Electronic Supplementary Material (ESI) for Chemical Communications.

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

Kristen A. Pace,[ab] Vladislav V. Klepov,[a] Gregory Morrison,[ab] and Hans-Conrad zur Loye*[ab]
[a] *Department of Chemistry and Biochemistry, University of South Carolina, Columbia, South Carolina 29208, United States*
[b] *Center for Hierarchical Wasteform Materials, University of South Carolina, Columbia, South Carolina 29208, United States*
Email: zurloye@mailbox.sc.edu

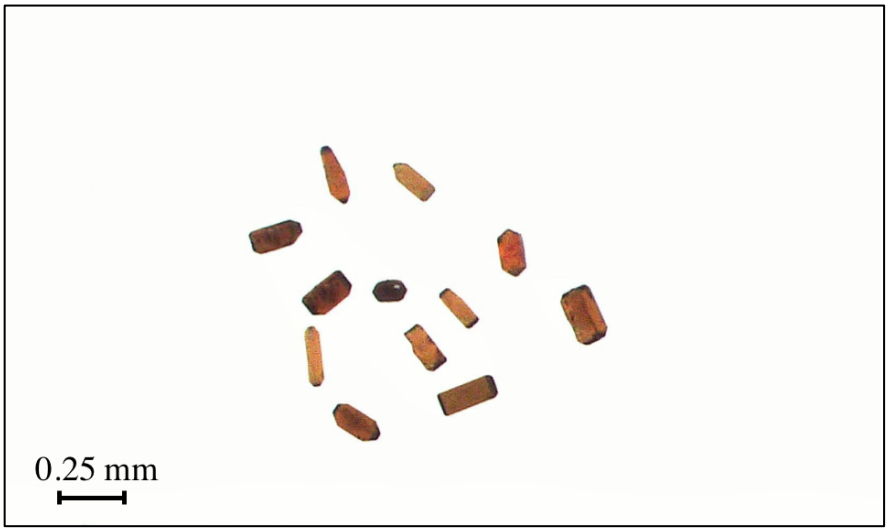

Figure S1 An image of amber tablet crystals of $Rb_2Na[(UO_2)_2(Si_2O_7)]$.

Table S1 Crystallographic data and refinement information

Formula	$Cs_2Na(UO)_2Si_4O_{12}$	$Rb_2Na(UO)_2Si_4O_{12}$	$K_2Na[(UO)_2(Si_2O_6)_2]$	$Cs_2Na[(UO_2)_2(Si_2O_7)]$	$Rb_2Na[(UO_2)_2(Si_2O_7)]$
Formula Weight (g mol^{-1} F. U.)	1101.23	1006.35	913.61	997.05	902.17
Temperature (K)	300(2)	300(2)	300(2)	300(2)	300(2)
Wavelength (Å)	0.71073	0.71073	0.71073	0.71073	0.71073
Crystal System	Orthorhombic	Orthorhombic	Orthorhombic	Orthorhombic	Orthorhombic
Space Group	*Cmmm*	*Cmmm*	*Imma*	*Pccn*	*Pccn*
Unit cell parameters:					
a (Å)	8.3837(3)	8.3008(2)	8.3067(2)	13.8327(3)	13.6169(4)
b (Å)	11.4748(4)	11.3013(3)	11.1188(3)	7.4187(2)	7.3529(2)
c (Å)	7.4900(3)	7.4374(2)	14.7604(4)	11.5783(3)	11.4921(4)
Volume ($Å^3$)	720.55(5)	697.70(3)	1363.28(6)	1188.17(5)	1150.63(3)
Z	2	2	4	4	4
Density (mg m^{-3})	5.076	4.790	4.451	5.574	5.208
Absorption coefficient (mm^{-1})	27.860	30.561	24.796	33.548	36.812
F(000)	946	874	1604	1684	1540
Crystal size (mm)	0.054 x 0.051 x 0.011	0.054 x 0.051 x 0.011	0.050 x 0.030 x 0.015	0.055 x 0.050 x 0.029	0.143 x 0.108 x 0.020
Theta range for data collection	2.719-32.499	2.739-29.991	3.665-33.123	3.579-33.138	3.546-33.128
Reflections	30 032	25 466	60 434	23 469	90 680
Independent reflections	769 (R_{int} = 0.0321)	604 (R_{int} = 0.0294)	1382 (R_{int} = 0.0286)	2146 (R_{int} = 0.0339)	2156 (R_{int} = 0.0572)
Completeness	100% to theta = 25.242°	100% to theta = 25.242°	100% to theta = 26.000°	100% to theta = 25.242°	100% to theta = 25.242°
Data/restraints/parameters	770/0/49	607/0/49	1436/0/66	2247/0/86	2193/0/86
Goodness of fit on F^2	1.207	1.196	1.144	1.180	1.232
Final *R* indices	R_1 = 0.0110 wR_2 = 0.0284	R_1 = 0.0243 wR_2 = 0.0701	R_1 = 0.0111 wR_2 = 0.0350	R_1 = 0.0155 wR_2 = 0.0351	R_1 = 0.0256 wR_2 = 0.0636
R indices (all data)	R_1 = 0.0110 wR_2 = 0.0284	R_1 = 0.0243 wR_2 = 0.0701	R_1 = 0.0117 wR_2 = 0.0354	R_1 = 0.0166 wR_2 = 0.0355	R_1 = 0.0261 wR_2 = 0.0639
Extinction coefficient	-	-	0.00039(3)	0.00156(8)	0.00165(12)
Largest diff. peak and hole (e^- $Å^{-3}$)	1.734 and -1.905	3.582 and -3.292	1.628 and -0.965	1.424 and -1.400	2.539 and -2.803

