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Moderate Supercritical Synthesis as a Facile Route to Mixed-Valent Uranium (IV,V) and (V,VI) Silicates

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Mixed-valent uranium (IV,V) and (V,VI) phases represent a unique subset of known uranium compounds. Efforts to develop our current understanding of these materials have pointed to hydrothermal methods as effective preparative techniques. Herein we report the successful use of moderate supercritical conditions for the synthesis of five new U(V) containing phases.

Uranium's ability to exist in multiple oxidation states (II, III, IV, V, VI) has resulted in a substantial number of compounds containing uranium in diverse, often oxidation state specific, coordination environments. Owing to the greater stability of U(IV) and U(VI), as compared to U(II), U(III), and U(V), divalent and trivalent uranium exists almost exclusively in molecular compounds, while pentavalent uranium remains a relatively undeveloped facet of uranium chemistry.[1]

U(V)-containing minerals are known, for example the dehydrated and hydrated forms of wyartite, $CaU^{V}(U^{VI}O_2)_2(CO_3)O_4(OH)(H_2O)_7$[2,3] and, like many minerals, their formation likely resulted from hydrothermal crystal growth processes. It stands to reason that to synthesize other U(V)-containing materials we can learn from nature and adopt this proven approach. The main challenge, of course, remains to identify and create the conditions that facilitate the formation and stabilization of U(V), as only a few examples of purely pentavalent uranium-containing compounds are known;[4] complex ternary and higher mixed valent U(IV,V) and U(V,VI) compositions are even less prevalent.

In recent years, a number of reports on the successful preparation of mixed-valent U(IV,V) and U(V,VI) compounds has highlighted synthetic techniques that are able to stabilize pentavalent uranium where, in particular, the hydrothermal method has emerged as one of the most prominent of these techniques. As an example, a U(V,VI) hydroxide reported by Cahill et al. was synthesized via a mild hydrothermal route from the partial reduction of $[UO_2]^{2+}$ by zinc and hydrazine, resulting in the stabilization of U(V) most likely attributable to the formation of U^{V}-U^{VI} dimers.[5] Using related methods, Wang et al. reported on the synthesis of a U(IV,V,VI) phosphonate; an extremely rare case in which all three oxidation states of uranium were stabilized simultaneously in a single structure.[6] This composition was prepared under mild solvothermal conditions in which methanol was used as a soft reducing agent. Interestingly, addition of zinc to this system resulted in the formation of a phase pure U(IV,VI) phosphonate, suggestive of U(V) disproportionation.

In contrast to mild conditions, Lii et al. demonstrated the viability of using high temperature high pressure (HTHP) hydrothermal methods at ca. 600°C and pressures of 150-170 MPa to synthesize an extensive family of pentavalent[7-9] and mixed-valent uranium silicates[10-12] and germanates,[13,14] as well as a mixed-valent uranium oxyhydroxide.[15] It is noteworthy that many of these compositions were prepared without the addition of a reducing agent, implying that the inherently reducing nature of hydrothermal synthesis conditions[16] are conducive to the stabilization of U(V). In addition to silicates and germanates, application of this technique to other systems has also been demonstrated successfully. Using similar HTHP conditions, Albrecht-Schmitt et al. prepared the first mixed-valent U(V,VI) borate.[17] A narrow range of stability restricts the formation of this phase, which is evident from the formation of an exclusively U(VI) phase as a result of an increase in reaction temperature from 600°C to 650°C; furthermore, stabilization of

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† Electronic Supplementary Information (ESI) available: Crystal image, crystallographic data, bond-valence sums, PXRD. For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/x0xx00000x

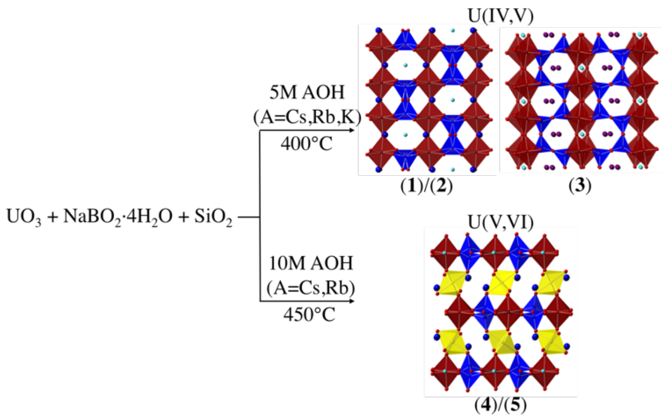
this phase was also suggested to be dependent on the high pH of the reaction mixture.

