Crystal Growth and Structure Characterization of Three Layered Uranyl Phosphates and Their Relation to the Phosphuranylite Family

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Supporting Information

ABSTRACT: Three new materials related to the phosphuranylite family were synthesized by using alkali chloride fluxes at 875 °C: CsNa_{1.7}[{(UO}_2)_2{(PO}_4)_2] (1), CsNa[{(UO}_2)_2{(PO}_4)_2] (2), and Rb_{1.7}[{(UO}_2)_2{(PO}_4)_2] (3). CsNa_{1.7}[{(UO}_2)_2{(PO}_4)_2] (1) crystallizes in the triclinic space group P1 with the lattice parameters, a = 6.9809(3) Å, b = 9.3326(4) Å, c = 12.9626(5) Å, α = 71.5620(10)°, β = 78.9430(10)°, and γ = 68.0840(1)°. CsNa[{(UO}_2)_2{(PO}_4)_2] (2) crystallizes in the triclinic space group P1 with the lattice parameters, a = 6.9890(3) Å, b = 12.9652(6) Å, c = 13.2086(6) Å, α = 96.224(2)°, β = 101.433(2)°, and γ = 105.459(2)°. And Rb_{1.7}[{(UO}_2)_2{(PO}_4)_2] crystallizes in the P2_1/m space group with the lattice parameters, a = 6.9225(3) Å, b = 24.773(1) Å, c = 7.07647(3) Å, and β = 90.741(1)°. The sheets of 1 are based on the phosphuranylite topology, while the sheets of 2 and 3 contain sheets based on the U_3O_7 and uranophane topologies but differ in the orientation of the phosphate tetrahedra. The regions between the sheets contain the alkali cations and are not all identical in structures 1 and 2. The geometrical isomers found in these sheet structures and their relationship to known sheet topologies are discussed.

INTRODUCTION

Layered uranium(VI) phosphate materials continue to receive attention in the actinide community due to their large structural variety and low solubility, which makes them of interest to the waste form community. Historically most investigations were focused on obtaining new uranium containing compositions and to crystallize them in novel structure types with the long-term goal being to better understand uranium crystal chemistry, in general, and the local coordination chemistry, in specific. The low solubility of actinide phosphates is a valuable property for nuclear waste applications, where issues including environmental mobility, environmental remediation, waste processing, and the development of novel nuclear waste storage materials are being investigated.

The phosphuranylite sheet anion topology is one of the most dominant structure types for uranium phosphate and arsenate minerals, and this sheet topology is also found in synthetic materials. To date, there are 17 synthetic compounds and 17 structurally characterized minerals belonging to the phosphuranylite class. The phosphuranylite materials are a compositionally varied class of materials composed of sheets, sometimes connected by U or Th polyhedra, separated by monovalent and/or divalent cations and water in mineral structures. The phosphuranylite sheet anion topology contains triangles, squares, pentagons, and hexagons where there are typically chains of UO_3 square bipyramids and dimers of UO_2 pentagonal bipyramids that are connected together by tetrahedral (P, As, V), trigonal pyramidal (Se, Te), or trigonal planar (C) building units. This arrangement always leads to vacant square coordination sites, and the hexagonal uranium sites can at times also be vacant, as seen in the johannite mineral, although materials that have vacant hexagons will not be considered further in this work. Also related to the family of phosphuranylite materials, are a few that are framework structures constructed of phosphuranylite-type chains, and these include A_6[Al_2O_3(PO_4)_3][(UO_2)_2O_5] (A = Rb, Cs), the arsenate mineral nielsbohrite, and [(UO_2)_3(PO_4)_2(OH)- (H_2O)_2](H_2O), which will be included in the discussion of synthetically derived phosphuranylite materials.

