Inorganic Chemistry
Article

Inorg. Chem. **2009**, *48*, 8357–8361 **8357**
DOI: 10.1021/ic901001n

Flux Synthesis of Salt-Inclusion Uranyl Silicates: $[K_3Cs_4F][(UO_2)_3(Si_2O_7)_2]$ and $[NaRb_6F][(UO_2)_3(Si_2O_7)_2]$

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Received May 23, 2009

Two salt-inclusion uranyl silicates, $[K_3Cs_4F][(UO_2)_3(Si_2O_7)_2]$ (compound **1**) and $[NaRb_6F][(UO_2)_3(Si_2O_7)_2]$ (compound **2**), have been synthesized at high temperature using mixtures of alkali metal fluorides as fluxes and structurally characterized by single-crystal X-ray diffraction. Both compounds contain UO_6 tetragonal bipyramids linked by disilicate groups to form three-dimensional framework structures with identical framework composition but different framework structures and salt inclusions. Both structures contain elliptical 12-ring channels where the K_2Cs_4F and Rb_6F units are located. They are the first examples of salt-inclusion uranium silicates. The frameworks of **1** and **2** are thermally stable up to 850 and 750 °C, as indicated from powder X-ray diffraction. The ^{19}F and ^{29}Si MAS NMR spectra and the second-harmonic-generation response of **1** are consistent with the crystal structure analysis results. Crystal data: $[K_3Cs_4F][(UO_2)_3(Si_2O_7)_2]$, $Cmc2_1$, $a = 7.8095(3)$ Å, $b = 22.2819(7)$ Å, $c = 14.0861(4)$ Å, and $Z = 4$; $[NaRb_6F][(UO_2)_3(Si_2O_7)_2]$, $Pnnm$, $a=11.1429(2)$ Å, $b=13.5151(3)$ Å, $c=7.8868(1)$ Å, and $Z=2$.

Introduction

We have been interested in the exploratory synthesis of metal silicates and germanates because of their interesting structural chemistry and potential applications. A good number of silicates and germanates of transition metals,[1a] main-group elements,[1b,c] lanthanides,[1d,e] and uranium[1f−h] have been synthesized by high-temperature, high-pressure hydrothermal and flux-growth reactions. For the flux techniques the alkali metal fluoride-MoO_3 fluxes have proven to be very useful in terms of synthesizing new compounds and retrieving crystals for structure determination.[2a,b] In some cases both alkali metal cations and fluoride anions from the fluxes are incorporated in host lattices, and this salt inclusion provides additional variety in structural features of the reaction products. For example, in the structure of $[Na_3F][SnSi_3O_9]$,[1b] the F^- and Na^+ ions are located in the structural channels and form a dimer with the *anti*-$Al_2Cl_6(g)$ structure. The salt-inclusion lanthanide silicates, $[K_9F_2]$-$[Ln_3Si_{12}O_{32}]$ (Ln = Sm, Eu, Gd),[1e] contain a F_2K_7 dimer with a structure similar to that of Cl_2O_7.

In addition to silicates,[3−5] a good number of salt-inclusion phosphates, arsenates, oxalates, and vanadates have also been synthesized by employing flux techniques at high temperatures[6−11] or a hydrothermal method at ~150 °C.[12−14] These salt-inclusion compounds contain some extraordinary structural features. Structural studies have also revealed that the incorporated salts provide structure-directing effects in the synthesis of non-centrosymmetric frameworks.

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Uranyl silicates exist as minerals and their structural chemistry has been extensively studied by Burns et al.[15] A good number of uranyl silicates which contain an organic amine or alkali metals as counter cations have been synthesized under mild hydrothermal conditions by Jacobson and co-workers.[16] During our continued exploratory synthesis of metal silicates, we synthesized two uranyl silicates, $[K_3Cs_4F][(UO_2)_3(Si_2O_7)_2]$ and $[NaRb_6F][(UO_2)_3(Si_2O_7)_2]$, by using mixtures of alkali metal fluorides as fluxes. They are the first examples of salt-inclusion uranium silicate. Both compounds adopt three-dimensional (3-D) framework structures with 12-ring channels and identical framework composition, although their framework structures and extra framework ionic species are different. In this work, we describe the synthesis, crystal structures, second harmonic generation, and solid-state NMR spectroscopy of these interesting compounds.

