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Flux Crystal Growth: A Versatile Technique to Reveal the Crystal Chemistry of Complex Uranium Oxides

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Abstract:

This frontier article focuses on the use of flux crystal growth for the preparation of new actinide containing materials, reviews the history of flux crystal growth of uranium containing phases, and highlights the recent advances in the field. Specifically, we discuss how recent developments in f-element materials, fueled by accelerated materials discover via flux crystal growth, have led to the synthesis and characterization of new families of complex uranium containing oxides, namely alkali/alkaline uranates, oxychlorides, oxychalcogenides, tellurites, molybdates, tungstates, chromates, phosphates, arsenates, vanadates, niobates, silicates, germanates, and borates. An overview of flux crystal growth is presented and specific crystal growth approaches are described with an emphasis on how and why they – versus some other method – are used and how they enable the preparation of specific classes of new materials.

Introduction

The numerous recent literature reports of novel uranium containing materials with extended structures are the result of multiple parallel efforts to explore the crystal chemistry of uranium containing materials, as well as of efforts aimed at improving the nuclear fuel cycle and environmental remediation projects. In addition, a recent push to develop new materials as a foundational basis for the development of new waste forms that can be used to more effectively immobilize nuclear waste has also contributed.[1] These combined efforts have resulted in an expansion of the synthetic approaches used to create novel structure types and have greatly increased the number of materials and structures containing uranium. The ability to obtain these materials in the form of single crystals has been instrumental for their discovery and the determination of their structures. In fact, one can safely state that the crystal growth process has been instrumental in the discovery of the majority of these new materials.

This frontier article focuses on the use of flux crystal growth for the preparation of new actinide containing materials, reviews the history of flux crystal growth of uranium containing phases, and highlights the recent advances in the field. The overall focus is on specific crystal growth approaches that are described with an emphasis on how and why they – versus some other method – are used and how they enable the preparation of specific classes of new materials, such as uranium containing oxides, fluorides or chalcogenides.[2] An attempt is made to realistically portray the underlying strategies of flux crystal growth experiments to create new compositions that hopefully exhibit the desired structures, or that, by serendipity, exhibit something different but perhaps even more exciting. In many sections of this article, we highlight one interesting structure or structural feature within the discussed class of compounds. More extensive discussions of the crystal chemistry of uranium are available elsewhere.[3–5] Likewise, the physical properties of uranium containing compounds which make them of particular interest, including their luminescent and magnetic properties, are not discussed in this work but are discussed elsewhere.[6–8]

The use of fluxes for crystal growth, of course, goes back many decades although only in the past two or three decades has flux crystal growth been applied in earnest to the preparation of new uranium containing phases. Uranium containing chalcogenides have been prepared via flux growth primarily by the Ibers group for some time and recent reviews summarize this body of work; for that reason is not covered herein.[9, 10] Furthermore, many new uranium and thorium containing structures have been prepared by Albrecht-Schmitt, Burns, Cahill, zur Loye, Obbade, Abraham, Loiseau, Dacheux, and Lii groups, among others, via hydrothermal routes, a synthetic method that, although extremely effective, is outside the scope of this frontier article which focuses on flux crystal growth of uranium containing oxides, including mixed anion oxides such as oxychlorides and oxychalcogenides.[11–32]

The preparation of a new material is not trivial as the targeted synthesis of an unknown compound is inherently challenging. In some relatively simple systems, there exists extensive literature that one can use to make targeted predictions of new compositions and the expected structural variants. For example, in the case of perovskite oxides, a simple set of rules exists to predict new compounds that will crystallize in the perovskite or related structure types. Unfortunately, this prediction becomes prohibitively difficult for more complex compositions and structures, especially when the crystal chemistry is not well-understood or the structure type is unknown. This is where flux crystal growth is incredibly useful as it facilitates the preparation of new complex compositions in the absence of a fully established crystal chemistry; and, since the new compositions are isolated as single crystals, their structures can readily be determined. In general, the flux growth of new materials involves, first, the determination of conditions which are suitable for crystal growth within a specific system, including reactant identities, dwell temperatures, reactant concentrations, and, importantly, the flux used. Once these conditions are determined, reaction conditions, especially reactant concentrations and dwell temperature, can be varied with the goal of avoiding known phases and growing new compounds. With this in mind, in this frontier article we will focus on the flux crystal growth of complex uranium containing oxides, including, silicates, germanates, and phosphates, with an emphasis on the reactions conditions that are conducive to crystal growth in these particular systems.

Flux Crystal Growth

The flux, typically an inorganic solid at room temperature, functions as the solvent at the high temperatures at which crystals are obtained via a *conceptually* well understood sequence of events, beginning with nucleation and finishing with growth.[33, 34] Our understanding of the step leading to the nucleation of *specific phases*, however, is still in its infancy, although we do understand, in general, the underlying reasons for nucleation to take place. In order for the nucleus, once formed, to grow and not re-dissolve, it must reach a critical size that is a function of the degree of supersaturation. In general, the higher the degree of supersaturation, the smaller the critical nucleus size can be. For that reason, it is preferred to use a flux that is able to dissolve a large quantity of the reagents and that exhibits a significant change in solubility with temperature to achieve this supersaturation. The nucleation process has a temperature dependence and requires a minimum temperature for nucleation to occur and, furthermore, has an optimum temperature range in which the nucleation is at its maximum. Finding these optimum conditions, which tend to be unique for each system and change for even minor compositional adjustments, is largely a matter of trial and error. Starting with a set of conditions that are known to yield crystals of a related composition or structure is a good first approach and adjustments in temperature, concentration, time, reagent identity, etc., are made as needed.

Fluxes

The flux is the high temperature solution that functions as the solvent for crystallization and, more often than not, consists of a single, simple inorganic compound, such as B_2O_3, KCl, KOH, PbO, Bi_2O_3, or Na_2CO_3, which melt at conveniently low temperatures (Figure 1). The combination of different solids to form eutectic compositions is one effective way to obtain an even lower melting flux. A “good” flux has certain attributes including the ability to dissolve a significant quantity of the reagents, a large change of the solubility with temperature, a low melting point, low volatility, low cost and finally, easily removed after crystal growth via dissolution in common solvents, ideally water. There is no “universal flux” although many fluxes can be used interchangeably and most crystals can be grown out of more than one solvent system; there are some advantages and disadvantages to all of them, however.

There are several chemical factors that influence the ability of a flux to dissolve the reagents and to promote crystal growth. For example, materials that are good fluxes include those that form a compound with the solute at lower temperatures or in different concentration ranges. The optimal concentration for flux crystal growth is individual to each system, although 1:10 molar ratio of reagents to flux is typically a good starting point. In addition, the presence of a common anion or cation in flux and the reagent can have a positive impact on the solution chemistry and solubility as will matching the polarizability of the solvent and the solute. One important advantage of choosing the flux by matching the physical and chemical properties is the formation high quality crystals. A detailed introduction to fluxes is given in the review by Bugaris and zur Loye.[33]

The reaction vessel used for crystal growth also is an important consideration, as many fluxes are highly reactive and will dissolve and/or chemically react with various containers. Therefore, one has to take into consideration the compatibility of the reaction vessel and the flux. “Inert” containers include platinum and gold, which however, are quite expensive and, in the case of gold, limit the crystal growth temperature to lie below 1064°C. Alumina crucibles are often used as a less expensive alternative and are considered chemically resistant towards halide but not fluoride melts, however can be dissolved by hydroxide fluxes, leading to the incorporation of aluminum into the product. Fluoride based fluxes cannot be used with alumina, as they readily react/dissolve alumina crucibles. Silver is a better alternative for both hydroxide and fluoride fluxes as silver is substantially inert towards them. Fused silica is a good choice for crystal growth experiments necessitating a sealed reaction environment, for example for growing crystals containing elements in reduced oxidation states, as long as a silica compatible flux is chosen. Numerous other refractories and metal containers have been used as appropriate for the flux used and there is no universal container that is ideal for all flux growth experiments.

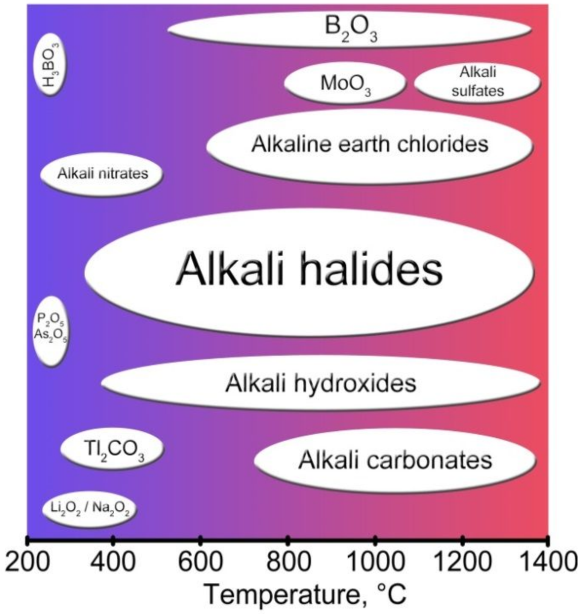


Figure 1. The variety of fluxes used for obtaining complex uranium oxides and their approximate operating temperature ranges.

Uranium in extended structures exists predominantly in the +6 oxidation state, uranium's most stable oxidation state in air, and the easiest to prepare. It is possible to prepare structures containing uranium in the +4 and the +5 (rare) oxidation states, but only if the syntheses are conducted in a controlled atmosphere and start with the appropriate, often pre-reduced, reagents. Depending on the target oxidation state, different fluxes should be used, for example carbonates and hydroxides for U(VI) containing materials and halides open to air for U(VI) and in sealed tubes for U(V) and U(IV) containing materials (Table 1). A more extensive version of Table 1 including the oxidation state of U, reagents, dwell time and temperature, cooling rate and temperature, crystal color, reaction vessel and wash method is available in the SI. This is best achieved by closely matching the bonding of the molten compound (flux) to that of the final product i.e. ionic to ionic, covalent to covalent. Since most materials are not strictly one or the other, compromises must be made. While it is possible to use a flux in which the bonding is very different from the desired product, the solubility of the reagents in such systems is often quite limited.