The phosphuranylite topology consists of chains of uranyl pentagonal and hexagonal bipyramids whose edges are decorated with tetrahedral building units that connect the chains into layers through edge and corner sharing (Figure 1a). Related to this phosphuranylite topology is the sheet anion topology observed in "extended phosphuranylite" systems, the structural relationship of which is illustrated in Figure 1b, c, which is observed in the synthetic materials Cs_{5.2}K_{14.1}[{(UO}_2)_3 O_6{(PO}_4)_2], Rb_{1.7}K_{4.4}[{(UO}_2)_2O_5{(PO}_4)_2], K_{10.6}[{(UO}_2)_3 O_6{(PO}_4)_2], and M_{14}[{(UO}_2)_3O_5{(VO}_3)_2] (M = K, Na), K_{10}[{(UO}_2)_5].
byproduct by loading 0.5 mmol of UF₄, 2 mmol of AlPO₄, 4 mmol of NaCl, and 20 mmol of CsCl into silver tubes measuring 5.7 cm tall by 1.8 cm wide. The reaction was heated to 875 °C in 1.5 h, held for 12 h, and slowly cooled to 400 °C at 6 °C/h. Both CsNa₃[(UO₂)₃O₅(PO₄)₁₂] (1) and Rb₆[(UO₂)₃O₅(PO₄)₁₂] (3) were synthesized in aluminia crucibles that were covered by larger inverted crucibles as previously described and heated under the same conditions as 2. To obtain the yellow single crystals of CsNa₃[(UO₂)₃O₅(PO₄)₁₂] (1) (Figure 2), 0.5 mmol of UF₄, 0.33 mmol of AlPO₄, 5 mmol of CsCl, and 5 mmol of NaCl were used. Rb₆[(UO₂)₃O₅(PO₄)₁₂] (3) was synthesized using 0.5 mmol of UF₄, 0.33 mmol of AlPO₄ and 20 mmol of RbCl, and this reaction produced orange plates of 3 and yellow rods of Rb₆[Al₆O₁₇(PO₄)₉][(UO₂)₃O₅(PO₄)₁₂].

**Structure.** Single crystal X-ray diffraction data were collected on a Bruker D8 Quest single crystal X-ray diffractometer equipped with a Mo Kα microfocus source (λ = 0.71073 Å). The raw data were reduced and corrected using SAINT+ and SADABS within the APEX 3 software. The SHELXT intrinsic phasing solution program was used to obtain an initial structure that was subsequently refined using SHELXL. PLATON programs ADDSYM and TwinRotMap were used to check for missing symmetry elements and minor twin components. Energy dispersive spectroscopy (EDS) performed on a TESCAN Vega-3 SBU equipped with an EDS detector was used to obtain qualitative elemental analysis in order to verify the elemental contents of the structures. All metal atoms were allowed to individually freely refine, and no significant deviation from unit was observed. Full crystallographic data are reported in Table 1, and tables of selected bond distances and bond valence sums are included in Tables S1–S3.

CsNa₃[(UO₂)₃O₅(PO₄)₁₂] (1) crystallizes in the triclinic space group PI with the lattice parameters, \(a = 6.9809(3)\) Å, \(b = 9.3326(4)\) Å, \(c = 12.9626(5)\) Å, \(α = 71.5620(10)^{\circ}\), \(β = 78.9430(10)^{\circ}\), and \(γ = 105.459(2)^{\circ}\). Within the asymmetric unit there are three U sites, two P sites, four Na sites, and 16 O sites where all lie on general positions. Similar to 1, all atoms lie on general positions, except Na3 and Na4 that lie on Wyckoff sites 1a and 1b, respectively, and have \(I\) symmetry.

CsNa₃[(UO₂)₃O₅(PO₄)₁₂] (2) crystallizes in the triclinic space group PI with the lattice parameters, \(a = 6.9809(3)\) Å, \(b = 12.9626(6)\) Å, \(c = 13.2086(6)\) Å, \(α = 96.224(19)^{\circ}\), \(β = 101.433(19)^{\circ}\), and \(γ = 105.459(2)^{\circ}\). The asymmetric unit contains five symmetrically unique U sites, two P sites, two Cs sites, five Na sites, and 23 O sites. Similar to 1, all atoms lie on general positions, except Na3 and Na5 that lie on Wyckoff sites 1c and 1g, respectively, with 1/2 symmetry.