The methods discussed have indeed proven to be productive synthetic routes to U(V)-containing materials. Nonetheless, a more facile method is desired to enable a systematic approach to the targeted synthesis of U(V) compounds. Ideally, such a method should maintain the intrinsic reducing conditions of HTHP hydrothermal synthesis. In order to meet these criteria, our group has probed the intermediate hydrothermal regime between 300-450°C; a range of conditions largely unexplored in comparison to HTHP (>500°C) and low temperature (<250°C) methods. We recently reported on the first entirely pentavalent uranium borate, the preparation of which was achieved using subcritical reaction conditions.[4] In our efforts to build on this system and promote further structural diversity through the incorporation of mixed oxoanions, namely borosilicate, we discovered that subtle changes in reaction temperature and hydroxide concentration resulted in the formation of five unique mixed-valent U(IV,V) and U(V,VI) phases, discussed herein.

Three of the five mixed-valent compounds reported herein are U(IV,V) phases having compositions of $Cs_2Na(UO)_2Si_4O_{12}$ (**1**), $Rb_2Na(UO)_2Si_4O_{12}$ (**2**), and $K_2Na[(UO)_2(Si_2O_6)_2]$ (**3**). All three phases were synthesized from a mixture of UO_3, $NaBO_2 \cdot 4H_2O$, and SiO_2 in 2 mL of a 5M alkali hydroxide solution in a molar ratio of U/Na/Si/(Cs,Rb,K) = 1:10:10:20. Each reaction was sealed in a silver tube that was placed inside a stainless-steel high-pressure vessel filled with water for counterpressure and heated at 400°C for 24 hours followed by a period of slow cooling, yielding well-faceted amber/black, tablet shaped crystals (Figure S1, ESI†). Based on the 32% fill level, an estimated 28 MPa of pressure was generated during the reactions. The other two mixed-valent phases contain U(V,VI) and were synthesized by the same method that resulted in compounds **1**-**3** (Scheme 1) however, employing the higher reaction temperature of 450°C and a molar ratio of U/Na/Si/(Cs,Rb) = 1:10:10:40 resulted in the formation of $Cs_2Na[(UO_2)_2(Si_2O_7)]$ (**4**), and $Rb_2Na[(UO_2)_2(Si_2O_7)]$ (**5**). Of the five phases presented, **3** can be obtained as a phase pure product, while **4** and **5** form in high yields along with a small amount of an unidentified side product. This impurity can be eliminated via a dropwise addition of concentrated (49-50%) HF during vacuum filtration of the bulk product, followed by sonication in deionized water.

Compounds **1** and **2** crystallize in the orthorhombic space group *Cmmm* and are isostructural to $Cs_2K(UO)_2Si_4O_{12}$, a previously reported composition synthesized under HTHP hydrothermal conditions by Lii et al.[11] The structures of **1** and **2** are characterized by chains of UO_6 octahedra exhibiting cation-cation interactions as a result of connections through the uranyl oxygens,[8,18] which extend down the *a*-axis and are connected to neighboring chains by corner-sharing Si_4O_{12} rings that lie within the [*ac*] plane. Disorder in the structure arises from oxygen atoms which lie just off the mirror planes (Figure 1a,b). Channels within the framework contain sodium and cesium or rubidium atoms. Identical synthesis conditions were used for the preparation of **3**, however, it exhibits unique structural features as compared to those of compounds **1** and **2**. Crystallizing in the orthorhombic space group *Imma*, compound **3** is composed of corrugated chains of UO_6 octahedra connected by uranyl oxygens, linked to neighboring chains by corner-sharing with Si_2O_6 chains that extend in the same direction as the uranium octahedra along the *a*-axis (Figure 2a,b). Sodium and potassium atoms reside within the channels of the framework.