Experimental Section

Synthesis. The title compounds were synthesized by using mixtures of alkali metal fluorides as fluxes. Compound **1** was synthesized by heating a mixture of 0.776 g of CsF (Alfa Aesar 99.9%), 0.224 g of KF (Merck, >99%), 0.282 g of UO_3 (Cerac, 99.8%), and 0.080 g of SiO_2 (Alfa Aesar 99.995%) (Cs/K/U/Si mole ratio = 15.5/12/3/4) in a 4 mL platinum crucible at 750 °C for 12 h. The crucible was then cooled to 550 at 2 °C/h and quenched at room temperature by removing the crucible from the furnace. The flux was dissolved with hot water, and the solid product was obtained by suction filtration. Yellow column crystals of **1** were obtained as the major product, along with a small amount of orange crystals of $Cs_2UO_3SiO_3$.[17] Yellow prismatic crystals of **2** were prepared as a major product by heating a mixture of 0.834 g of RbF (Alfa Aesar 99.7%), 0.166 g of NaF (Merck, >99%), 0.094 g of UO_3 (Cerac, 99.8%), and 0.040 g of SiO_2 (Alfa Aesar 99.995%) (Rb/Na/U/Si mole ratio = 24.4/12/1/2) under similar reaction conditions except that the crucible was slowly cooled to 600 °C, and then quenched at room temperature. The reaction products also contained a small amount of orange column crystals of $Rb_2UO_3SiO_3$, which is isostructural to $Cs_2UO_3SiO_3$ as indicated by powder X-ray diffraction.

The heating programs for the two compounds are very similar, but the molar ratios of the reactants are considerably different. A reaction with the Cs/K/U/Si mole ratio of 24.4/12/1/2 under the same reaction conditions as those for **1** produced orange crystals of $Cs_2UO_3SiO_3$ and a very small amount of unknown yellow plate crystals. A comparison reaction with the Rb/Na/U/Si molar ratio of 15.5/12/3/4 under the reaction conditions for **2** was also performed, and the reaction product contained nearly pure compound **2** along with a trace of poorly crystalline orange material. The above results indicate that compounds **1** and **2** do not coexist.

The title compounds could be manually separated from the side products, giving pure samples, as indicated by powder X-ray diffraction (Supporting Information, Figure S1). Powder diffraction data were collected in the range of 5° ≤ 2θ ≤ 50° on a Shimadzu XRD-6000 automated powder diffractometer using θ-2θ mode in a Bragg−Brentano geometry. Energy dispersive X-ray analysis of several crystals showed the presence of Cs, K, U, Si, and F in **1** and Na, Rb, U, Si, and F in **2**. The yields were 65.3% and 48.3% for **1** and **2**, respectively, based on uranium. To investigate the thermal stabilities of the title compounds, X-ray diffraction patterns were taken on powder samples which had been heated at several temperatures in the range of 500 to 900 °C. The results indicate that the framework structures of **1** and **2** retain up to 850 and 750 °C, and transform to unknown phases at higher temperatures (Supporting Information, Figures S2 and S3).