Rb₆[(UO₂)₃O₅(PO₄)₁₂] crystallizes in the \(P2_1/m\) space group with the lattice parameters, \(a = 6.9255(3)\) Å, \(b = 24.773(1)\) Å, \(c = 7.07647(3)\) Å, and \(β = 90.741(1)^{\circ}\). The solution was refined as a two-component twin using twin law \(-1 0 0 1 0 0 0 1 \) with a volume fraction of 1%. The addition of the twin law with small volume fraction significantly improved the \(R_b\) value from 0.0272 to 0.0232 and the maximum and minimum residual density peaks from

**Crystal Growth.** Crystals of all three phases were obtained using molten alkali chloride fluxes. Small orange needles of CsNa₃[(UO₂)₃O₅(PO₄)₁₂] (2) were produced in a large excess of AgCl

### EXPERIMENTAL SECTION

UF₄ (International Bio-Analytical Industries, powder, ACS grade), AlPO₄ (Alfa Aesar, powder, 99.9%) and NaCl (Alfa Aesar, powder, 98%), RbCl (Alfa Aesar, powder, 99.8%); Caution! Although the uranium precursor used contained depleted uranium, standard safety measures for handling radioactive substances must be followed.

Crystals of all three phases were obtained using molten alkali chloride fluxes. Small orange needles of CsNa₃[(UO₂)₃O₅(PO₄)₁₂] (2) were produced in a large excess of AgCl.
Typically, uranium phosphates crystals have been obtained by hydrothermal, solid state, or molten flux methods. Regardless of the synthesis route, UO₂(NO₃)₂ is among the most widely used uranium source, although the common uranium oxides U₂O₅, U₂O₃, and U₂O₄ are also used. The phosphate sources are more widely varied where wet chemical routes tend to use solutions of H₃PO₄ or H₃PO₃, and less commonly solutions of Na₃P₂O₇ and K₃P₂O₇ where solid state and molten flux synthetic routes most often use P₂O₅ (NH₄)₂HPO₄ or NH₄H₂PO₄. While P₂O₅ is very common in solid state and molten flux synthesis, sometimes as a flux, it is better suited for synthesis in closed systems due to the fact that P₂O₅ is very reactive to atmospheric water and should be handled in the glovebox for accurate masses. (NH₄)₂HPO₄ and NH₄H₂PO₄, where (NH₄)₂HPO₄ loses NH₃ at 70 °C to become NH₄H₂PO₄, are often used instead of P₂O₅ due to the ease of handling the ammonium based reagents in air. AlPO₄ is a fairly unique phosphate source for molten flux methods and can lead to the synthesis of both phosphates and aluminophosphates and leads to the synthesis of different phosphate products as compared to the use of (NH₄)₂HPO₄ and NH₄H₂PO₄ phosphate sources. Thus far, the AlPO₄ starting material has led to the discovery of 15 new uranium phosphates/aluminophosphates including those described in this article. The large variety of phosphate sources available to the solid state chemist including, BPO₄, Al₂P₂O₇ (A = Na, K), AlPO₄, Na₃PO₄, APO₃ (A = Na, K), Al₂(H₂O)₅PO₄ (A = Na, K), and Al₂HPO₄ (A = Na, K), are undergone in uranium phosphate chemistry with few examples of syntheses using...
these reagents. The use of different phosphate sources should be studied in order to obtain new and unique structures as well as to increase our understanding of why different phosphate sources lead to different products.

