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Targeted Crystal Growth of Uranium Gallophosphates via the Systematic Exploration of the UF_4-$GaPO_4$-ACl (A = Cs, Rb) Phase Space

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Table S1: Phase space summary of UF_4-$GaPO_4$-RbCl in 5mL fused silica crucibles.

mmols of RbCl	1.5:1	1:1
		---875°C ---775°C
20	? poor xtals	$[Rb_{5.93}Cl_{0.93}][(UO_2)_5(PO_4)_5]$ ‡ + ?
		$[Rb_{5.93}Cl_{0.93}][(UO_2)_5(PO_4)_5]$ ‡ + ?
10	$Rb_6[(UO_2)_5O_2(PO_4)_4]$‡	$Rb_{11}U_{12}P_3O_{48}F_2$[23]
		$[Rb_{5.93}Cl_{0.93}][(UO_2)_5(PO_4)_5]$ ‡

Molar ratio of UF_4:$GaPO_4$

NOTE: The lack of more than one phase listed does not imply a phase pure product, but rather that only the major phase is reported. In many cases small impurities could not be identified

‡Structures from this work, [37]Reference 37

Table S2: Phase space summary of UF_4-$GaPO_4$-RbCl in 5mL Pt crucibles.

mmols of RbCl	1.5:1	1:1	1:2
			---875°C ---775°C
20	$Rb_{11}[(UO_2)_8(PO_4)_9]$‡	$Rb_9U_5P_6O_{34.5}$*	$Rb_9U_5P_6O_{34.5}$* + $GaPO_4$ + Ga_2O_3
	$Rb_6[(UO_2)O_5(PO_4)_2]$[25] + $Rb_4[(UO_2)_3O_2(PO_4)_2]$[25,27] + $Rb_9U_5P_6O_{34.5}$*	$Rb_9U_5P_6O_{34.5}$*	$Rb_9U_5P_6O_{34.5}$*
10	$Rb_6[(UO_2)_5O_2(PO_4)_4]$[25] + $Rb_6[(UO_2)_5O_5(PO_4)_2]$‡ + $Rb_9U_5P_6O_{34.5}$*	$Rb_9U_5P_6O_{34.5}$*	$Rb_9U_5P_6O_{34.5}$* $GaPO_4$ + Ga_2O_3
	$Rb_4U_5O_{17}$[28] + $Rb_9U_5P_6O_{34.5}$*	$Rb_{11}[(UO_2)_8(PO_4)_9]$‡	$Rb_{11}[(UO_2)_8(PO_4)_9]$‡ + $Rb_9U_5P_6O_{34.5}$*

Molar ratio of UF_4:$GaPO_4$

NOTE: The lack of more than one phase listed does not imply a phase pure product, but rather that only the major phase is reported. In many cases small impurities could not be identified

*Crystal quality poor with extensive disorder, a = 13.7939(7) Å, c = 9.5213(6) Å, α= β = ɣ = 90°, R_1 = 0.0886

‡Structures from this work, all other superscript numbers correspond to references in main text

[25,27]Analogous to other layered phosphuranylite structures in ref. 21, 22, expected corrugation based on $Rb_6[(UO_2)O_5(PO_4)_2]$, poor crystal quality, a = 6.9127(6) Å, b = 7.0226(7) Å, c = 16.9750(15) Å, α = 89.981(4), β = 89.989(4), ɣ = 89.595(4), R_1 = 0.01443

Table S3: Phase space summary of UF_4-$GaPO_4$-CsCl in 5mL Pt crucibles.

mmols of CsCl	1.5:1	1:1	1:2
			---875°C ---775°C
20	$Cs_6[(UO_2)_7O_4(PO_4)_4]$[30]	$[Cs_4Cs_4Cl][(UO_2)_4(PO_4)_5]$[14]	$Cs_4[(UO_2Ga_2(PO_4)_4]$‡
	$Cs_6[(UO_2)_7O_4(PO_4)_4]$[30]	$Cs_2(UO_2)_2(PO_4)_2$[29]	$Cs_4[(UO_2Ga_2(PO_4)_4]$‡
10	$Cs_6[(UO_2)_7O_4(PO_4)_4]$[30]	??	$Cs_4[(UO_2Ga_2(PO_4)_4]$‡ + $[Cs_4Cs_4Cl][(UO_2)_4(PO_4)_5]$[14]
	$Cs_6[(UO_2)_7O_4(PO_4)_4]$[30]	$Cs_2(UO_2)_2(PO_4)_2$[29]	$Cs_2(UO_2)_2(PO_4)_2$[29]

Molar ratio of UF_4:$GaPO_4$

NOTE: The lack of more than one phase listed does not imply a phase pure product, but rather that only the major phase is reported. In many cases small impurities could not be identified

‡Structures from this work, all other superscript numbers correspond to references in main text

?? Single crystals were not of sufficient quality to determine a reliable unit cell or unit cell contents

Table S4: BVS and bond distances for $Cs_2UO_2Ga_2O_5$ (**2**).