Table 1. List of flux grown uranium oxides and the flux used organized by category

Compound	Flux	Ref	Compound	Flux	Ref	Compound	Flux	Ref
Uranates			Mixed Oxides			Oxychalcogenides		
K_2UO_4	KOH	35	Ba_2CuUO_6	K_2CO_3	36	$UYb_2O_2S_3$	Sb_2S_3	37
Na_4UO_5	NaOH	35	Ba_2NiUO_6	K_2CO_3	36	$UY_2O_2S_3$	Sb_2S_3	37
Sr_3UO_6	K_2CO_3	36	Ba_2ZnUO_6	K_2CO_3	36	$Na_2Ba_2((UO_2)S_4)$	Na_2O_2	38
$Ba_2Na_{0.83}U_{1.17}O_6$	Na_2CO_3	39	$MnUO_4$	CsCl	40	$UY_4O_3S_5$	Sb_2S_3	41
$BaK_4U_3O_{12}$	K_2CO_3	39	$FeUO_4$	$BaCl_2$	40	$UTa_2O(S_2)_3Cl_6$	TaS_2	42
$Na_3Ca_{1.5}UO_6$	Na_2CO_3	39	NiU_2O_6	KCl	40	$UYb_2O_2Se_3$	Sb_2Se_3	43
$CaUO_4$	K_2CO_3	44	$Cs_2Mn_3U_6O_{22}$	CsCl	45	$U_2Pr_2O_4Se_3$	Sb_2Se_3	43
β-Ca_3UO_6	K_2CO_3	44	$K_2MnU_3O_{11}$	KCl	46	$U_2Sm_2O_4Se_3$	Sb_2Se_3	43
$K_4CaU_3O_{12}$	K_2CO_3	44	$Rb_2MnU_3O_{11}$	RbCl	46	$U_2Gd_2O_4Se_3$	Sb_2Se_3	43
$K_4SrU_3O_{12}$	K_2CO_3	44	$Li_{3.2}Mn_{1.8}U6O_{22}$	LiCl	46	$U_7O_2Se_{12}$	CsCl	47
$K_8U_7O_{24}$	KF	48	$Na_{4.5}Nd_{0.5}UO_6$	NaOH/KOH	49	UOS	Sb_2S_3	50
$Cs_{2.2}U_5O_{16}$	CsCl	51	Pb_3UO_6	PbO	52	UOSe	Sb_2Se_3	50
$Cs_2U_4O_{13}$	CsCl	51	β-$CdUO_4$	$CdCl_2$	53	$UEr_2O_2S_3$	Sb_2S_3	54
$Rb_4U_5O_{17}$	Sb_2O_5	55	$PbUO_4$	PbClF	56			
$Ca(K_6Ba_2)U_6O_{24}$	K_2CO_3	57	$K_9BiU_6O_{24}$	B_2O_3	58	Molybdates		
$KUO_{3.5}$ ($K_2U_2O_7$)	KCO_3	59	Oxychlorides			$Cs_2((UO_2)O(MoO_4))$	Cs_2CO_3	60
$Na_8Ca_{3.11}U_{3.7}O_{17.52}$	Na_2CO_3, $CaCO_3$	61	$K_4U_5O_{16}Cl_2$	KCl	62	$Li_4((UO_2)_{10}O_{10}(Mo_2O_8))$	Li_2CO_3	63
$Cs_2U_4O_{12}$	Cs_2SO_4	64	$Rb_4U_5O_{16}Cl_2$	RbCl	62	$Cs_6[(UO_2)_2(MoO_4)_3(MoO_5)]$	Cs_2CO_3	65
$BaUO_4$	$BaCl_2$	66	$Cs_5U_7O_{22}Cl_3$	CsCl	62	β-$Cs_2[(UO_2)_2(MoO_4)_3]$	$Cs(COOCH_3)/MoO_3$	67
$Cs_4U_5O_{17}$	CsCl	68	$RbUO_3Cl$	RbCl	62	$Ag_6[(UO_2)_3O(MoO_4)_5]$	$AgNO_3/MoO_3$	69
$MgUO_4$	$MgCl_2$	70	$CsUO_3Cl$	CsCl	62	$K2(UO_2)_2(MoO_4)O_2$	K_2CO_3	71
$CaUO_4$	$CaCl_2$	72	KUO_3Cl	KCl	73	$K_8(UO_2)_8(MoO_5)_3O_6$	K_2CO_3	71
$SrUO_4$	$SrCl_2$	72	$Cs_x(UO_2)OCl_x$	CsCl	74	$K_2(UO_2)(MoO_4)_2$	MoO_3	75
α-Li_2UO_4	LiCl	76	$Cs_2UNb_6Cl_{15}O_3$	CsCl	77	$Rb_2U_2MoO_{10}$	MoO_3	78
$MgUO_4$	$MgCl_2$	79	KUO_3Cl	KCl	73	$(Cu,Mn)UMo_3O_{12}$	MoO_3	80
β-Li_6UO_6	Li_2O_2	81						
α-Li_6UO_6	Li_2O_2	81	Tungstates		82	Niobates		
$Na_2(UO_4)$	Na_2CO_3	83	$Bi_2(W_{0.7}U_{0.3})O_6$	K_2SO_4/Na_2SO_4	82	$Cs_9((UO2)_8O_4(NbO_5)(Nb_2O_8)_2)$	Cs_2CO_3	84
$Cs_2U_4O_{12}$	Cs_2SO_4	64	$Bi_2(W_{0.4}U_{0.6})O_6$	K_2SO_4/Na_2SO_4	85	$TlNb_2U2O_{11.5}$	Tl_2CO_3	86
$K_9U_6O_{22.5}$	K_2CO_3	57	$Rb_8((UO_2)_4(WO_4)_4(WO_5)_2)$	Rb_2CO_3	85	$UTiNb_2O_{10}$	H_3BO_3	87
			$Cs_8((UO_2)_4(WO_4)_4(WO_5)_2)$	Cs_2CO_3	85	$TlNb_2U_2O_{11.5}$	Tl_2CO_3	86
Tellurites			$Rb_6((UO_2)_2O(WO_4)_4)$	Rb_2CO_3	88	$KNbUO_6$	K_2CO_3	86

$K_2[(UO_2)_3(TeO_3)_2O_2]$	KCl	89	$Li_4((UO_2)_2(W_2O_{10}))$	Li_2CO_3	90	$RbNbUO_6$	Rb_2CO_3	86
$Rb_2[(UO_2)_3(TeO_3)_2O_2]$	RbCl	89	$Na_2Li_8[(UO_2)_{11}O_{12}(WO_5)_2]$	Li_2CO_3/Na_2CO_3		$CsNbUO_6$	Cs_2CO_3	91
$Cs_2[(UO_2)_3(TeO_3)_2O_2]$	CsCl	89			92	$KNbUO_6$	K_2CO_3	86
$Ca_2(UO_3)(TeO_3)_2$	H_6TeO_6	93	Chromates		92	$Nb_{7.6}U_{2.4}Ba_{5.2}K_{0.8}O_{30}$	K_2CO_3	94
$K_2(UO_2)_2O_2(TeO_3)$	H_6TeO_6	93	$Cs_2(UO_2)(CrO_4)_2$	$CsNO_3$				
$K_4[(UO_2)_5(TeO_3)_2O_5]$	KCl	95	$Rb_2(UO_2)(CrO_4)_2$	$RbNO_3$				

Table 1. cont. List of flux grown uranium oxides and the flux used organized by category

Compound	Flux	Ref	Compound	Flux	Ref	Compound	Flux	Ref
Silicates			Germanates			Phosphates		
Rb_2USiO_6	RbF	96	$K_4((UO_2)Eu_2(Ge_2O_7)_2)$	MoO_3-KF	97	$Rb_6[(UO_2)_7O_4(PO_4)_4]$	RbCl	98
Cs_2USiO_6	CsF	96	$[Cs_2Cs_5F][(UO_2)_3(Ge_2O_7)_2]$	CsF	99	$Cs_6[(UO_2)_7O_4(PO_4)_4]$	CsCl	98
$K_4CaUSi_4O_{14}$	KF/CaF2 eu	100	$[Cs_6Ag_2Cl_2][(UO_2)_3(Ge_2O_7)_2]$	CsCl	99	$A_4(PO_4)_2[(UO_2)_3O_2]$	ACl	101
$K_2USi_6O_{15}$	KF/KCl eu	102	$[Cs_6Na_2Cl_2][(UO_2)_3(Ge_2O_7)_2]$	CsF/CsCl/NaCl	103	$Li_6((UO_2)_{12}(PO_4)_8(P_4O_{13}))$	P_2O_5	104
$Rb_2USi_6O_{15}$	RbF/RbCl eu	102	$[Cs_6Ag_xNa_{2-x}Cl_2][(UO_2)_3(Ge_2O_7)_2]$	CsF/CsCl eu	99	$Li((UO_2)(PO_4))$	P_2O_5	105
$Cs_2USi_6O_{15}$	CsF/CsCl eu	102	$[Cs_6K_{2-x}Ag_xCl_2][(UO_2)_3(Ge_2O_7)_2]$	CsF/CsCl eu	99	$Li_2((UO_2)_3(P_2O_7)_2)$	P_2O_5	105
$[NaK_6F][(UO_2)_3(Si_2O_7)_2]$	KF/NaF eu	106	$[KK_6Cl][(UO_2)_3(Ge_2O_7)_2]$	KF/KCl eu	99	$Cs_3(UO_2)_2(PO_4)O_2$	CsI	107
$[KK_6Cl][(UO_2)_3(Si_2O_7)_2]$	KF/NaF eu	106	$[NaK_6Cl][(UO_2)_3(Ge_2O_7)_2]$	Na_2CO_3/KF/KCl	103	α-$Ba_2[UO_2(PO_4)_2]$	B_2O_3	108
$K_8(K_5F)U_6Si_8O_{40}$	KF/KBr	109	$[KK_6Br_{0.6}F_{0.4}][(UO_2)_3(Ge_2O_7)_2]$	KF/KBr eu	99	β-$Ba_2[UO_2(PO_4)_2]$	H_3BO_3	108
$Cs_2USi_2O_8$	CsCl	110	$[Na_{0.9}Rb_{6.1}F][(UO_2)_3(Ge_2O_7)_2]$	RbF/NaF eu	99	α-$K[(UO_2)(P_3O_9)]$	P_2O_5	111
$[Cs_3F][(UO_2)(Si_4O_{10})]$	CsCl	110	$[KK1.8Cs4.2F]\ [(UO_2)_3(Ge_2O_7)_2]$	CsF/KF eu	99	β-$K[(UO_2)(P_3O_9)]$	P_2O_5	111
$[Cs_2Cs_5F][(UO_2)_3(Si_2O_7)_2]$	CsCl	110	$[Cs_6Cs_{0.71}Cl_{0.71}][(UO_2)_3O_3(Ge_2O_7)]$	CsCl	99	$K[(UO_2)_2(P_3O_{10})]$	P_2O_5	111
$[Cs_2Cs_5F][(UO_2)_2(Si_6O_{17})]$	CsCl	110	$K_2(UO_2)GeO_4$	K_2CO_3/WO_3	103	$Cs_{11}Eu_4(UO_2)_2(P_2O_7)_6(PO_4)$	$CsPO_3/Cs_4P_2O_7$	112
$[Cs_9Cs_6Cl][(UO_2)_7(Si_6O_{17})_2(Si_4O_{12})]$	CsCl	110	$K_6(UO_2)_3Ge_8O_{22}$	K_2CO_3/MoO_3/PbO	103	$(Nd_{0.38}U_{0.62})(PO_3)_4$	conc. H_3PO_4	113
$Rb_2(UO_2)Si_2O_6$	RbF/RbCl eu	114	α-$Cs_2(UO_2)Ge_2O_6$	Cs_2CO_3/V_2O_5/CsF	103	$Rb_2(UO_2)(P_2O_7)$	$Rb_4P_2O_7$	115
$Cs_2(UO_2)Si_2O_6$	CsF/CsCl eu	114	β-$Cs_2(UO_2)Ge_2O_6$	CsCl/CsF	103	$Cs_2(UO_2)(P_2O_7)$	CsCl	115
$(K_3Cs_4F)((UO_2)_3(Si_2O_7)_2)$	CsF-KF	116	$Cs_2(UO_2)GeO_4$	Cs_2CO_3/V_2O_5/CsF	103	$(UO_2)_2P_6O_{17}$	Polyphosphoric acid	117
$(NaRb_6F)((UO_2)_3(Si_2O_7)_2)$	RbF-NaF	116				$Rb_2((UO_2)_3(P_2O_7)(P_4O_{12}))$	P2O5	118
$(Ca_{0.5}Na_{0.5})_2NaUSi_8O_{20}$	Na_2WO_4	119	Arsenates			$CsU_2(PO_4)_3$	CsCl	120
			$Ag_6[(UO_2)_2(As_2O_7)(As_4O_{13})]$	As_2O_5	121	$U(PO_3)_4$	conc. H_3PO_4	113
Borates			$Ag_6[(UO_2)_2(AsO_4)_2(As_2O_7)]$	As_2O_5	121	$U(P_4O_{12})$	conc. H_3PO_4	113
$LiBUO_5$	B_2O_3	122	$Na_6[(UO_2)_2(AsO_4)_2(As_2O_7)]$	As_2O_5	121			