Table S2. Bond Lengths and U B.V.S.	Representative Interatomic Distances(Å)		B.V.S. (v.u.)	Ref.
(**1**) $Cs_2Na(UO)_2Si_4O_{12}$	U(1)-O(1) x 2 U(1)-O(2) x 2 U(1)-O(4) x 2	2.229(3) 2.239(3) 2.1280(10)	U(1) = 4.54	present work
(**2**) $Rb_2Na(UO)_2Si_4O_{12}$	U(1)-O(1) x 2 U(1)-O(2) x 2 U(1)-O(0AA) x 2	2.234(7) 2.227(6) 2.114(3)	U(1) = 4.60	present work
(**3**) $K_2Na[(UO)_2(Si_2O_6)_2]$	U(1)-O(00A) U(1)-O(007) U(1)-O(008) x 2 U(1)-O(009) x 2	2.1265(5) 2.0641(6) 2.2403(15) 2.2351(17)	U(1) = 4.63	present work
(**4**) $Cs_2Na[(UO_2)_2(Si_2O_7)]$	U(1)-O(3) x 2 U(1)-O(6) x 2 U(1)-O(7) x 2 U(2)-O(2) x 2 U(2)-O(3) x 2 U(2)-O(4) x 2	2.039(2) 2.194(3) 2.207(3) 2.214(2) 2.251(2) 1.838(2)	U(1) = 5.05 U(2) = 5.84	present work
(**5**) $Rb_2Na[(UO_2)_2(Si_2O_7)]$	U(1)-O(1) x 2 U(1)-O(2) x 2 U(1)-O(5) x 2 U(2)-O(1) x 2 U(2)-O(4) x 2 U(2)-O(6) x 2	2.039(4) 2.201(5) 2.178(5) 2.236(3) 1.838(4) 2.222(4)	U(1) = 5.11 U(2) = 5.85	present work
$CaU(UO_2)_2(CO_3)O_4(OH)(H_2O)_7$	U(3)-O(3) U(3)-O(4) U(3)-O(7) U(3)-O(8) U(3)-O(9) U(3)-O(11) U(3)-O(14)	2.141 2.082 2.076 2.063 2.432 2.479 2.475	U(3) = 5.07	4
$[U(H_2O)_2(UO_2)2O_4(OH)](H_2O)_4$	U(1)-O(1) U(1)-O(2) U(1)-O(3) x 4 U(2)-O(3) x 2 U(2)-O(3) x 2 U(2)-O(4) U(2)-O(5) U(2)-O(6)	2.41(3) 2.44(2) 2.059(7) 2.364(7) 2.393(7) 1.784(13) 1.788(11) 2.312(6)	U(1) = 4.91 U(2) = 6.07	7
$K_{13}[(UO_2)_{19}(UO_4)(B_2O_5)_2(BO_3)_6(OH)_2O_5]\cdot H_2O$	U(11)-O(10) x 2 U(11)-O(17) x 2 U(11)-O(32) x 2	2.13(1) 1.99(1) 2.33(3)	U(11) = 5.30	18
$Cs_2K(UO)_2Si_4O_{12}$	U(1)-O(2) x 4 U(1)-O(4) x 2	2.234(3) 2.12320(17)	U(1) = 4.56	13
$Cs_4(UO)(UO)_2(Si_2O_7)_2$	U(1)-O(1) x 4 U(1)-O(5) x 2 U(2)-O(2) x 2 U(2)-O(3) x 2 U(2)-O(5) U(2)-O(6)	2.196(4) 2.058(6) 2.246(4) 2.217(4) 2.179(6) 2.1301(6)	U(1) = 5.00 U(2) = 4.47 	15

*Bond valence sums for compositions presented in this work were calculated using the parameters r_o = 2.051 and B = 0.519.