Compounds **1**-**3** each exhibit a single uranium site on which U(IV) and U(V) co-exist; in contrast, compounds **4** and **5** contain two unique uranium sites with full occupancy of U(V) on one site and U(VI) on the second. Tables S1 and S2 summarizing all relevant crystallographic information, comparisons of representative U-O bond lengths with those of other known



Scheme 1 A synthetic scheme for compounds **1**-**5**, where polyhedra containing U(V) and U(VI) are shown in red and yellow, respectively.

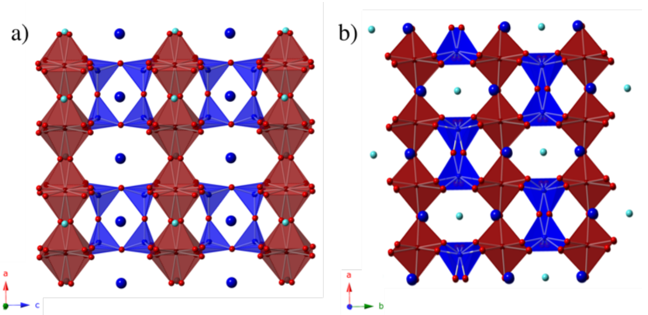


Figure 1 Structural disorder of $A_2Na(U^{IV,V}O)_2Si_4O_{12}$ (A = Cs (**1**), Rb (**2**)) within a) $U^{IV,V}O_6$ chains and b) Si_4O_{12} rings, where red polyhedra represent $U^{IV,V}O_6$, blue tetrahedra are SiO_4 groups, dark blue spheres are Cs or Rb, and light blue is Na.

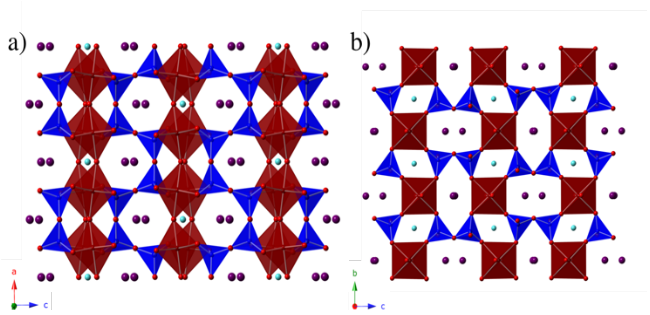


Figure 2 Structure of $K_2Na[(U^{IV,V}O)_2(Si_2O_6)_2]$ (**3**) showing a) corrugated $U^{IV,V}O_6$ chains linked by Si_2O_6 chains and b) a view of the connectivity of Si_2O_6 chains and $U^{IV,V}O_6$ octahedra.

U(V)-containing phases, and bond valence sums for each composition are tabulated in the supporting information. Compounds **4** and **5** are isostructural and crystallize in the space group *Pccn*. The structure can be described as consisting of layers composed of isolated U^VO_6 octahedra that corner-share with four Si_2O_7 groups to form $(UO)_2(Si_2O_7)$ sheets within the [*bc*] plane (Figure 3a). The sheets are connected by $U^{VI}O_6$ octahedra that corner-share each equatorial oxygen with two opposing U^VO_6 octahedra and two opposing SiO_4 tetrahedra (Figure 3b). The axial uranyl oxygens of the U^VO_6 octahedra are corner-shared by the $U^{VI}O_6$ octahedra, while the uranyl oxygens of the $U^{VI}O_6$ octahedra point inwards toward channels that are occupied by sodium and cesium or rubidium atoms.

