



Solid-state syntheses and single-crystal characterizations of three tetravalent thorium and uranium silicates



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ABSTRACT

Colorless crystals of ThSiO_4 (huttonite) (**1**) and $(\text{Ca}_{0.5}\text{Na}_{0.5})_2\text{NaThSi}_8\text{O}_{20}$ (**2**) have been synthesized by the solid-state reactions of ThO_2 , CaSiO_3 , and Na_2WO_4 at 1073 K. Green crystals of $(\text{Ca}_{0.5}\text{Na}_{0.5})_2\text{NaUSi}_8\text{O}_{20}$ (**3**) have been synthesized by the solid-state reactions of UO_2 , CaSiO_3 , and Na_2WO_4 at 1003 K. All three compounds have been characterized by single-crystal X-ray diffraction. Compound **1** adopts a monazite-type three-dimensional condensed structure, which is built from edge- and corner-shared ThO_9 polyhedra and SiO_4 tetrahedra. Compounds **2** and **3** are isostructural and they crystallize in a steacyite-type structure. The structure consists of discrete pseudocubic $[\text{Si}_8\text{O}_{20}]^{8-}$ polyanions, which are connected by An^{4+} cations into a three-dimensional framework. Each An atom coordinates to eight monodentate $[\text{Si}_8\text{O}_{20}]^{8-}$ moieties in a square antiprismatic geometry. Na^+ and Ca^{2+} ions reside in the void within the framework. Raman spectra of **1**, **2**, and **3** were collected on single crystal samples. **1** displays more complex vibrational bands than thorite. Raman spectra of **2** and **3** are analogous with most of vibrational bands located at almost the same regions.

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1. Introduction

The natural formation of silicate minerals has involved a range of processes that include partial melting and crystallization. Because silicate phases are a significant class of minerals observed for natural actinides [1–8], as exemplified by thorite (ThSiO_4) [1] and coffinite (USiO_4) [3], we are interested in developing synthetic routes from melts that can be used to extend this chemistry to the man-made heavier actinides, Np and Pu. Knowledge in this area is critical to furthering our predictive capabilities regarding the fate and transport of transuranic contaminants in the geosphere [9,10].

The current research of actinide silicates, particularly those containing lower-valent actinides (III/IV) has been largely hindered by the difficulty in the material syntheses [11–15]. For example, synthesis of pure USiO_4 proves to remain challenging to date, which has prevented the determination of accurate thermodynamic values until recently [12,14,15]. Binary actinide and silicon oxides and most of metal silicates have low solubility in common solvents and high melting points (e.g. ThO_2 : insoluble in water with a melting point of 3660 K). Harsh synthetic conditions such as high pressure and high temperature (> 1273 K) are typically required to allow the reactants to reach reasonable

diffusion rates [11,13,16,17]. Most actinides except Th are redox active, which poses additional challenges over the syntheses [18]. Hydrothermal methods have been widely used to prepare silicate materials including uranyl silicates [19,20], however there is limited success in stabilizing lower-valent actinides under these conditions [12,13]. As a result, the number of actinide (III/IV) silicates reported in the literature is rather small even for Th or U phases [5–8,13,21–24]. Most of studies have focused on actinide orthosilicates and a few of other actinide-contained silicate minerals such as arapovite $((\text{CaNa})_2(\text{K}_{1-x}\text{U})\text{USi}_8\text{O}_{20})$ [8] and ekanite $(\text{Ca}_2\text{ThSi}_8\text{O}_{20})$ [25]. The only additions to the minerals and their related phases are recently discovered $\text{Cs}_2\text{ThSi}_6\text{O}_{15}$ [22], $\text{Cs}_2\text{U-Si}_6\text{O}_{15}$ [13], and several U(IV)-contained mixed-valent uranium silicates [26–28] in laboratories.