Table 1. Crystallographic Data for $[K_3Cs_4F][(UO_2)_3(Si_2O_7)_2]$ (**1**) and $[NaRb_6F][(UO_2)_3(Si_2O_7)_2]$ (**2**)

	1	**2**
a/Å	7.8095(3)	11.1429(2)
b/Å	22.2819(7)	13.5151(3)
c/Å	14.0861(4)	7.8868(1)
V/Å^3	2451.13(14)	1187.73(4)
Z	4	2
fw	1814.39	1701.26
space group	$Cmc2_1$ (No. 36)	$Pnnm$ (No. 58)
T (°C)	21	21
λ (Mo Kα), Å	0.71073	0.71073
D_{calc}/ g cm^{-3}	4.917	4.757
μ(Mo Kα)/ mm^{-1}	26.422	32.93
$R_1{}^a$	0.0262	0.0156
$wR_2{}^b$	0.0694	0.0318

[a] $R_1 = \sum||F_o| - |F_c||/\sum|F_o|$. [b] $wR_2 = [\sum w(F_o{}^2 - F_c{}^2)^2/\sum w(F_o{}^2)^2]^{1/2}$, $w = 1/[\sigma^2(F_o{}^2) + (aP)^2 + bP]$, $P = [\max(F_o,0) + 2(F_c)^2]/3$, where $a = 0.0353$ and $b = 44.82$ for **1** and $a = 0.0077$ and $b = 4.53$ for **2**.

Single-Crystal X-ray Diffraction. Yellow crystals of dimensions 0.175×0.025×0.025 mm^3 for **1** and 0.075×0.075×0.05 mm^3 for **2** were selected for indexing and intensity data collection on a Bruker APEX diffractometer equipped with a normal-focus 2 kW sealed tube X-ray source. Intensity data were collected at room temperature in 7035 frames for **1** and 6420 frames for **2** with ω scans (width 0.30° per frame), and the space groups were determined to be $Cmc2_1$ for **1** and $Pnnm$ for **2**. The program SADABS was used for absorption correction ($T_{min/max} = 0.379/0.746$ for **1** and 0.587/0.746 for **2**).[18] The structures were solved by Patterson methods and difference Fourier syntheses. The final cycles of least-squares refinement including atomic coordinates and anisotropic thermal parameters for all atoms converged at $R_1 = 0.0262$ and $wR_2 = 0.0694$ for **1** and $R_1 = 0.0156$, $wR_2 = 0.0318$ for **2**. The residual electron densities in the final difference maps were close to U(1) in **1** and Rb(1) in **2** atoms ($\Delta\rho_{max,min} = 1.601, -2.326$ e Å^{-3} for **1** and 1.067, −0.898 e Å^{-3} for **2**). All calculations were performed using the SHELXTL version 5.1 software package.[19] Crystallographic data for **1** and **2** are given in Table 1.

Solid-State NMR Measurements. The ^{19}F and ^{29}Si MAS NMR spectra of **1** were acquired at 293 K on a Varian Infinityplus-500 NMR spectrometer equipped with a 4 mm Chemagnetics T3 HFX probe. The ^{19}F MAS NMR spectrum was acquired with a 90° pulse of 4.5 μs and a recycle delay of 10 s. A 45° pulse of 3.0 μs and a recycle delay of 60 s were used to acquire the ^{29}Si NMR spectra. The spinning speeds were set to 20 and 5 kHz for ^{19}F and ^{29}Si NMR, respectively. ^{19}F and ^{29}Si NMR chemical shifts were externally referenced to CCl_3F and tetramethylsilane (TMS) at 0 ppm, respectively.

Second-Harmonic-Generation (SHG) Measurements. Compound **1** crystallizes in a non-centrosymmetric space group,

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[17] Crystal data for $Cs_2UO_3SiO_3$: orange crystal of dimensions 0.2×0.05×0.02 mm, orthorhombic, space group $Immm$, $M_r = 627.94$, $a = 8.5514(7)$ Å, $b = 12.8190(11)$ Å, $c = 14.0179(12)$ Å, $V = 1536.6(2)$ Å^3, $Z = 8$, $d_{calcd} = 5.429$ g cm^{-3}, μ(Mo Kα) = 305.94 cm^{-1}. A total of 5678 reflections were measured on a CCD diffractometer at 294 K, which gave 1099 independent reflections with $R_{int} = 0.0258$. Final refinement converged at $R1 = 0.0480$ and $wR2 = 0.1334$ for 1034 reflections with $I > 2\sigma(I)$ and 66 parameters.