The magnetic susceptibilities of **3**-**5** were measured from 2 to 375 K in an applied magnetic field of 0.1 T. We were unable to obtain phase pure samples of **1** and **2** and, therefore, no magnetic measurements of these two compositions were made. All three materials exhibit paramagnetic behavior at low temperature (Figure 4a), but do not obey the Curie-Weiss law for all temperatures. High temperature effective magnetic moments were therefore obtained from a plot of χT *versus* T (Figure 4b), resulting in moments at 300 K of 2.497 μ_B for **3**, 1.787 μ_B for **4**, and 1.347 μ_B for **5**, where the larger moment of compound **3** is due to the fact that the structures of **4** and **5** contain U(V) and non-magnetic U(VI), versus **3** that contains both U(V) and magnetic U(IV). Corrections for the diamagnetic contribution of uranium were applied to the data using Pascal's constants.[19] The magnetic moments obtained are consistent with reported room-temperature magnetic moments for U(IV) and U(V), which fall into the ranges of approximately 1.3-3.8 μ_B and 1.2-3.7 μ_B, respectively.[20]

The electronic structures of **3**-**5** were probed using diffuse reflectance UV-visible spectroscopy. All three compounds were found to exhibit a charge-transfer band in the region of approximately 200-400 nm (Figure 5). This absorption feature arises from equatorial ligand to metal charge transfer ($LMCT_{eq}$) transitions and is characteristic of both U(VI) and U(V); however, charge-transfer bands associated with U(VI) are typically narrower than those for U(V).[6,21] This is consistent with our observations, in which the U(IV,V)-containing compound **3** exhibits a significantly broader $LMCT_{eq}$ band than the U(V,VI)-containing compounds **4** and **5**. The large, broad feature at approximately 500 nm in the spectra of all three compounds is associated with the charge transfer of the U(V), UO_2^+ moiety.[17]

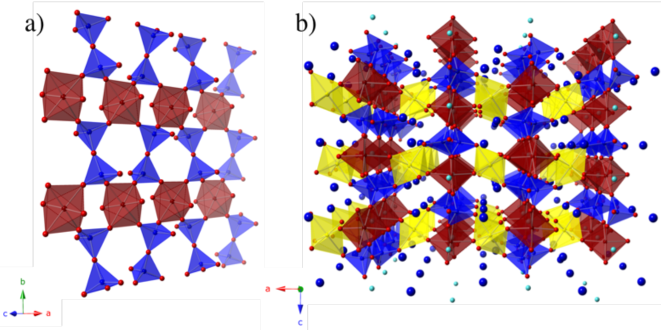


Figure 3 Structure of $A_2Na[(U^{V,VI}O_2)_2(Si_2O_7)]$ (A = Cs (**4**), Rb (**5**)) composed of a) $(U^VO)_2(Si_2O_7)$ sheets connected by b) corner-sharing $U^{VI}O_6$ octahedra, shown in yellow.

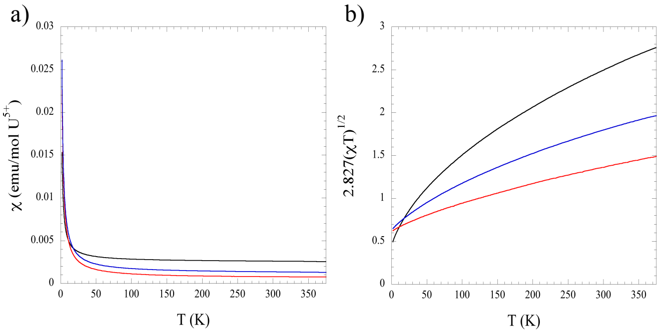


Figure 4 a) Magnetic susceptibilities and b) χT *vs.* T plots for $K_2Na[(U^{IV,V}O)_2(Si_2O_6)_2]$ (black), $Cs_2Na[(U^{V,VI}O_2)_2(Si_2O_7)]$ (blue), and $Rb_2Na[(U^{V,VI}O_2)_2(Si_2O_7)]$ (red).

