm^{-1}, which can be assigned to the stretching modes of uranyl groups (Figure S2). The strong bands at 783, 751, and 729 cm^{-1} can be assigned to the asymmetric stretching vibrations of Ge−O bonds. The peaks at 525 and 407 cm^{-1} are attributed to the symmetric stretching and bending vibrations of germanate groups. The bands in the regions 1600−1700 and 3000−3600 cm^{-1} are typical for water molecules. The ^{133}Cs MAS NMR spectrum was measured on a 200 mg powder sample of **1** at 65.39 MHz. The spectrum displays three sharp isotropic peaks at 99.1, 59.8, and 10.7 ppm (Figure S3). The three peaks correspond to three unique Cs sites as determined from X-ray diffraction. A combination of variable-temperature (30−900 °C, under N_2) in situ powder X-ray diffraction (Figure S4) and TG analysis (Figure S5) of **1** shows that the dehydration is completed at ~600 °C, the framework structure is retained up to 700 °C, and the transformation from **1** to an unknown material occurs at ~800 °C. The TGA curve (Figure S5a) shows a weight loss of 3.38% between 55 and 650 °C and confirms the presence of two lattice water molecules (3.28%). To study guest desorption−sorption properties, a dehydrated sample was exposed to moist air at room temperature for 2 days and then was heated to 650 at 10 °C min^{-1} by using the same thermal analyzer. The results show that the dehydrated compound can absorb water reversibly (Figure S5b). Attempts to determine the crystal structure of the dehydrated form of **1** by single-crystal X-ray diffraction were unsuccessful because of poor crystal quality.

The structure of **1** is constructed from the following distinct structural elements: two UO_6 polyhedra, two GeO_4 tetrahedra, three Cs^+ cations, and two lattice water molecules. All the atoms are in general positions except U(2), which is at an inversion center. Both GeO_4 tetrahedra are slightly distorted, as indicated by the Ge−O bond lengths (1.720−1.773 Å, average 1.741 Å for Ge(1); 1.728−1.766 Å, average 1.746 Å for Ge(2)) and O−Ge−O bond angles (101.4°−113.5° for Ge(1); 103.9°−115.2° for Ge(2)). Every GeO_4 tetrahedron shares a corner with another tetrahedron to form a Ge_2O_7 dimer, with the bond angle at the bridging oxygen atom being 130.0(2)°. In the $U(1)O_6$ and $U(2)O_6$ tetragonal bipyramids (designated as $Ur\phi_4$), the U(1) and U(2) atoms have unsymmetrical oxygen coordination environments: two U═O bonds are short (1.831 and 1.832 Å for U(1); 1.837 Å (2×) for U(2)), forming linear uranyl (Ur) units, which are typical for uranium(VI) compounds; the four U−O bonds in the plane normal to the O═U═O axis are longer (2.212−2.241 Å for U(1); 2.196−2.213 Å for U(2)). The bond-valence sums at the U(1) and U(2) sites, calculated with the coordination-specific parameters of Burns et al.,[9] are 6.14 v.u. and 6.23 v.u., respectively, consistent with the occurrence of U^{6+} ions in these sites.

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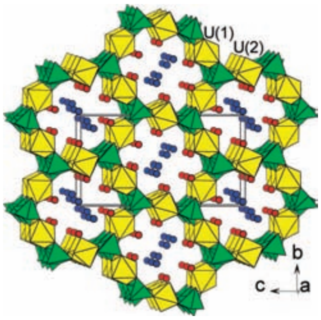

Figure 1. Structure of **1** viewed along the *a* axis. Red and blue circles are Cs$^+$ cations and water oxygen atoms, respectively.

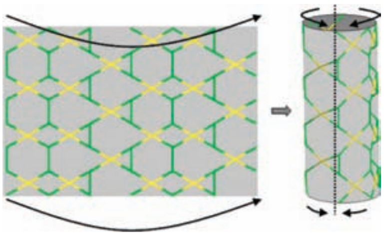

Figure 2. (Right) The topological structure of the 12-rig channel in **1**. (Left) The unrolled channel wall. In these diagrams, the U (in yellow) and Ge (in green) atoms are located at the intersections of the lines, as O bridges are made by corner sharing from the vertexes of the tetragonal bipyramid and the tetrahedron.