$CaB_2U_2O_{10}$	B_2O_3	123	$Li_5((UO_2)_{13}(AsO_4)_9(As_2O_7))$	As_2O_5	104			
$Ni_7B_4UO_{16}$	B_2O_3	124	$Li((UO_2)_4(AsO_4)_3)$	As_2O_5	104			
UB_2O_6	B_2O_3	125	$Li_3((UO_2)_7(AsO_4)_5O)$	As_2O_5	104			
$NaBUO_5$	B_2O_3	126	$Ba_4((UO_2)_2(As_2O_7)_3)$	As_2O_5	127			
MgB_2UO_7	B_2O_3	128	$Ba_3((UO_2)_2(AsO_4)_2(As_2O_7))$	As_2O_5	127			
$Sr[(UO_2)_2(B_2O_5)O]$	$H_3BO_3/Li_2B_4O_7$	12	$Ba_5Ca((UO_2)_8(AsO_4)_4O_8)$	As_2O_5	127			
$Cs_6[(UO_2)_{12}(BO_3)_8O_3](H_2O)_6$	B_2O_3	129	$K_2((UO_2)As_2O_7)$	As_2O_5	130			
$Rb_6[(UO_2)_{12}(BO_3)_8O_3](H_2O)_6$	B_2O_3	129	$Li((UO_2)(AsO_4))$	As_2O_5	105			
$K_4Sr_4[(UO_2)_{13}(B_2O_5)_2(BO_3)_2O_{12}]$	$H_3BO_3/K_2B_4O_7$	129	$Li((UO_2)(AsO_4))$	As_2O_5	105			
$(UO_2)(B_2O_4)$	Boric Acid	131	$Rb((UO_2)_2(As_3O_{10}))$	As_2O_5	118			
			$Ba_2[UO_2(AsO_4)_2]$	B_2O_3	108			
			$Ba_4[(UO_2)_7(UO_4)(AsO_4)_2O_7]$	As_2O_5	132			

Alkali, Alkaline Earth, and Select Mixed Metal Uranates

The first synthesis and investigation of alkali metal uranates dates back to the mid 20th century where the early samples were compositionally, but rarely structurally, characterized. A variety of synthetic approaches were used to prepare these phases, most of which resulted in polycrystalline samples that were structurally investigated by powder X-ray diffraction. The development of single crystal X-ray diffraction prompted numerous research groups to pursue the growth of single crystals in order to precisely elucidate the structures of this class of materials and, beginning in the 1980's, numerous reports on the crystal growth and structural determination began to appear in the literature. These researchers typically relied on the use of flux crystal growth to obtain the crystals needed for structural determination and soon a significant number of lithium, sodium, potassium and especially cesium uranates were grown as single crystals and structurally characterized. Thus, Wolf et al. published on the flux crystal growth of alpha and beta Li_6UO_6, which were obtained by dissolving U_3O_8 or UO_3, contained in a sealed gold capsule, in a Li_2O_2 flux for many days followed by slow cooling.[81] The lemon-yellow crystals were obtained in good yield and were observed to change to an orange color after a few hours of exposure to air. Subsequent flux crystal growth experiments on the other alkali uranates suggest that these times are likely longer than needed as many flux growth experiments are complete after 12-24 hours.

The sodium uranates exhibit more structural variety when compared to lithium, and have been obtained from a variety of fluxes. Beta-Na_2UO_4 was crystallized by Gasperin using a complex Na_2CO_3-Nb_2O_5 flux by heating U_3O_8 in this mixture at 1190°C for 15 hours.[83] This composition crystallizes in a K_2NiF_4 related structure. Orange-yellow plate crystals of Na_4UO_5 were grown by Roof et al. at much lower temperatures out of a molten hydroxide flux at only 750°C for 1 d followed by slow cooling. Using the same conditions, Roof et al. also obtained orange yellow plate crystals of K_2UO_4 (Figure 2), which crystallizes in the K_2NiF_4 structure.[36] The hydroxide fluxes, which are known to be highly effective for the crystal growth of oxides containing transition metals in high oxidation states work exceedingly well for the synthesis of K_2UO_4 and Na_4UO_5, which readily crystallize out of hydroxide fluxes. Unfortunately, these two compositions are strongly favored no matter what other elements are present in the melt, limiting the use of hydroxides for the exploration of more complex uranium containing structures. Jove et al. grew orange crystals of $Na_2U_2O_7$ out of a Na_2CO_3-Nb_2O_5 flux charged with U_3O_8 and orange crystals of $K_2U_2O_7$ out of a K_2CO_3-Nb_2O_5 flux charged with U_3O_8; in both cases the fluxes were heated to

1150°C in air.[59, 133] The two compositions are isostructural with $K_2Np_2O_7$. Read et al. crystallized a novel cubic phase, $K_8U_7O_{24}$, in a uranium deficient KUO_3 structure, out of a KF flux contained in a copper tube at 950°C followed by slow cooling. The uranium source was UO_2 and care was taken to eliminate water and oxygen from the reaction. The reaction yielded a mixture of yellow $K_2U_2O_7$ crystals and black cubes of $K_8U_7O_{24}$.[48] This is a rare example of an alkali uranate containing uranium in an oxidation state less than +6. A more complex potassium uranate, $K_9U_6O_{22.5}$ was crystallized by Saine et al, out of a K_2CO_3-Nb_2O_5 flux charged with U_3O_8.[57] The cubic structure containing all U(VI) differs from the all U(V) containing cubic KUO_3 structure by virtue of the uranyl (UO_2^{2+}) species that tetragonally distort the UO_6 octahedra.

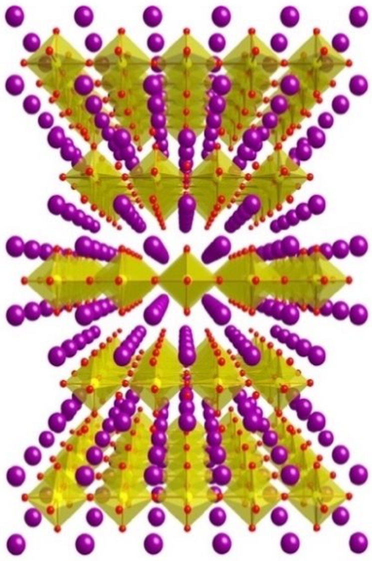


Figure 2. Structure of K_2UO_4 with uranium polyhedra in yellow, oxygen atoms in red, and potassium atoms in purple.

$Rb_4U_5O_{17}$, was reported by Saad et al, who grew yellow crystals out of a U_3O_8 containing Rb_2O-Sb_2O_3 flux by heating the mixture at 1300°C for 2 d followed by slow cooling to RT.[55] This composition is isostructural to the cesium analog, $Cs_4U_5O_{17}$. The cesium uranates are the most numerous among the alkali uranates and were extensively investigated by Egmond, who grew numerous cesium uranate crystals for structure determination, including yellow crystals of the aforementioned $Cs_4U_5O_{17}$ as well as Cs_2UO_4, $Cs_2U_4O_{12}$, $Cs_2U_7O_{22}$, and $Cs_2U_{15}O_{46}$ out of a CsCl flux.[64, 68] These structures tend to be related to the UO_2 structure where cesium atoms take the place of the uranium. This work was extended by Morrison et al, who reported the crystal growth of $Cs_{2.2}U_5O_{16}$ and $Cs_2U_4O_{13}$, also from a CsCl flux.[51] The structure of $Cs_{2.2}U_5O_{16}$ is closely related to $Cs_2U_5O_{16}$ via the addition of extra Cs to the channels, while $Cs_2U_4O_{13}$, seemingly related to the reduced $Cs_2U_4O_{12}$, crystallizes in a quite different structure.

A natural extension of the alkali uranates are both the alkaline earth uranates and mixed alkali-alkaline earth uranates. The latter can be crystallized out of carbonate melts, for instance $Ba_2Na_{0.83}U_{1.17}O_6$, $Na_3Ca_{1.5}UO_6$, and $K_4BaU_3O_{12}$ reported by Roof et al., and the isostructural $K_4CaU_3O_{12}$ and $K_4SrU_3O_{12}$ reported by Read et al.[39, 44] In both cases, Na_2CO_3 and K_2CO_3 fluxes were used at temperatures ranging from 900 – 1050 °C followed by slow cooling. These structures crystallize in perovskite related structures with fairly complex cation ordering. The exception is $Na_3Ca_{1.5}UO_6$, structurally related to $Na_{4.5}Nd_{0.5}UO_6$, which crystallizes in a unique ordered rock salt superstructure in which NaO_6, CaO_6 and UO_6 octahedra are edge and corner shared to create the overall 3D structure. An extremely complex composition, $Na_8U_2U_{0.81}(U_{0.89}Ca_{3.11})O_{17.35}$, (nominally a perovskite of the type $A_8B_8O_{24}$) was reported by Gasperin et al. in which U(VI) and Ca(II) occupy the same sites in the structure.[61] It is a mixed valent structure and contains a mixture of U(V) and U(VI) with an overall average oxidation state of +5.5.