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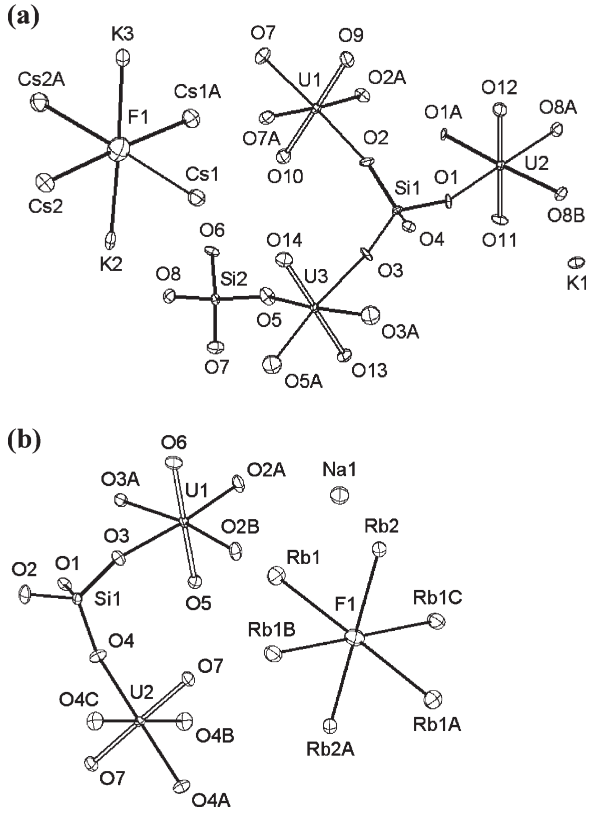

Figure 1. Building units of **1** (a) and **2** (b) showing the atom labeling scheme. Thermal ellipsoids are shown at 50% probability. The U=O bonds are represented by double lines.

Cmc2_1. Because SHG provides a highly sensitive and definite test of the absence of a center of symmetry of crystalline materials, the SHG response of a powder sample of **1** was measured.[20] The experimental setup mainly consists of an actively Q-switched Nd:YAG laser of wavelength 1.064 μm as the fundamental pump source, a ~0.013 nm-resolution grating monochromator as the spectral analyzer, and a photomultiplier tube as the signal detector. The Q-switched laser has a peak power of ~1200 kW with a pulse width of 5.3 ns and a repetition rate of 10 Hz. The sample powder was placed between microscope slides for measurement.

Results and Discussion

Structure. Both compounds adopt 3-D framework structures with identical framework composition, although their framework structures and extra framework species are different. Compound **1** crystallizes in a non-centrosymmetric space group with a unit cell volume about twice of that for **2**. The asymmetric units of the two compounds are shown in Figure 1. The structure of **1** is constructed by the following structural elements: two cesium sites, three potassium sites, one fluoride site, three UO_6 polyhedra, and two SiO_4 tetrahedra. All Cs and Si atoms are in general positions, whereas the other metal atoms and F atom lie in mirror planes. The observed Si−O bond lengths (1.590(9)−1.665(5) Å, average 1.627 Å) and O−Si−O bond angles (105.3(5)−113.7(5)°) are typical values falling within the normal range.[21] Every SiO_4 tetrahedron shares a corner with another tetrahedron to form a Si_2O_7 dimer, with the bond angle at the bridging oxygen atoms being 139.9(7)° for Si(1) and 141.9(7)° for Si(2). In the $U(1)O_6$, $U(2)O_6$, and $U(3)O_6$ tetragonal bipyramids (designated as $Ur\phi_4$), the U atoms have unsymmetrical oxygen coordination environments: two U=O bonds are short (1.811(13), 1.818(13) Å for U(1); 1.828(12), 1.840(12) Å for U(2); 1.807(12), 1.825(13) Å for U(3)), forming a linear uranyl (Ur) unit, which is typical for uranium(VI) compounds; and four U−O bonds in the plane normal to the O=U=O axis are longer (2.213(9)−2.253(9) Å). The bond-valence sums at the U(1), U(2), and U(3) sites are 5.99, 5.76, and 5.97, respectively, consistent with the occurrence of U^{6+} ions in these sites.[22] All Cs, K, and F sites are fully occupied. Each fluoride anion is bonded to two K^+ and four Cs^+ cations to form an octahedron as shown in Figure 1(a). It should be noted that K(1) is bonded to framework oxygen atoms only. On the basis of the maximum cation−anion distance by Donnay and Allmann,[23] limits of 3.70 and 3.35 Å were set for Cs−O and K−O interactions, respectively, which give the following coordination numbers: Cs(1), 8-coordinate, including one F atom at 2.879(12) Å; Cs(2), 8-coordinate, including one F atom at 2.900(12) Å; K(1), 7-coordinate, bonded to oxygen atoms only; K(2), 8-coordinate, including one F atom at 3.057(19) Å; K(3), 7-coordinate, including one F atom at 3.018(19) Å.