Interaction	Distance	Interaction	Distance
U1 – O1 x 2	1.849(4)	Ga2 – O2	1.849(4)
U1 – O2 x 4	2.401(4)	Ga2 – O3 x2	1.806(2)
U1 – O4	2.425(6)	Ga2 – O4	1.8229(13)
BVS U1	**5.926**	**BVS Ga2**	**3.132**

Table S5: BVS and bond distances for $[Rb_{5.93}Cl_{0.93}][(UO_2)_5(PO_4)_5]$(**3**).

Interaction	Distance	Interaction	Distance	Interaction	Distance
U1 – O9	2.428(9)	U2 – O12	2.241(12)	U3 – O1	2.443(15)
U1 – O10	2.492(9)	U2 – O15	2.257(12)	U3 – O4	2.672(13)
U1 – O10	2.384(9)	U2 – O18	2.263(11)	U3 – O5	2.294(11)
U1 – O14	2.248(10)	U2 – O19	2.210(11)	U3 – O20	2.270(10)
U1 – O16	2.244(10)	U2 – O23	1.803(11)	U3 – O25	1.781(11)
U1 – O21	1.774(10)	U2 – O24	1.778(12)	U3 – O30	1.782(11)
U1 – O22	1.786(10)	**BVS U2**	**6.07**	**BVS U3**	**6.07**
BVS U1	**6.18**	U5B – O2	2.255(16)	U5C – O2	2.671(18)
U5A – O2	2.440(14)	U5B – O2	3.03(3)	U5C – O2	3.17(3)
U5A – O2	2.641(18)	U5B – O4	3.00(4)	U5C – O4	2.800(19)
U5A – O4	2.425(14)	U5B – O6	2.489(13)	U5C – O6	2.096(17)
U5A – O6	2.296(12)	U5B – O8	1.784(14)	U5C – O8	1.835(17)
U5A – O8	2.308(13)	U5B – O28B	1.75(4)	U5C – O28B	1.96(4)
U5A – O28A	1.803(14)	U5B – O29	1.808(12)	U5B – O29	1.654(14)
U5A – O29	1.738(10)	**BVS U5B**	**6.49**	**BVS U5C**	**6.43**
BVS U5A	**5.95**	P1 – O1	1.530(16)	P2 – O5	1.511(11)
U4 – O3	2.297(11)	P1 – O2	1.436(13)	P2 – O6	1.521(13)
U4 – O7	2.245(12)	P1 – O3	1.486(11)	P2 – O7	1.486(14)
U4 – O11	2.257(10)	P1 – O4	1.600(14)	P2 – O8	1.529(14)
U4 – O13	2.291(10)	**BVS P1**	**5.37**	**BVS P2**	**5.26**
U4 – O26	1.809(11)	P4 – O10	1.547(11)	P5 – O17	1.527(11)
U4 – O27	1.690(12)	P4 – O14	1.508(10)	P5 – O18	1.505(11)
BVS U4	**6.071**	P4 – O15	1.515(12)	P5 – O19	1.522(11)
P3 – O9	1.532(8)	P4 – O16	1.515(10)	P5 – O20	1.527(10)
P3 – O10	1.547(10)	**BVS P4**	**5.19**	**BVS P5**	**5.20**
P3 – O11	1.504(11)				
P3 – O12	1.514(12)				
BVS P3	**5.15**				

Table S6: BVS and bond distances for $Rb_{11}[(UO_2)_8(PO_4)_9]$ (**4**).