By comparison, the all-alkaline earth uranates are fairly simple. They primarily form with the compositions of AUO_4 and A_3UO_6, and have been reported for Mg, Ca, Sr, and Ba. $MgUO_4$, $CaUO_4$, and $SrUO_4$ were reported by Zachariasen in 1948 and 1954, representing some of the first uranate single crystal structures reported, and the barium analog was reported by Reis et al. in 1976.[66, 70, 72] The yellow green A_2UO_4 crystals were grown out of an $MgCl_2$ $CaCl_2$, $SrCl_2$ or $BaCl_2$ melt, respectively, using U_3O_8 as the uranium source. The series is not isostructural due to the size differences of the alkaline earths resulting in structural distortions and the compositions crystallize in a number of different space groups. The double perovskites Ca_3UO_6 and Sr_3UO_6 (A_2ABO_6) were obtained as single crystals from a Na_2CO_3 and K_2CO_3 melt with $CaCO_3$ and $SrCO_3$ providing the Ca and Sr, respectively; UO_2 or U_3O_8 were used to supply the uranium.[36]

The specific identity of the uranium source, other than for the crystallization of phases containing reduced uranium, does not seem exceedingly critical for product formation. The variety of fluxes used, alkali and alkaline earth halides, alkali carbonates, and alkali oxides, have all demonstrated their ability to dissolve a variety of uranium sources, such as UO_2, U_3O_8 and UO_3. From the compositions listed, it is clear that "in-fill" compositions to complete a number of the above mentioned structural and compositional series should in all likelihood be readily obtained using one of the methods described above.

Related phases containing transition and main group elements in place of the alkaline earth cations have been prepared in recent years. The series Ba_2MUO_6 with M = Cu, Ni, Zn, is isostructural to Sr_3UO_6 discussed above.[36] Crystals of these oxides were grown out of carbonate melts, as already used for Sr_3UO_6. In all cases the uranium is in the +6 oxidation state and Cu, Ni and Zn are divalent. The compositionally, but not structurally related Pb_3UO_6 was crystallized out of molten PbO and the crystals mechanically extracted. The expectation was that Pb_3UO_6 would be structurally related to Ba_3UO_6, however, the irregular coordination environment of the lead cation results in the formation of unique $(UO_5)_\infty$ chains, yielding a novel structure type.[52] Analogs to the AUO_4 structure also exist with, however, in some cases exhibiting unique differences in oxidation states.[56] $CdUO_4$, which could be obtained out of a $CdCl_2$ melt, is structurally related to the AUO_4 series.[53] $MnUO_4$, $FeUO_4$ and NiU_2O_6 are an interesting series of transition metal uranates that can be grown out of chloride fluxes.[40] $MnUO_4$ is isostructural to $MgUO_4$, however, $FeUO_4$ is not. While $MnUO_4$ contains Mn(II) and U(VI), $FeUO_4$ contains Fe(III) and U(V), making the latter a rare example of a U(V) containing material. Similarly, NiU_2O_6, also contains U(V), this time alongside Ni(II).

More complex transition metal uranates can be crystallized out of alkali chloride melts, specifically $K_2MnU_3O_{11}$ (Figure 3), $Rb_2MnU_3O_{11}$, $Cs_2Mn_3U_6O_{22}$ and $Li_{3.2}Mn_{1.8}U_6O_{22}$, whose structures are related to the mineral Natrotantite, $Na_2Ta_4O_{11}$.[45, 46] The potassium and rubidium containing quaternary uranates contain U_3O_8 topological type layers connected via MnO_6 octahedra and K^+ cations, resulting in a layered intergrowth type structure. The Cs containing material is more complex and is based on U_3O_8 topological type layers connected via layers consisting exclusively of MnO_6 octahedra and layers consisting entirely of Cs^+ cations, resulting in a doubled unit cell with ordered layers. This arrangement separates the MnO_6 layers by over 13 Å, leading to two dimensional magnetic properties best described as a frustrated spin lattice and ferromagnetic like ordering at 12K.

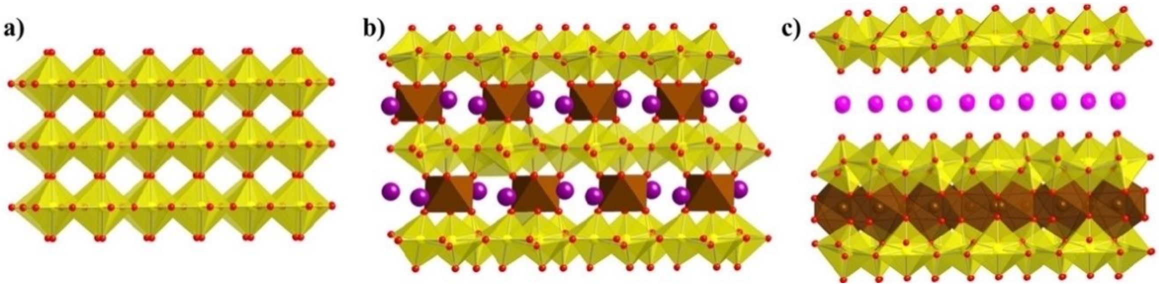


Figure 3. Crystal structures of a) U_3O_8, b) $K_2MnU_3O_{11}$, and c) $Cs_2Mn_3U_6O_{22}$ where uranium polyhedra are in yellow, manganese in brown, and potassium and cesium ions in purple and pink, respectively.

Oxychlorides

Uranium oxychlorides were first studied in the 1960s and have continued to receive attention. Multiple synthesis techniques have been used to prepare these compounds including solid state methods, flux growth, mild hydrothermal techniques, and most commonly, by crystallization from hydrochloric acid solutions.

All of the flux grown uranium oxychlorides, of which there are ten, have been synthesized using alkali chloride fluxes, typically in a sealed fused silica tube.[74] For example, the first reported flux growth by Allpress and Wadsley heated amorphous UO_3 in excess CsCl at 600 ºC in a sealed glass capsule for several weeks to form $Cs_x(UO_2)OCl_x$ ($x \sim 0.9$).[62, 73, 74, 77, 134] Read et al. reported that a sealed system and well dried reactants were instrumental in the formation of oxychlorides over pure oxides.[62] However, in rare instances, oxychlorides can form in open systems. KUO_3Cl was synthesized from a mixture of U_3O_8, $CoCl_2{\cdot}6H_2O$, and KCl flux in a covered alumina crucible heated to 900 ºC, where the role of $CoCl_2{\cdot}6H_2O$ was unclear but necessary.[73] $M_7(UO_2)_8(VO_4)_2O_8Cl$ (M = Rb, Cs) were obtained from the reaction of $(UO_2)_3(VO_4)_2{\cdot}5H_2O$ with a large excess of MCl flux in a Pt crucible at 750 ºC.[134]

An interesting pair of uranium oxychlorides, $A_4U_5O_{16}Cl_2$ (A = K, Rb) shown in Figure 4, were synthesized from the reaction of UO_3 and ACl flux in sealed fused silica tubes and contain 2-D uranyl sheets composed of UO_6, UO_7, and UO_4Cl_2 polyhedra. In these compounds, the bulky Cl ligands are directed out of the sheets forcing the uranyl oxygens to lie within the plane of the sheet thus forming sterically mediated cation-cation interactions (CCI), i.e. coordination of uranium(VI) atoms by the –yl oxygens of another uranyl groups.[135, 136] In contrast, $RbUO_3Cl$

contains 1-D uranyl chains of UO_6, UO_7, and UO_4Cl_2 polyhedra. This 1-D topology allows both the bulky chloride atoms and the uranyl oxygens to stick out of the chain and no cation-cation interactions exist in this structure.[62]

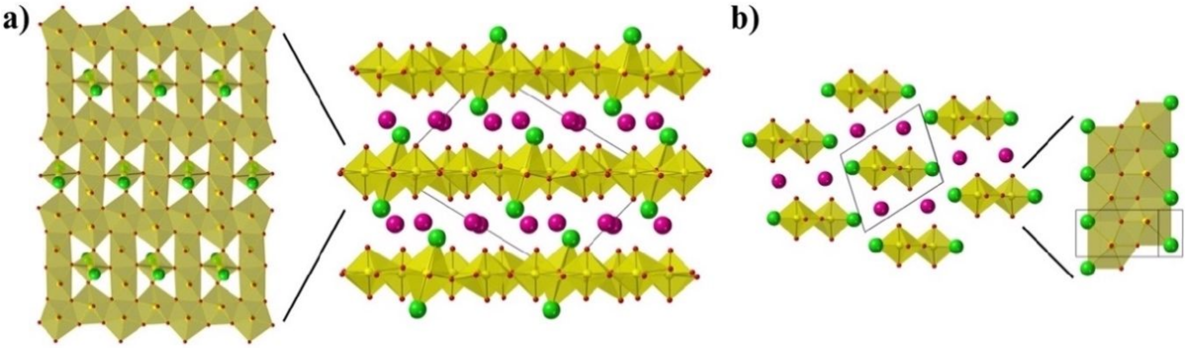


Figure 4. a) The layered structure of $A_4U_5O_{16}Cl_2$ with the uranyl bonds of the CCIs shown in bold and b) the 1-D structure of $RbUO_3Cl$ where uranium polyhedra are shown in yellow, cesium atoms in pink, chlorine atoms in green, and oxygen in red.

Oxychalcogenides

Uranium-containing oxychalcogenides obtained via flux growth are not very numerous and almost exclusively have been reported by the Ibers group.[37, 43, 47, 50, 54, 137–139] Many more oxychalcogenide compounds, however, were obtained via solid state synthesis, a method which proved useful for the synthesis of this class of compounds. The solid state synthesis of oxychalcogenides requires very precise control over the oxygen content in the system because of the high stability of both UOS and UO_2, which can compete with the targeted oxychalcogenide phase.[47] Other oxychalcogenides were obtained serendipitously from reactions that were thought to be oxygen free; however, the resulting product contained oxygen that had come either from the reaction vessel (typically, evacuated fused silica tube) or from an impurity in the starting materials.[139]

One of the unique aspects of oxychalcogenide flux crystal growth is that fluxes were typically used for the recrystallization of a powder phase obtained via solid state route, rather than from a mixture of dissolved simple starting materials, which is typically done in the flux crystal growth of other systems. The recrystallization approach limits the flux choices as the flux must both be inert towards the target phase and yet dissolve a good amount of it at the same time. Another requirement for the flux used in oxychalcogenide flux crystal growth is that it must be either easily separable from the target phase (e.g. either the flux or the target phase should form large single crystals readily available for handpicking) or be soluble in the most common dry solvents, such as methanol, ethanol, DMF, acetonitrile, etc. A flux that meets both these requirements is antimony chalcogenide Sb_2Q_3 (Q = S or Se), which has been employed successfully for the recrystallization of oxysulfides and oxyselenides, respectively. Although this flux is not readily soluble, it ends up in the form of large crystals that can be physically removed from the target product. A typical quantity of this flux used for recrystallization is approximately equal to the mass of the uranium-containing product phase.