Herein, we report the single-crystal growth of ThSiO_4 (huttonite) (**1**) and two new compounds, $(\text{Ca}_{0.5}\text{Na}_{0.5})_2\text{NaThSi}_8\text{O}_{20}$ (**2**), and $(\text{Ca}_{0.5}\text{Na}_{0.5})_2\text{NaUSi}_8\text{O}_{20}$ (**3**) using a ternary precursor and a Na_2WO_4 flux in silica ampoules at much lower temperatures (several hundreds of degrees) than previous solid-state studies. Naturally occurring huttonite has been synthesized in powder form by a hydrothermal process [11] or from sintering ThO_2 and SiO_2 at 1773 K [29]. Alternatively, single-crystal samples have been obtained by heating two binary oxides in a Li_2WO_4 or a Na_2WO_4 melt at 1523 K [16,17]. It is noted that, compounds **2** and **3** are closely related to the minerals, steacyite and turkestanite $((\text{CaNa})_2(\text{K}_{1-x}\text{U})\text{ThSi}_8\text{O}_{20}(\text{H}_2\text{O})_n)$ [5,6], and arapovite $((\text{CaNa})_2(\text{K}_{1-x}\text{U})\text{USi}_8\text{O}_{20})$ [8]. Powder samples of synthetic analogous of Th minerals, $\text{KNaCaThSi}_8\text{O}_{20}$ [23]

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and RbNaCaThSi₈O₂₀ [24] have been synthesized very recently from solid-state reactions of metal nitrates and silicon oxides at 1420 K.

We also report structural and Raman spectroscopic studies on single crystal samples of **1**, **2**, and **3**. Raman spectroscopy has been widely used to gain structural and compositional information of silicate materials [30]. Extensive Raman studies on zircon-type compounds including ZrSiO₄, HfSiO₄, ThSiO₄ (thorite), and USiO₄ have been reported in the literature [31–33]; However no study has been conducted on huttonite, which is the high-temperature polymorph of thorite. To our knowledge, this is the first reported Raman spectrum for single crystals of huttonite. Recently, Clavier et al. have demonstrated the use of Raman spectroscopy as a promising tool for the semi-quantitative determination of chemical composition of uranothorite samples (Th_{1-x}U_xSiO₄) [33]. Our results on isostructural compounds **2** and **3** are used to further assess this potential application of Raman spectroscopy for actinide silicate materials.

2. Experiments

Cation ! ²³²Th and ²³⁸U are α emitting radioisotopes and as such are considered a health risk. Their use requires appropriate infrastructure and personnel trained in the handling of radioactive materials.

2.1. Syntheses

ThO₂ (International Bio-Analytical Industries, Inc.), UO₂ (International Bio-Analytical Industries, Inc.), CaSiO₃ (Cerac, 99.5%), and Na₂WO₄ (MP Biomedicals) were used as received. For both reactions, the reactants were loaded into carbon coated fused-silica ampoules and then flame-sealed under vacuum. The reaction mixtures were placed in a computer-controlled furnace and heated to 1073 K (Th reaction) or 1003 K (U reaction) in 30 h, held at this temperature for 140 h, slowly cooled to 748 K (Th reaction) or 703 K (U reaction) in 150 h, and then cooled to 298 K in 6 h. The reaction products were washed with water and dried with acetone. Crystals found in these reactions were characterized by single-crystal X-ray diffraction methods.

ThSiO₄ (1) and (Ca_{0.5}Na_{0.5})₂NaThSi₈O₂₀ (2). 0.020 g (0.076 mmol) of ThO₂ and 0.016 g (0.138 mmol) of CaSiO₃ were thoroughly ground together before loading into an ampoule with 0.090 g (0.306 mmol) of Na₂WO₄. A large number of colorless prismatic crystals of **1** and colorless cubic crystals of **2** co-formed in the same bulk reaction products. Both compounds are stable in air. The yields of **1** and **2** are difficult to estimate owing to the similar appearance of crystals and broken glass pieces.

(Ca_{0.5}Na_{0.5})₂NaUSi₈O₂₀ (3). 0.010 g (0.037 mmol) of UO₂ and 0.034 g (0.293 mmol) of CaSiO₃ were thoroughly ground together before loading into an ampoule with 0.080 g (0.273 mmol) of Na₂WO₄. The reaction products included green cubic crystals of **3**, which grow among other powder products including unreacted brown UO₂, white CaWO₄, and some unidentified white phases. A complete separation of green crystals from other products failed. The yield of **3** is estimated to around 70% from a visual inspection. After removing the broken glass, the products were ground into a powder and characterized by powder X-ray diffraction measurements.