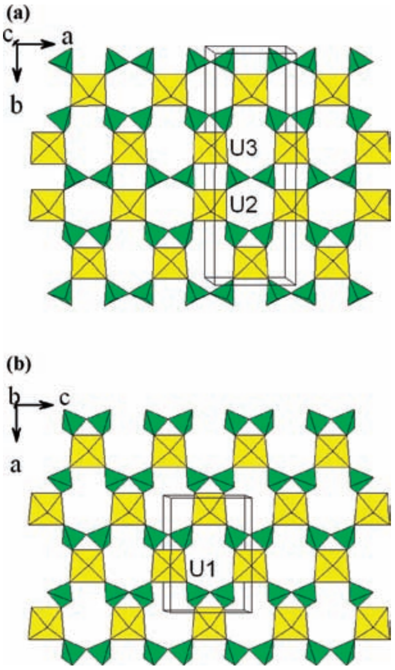

Figure 2. Slice of the structure of **1** in the *ab* plane (a) and **2** in the *ac* plane (b). The yellow and green polyhedra represent UO_6 tetragonal bipyramids and SiO_4 tetrahedra, respectively.

The $Ur\phi_4$ units have four equatorial oxygen atoms (ϕ, O_{eq}) that are shared with SiO_4 tetrahedra, and two apical uranyl oxygen atoms that are unshared. The $U(2)O_6$ tetragonal bipyramid is connected to four different Si_2O_7 groups and $U(3)O_6$ to three Si_2O_7 groups to form 2-D layers in the *ab* plane (Figure 2(a)). Adjacent layers

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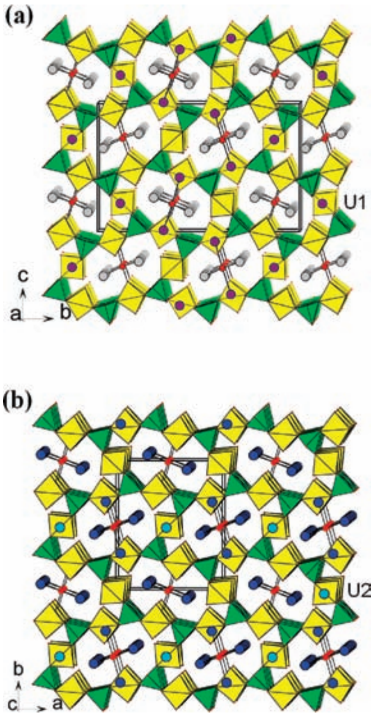

Figure 3. Structure of **1** (a) and **2** (b) viewed along the *a* axis and *c* axis, respectively. Key: yellow polyhedron, UO_6; green tetrahedron, SiO_4; gray circle, Cs^+; purple circle, K^+; cyan circle, Na^+; blue circle, Rb^+; red circle, F^-.