For purpose of discussing specific examples of oxychalcogenide crystals grown by the flux method, it is worth starting with the examples of UOS and UOSe. The structures of these two compounds were deduced from PXRD patterns dating back to 1949, while the single crystal structures of these two compounds were reported significantly later, when Bang Jin et al. recrystallized UOS and UOSe powders from Sb_2S_3 and Sb_2Se_3 fluxes at temperatures of 1000 °C and 950 °C, respectively.[50] Among the products, plate-like black crystals were found to be the corresponding oxychalcogenides.

A number of other oxysulfide and oxyselenide phases have been obtained from the antimony chalcogenide flux, i.e. rare-earth element containing phases $UYb_2O_2S_3$, $UY_2O_2S_3$, $UY_4O_3S_5$, $UYb_2O_2Se_3$, $U_2Pr_2O_4Se_3$, $U_2Sm_2O_4Se_3$, $U_2Gd_2O_4Se_3$, and $UEr_2O_2S_3$.[37, 43, 54] The synthesis of all of these, with the exception of $UYb_2O_2S_3$, follow the abovementioned two-step procedure, i.e. all compounds were obtained via solid state routes and then recrystallized in a Sb_2Q_3 flux. An attempt of obtaining $UYb_2O_2S_3$ compound from KCl flux was undertaken, but it was unsuccessful due to a reaction between the starting reagents and the flux, resulting in the formation of $K_3Yb_7S_{12}$, which illustrates the importance of proper flux selection.[37] However, the use of 100 mg of CsCl flux in a reaction between uranium, SeO_2, and Se resulted in crystals of $U_7O_2Se_{12}$, showing no flux component incorporation into the final product.[47]

Although antimony chalcogenides are typical fluxes for uranium oxychalcogenides synthesis, there is an interesting example in which UCl_4 plays the role of a flux. A reaction between TaS_2 and excess of UCl_4 (1.6:1 ratio) in an evacuated fused silica tube at 610 °C, which is only 20 °C above the melting point of UCl_4, afforded crystals of $UTa_2O(S_2)Cl_6$ in an approximately 40% yield.[139] The source of oxygen for the resulting product is not known for certain, but most likely resulted from an oxide impurity in the TaS_2 reagent.

Concluding this section, a unique example of a uranyl sulfide compound, $Na_2Ba_2(UO_2)S_4$, highlights the importance of using new, unconventional fluxes for obtaining crystals of new materials.[138] A reaction between uranium, Na_2O_2, sulfur, and BaS, with an excess of the second component, Na_2O_2, results in single crystals of the phase $Na_2Ba_2(UO_2)S_4$. This compound exhibits a unique $[(UO_2)S_4]^{6-}$ unit (Figure 5) and allows one to speculate that highly oxidative fluxes, such as Na_2O_2, do not necessarily oxidize sulfur and, at the same time, maintain uranium in the highest oxidation state.

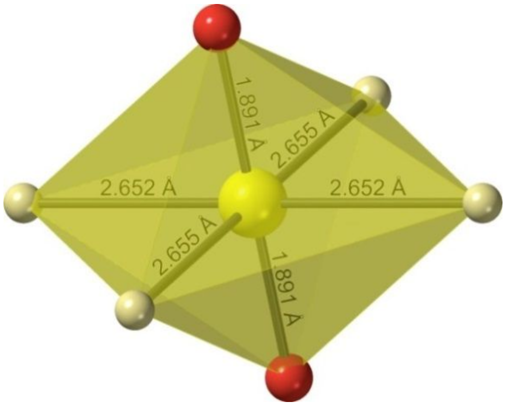


Figure 5. Uranium(VI) coordination polyhedron in the structure of $Na_2Ba_2(UO_2)S_4$.

Tellurites

Uranyl tellurites represent a unique class of materials that exhibit an extensive array of structural topologies. While historically hydrothermal synthesis routes were the predominant methods used to synthesize uranyl tellurites, flux crystal growth has more recently been shown to also be a viable synthetic route to uranyl tellurites. Moreover, it has enabled access to compositions that have revealed further structural diversity amongst the variety of phases in this class of materials. Extended structures containing uranium(VI) are often characterized by two-dimensional sheet structures as a result of the presence of the "uranyl" UO_2^{2+} unit, which preferentially forms bonding interactions along the equatorial plane. Compounds containing both uranyl and a main group element with a stereochemically active lone-pair, however, tend to form one-dimensional structures. Despite this, the compositions obtained via flux crystal growth deviate from this trend, indicating that a more comprehensive understanding of uranyl tellurite structural chemistry is desirable.

One such deviation from this structural trend is observed in $A_2[(UO_2)_3(TeO_3)_2O_2]$ (A = K, Rb, Cs), a family of layered alkali uranyl tellurites prepared by Woodward et al.[89] Compositions in the $A_2[(UO_2)_3(TeO_3)_2O_2]$ family were synthesized by flux crystal growth, where the combination of ACl (A = K, Rb, or Cs), UO_3, and TeO_3 in a 4:4:2 molar ratio resulted in yellow needle crystals when heated to temperatures between 650°C to 850°C for anywhere from one to six days. The target phases contain the A, U, and Te elements in a 2:3:2 molar ratio, suggesting that there is an excess of both ACl salts and UO_3. A wide temperature range was determined to be conducive to the formation of $A_2[(UO_2)_3(TeO_3)_2O_2]$ crystals, although it was noted that reaction temperatures above 650°C were needed to achieve the reduction of Te^{6+} to Te^{4+}. The reaction was found to be successful in either sealed silica ampoules or open ceramic crucibles, however, sealed reactions resulted in products with improved crystal quality.

$K_4[(UO_2)_5(TeO_3)_2O_5]$, a similar composition, was also synthesized by Woodward et al. using similar reaction conditions.[95] Yellow prisms of $K_4[(UO_2)_5(TeO_3)_2O_5]$ were grown from a mixture of KCl, UO_3, and TeO_3 in a molar ratio of 16:3:2: (U:Te:K), which was placed into an alumina crucible and heated to 800°C for three days, followed by slow cooling. In contrast to the previous three reactions, a large excess of KCl is used as a flux, leading to crystallization from a more diluted salt solution. As shown in Figure 6, a staircase topology analogous to the aforementioned $A_2[(UO_2)_3(TeO_3)_2O_2]$ series is observed in the structure of $K_4[(UO_2)_5(TeO_3)_2O_5]$. The structural similarities between the $K_4[(UO_2)_5(TeO_3)_2O_5]$ and the $A_2[(UO_2)_3(TeO_3)_2O_2]$ phases suggest that minor variations in synthetic parameters during the flux growth of uranyl tellurites could be an effective method to develop our understanding of existing trends in their structural chemistry.

As an alternative to the use of alkali metal salts as fluxes, Zadoya et al. investigated the use of a telluric acid flux to synthesize $Ca_2(UO_3)(TeO_3)_2$ and $K_2(UO_2)_2O_2(TeO_3)$, which exhibit an unusual tetraoxido core coordination and a new layer topology, respectively.[93] Mixtures of CaO or KCl, $(UO_2)(NO_3)_2{\cdot}6H_2O$, and H_6TeO_6 were added to a platinum crucible in a molar ratio of 1:2:3 (Ca/K:U:Te) and heated to 700°C and then slow cooled, resulting in yellow needles of the product phases. In both cases telluric acid was present in excess, playing the role of the flux.

To conclude, although the tellurite system offers a lot of compositional and structural flexibility, only a few fluxes have been employed to study this system so far. Further investigations on flux crystal growth in this system employing the alkali halide fluxes with tellurium oxide or telluric acid could be a promising direction for novel compositions. Also, it is important to note that almost no physical properties of the compounds in this class were reported, representing an additional impetus for the further development of this class of materials.

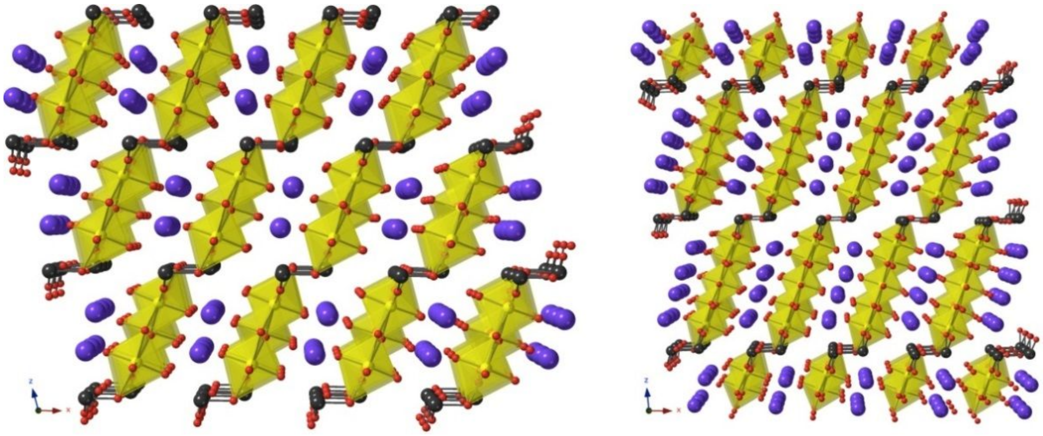


Figure 6. The staircase layers in the structures of $K_2[(UO_2)_3(TeO_3)_2O_2]$ (left) and $K_4[(UO_2)_5(TeO_3)_2O_5]$ (right).

Molybdates, Tungstates, and Chromates

To date, single crystals of uranium molybdates were obtained either from MoO_3 or carbonate fluxes. The use of the MoO_3 flux was found to be very convenient for obtaining single crystals of new molybdates as it functions as the molybdenum source, has a relatively low melting point, 795 °C, and partially evaporates at high temperatures, thereby saturating the melt with respect to uranium and prompting the growth of large single crystals. Alkali carbonates, such as K_2CO_3 and Cs_2CO_3 have also been used successfully for the growth of uranium molybdates. In addition to dissolving the starting materials, the carbonate fluxes also serve as a source of the alkali cations, eliminating the necessity of adding another alkali source, such as nitrates, to the reaction. A combination of the two fluxes, a mixture of both alkali carbonate/nitrate and MoO_3, has also been shown to favor the growth of single crystals of uranium molybdates. The latter is a more complicated process as it involves a reaction between the alkali salt and molybdenum oxide to form a low melting point molybdate which then functions as the flux. For example, the melting point of Na_2MoO_4 is 687 °C, which is about 100 °C lower than the melting point of MoO_3, 795 °C. Noteworthy, all uranyl molybdate compounds have been obtained in a temperature range 850 – 1000 °C, above the melting point of molybdenum oxide.