2.2. Structure determination

Single-crystal X-ray diffraction data for ThSiO₄ (**1**), (Ca_{0.5}Na_{0.5})₂NaThSi₈O₂₀ (**2**), and (Ca_{0.5}Na_{0.5})₂NaUSi₈O₂₀ (**3**) were collected with the use of graphite-monochromatized Mo Kα radiation (λ=0.71073 Å) at 100 K on a Bruker APEX2 diffractometer [34]. The crystal-to-detector distance was 5.106 cm. Data were collected by a scan of 0.3° in ω

Table 1

Crystal data and structure refinements for (Ca_{0.5}Na_{0.5})₂NaAnSi₈O₂₀ (An=Th, U)^a.

	(Ca _{0.5} Na _{0.5}) ₂ NaThSi ₈ O ₂₀	(Ca _{0.5} Na _{0.5}) ₂ NaUSi ₈ O ₂₀
Fw	862.82	868.81
a (Å)	7.497(2)	7.438(2)
c (Å)	14.886(4)	14.888(3)
V (Å ³)	836.6(4)	823.7(3)
ρ _c (g/cm ³)	3.425	3.503
μ (cm ⁻¹)	99.58	109.15
R(F) ^b	0.0231	0.0292
R _w (F _o ²) ^c	0.0563	0.0793

^a For both structures, Z=2, space group=P4/mcc, λ=0.71073 Å, and T=100(2) K.

^b R(F)=Σ||F_o|-|F_c||/Σ|F_o| for F_o²>2σ(F_o²).

^c R_w(F_o²)=[Σ[w(F_o²-F_c²)²]/ΣwF_o⁴]^{1/2} for all data. w⁻¹=σ²(F_o²)+(qF_o²)² for F_o²≥0; w⁻¹=σ²(F_o²) for F_o²<0. q=0.0289 for (Ca_{0.5}Na_{0.5})₂NaThSi₈O₂₀, 0.0450 for (Ca_{0.5}Na_{0.5})₂NaUSi₈O₂₀.

in groups of 600 frames at φ settings of 0°, 90°, 180°, and 270°. The exposure time was 20 s/frame for **1**, 80 s/frame for **2**, and 50 s/frame for **3**. The collection of intensity data as well as cell refinement and data reduction were carried out with the use of the program APEX2 [34]. Absorption corrections, incident beam, and decay corrections were performed with the use of the program SADABS [35]. The structures were solved with the direct-methods program SHELXS and refined with the least-squares program SHELXL [36]. The structural refinements for **1** were straightforward. In cases of **2** and **3**, disordering of Ca and Na atoms at the 4f (0, 1/2, 1/4) site is required to reach reasonable thermal parameters. Unrestricted anisotropic models for both **2** and **3** refined successfully and led to Ca:Na close to 1:1. The restricted refinements with Ca:Na equal to 1:1 also yielded similar thermal parameters. Similar disordering behavior of Ca and Na at this position has been observed in other isostructural minerals and compounds [6,8,23]. Final refinements included anisotropic displacement parameters for all atoms. The program STRUCTURE TIDY was used to standardize the positional parameters [37]. Additional experimental details are given in Table 1 and in the crystallographic information files included in the Supporting material.

2.3. X-ray powder diffraction measurements

X-ray powder diffraction patterns were collected with a Scintag X1 diffractometer with the use of Cu Kα radiation (λ=1.5418 Å). The powder sample was loaded into an encapsulated container with curved Kapton windows to minimize the X-ray absorption by the Kapton.

2.4. Raman spectroscopy

Raman spectra of single-crystal samples of ThSiO₄ (**1**), (Ca_{0.5}Na_{0.5})₂NaThSi₈O₂₀ (**2**), and (Ca_{0.5}Na_{0.5})₂NaUSi₈O₂₀ (**3**) were collected on a Renishaw inVia Raman Microscope with excitation lines of 532 nm and 785 nm. For each compound, at least six different spots were collected on numerous crystals to obtain reproducible data. Due to the radiological hazards associated with ²³²Th and ²³⁸U, each sample was placed on a glass drop-slide covered with a transparent coverslip, which was sealed to the slide using an epoxy sealant.

3. Results and discussion

3.1. Syntheses

Recent experimental studies and theoretical calculations have shown that thorite and huttonite are thermodynamically

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