are linked together by $U(1)O_6$ tetragonal bipyramids which share corners with three different Si_2O_7 groups to form a 3-D framework (Figure 3(a)). One type of elliptical 12-ring channel which is formed by the edges of six $Ur\phi_4$ units and six SiO_4 tetrahedra are observed along the *a* axis. Lateral 7-ring channels which are formed by the edges of three $Ur\phi_4$ units, one Si_2O_7 group, and two SiO_4 tetrahedra are observed along the [1 1 0] and [1 −1 0] directions. The K_2Cs_4F octahedron is located in the 12-ring channel, whereas K(1) is in the lateral 7-ring channel.

As shown in Figure 1(b), the structure of **2** is constructed from the following structural elements: two rubidium sites, one sodium site, one fluoride site, two UO_6 polyhedra, and one SiO_4 tetrahedron. Si(1) and Rb(1) are in general positions, whereas Na(1), U(2), and F(1) are at inversion centers and Rb(2) and U(1) in mirror planes. U(1) and U(2) also have unsymmetrical oxygen coordination environments which are typical for uranium(VI) compounds. All of the Rb, Na, and F sites are fully occupied. F(1) is bonded to six Rb cations to form an octahedron. Both Rb(1) and Rb(2) are coordinated by one F and six oxygen atoms, and Na(1) by eight oxygen atoms only. Each $U(1)O_6$ is connected to three Si_2O_7 groups forming two-dimensional (2-D) layers in the *ac* plane (Figure 2(b)). Adjacent uranyl silicate layers are linked together by $U(2)O_6$ tetragonal bipyramids which share corners with four different Si_2O_7 groups to form a 3-D framework (Figure 3(b)). Elliptical 12-ring channels along the *c* axis and lateral 6-ring channels along the *a* axis are observed. The octahedral Rb_6F units are located in the 12-ring channels with the Na cations in the lateral 6-ring channels.

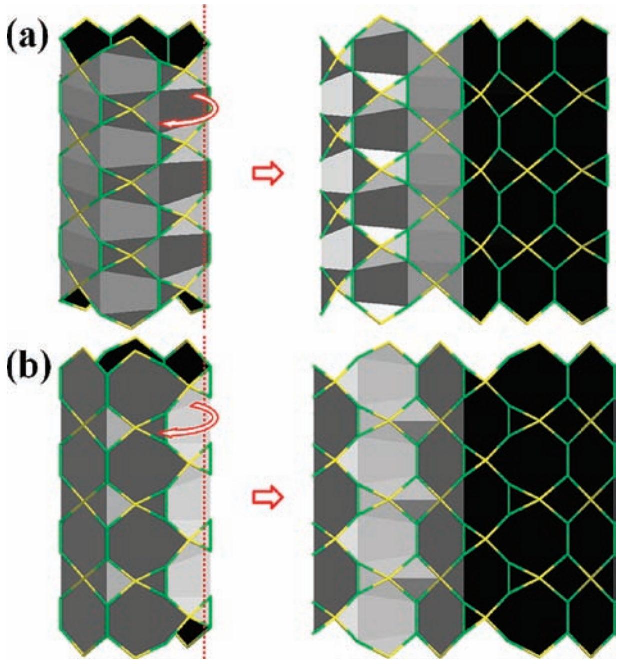

Figure 4. (Left) Topological structure of the 12-ring channel in **1** (a) and **2** (b). (Right) Unrolled channel walls. In these diagrams, the U (in yellow) and Si (in green) atoms are located at intersections of the lines, as O bridges are made by corner sharing from the vertexes of the tetragonal bipyramid and the tetrahedron. Gray and black tiles represent the front and rear part of channels.