Single crystals of $Li_4[(UO_2)_{10}O_{10}(Mo_2O_8)]$, $K_2[UO_2(MoO_4)_2]$, $Rb_2[(UO_2)_2MoO_4O_2]$, $Cs_2[(UO_2)_2(MoO_4)_3]$, $Ag_6[(UO_2)_3O(MoO_4)_5]$, among others, have been obtained from MoO_3 flux with an addition of nitrate or carbonate alkali metal source.[63, 67, 69, 78, 140, 141] It is noteworthy that several of these reactions, although called solid state reactions by the authors, involve non-stoichiometric ratios of the starting reagents, enabling an excess component to function as a flux.[140, 141] $Cs_6[(UO_2)_2(MoO_4)_3(MoO_5)]$, $K_2(UO_2)_2(MoO_4)O_2$, and $K_8(UO_2)_8(MoO_5)_3O_6$, two of which exhibit MoO_5 trigonal bipyramidal units (Figure 7) are related examples where the use of a large excess of alkali carbonates resulted in the crystal formation.[65, 71] Further investigation of related compositions would be of interest and it is noteworthy that no uranium molybdates have been reported grown from an alkali halide flux to date, suggesting that this might be an alternative approach for the crystal growth of this class of materials.

Alekseev et al. reported the flux crystal grwoth of several uranium tungstates, e.g. $Na_2Li_8[(UO_2)_{11}O_{12}(WO_5)_2]$, $Li_4[(UO_2)_2(W_2O_{10})]$, $A_8[(UO_2)_4(WO_4)_4(WO_5)_2]$ (A = Rb, Cs) and $Rb_6[(UO_2)O(WO_4)_4]$.[85, 88, 90] Crystals of these phases were obtained by heating a mixture of uranyl acetate $UO_2(CH_3CO_2)_2{\cdot}2H_2O$, alkali carbonate A_2CO_3, and tungsten oxide WO_3 in a platinum crucible at roughly 950 °C. There is no apparent excess of any of the reagents, suggesting that therefore there is no readily identifiable flux in these system; however, complex products, such as $Li_2(UO_2)_4(WO_4)_4$, obtained along with the target phase $Na_2Li_8[(UO_2)_{11}O_{12}(WO_5)_2]$ suggests, that there are multiple competing processes occurring in the reaction mixture.[90] It has been shown by Charkin et. al. that an eutectic K_2SO_4–Na_2SO_4 mixture can be used to recrystallize uranium-containing tungstates.[82] No other fluxes have been used to probe the A_2O–UO_3–WO_3 (A = alkali earth element) systems so far.

Given the tendency of the chromate(VI) groups to decompose at high temperatures, only fluxes with low melting points can be employed to grow crystals of uranium chromates. There are two compounds reported to date, $Rb_2(UO_2)(CrO_4)_2$ and $Cs_2(UO_2)(CrO_4)_2$, that have been grown at a temperature of 270 °C from a CrO_3 flux, which served as a source of the chromate anions for the target phases as well. However, even at that low temperature CrO_3 undergoes decomposition, contaminating the sample with the highly inert Cr_2O_3. Recently, we have demonstrated the successful application of eutectic nitrate fluxes with low melting points, to grow thorium fluorides,[142] avoiding the formation of the inert ThO_2. A similar approach might be employed to grow crystals of additional chromate phases.

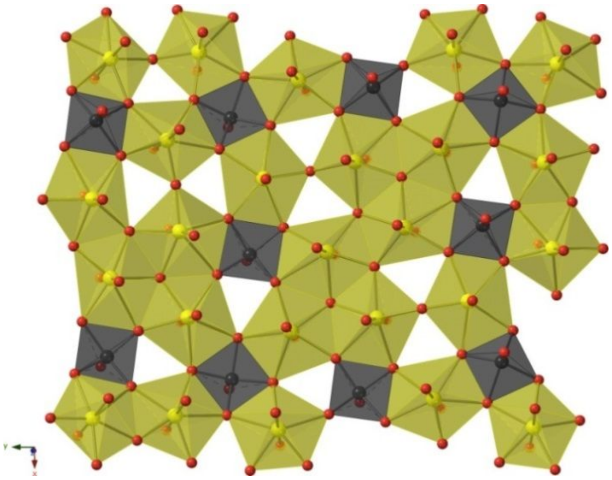


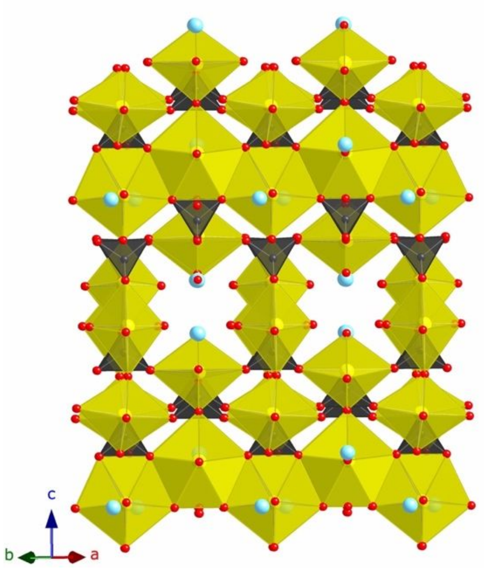
Figure 7. A layer consisting of UO_2O_5 and MoO_5 polyhedra in the structure of $K_8(UO_2)_8(MoO_5)_3O_6$.

Phosphates and Arsenates

The flux synthesis of uranium phosphates and arsenates is a relatively new area of synthesis, considering that there are only two publications prior to the turn of the century, as compared to the alkali and alkaline uranates that garnered significant attention in the 1980s. The hydrothermal and solution based syntheses of hydrated phosphates and arsenates received significant attention for their relationship to the uranium phosphate and arsenate mineral class, one of the largest for uranium containing minerals. By comparison, the anhydrous phosphate and arsenate phases synthesized at high temperatures by various synthetic routes, including flux synthesis, have received comparatively less attention. To date, the Depmeier and Alekseev groups have published all of the reported uranium arsenates and half of the phosphates synthesized by flux methods, with additional contributions to the expansion of this class of materials by the zur Loye, Obadde, and Ibers groups.[98, 101, 104, 105, 107, 108, 111–113, 117, 118, 120, 121, 127, 130, 143]

The general synthesis route for crystalizing uranium arsenates established by Depmeier and Alekseev consists of loading uranyl nitrate, As_2O_5, and nitrates or carbonates of desired cations, such as Li, Na, K, Rb, Ca, Ba, and Ag, into a platinum crucible and heating to 780-850 °C followed by slow cooling at 5-7 °C/h to 50-60 °C. As_2O_5 functions as a very low melting point (315 °C) flux for these reactions that produced crystals of layered structures

Figure 8. The structure of $Li_3((UO_2)_7(AsO_4)_5O)$ which contains perpendicular chains of pentagonal bipyramids as observed in the uranophane topology connected by cation-cation interactions. Uranium polyhedra are shown in yellow, arsenate tetrahedra in gray, oxygen atoms in red, and lithium atoms in light blue.



$Ag_6[(UO_2)_2(As_2O_7)(As_4O_{13})]$, $Ag_6[(UO_2)_2(AsO_4)_2(As_2O_7)]$, $Na_6[(UO_2)_2(AsO_4)_2(As_2O7)]$, three dimensional structures $Li_5((UO_2)_{13}(AsO_4)_9(As_2O_7))$, $Li((UO_2)_4(AsO_4)_3)$, $Li_3((UO_2)_7(AsO_4)_5O)$, $Li((UO_2)(AsO_4))$, $Ba_3((UO_2)_2(AsO_4)_2(As_2O_7))$, $K_2((UO_2)As_2O_7)$, $Rb((UO_2)_2(As_3O_{10}))$, and the 1-D chain structure $Ba_4((UO_2)_2(As_2O_7)_3)$.[104, 105, 118, 121, 127, 130] Additionally, the layered $Ba_5Ca((UO_2)_8(AsO_4)_4O_8)$ and three dimensional $Ba_4[(UO_2)_7(UO_4)(AsO_4)_2O_7]$ were prepared by methods similar to those described above, with an increased heating temperature of 1150 °C.[127] $Ba_2[UO_2(AsO_4)_2]$, the only reported arsenate synthesis to use a non-As_2O_5 flux, was prepared by loading uranyl nitrate, barium nitrate, ammonium dihydrogen arsenate, and B_2O_3 flux into a Pt crucible that was heated to 1000 °C, held for 5 h, and slow cooled to 300 °C at 5 °C/h. This structure consists of layers of isolated uranyl bipyramids connected through corner sharing of arsenate tetrahedra.[108]

Among the structures mentioned above, the lithium uranyl arsenates, $Li_5((UO_2)_{13}(AsO_4)_9(As_2O_7))$, $Li((UO_2)_4(AsO_4)_3)$, and $Li_3((UO_2)_7(AsO_4)_5O)$ exhibit the most interesting structures as they contain cation-cation interactions which occur in less than 2% of all U^{6+} containing materials.[104] $Li_5((UO_2)_{13}(AsO_4)_9(As_2O_7))$ is constructed of well-defined tubular units that when unfolded onto a 2D plane exhibit the ubiquitous uranophane topology. $Li((UO_2)_4(AsO_4)_3)$ is comprised of uranophane type chains and perpendicular chains parallel to the *a* direction and the *b* direction are connected through uranyl square bipyramids via cation-cation interactions to form a complex 3D structure. $Li_3((UO_2)_7(AsO_4)_5O)$, shown in Figure 8, is very similar to $Li((UO_2)_4(AsO_4)_3)$ with additional cation-cation interactions between two uranyl pentagonal bipyramids of perpendicular uranophane-type chains.