In the synthesis of CsNa\(_2\)\([\text{(UO}_2\text{)}_3\text{O}_5\text{(PO}_4\text{)}_2]\) (2), the large amount of AgCl produced by the chloride flux interaction with the silver reaction vessel during the synthesis made isolating the very small and brittle orange needles difficult. As in the recently reported synthesis of the A\(_4\)\([\text{(UO}_2\text{)}_3\text{O}_5\text{(PO}_4\text{)}_2]\) family, reactions with the same reactant loading and heating were carried out in alumina reaction vessels. All attempts in alumina crucibles, including conducting multiple crystal growth reactions utilizing different amounts of flux, yielded only the yellow crystals of CsNa\(_2\)\([\text{(UO}_2\text{)}_3\text{O}_5\text{(PO}_4\text{)}_2]\) (1). In the synthesis of the A\(_4\)\([\text{(UO}_2\text{)}_3\text{O}_5\text{(PO}_4\text{)}_2]\) materials, it was shown that increasing the flux to 40 mmol improved the yield of the desired phase, A\(_4\)\([\text{(UO}_2\text{)}_3\text{O}_5\text{(PO}_4\text{)}_2]\), over side products of A\(_2\)\([\text{(UO}_2\text{)}_3\text{O}_5\text{(PO}_4\text{)}_2]\). In order to target CsNa\(_2\)\([\text{(UO}_2\text{)}_3\text{O}_5\text{(PO}_4\text{)}_2]\) (2), the reverse was attempted. However, decreasing the flux to 5 mmol was unsuccessful and the CsNa\(_2\)\([\text{(UO}_2\text{)}_3\text{O}_5\text{(PO}_4\text{)}_2]\) (1) phase still preferentially formed.

Rb\(_6\)\([\text{(UO}_2\text{)}_3\text{O}_5\text{(PO}_4\text{)}_2]\) (3) also proved difficult to isolate over the recently published products Rb\(_6\)\([\text{(UO}_2\text{)}_3\text{O}_5\text{(PO}_4\text{)}_2]\)\(^{36}\), Rb\(_6\)\([\text{Al}_2\text{O}_5\text{(PO}_4\text{)}_2]\)\([\text{(UO}_2\text{)}_3\text{O}_5]\), and Rb\(_6\)\([\text{Al}_2\text{O}_5\text{(PO}_4\text{)}_2]\)\([\text{(UO}_2\text{)}_3\text{O}_5\text{(PO}_4\text{)}_2]\). All form under similar conditions of 0.5 mmol of UF\(_6\) 0.2–0.5 mmol of AlPO\(_4\) 10/20 mmol of RbCl, and 775–875 °C reaction temperature. The lower temperature of 775 °C favored the formation of Rb\(_6\)\([\text{Al}_2\text{O}_5\text{(PO}_4\text{)}_2]\)\([\text{(UO}_2\text{)}_3\text{O}_5]\), while 10 mmol of RbCl flux at 875 °C primarily produced Rb\(_6\)\([\text{(UO}_2\text{)}_3\text{O}_5\text{(PO}_4\text{)}_2]\)\([\text{(UO}_2\text{)}_3\text{O}_5\text{(PO}_4\text{)}_2]\), and 20 mmol produced Rb\(_6\)\([\text{Al}_2\text{O}_5\text{(PO}_4\text{)}_2]\)\([\text{(UO}_2\text{)}_3\text{O}_5\text{(PO}_4\text{)}_2]\) with small amounts of the title compound Rb\(_6\)\([\text{(UO}_2\text{)}_3\text{O}_5\text{(PO}_4\text{)}_2]\) (3). Attempts to optimize the synthesis for Rb\(_6\)\([\text{(UO}_2\text{)}_3\text{O}_5\text{(PO}_4\text{)}_2]\) (3) by changing the amount of flux (2.5–40 mmol), varying the temperature, and using a non-Al containing phosphorus source, (NH\(_4\)\(_2\))HPO\(_4\) were unsuccessful. Reactions using (NH\(_4\)\(_2\))HPO\(_4\) as the phosphate source favored the synthesis of the Rb\(_6\)\([\text{(UO}_2\text{)}_3\text{O}_5\text{(PO}_4\text{)}_2]\) phase regardless of the uranium to phosphorus ratio used, and 3 could not be obtained with this reagent.