Interaction	Distance	Interaction	Distance	Interaction	Distance
U1 – O1	1.810(10)	U2 – O6A	2.23(3)	U3 – O10B	2.483(12)
U1 – O2	1.787(10)	U2 – O6B	2.39(3)	U3 – O12A	2.34(3)
U1 – O3 x 2	2.270(8)	U2 – O7	1.766(10)	U3 – O12B	2.41(3)
U1 – O10A	2.413(13)	U2 – O8	1.822(14)	U3 – O13	1.778(10)
U1 – O11A	2.43(2)	U2 – O9A	2.22(2)	U3 – O14	1.780(10)
U1 – O11B	2.323(19)	U2 – O9B	2.532(18)	U3 – O15A	2.26(3)
BVS U1	**6.14**	U2 – O10B	2.490(11)	U3 – O15B	2.28(3)
U4 – O4A	2.506(19)	**BVS U2**	**6.06**	**BVS U4**	**6.20**
U4 – O4A	2.359(17)	P1(A) – O15A x 4	1.52(3)	P1(B) – O15B x 4	1.56(3)
U4 – O4B	2.25(2)	**BVS P1(A)**	**5.20**	**BVS P1(B)**	**4.67**
U4 – O5A	2.385(14)	P2A – O9A	1.49(2)	P2B – O9B	1.515(17)
U4 – O5B	2.246(14)	P2A – O10A	1.556(15)	P2B – O10B	1.579(13)
U4 – O16	1.804(12)	P2A – O11A	1.49(2)	P2B – O11B	1.47(2)
U4 – O17	1.807(15)	P2A – O12A	1.55(3)	P2B – O12B	1.50(3)
BVS U4	**6.07**	**BVS P2A**	**5.20**	**BVS P2B**	**5.29**
		P3A – O3	1.487(16)	P3B – O3	1.533(16)
		P3A – O4A	1.565(18)	P3B – O4B	1.505(19)
		P3A – O5A	1.536(18)	P3B – O5B	1.511(19)
		P3A – O6A	1.48(3)	P3B – O6B	1.55(3)
		BVS P3A	**5.36**	**BVS P3B**	**5.14**

Table S7: BVS and bond distances for $Rb_{7.6}[(UO_2)_8O_{8.6}F_{0.4}(PO_4)_2]$(**5**).

Interaction	Distance	Interaction	Distance	Interaction	Distance
U1 – O1	1.811(11)	U4A – O4/F4	2.177(10)	U4B – O4/F4	**2.464(10)**
U1 – O2	1.817(11)	U4A – O8	2.343(13)	U4B – O8	2.133(15)
U1 – O3	2.328(10)	U4A – O11	2.890(19)	U4B – O11	2.484(19)
U1 – O3	2.293(10)	U4A – O14	2.297(11)	U4B – O14	2.547(11)
U1 – O4/F4	2.354(10)	U4A – O15	1.796(13)	U4B – O15	1.820(13)
U1 – O12	2.342(10)	U4A – O16	1.837(13)	U4B – O16	**1.818(13)**
U1 – O17	2.343(12)	U4A – O17	2.246(12)	U4B – O17	2.061(12)
BVS U1	**6.07**	**BVS U4A**	6.01	**BVS U4B**	**6.20**
U2 – O7	2.612(14)	U3 – O3	2.294(10)	P1 – O7	1.572(14)
U2 – O8	2.228(11)	U3 – O4/F4	2.221(9)	P1 – O12	**1.543(11)**
U2 – O9	1.824(12)	U3 – O5	1.800(11)	P1 – O13	1.497(17)
U2 – O10	1.833(11)	U3 – O6	1.799(11)	P1 – O14	1.567(10)
U2 – O11	2.31(2)/2.13(2)	U3 – O7	2.481(13)	**BVS P1**	4.87
U2 – O12	2.435(11)	U3 – O8	2.381(13)		
U2 – O17	2.207(11)	U3 – O14	2.547(11)		
BVS U2	**6.07**	**BVS U3**	5.94		

Table S8: BVS and bond distances for $Rb_6[(UO_2)_5O_2(PO_4)_4$ (**5**).

Interaction	Distance	Interaction	Distance	Interaction	Distance
U1 – O1	2.308(3)	U2 – O2	2.326(3)	U3 – O7 x 2	2.414(3)
U1 – O3	2.398(3)	U2 – O2	2.517(3)	U3 – O11 x 2	1.813(4)
U1 – O5	2.292(3)	U2 – O3	2.423(3)	U3 – O12 x 2	2.199(3)
U1 – O6	2.451(3)	U2 – O6	2.277(3)	**BVS U3**	**5.661**
U1 – O12	2.318(3)	U2 – O9	1.802(3)	P1 – O1	1.526(3)
U1 – O13	1.795(3)	U2 – O10	1.804(4)	P1 – O2	1.576(3)
U1 – O14	1.812(3)	U2 – O12	2.248(3)	P1 – O3	1.565(3)
BVS U1	**6.033**	**BVS U2**	**6.041**	P1 – O4	1.488(4)
				BVS P1	**4.964**