Alekseev and Depmeier also synthesized several phosphates, $Li_6((UO_2)_{12}(PO_4)_8(P_4O_{13}))$, $Li((UO_2)(PO_4))$, $Li_2((UO_2)_3(P_2O_7)_2)$, α-$K[(UO_2)(P_3O_9)]$, β-$K[(UO_2)(P_3O_9)]$, $K[(UO_2)_2(P_3O_{10})]$, and $Rb_2((UO_2)_3(P_2O_7)(P_4O_{12}))$, using a method similar to the one used for arsenates by simply substituting As_2O_5 with P_2O_5 that melts at 580 °C. [104, 105, 111, 118, 143] The structures of these phosphates are three dimensional where $Li_6((UO_2)_{12}(PO_4)_8(P_4O_{13}))$ and $Li((UO_2)(PO_4))$ are structurally related to $Li_5((UO_2)_{13}(AsO_4)_9(As_2O_7))$ and $Li((UO_2)_4(AsO_4)_3)$, while α-$K[(UO_2)(P_3O_9)]$, β-$K[(UO_2)(P_3O_9)]$, $K[(UO_2)_2(P_3O_{10})]$, and $Rb_2((UO_2)_3(P_2O_7)(P_4O_{12}))$ all contain polyphosphate units which are not found in minerals, and are uncommon among uranyl phosphates. The use of a B_2O_3 flux was successful for the synthesis of a barium uranyl arsenate, $Ba_2[UO_2(AsO_4)_2]$, and was also successful for the synthesis of α- and β- $Ba_2[UO_2(PO_4)_2]$ which are comprised of 1D chains and synthesized using uranyl nitrate, barium carbonate, and boron phosphate.[108] The reactants were loaded into a platinum crucible along with the B_2O_3 flux and where heated to 1000 and 1300 °C, respectively, held for 2 h and slow cooled to 300 °C at 7 °C/h.

The reported phosphate flux syntheses utilized a more diverse collection of fluxes when compared to the arsenates, including the previously discussed P_2O_5, H_3PO_4 acid, polyphosphoric acid, a mixed $CsPO_3/Cs_4P_2O_7$ flux, and alkali halide fluxes. P_2O_5 is difficult to weigh out in air considering it is extremely hygroscopic and reacts with water to form phosphoric acid. Diammonium phosphate or dihydrogen ammonium phosphate are easier solids to weigh out, although it is important to note that both of these reagents ultimately decompose into metaphosphoric acid (as do phosphoric and polyphosphoric acid) to form a glassy melt that acts as a flux; thus, fluxes of P_2O_5 vs diammonium phosphate or dihydrogen ammonium phosphate are significantly different. The use of the phosphoric and polyphosphoric acid fluxes allowed the use of low reaction temperatures of 500 °C and 400-420 °C, respectively. $(Nd_{0.38}U_{0.62})(PO_3)_4$, $U(PO_3)_4$, and $U(P_4O_{12})$ were produced from phosphoric acid fluxes where the former where made from the reaction of uranyl nitrate, neodymium nitrate, and sodium carbonate, while the latter was synthesized from U_3O_8.[113] It's interesting to note, that while all of the other phosphates and arsenates synthesized in air result in compounds containing U^{6+}, those synthesized using the phosphoric acid flux resulted in U(IV) containing products. The use of the polyphosphoric acid flux and the UO_3 reagent produced a U(VI) containing compound, $(UO_2)_2P_6O_{17}$, [117] suggesting that polyphosphoric acid is not as reducing towards U(VI) as phosphoric acid, which is interesting considering both starting reagents effectively result in a metaphosphoric acid flux; however, it would be difficult to determine when during the decomposition of the phosphorus containing reagent the product forms. U(IV) phosphates can also be synthesized by combining UP_2, Se, and CsCl flux in a sealed silica tube, heating to 950 °C and dwelling for 192 h before cooling to 550 °C in 120 h. This synthesis reported by the Ibers group produced blue-purple dichroic crystals of $CsU_2(PO_4)_3$.[120] Using the mixed $CsPO_3/Cs_4P_2O_7$ flux with UO_3 and Eu_2O_3 starting materials in a platinum crucible, heated at 600 °C for 2 days, and 850 °C for 10 days, and slow cooling to 720 at 1 °C/h resulted in orange, luminescent crystals of $Cs_{11}Eu_4(UO_2)_2(P_2O_7)_6(PO_4)$, reported by Pobedina et al.[112]

Alkali halide fluxes have also been used in reaction vessels open to air. The Obbade group reported the synthesis of $Cs_3(UO_2)_2(PO_4)O_2$ obtained by using $(UO_2)_3(PO_4)_2(H_2O)_4$ as the uranium and phosphate source and CsI as the flux.[107] These powders were loaded into a platinum crucible in a 1:30 ratio and heated at 750 °C for 10 h before slow cooling at 7 °C/h. The zur Loye group utilized UF_4 and $AlPO_4$ and alkali chloride fluxes and heated mixtures with general molar ratios of 3:2:120 in alumina crucibles at 875 °C for 12 h before cooling to 400 °C at 6 °C/h. The excess flux is washed away with water to yield yellow or orange crystals of $A_6[(UO_2)_7O_4(PO_4)_4]$ (A = Rb, Cs), $A_4[(UO_2)_3O_2(PO_4)_2]$ (A = K, Rb/K, Cs/K), and $A_6[(UO_2)_5O_5(PO_4)_2]$ (A = Cs/K, Rb/K).[98, 101] While the latter two families adopt layered structures of known topologies, the $A_6[(UO_2)_7O_4(PO_4)_4]$ structure type features chains of phosphuranylite type units connected into 2D sheets through uncommon uranyl cation-cation interactions.

Vanadates

Numerous vanadates have been obtained via hydrothermal synthesis. The higher temperature flux crystal growth, however, can make compositions accessible that cannot readily be prepared via hydrothermal methods; specifically, anhydrous compositions are more conveniently obtained by flux crystals growth. The work by Abraham et. al.[27, 144–146] which resulted in a large number of anhydrous vanadates via halide flux crystal growth, is one example. They used a KCl flux at temperatures just above its melting point (reaction temperature 775 vs. 770 °C melting point) to dissolve $(UO_2)_3(VO_4)_2 \cdot 5H_2O$ and to obtain single crystals of $K_6(UO_2)_5(VO_4)_2O_5$.[144] A related composition, $Na_6(UO_2)_5(VO_4)_2O_5$, was obtained by melting Na_2UO_4 and V_2O_5 in a 3:2 molar ratio at a temperature of 800 °C. In this crystal growth reaction, one can consider the excess V_2O_5 with a melting point of 690 °C to function as the flux. Single crystals of two polymorphs of the rubidium analog, α- and ß-$Rb_6(UO_2)_5(VO_4)_2O_5$,[145] were also obtained; the former was crystallized from a RbI flux at a temperature 8 °C above the flux melting point of 642 °C, and the other one from a mixture of U_3O_8 and a V_2O_5/Rb_2CO_3 flux in a 0.67:1:2 molar ratio at a temperature of 1200 °C. In the latter case, the excess of Rb_2CO_3 and V_2O_5 can be considered as a flux. Similarly, single crystals of $Na(UO_2)_4(VO_4)_3$ were obtained by melting a mixture of V_2O_5, U_3O_8, and Na_2CO_3 in a 12:11:3 molar ratio.[146]

Alkali halides or vanadium(V) oxide, as in the previous examples, are rather intuitive choices for a flux employed to crystallize uranyl vanadates. A less conventional approach is the synthesis resulting in $[La(UO_2)V_2O_7][(UO_2)(VO_4)]$, which was obtained by melting $LaCl_3 \cdot 7H_2O$ and $U_2V_2O_{11}$ in a 2:3 molar ratio at 870 °C.[27] The structure of this compound represents a 3D structure resulting from the stacking of $[La(UO_2)V_2O_7]^+$ double layers and sheets of $[(UO_2)(VO_4)]^-$.

Niobates

In addition to high-temperature solid-state methods, flux growth has been used to synthesize several uranium niobates. Chevalier and Gasperin first reported on $UTiNb_2O_{10}$, which they obtained in single crystal form from a mixture of U_3O_8, Nb_2O_5, and TiO_2 heated in a H_3BO_3 flux at 1200°C.[87] Gasperin later reported on the use of carbonate fluxes to prepare $TlNb_2U_2O_{11.5}$, $KNbUO_6$, and $RbNbUO_6$, which were grown in platinum crucibles heated to temperatures in excess of 1150 °C from mixtures of U_3O_8, Nb_2O_5 and Tl_2CO_3 or K_2CO_3/Rb_2CO_3 in a 1:1:2 and 1:1:6 molar ratio (U:Nb:Tl,K/Rb), respectively.[86] $CsNbUO_6$ was later reported by Gasperin who synthesized it using methods identical to those used to prepare $KNbUO_6$ and $RbNbUO_6$, only changing the molar ratio of U_3O_8, Nb_2O_5 and Cs_2CO_3 to 1:1:2.5.[86]

Similarly, a mixed alkali/alkaline earth metal uranium niobate $(Nb_{7.6}U_{2.4})(Ba_{5.2}K_{0.8})O_{30}$ was prepared by Saine using a K_2CO_3 flux, representing an unusual composition in which the U(VI) site is surprisingly shared by Nb(V) and Nb(IV).[94] Crystals of this composition were grown from a 1:1:1 mixture of U_3O_8, Nb_2O_5 and $BaCO_3$ heated to 1250°C for fifteen hours.

Silicates and Germanates

Uranium silicates constitute an abundant class of materials with over 60 compounds known, including nearly 20 minerals. Many of the synthetic uranium silicates have been grown under hydrothermal conditions which mimic the conditions under which natural minerals often form. However, in the past decade, the flux growth of uranium silicates has received considerable attention and resulted in the discovery of 19 new compounds.[96, 100, 102, 106, 109, 110, 114, 116, 119]

Alkali fluoride containing fluxes have been found to be very effective fluxes for the growth of complex uranium silicates and all but one of the syntheses reported in literature use such a flux. However, single species fluxes have had limited success, with KF typically producing a layered potassium uranium oxide that decomposes when exposed to water during flux removal and RbF and CsF preferentially crystallizing Rb_2USiO_6 and Cs_2USiO_6, respectively. [114] For this reason, the flux crystal growth of uranium silicates has almost exclusively been conducted in mixed alkali fluoride containing fluxes, most commonly AF-BF and AF-ACl fluxes (A, B = alkali metals), where the fluoride is important to facilitate SiO_2 dissolution in the melt. For example, $Rb_2(UO_2)Si_2O_6$ was grown by heating a mixture of UF_4 and SiO_2 in a RbF/RbCl flux at 800 ºC. In a couple instances, more complex alkali fluoride fluxes were used. Namely, $K_6(UO_2)_3Si_8O_{22}$ was synthesized from UO_3 and SiO_2 in a KF/KVO_3 flux at 700 ºC and $K_4CaUSi_4O_4$ was synthesized from the reaction of U_3O_8 and SiO_2 in a KF/CaF_2 flux at 900 ºC.[100, 147]

The one example of a non-alkali fluoride containing flux in the growth of uranium silicates is the synthesis of $(Ca_{0.5}Na_{0.5})_2NaUSi_8O_{20}$, which was obtained from the reaction between UO_2 and $CaSiO_3$ in a Na_2WO_4 flux at 730 ºC.[119] This synthesis is also notable in that it produces a U(IV) silicate. To prevent the oxidation of the uranium during flux growth, the reaction was loaded into a flame-sealed, evacuated, carbon coated, fused silica ampoule. Three other U(IV) silicates, $A_2USi_6O_{15}$ (A = K, Rb, Cs), have been obtained by flux growth.[102] These were grown via the reaction of UO_2, SiO_2 and an AF/ACl flux in sealed Cu tubes. The copper tubes had to be heated in a N_2 flow to prevent the copper from oxidizing; the copper tubes are, however, relatively inert to fluoride fluxes which is not the case with the more prevalent fused silica tubes.