**Figure 3.** Known geometric isomers of the phosphuranylite topology where uranyl polyhedra are yellow, tetrahedra or trigonal pyramids in the up orientation are pink, and those in the down orientation are purple. Examples of compounds exhibiting these isomers are (a) CsNa\(_2\)\([\text{(UO}_2\text{)}_3\text{O}_5\text{(PO}_4\text{)}_2]\) (1), (b) A\(_4\)\([\text{Kz}[\text{(UO}_2\text{)}_3\text{O}_5\text{(PO}_4\text{)}_2]\)]\(^{35}\), (c) vanmeerscheite,\(^{33}\) (d) Sr\(_2\)\([\text{(UO}_2\text{)}_3\text{SeO}_3\text{O}_2]\)\([\text{(H}_2\text{O})_4]\)\(^{34}\) (e) phosphuranylite,\(^{35}\) (f) phurcalite,\(^{35}\) and (g) bergeite.\(^{35}\)

**Figure 4.** Structure of CsNa\(_2\)\([\text{(UO}_2\text{)}_3\text{O}_5\text{(PO}_4\text{)}_2]\) (1) where the sheet topology and the overlaid cations are shown in (a) and (b), and the sheet stacking is shown in (c). The structure of CsNa\(_2\)\([\text{(UO}_2\text{)}_3\text{O}_5\text{(PO}_4\text{)}_2]\) (2) is depicted in an analogous way in (d)–(f). Uranyl polyhedra are yellow, oxygen atoms are red, and phosphate tetrahedra are magenta.
direction. Unlike other reported phosphuranylite-type layered systems, the layers within I are not all the same, the phosphate tetrahedra in subsequent layers point in opposite directions, and the phosphate tetrahedra do not align vertically (Figure 4). As a consequence, this creates two different interlayer distances where there is a smaller distance between layers in which the phosphate tetrahedra point toward each other, and larger distances where they point away from each other. This is likely a consequence of having two significantly different sized cations, Cs and Na, and as expected solely Na cations lie between layers where PO₄ units point in toward each other, whereas both Cs and Na cations lie between layers in which PO₄ units point away from each other. In these latter layers, the larger Cs cations are located in the gap created by the outward pointing PO₄ units and the Na cations lie between uranyl polyhedra. This follows a similar trend as observed in the A₄K₆[UO₂]₂(PO₄)₂ (A = Rb, Cs) structures, where the sites between phosphate tetrahedra were occupied by a mixture of K and Cs or Rb, and the site between uranyl polyhedra were solely K.

Cs₅Na₄[(UO₂)₂O₃(PO₄)₂] (2) and Rb₅[(UO₂)₂O₃(PO₄)₂] (3), shown in Figures 4 and 5, both adopt new isomers of the "extended phosphuranylite" sheet topology. These layered uranyl phosphates contain chains of edge-sharing uranyl pentagonal bipyramids that are connected to a mirror image uranyl pentagonal bipyramid chain through edge sharing with an additional uranyl polyhedron (referred to as the interior U), as in the U₃O₈ structure. These [(UO₂)₆]O₃ units are connected via edge-sharing and corner-sharing phosphate tetrahedra, similar to the uranophane topology. The extended phosphuranylite sheet topology can contain either α-U₃O₈ or β-U₃O₈ units (Figure 6d) depending on the coordination of the interior uranyl polyhedron. In order to determine which best describes the structures Cs₅Na₄[(UO₂)₂O₃(PO₄)₂] (2) and Rb₅[(UO₂)₂O₃(PO₄)₂] (3), the U–O bond distances and bond valence sums were investigated for the uranium in question, which is U1 and U3 for structures 2 and 3, respectively. Bond valence sums (BVS) were calculated using Rₚ and b parameters by Burns.