The Urϕ_4 tetragonal bipyramids have four equatorial oxygen atoms (ϕ, O$_{eq}$) that are shared with GeO$_4$ tetrahedra and two apical uranyl oxygen atoms that are unshared. Every U(1)O$_6$ tetragonal bipyramid shares four oxygen atoms with one Ge$_2$O$_7$ group and two GeO$_4$ tetrahedra belonging to two different Ge$_2$O$_7$ groups to form 2D layers in the *ab* plane. Adjacent layers are linked together by U(2)O$_6$ tetragonal bipyramids which share corners with four different Ge$_2$O$_7$ groups to form a 3D framework (Figure 1). One type of 12-ring channels which are formed by the edges of six UO$_6$ tetragonal bipyramids and six GeO$_4$ tetrahedra is observed along the *a* axis. The shortest O···O distance across the 12-ring window is 7.0 Å. Lateral 6-ring and 7-ring windows are observed on the wall of the 12-ring channel. The topological structure of the channel and its idealized unfolded version are shown in Figure 2. The structure of the unrolled channel wall is considerably different from those of the uranyl selenate nanotubules[12] and has not been observed previously in any uranyl silicate sheet structure. All three cesium sites are located near the edge of the 12-ring channel and the two lattice water sites in the central area. All these sites are fully occupied and ordered. The coordination number (CN) of the Cs atom was determined on the basis of the maximum cation−anion distance.[10] A limit of 3.70 Å was set for Cs−O interactions, which gives the following CN's: Cs(1), CN = 6 + 1, the first number referring the number of neighboring atoms at shorter distances; Cs(2), CN = 9; Cs(3), CN = 8 + 1. The bond-valence sums at Cs(1), Cs(2), and Cs(3) sites are 0.82, 0.86, and 1.15,[11] respectively, indicating that Cs(3) is more tightly bound than the other two Cs atoms, consistent with their thermal parameters. Hydrogen bonding exists between water molecules and between water molecules and framework oxygen atoms as indicated by short O···O distances (Ow···Ow = 2.745 Å, Ow(1)···O = 2.694, 2.841 Å, Ow(2)···O = 2.985 Å).

Open-framework materials with extra-large pores are of interest because they could potentially process larger hydrocarbon molecules. Given the limited stability of phosphate-based materials, new extra-large pore crystalline silicates and germanates are much in demand. Several new aluminosilicate zeolites, UTD-1,[13] CIT-5,[14] and OSB-9[15] containing 14-ring openings, a germanium-containing zeolite, IM-12,[16] with 2D channels formed by 14 and 12 rings, and a new gallosilicate, ECR-34,[17] with 18-ring openings have been synthesized. The thermal stabilities of most of these materials are comparable to the stabilities of other zeolites containing smaller rings within their structures. Many attempts have been made to modify the physical and catalytic properties of zeolite frameworks by the incorporation of other metal ions. While there are a few examples of transition metal silicates, ETS-10[18] and AM-6[19] containing extra-large pores, there was only one U silicate, USH-8,[2a] having 12-ring openings. However, TG analysis combined with PXRD indicates that the structure of USH-8 collapses after loss of the organic species between 300 and 600 °C. In contrast, compound **1** is stable up to 700 °C and is able to absorb water reversibly. To our knowledge, **1** is also the first crystalline material with 12-ring pore openings which is synthesized under high-temperature, high-pressure hydrothermal conditions. The existence of **1** suggests the potential of synthesizing other thermally stable silicate and germanate materials with extra-large pores.

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Supporting Information Available: X-ray crystallographic data in CIF format, PXRD patterns, IR and NMR spectra, and TGA curve. This material is available free of charge via the Internet at http://pubs.acs.org.

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(8) Crystal data for **1**: Yellow prismatic crystal of dimensions 0.34 × 0.05 × 0.04 mm^3, monoclinic, space group $P2_1/n$, M_r = 2193.97, a = 7.6417(4) Å, b = 10.3281(6) Å, c = 18.855(1) Å, β = 92.941(2)°, V = 1486.1(1) Å^3, Z = 2, d_{cal} = 4.903 g cm^{-3}, μ(Mo Kα) = 275.99 cm^{-1}. 12 951 reflections were measured on a CCD diffractometer at 293 K, which gave 3704 independent reflections with R_{int} = 0.0256. An empirical absorption correction was made ($T_{min/max}$ = 0.450/0.969). Final refinement converged at R1 = 0.0197 and wR2 = 0.0410 for 3370 reflections with $I > 2\sigma(I)$ and 170 parameters.
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