One noteworthy class of materials amongst the uranium silicates are the salt-inclusion materials, SIMs. These materials consist of a covalent metal oxide framework that surrounds an ionic salt lattice, often an alkali halide. While many varieties of SIMs are known, the uranyl silicate SIMs are particularly abundant. The first reported uranyl silicate SIMs, $[NaRb_6F][(UO_2)_3(Si_2O_7)_2]$ and $[K_3Cs_4F][(UO_2)_3(Si_2O_7)_2]$, were crystallized from a mixture of UO_3 and SiO_2 in a NaF/RbF or KF/CsF flux heated to 750 ºC in a Pt crucible.[116] Later research found that limiting the availability of oxygen to the melt by reducing the reaction surface area and by using halide as opposed to oxide precursors promoted the formations of SIMs. Using these enhancements, 7 more uranyl silicate SIMs were discovered. For example, $[Cs_3F][(UO_2)(Si_4O_{10})]$ was grown at 800 ºC from a mixture of UF_4, SiO_2, and a CsF/CsCl flux in a high aspect ratio cylindrical Ag crucible (Figure 9).[106, 110]

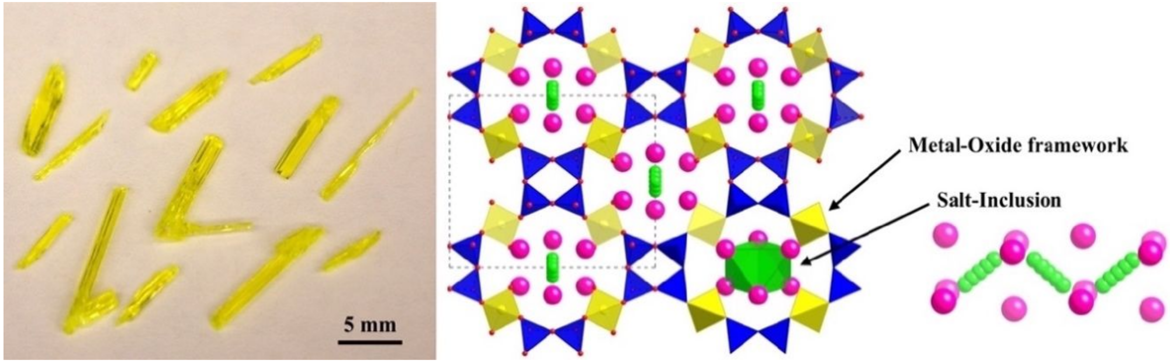


Figure 9. Optical images of crystals and framework structure of $[Cs_3F][(UO_2)(Si_4O_{10})]$, where uranium polyhedra are in yellow, silicate tetrahedra in blue, cesium atoms in pink, chlorine atoms in green, and oxygen atoms in red.

Uranium germanates are considerably less well studied than their silicate counterparts. However, three recent papers have reported their flux growth and thereby greatly increased the number of known uranium germanates. In general, the flux synthesis of germanates is similar to that of silicates. One notable difference is that GeO_2 is able to be solubilized by chloride melts, so fluoride free alkali halide fluxes can be used. For example, $[Cs_6Ag_2Cl_2][(UO_2)(Ge_2O_7)]$, a SIM that crystallizes in the same structure type as some of the silicate SIMs, was synthesized from the reaction of UF_4 and GeO_2 in a CsCl flux heated to 875 ºC in a silver crucible. Eleven other compounds with the same uranyl germanate framework and different salt-inclusions were synthesized by varying the composition of the flux.[99] The second reported flux synthesis of a uranyl germanate was that of $K_4[(UO_2)Eu_2(Ge_2O_7)_2]$, which was synthesized from UO_3, Eu_2O_3, and GeO_2 in a KF/MoO_3 flux at 950 ºC.[97] Finally, the synthesis of seven open-framework uranyl germanates, including two SIMs, were reported from the reaction of uranyl nitrate and GeO_2 in a variety of fluxes, namely K_2CO_3-WO_3, K_2CO_3-MoO_3-PbO, Cs_2CO_3-V_2O_5-CsF, CsF-CsCl, Na_2CO_3-KF-KCl, and CsF-CsCl-NaCl.[103]

Borates

The relevance of uranium borates has primarily resulted from research efforts focused on developing an understanding of the behavior of actinides in nuclear waste disposal processes in which, under certain process conditions, crystalline regions tended to form within borosilicate glass matrices.[148] Hydrothermal synthesis methods have proven to be highly effective for the preparation of uranium borates and many examples of these compounds have been synthesized from low temperature boric acid fluxes using mild hydrothermal methods by the Albrecht-Schmitt and Alekseev groups; however, this extensive body of work has been reviewed elsewhere.[148] To date, the application of high temperature, ambient pressure flux growth techniques to the preparation of uranium borates has resulted in several compounds, the majority of which have been prepared from B_2O_3 melts.

The first of these compounds was reported by Hoekstra, in which single crystals of $UO_2(BO_2)_2$ were prepared by reacting U_3O_8 with an excess of B_2O_3 at approximately 1100°C.[94] It was later reported by Holcombe and Johnson that polycrystalline powders of the same composition could be obtained using ammonium diuranate as the uranium source in an excess of B_2O_3; single crystals were then obtained by heating the powder to 850-900°C in a B_2O_3 flux. [125] The first alkali and alkaline earth metal uranium borates, $Li(UO_2)(BO_3)$, $Na(UO_2)(BO_3)$, $Mg(UO_2)B_2O_5$, and $Ca(UO_2)_2(BO_3)_2$, reported by Gasperin, were obtained from mixtures of U_3O_8 and the respective alkali/alkaline earth carbonate salts heated in B_2O_3 melts at temperatures between 1100-1200°C.[122, 123, 126, 128]

Nearly three decades after Gasperin's successful preparation of several uranium borates using B_2O_3 as a flux, Alekseev et al. reported on the use of a mixed $Li_2B_4O_7/H_3BO_3$ flux to synthesize $Sr[(UO_2)_2(B_2O_5)O]$ from $(UO_2)(NO_3)_2{\cdot}6H_2O$ and $Sr(NO_3)_2$ precursors heated to 965°C.[12] It was noted that attempts to prepare $Sr[(UO_2)_2(B_2O_5)O]$ by substitution of $Li_2B_4O_7$ with increased stoichiometric ratios of H_3BO_3 were unsuccessful, leading the authors to deduce that addition of $Li_2B_4O_7$ is necessary for the stabilization of this phase. Attempts were also made to prepare the barium analogue using $Ba(NO_3)_2$ as a precursor; however, this phase could only be synthesized from mild hydrothermal methods. Alekseev et al. later reported on $A_6[(UO_2)_{12}(BO_3)_8O_3](H_2O)_6$ (A = Rb, Cs) and $K_4Sr_4[(UO_2)_{13}(B_2O_5)_2(BO_3)_2O_{12}]$, synthesized using B_2O_3 and mixed $K_2B_4O_7/H_3BO_3$ fluxes, respectively.[12] The $A_6[(UO_2)_{12}(BO_3)_8O_3](H_2O)_6$ compounds were prepared from mixtures of $(UO_2)(NO_3)_2{\cdot}6H_2O$ and the respective alkali metal nitrate salt heated to 1000°C, while $K_4Sr_4[(UO_2)_{13}(B_2O_5)_2(BO_3)_2O_{12}]$ was prepared from a mixture of $(UO_2)(NO_3)_2{\cdot}6H_2O$ and $SrCO_3$ heated to 980°C. Since both the $A_6[(UO_2)_{12}(BO_3)_8O_3](H_2O)_6$ phases have been obtained at a high temperature, it is very likely that the hydration of these compounds took place during dissolving the flux with water, which also explains the low quality of the crystals. Although B_2O_3 melts have resulted in many compounds, this recent work by the Alekseev group demonstrates the viability of preparing novel uranium borate phases from variable borate fluxes and, thus, highlights a potential area for future work.

Summary and Outlook

Understanding the crystal chemistry of uranium and other actinides has become more pressing as efforts to enhance the nuclear fuel cycle, studies to create new materials in which to immobilize nuclear waste, and investigations to improve environmental remediation projects are being expected to emerge with new materials that can help solve existing problems. To address these and other issues, over the past decades, numerous research groups have used fluxes to grow crystals of diverse classes of uranium containing materials, and in the process have established flux growth as an important tool for materials chemistry and for improving our understanding of the crystal chemistry of uranium in general. Clearly, the utility of fluxes for materials discovery of uranium containing materials via exploratory crystal growth has been and continues to be a rewarding undertaking.

The challenge of materials discovery is present in all areas of materials chemistry where the desire to find new or create chemically modified versions of materials that exhibit desired structures and physical behavior has driven research for many decades. The use of fluxes for materials discovery has been reviewed by a number of investigators, each one typically focusing on a discrete area of materials chemistry, ranging from intermetallics to complex oxides.[149] In this frontier article we focused on providing an overview of the history of flux crystal growth of uranium containing phases, and highlighting the recent advances in the field, limiting ourselves to uranium containing oxides, including mixed anion oxides.

In order to grow crystals of desired materials, such as uranium containing phases, including quaternary and higher phases, the flux, by necessity, must be able to solubilize simultaneously a diverse mix of oxide reagents. We highlighted a number of fluxes that work eminently well for uranium containing oxides, including phosphates, silicate, borates, and arsenates; nonetheless, it is important to keep in mind that simple fluxes may not be up to this task, and for that reason the use of more complex fluxes may be required to target phases that are more compositionally demanding. It will be up to the researchers to adapt and modify existing fluxes for this purpose and, ideally, this frontier article will provide a useful starting point. The crystal growth from high temperature solutions is an adaptive field and we expect that new flux combinations will come into use and lead to the growth of additional new uranium containing complex oxides.

Finally, there remains the ever present tension between crystal size and crystal growth throughput. It is therefore important to keep in mind that adapting a growth process that has yielded a desired phase to one that produces multi millimeter crystals of the same phase is on the one hand very time consuming, yet on the other hand very rewarding for the research opportunities that are opened up.

The rapid progress enabled by flux crystal growth, especially in the last few years, is expected to motivate other groups to also utilize fluxes for materials discovery, not only in uranium containing materials, but in a wide range of materials classes and to further expand our knowledge of crystal chemistry in these areas.

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Graphical abstract

Molten flux crystal growth is a thriving field for the discovery uranium oxides.