Although the title compounds have identical framework composition, their framework structures are different. These results show that the incorporated salts, K_2Cs_4F and Rb_6F, provide structure-directing effects. Hwu and co-workers have also shown the utility of chlorine-centered salts as structure-directing agents in the synthesis of non-centrosymmetric phosphate and silicate frameworks.[4,5,9] Figure 4 shows the topological structures of the elliptical 12-ring channels and their idealized unfolded versions of the title compounds. The structures of unrolled channel walls are considerably different. Recently, we reported high-temperature, high-pressure hydrothermal synthesis of a new uranyl germanate, $Cs_6[(UO_2)_3(Ge_2O_7)_2]\cdot 4H_2O$,[1h] having a structure that contains circular 12-ring channels. The topological structure of the unrolled channel wall of this germanate is interestingly found to be identical to that of **2**.

Solid-State NMR Spectroscopy and SHG. The ^{29}Si MAS NMR spectrum of **1** shows one resonance with its maximum intensity at −75.9 ppm (Supporting Information, Figure S4(a)). Although there are two unique Si(1Si,3U) sites in the structure, both Si environments are too similar to be distinguished, so the resonance can be ascribed to overlapping peaks. The ^{29}Si chemical shift for **1** has a less negative value as compared with that of −81.3 ppm for the Si(2Si,2U) sites in the uranyl silicate USH-5Cs.[16b,24] These results are consistent with the general observations that the ^{29}Si chemical shift becomes increasingly negative with each additional Si−O−Si linkage because of increased electronic shielding of the central Si.[25] The ^{19}F MAS NMR spectrum of **1** (Supporting Information, Figure S4(b)) shows one resonance at −30.7 ppm, which corresponds to the single F(4Cs, 2K) environment in the structure.

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For comparison, the ^{19}F NMR chemical shifts of KF and CsF relative to CCl_3F are −136 and −14 ppm, respectively.[26]

To confirm that compound **1** crystallized in a noncentrosymmetric space group, *Cmc*2_1, the SHG response of powder of **1** was measured. After collimating and properly focusing the laser beam onto the surface of the loaded powder with an incident angle of 45°, the SHG signal was collected at 90° direction. The use of a focused beam is to enhance the SHG efficiency, and the collection of the SHG signal in the backward direction is to minimize the effect of absorption. The urea powder, with nonlinear coefficient estimated as 1.4 $pm \cdot V^{-1}$, was also measured under the same condition for comparison.[27] The SHG peak intensity ($\lambda = 0.532$ μm) of **1** was approximately 13% of that for urea (Supporting Information, Figure S5).

In summary, the molten-salt synthesis and crystal structures of the first examples of salt-inclusion uranyl silicates have been reported. Both compounds have identical framework composition but with different framework structures and salt inclusions. The ^{19}F and ^{29}Si MAS NMR spectra of **1** are consistent with the crystal structure as determined from X-ray diffraction. Although both compounds contain elliptical 12-ring channels, the structures of their unrolled channel walls are considerably different. Interestingly, the unrolled channel wall of **2** is the same as that of $Cs_6[(UO_2)_3(Ge_2O_7)_2]\cdot 4H_2O$ which contains a circular 12-ring channel. On the basis of powder X-ray diffraction, the framework structures of **1** and **2** retain up to 850 and 750 °C, respectively. SHG measurement results confirm that **1** crystallizes in a non-centrosymmeric space group. The flux techniques allow new discoveries to be made through different fluxes and altered reaction conditions. Further research on the exploratory synthesis of metal silicates and germanates in molten salts is in progress.

Acknowledgment. The authors thank Prof. H.-M. Kao at the Department of Chemistry of National Central University for solid state NMR measurements, and the National Science Council of Taiwan for financial support.

Supporting Information Available: Crystallographic data for $[K_3Cs_4F][(UO_2)_3(Si_2O_7)_2]$ and $[NaRb_6F][(UO_2)_3(Si_2O_7)_2]$ in CIF format, experimental and simulated X-ray powder patterns, solid state NMR spectra, and SHG measurement results. This material is available free of charge via the Internet at http://pubs.acs.org.

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