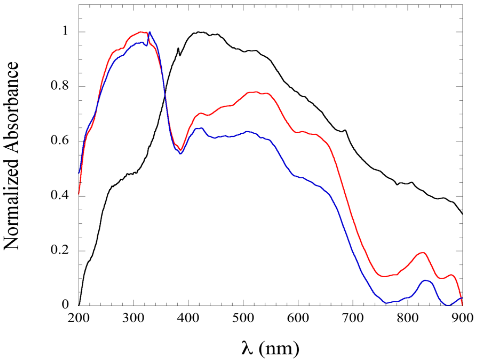


Figure 5 The UV-visible absorption spectra of $K_2Na[(U^{IV,V}O)_2(Si_2O_6)_2]$ (black), $Cs_2Na[(U^{V,VI}O_2)_2(Si_2O_7)]$ (blue), and $Rb_2Na[(U^{V,VI}O_2)_2(Si_2O_7)]$ (red).

In the spectrum of **3**, the fine structure of the absorption feature occurring between 400-800 nm reveals weak f-f transitions, indicating the presence of U(IV).[6]

The IR spectra of **3**-**5** lend additional support to these findings (Figure S2, ESI†). A strong band is observed in the spectra of **4** and **5** at 791 cm^{-1}, corresponding to the asymmetric stretching modes ν_3 of U(VI); this band is absent in the spectrum of **3**. In the case of **4** and **5**, bands corresponding to the U(VI) ν_3 stretching modes exhibit lower wavenumbers than are often reported due to the elongated U(VI) uranyl bond lengths of 1.838 Å. The weak band occurring at 637 cm^{-1} for **3** and **5**, and 647 cm^{-1} for **4** is assigned to the ν_3 stretching modes of U(V) and is consistent with the elongated uranyl bond lengths of 2.039 Å for **4** and **5**, and 2.0641 Å for **3**. Peak assignments were made based on the work of Veal et al.[22] These results are consistent with the IR spectra of other U(V)-containing phases reported elsewhere[5,23] and clearly demonstrate the presence of U(VI) in **4** and **5** while confirming the absence of U(VI) in **3**.

Thermogravimetric analysis was used to determine the thermal stability and identity of oxidation products for **3**-**5**. Compound **3** was heated in air to 900°C at 10°C per minute, during which time a 0.61% weight gain was observed followed by decomposition of the sample beginning at 600°C (Figure S3, ESI†). Powder X-ray diffraction analysis of the sample revealed the presence of UO_3 as well as an unidentified amorphous component. Similarly, compounds **4** and **5** were heated in air to 800°C at 10°C per minute. In contrast to the thermal behavior of **3**, mass losses of 1.54% and 0.60% were observed for **4** and **5**, respectively (Figure S4 and S5, ESI†). PXRD analysis of the products showed no change in the powder patterns before and after TGA measurements, indicating that **4** and **5** are highly stable phases. The nature of the observed weight loss is not yet clear; however, loss of oxygen during heating in air has been reported in the case of U_3O_8.[24]

There is currently no formal designation for the range of supercritical conditions existing below 500°C but above the critical temperature and pressure of water. We have coined the term "moderate supercritical synthesis" to distinguish this method from mild and HTHP hydrothermal methods. It is intriguing that this method enables the preparation of compositions similar to those previously thought to be accessible only under more extreme conditions, such as in the case of compounds **1** and **2**, in addition to providing a route to novel U(V)-containing compositions. Furthermore, these compositions can be made in high yields; three of the five compositions presented can be obtained as pure phases (Figure S6, S7, and S8, ESI†) while the remaining two phases can be obtained in approximately 80% yield based on uranium.

In summary, we have presented a highly effective synthetic approach for the synthesis of mixed-valent U(V)-containing compounds. Through the use of moderate supercritical synthesis, we have successfully prepared five novel mixed-valent uranium silicates and characterized them by single crystal X-ray diffraction, magnetic susceptibility measurements, UV-visible and IR spectroscopy, and TGA.

We note that the moderate supercritical synthesis is a facile and direct method for the crystal growth of mixed-valent uranium (IV,V) and (V,VI) silicates, facilitating our continued efforts to advance our understanding of mixed-valent uranium-containing materials.

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Conflicts of interest

There are no conflicts to declare.

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