![Figure 5. Structure of Rb₅[(UO₂)₂O₃(PO₄)₂] (3) with views in the (a) cb plane and the (b) ab plane. Uranyl polyhedra are yellow, oxygen atoms are red, and phosphate tetrahedra are magenta.](image)

![Figure 6. Known geometric isomers of the extended phosphuranylite topology where uranium polyhedra are yellow, tetrahedra or trigonal pyramids in the up orientation are pink, and those in the down orientation are purple. Examples of compounds exhibiting these isomers are (a) Cs₅Na₄[(UO₂)₂O₃(PO₄)₂] (2), (b) Cs₅K₆[(UO₂)₂O₃(PO₄)₂], (c) Rb₅[(UO₂)₂O₃(PO₄)₂] (3), (d) α-Rb₅[(UO₂)₂O₃(PO₄)₂] and K₆[(UO₂)₅(AsO₃)O₃].](image)
latter two, $\alpha$-Rb$_2$[(UO$_2$)$_5$(VO$_2$)$_3$]$^{4+}$ and K$_3$[(UO$_2$)$_7$-(TeO$_2$)$_2$O$_3$],$^{12}$ both adopt the udududO isomer, while the rest of the named compositions contain the uuuuuuO isomer. The trigonal pyramidal (TeO$_2$)$^{2-}$ units in K$_3$[(UO$_2$)$_7$(TeO$_2$)$_2$O$_3$] can be described in similar manners as (TO$_4$)$^{2-}$ (T = P, As, V) tetrahedra due to the lone pair on Te that causes a pyramid rather than a planar geometry. $\alpha$-Rb$_2$[(UO$_2$)$_5$(VO$_2$)$_3$] and K$_3$[(UO$_2$)$_7$(TeO$_2$)$_2$O$_3$] are also set apart by the difference in the interior U coordination. In the vanadate, the interior uranium is best considered as 7-coordinate, while in the tellurite it is a 6-coordinate square bipyramid. The ordering of the middle U pentagonal bipyramids in the udududO isomer is analogous to that in udududs as described for Rb$_2$[(UO$_2$)$_5$(PO$_4$)$_2$]$^3$ (3). It is natural to wonder if the remaining 3 phosphuranylite isomers (Figure 3e–g) can be synthesized in extended phosphuranylite structures, given that there are already four common isomers between the two families.

**CONCLUSION**

Three new crystal structures belonging to the phosphuranylite and extended phosphuranylite families have been synthesized as single crystals and structurally characterized. Each adopts a new geometrical isomer of the fairly well-known topologies. The synthetic methods used to obtain the phosphuranylite and extended phosphuranylite materials were discussed, and the alkali molten flux growth method has produced the majority of the reported materials including phosphates, vanadates, and tellurites, while hydrothermal methods have been used for selenites and arsenates. Future studies should continue to explore this diverse family of materials and aim to incorporate polyhedral building blocks containing Cr, As, Al, and Se via the molten flux method.

**ASSOCIATED CONTENT**

* Supporting Information
  The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.cgd.8b01643.

Bond valence sums and selected bonded distances of compounds 1, 2, and 3 (PDF)

**Accession Codes**

CCDC 1874954–1874956 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/data_request cif, or by emailing data_request@ccdc.cam.ac.uk, or by contacting The Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336033.

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**Funding**
Research was conducted by the Center for Hierarchical Waste Form Materials (CHWM), an Energy Frontier Research Center (EFRC). Research was supported by the U.S. Department of Energy, Office of Basic Energy Sciences, Division of Materials Sciences and Engineering, under Award DE-SC0016574. C.A.J. is additionally supported by an NSF IGERT Graduate Fellowship under grant number 1250052.

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