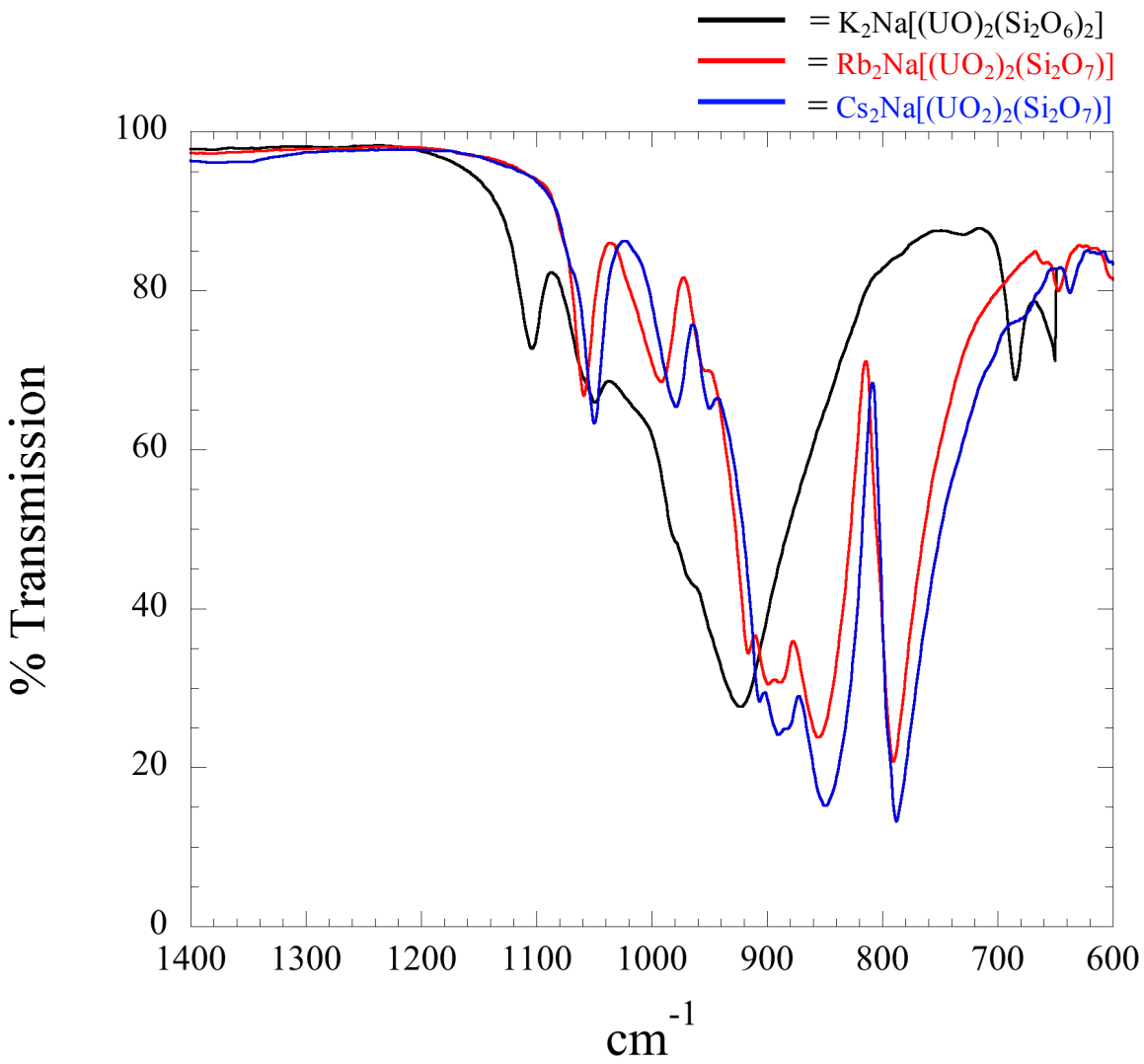

Figure S2 The IR spectra of $K_2Na[(U^{IV,V}O)_2(Si_2O_6)_2]$ (**3**), $Cs_2Na[(U^{V,VI}O_2)_2(Si_2O_7)]$ (**4**), and $Rb_2Na[(U^{V,VI}O_2)_2(Si_2O_7)]$ (**5**).

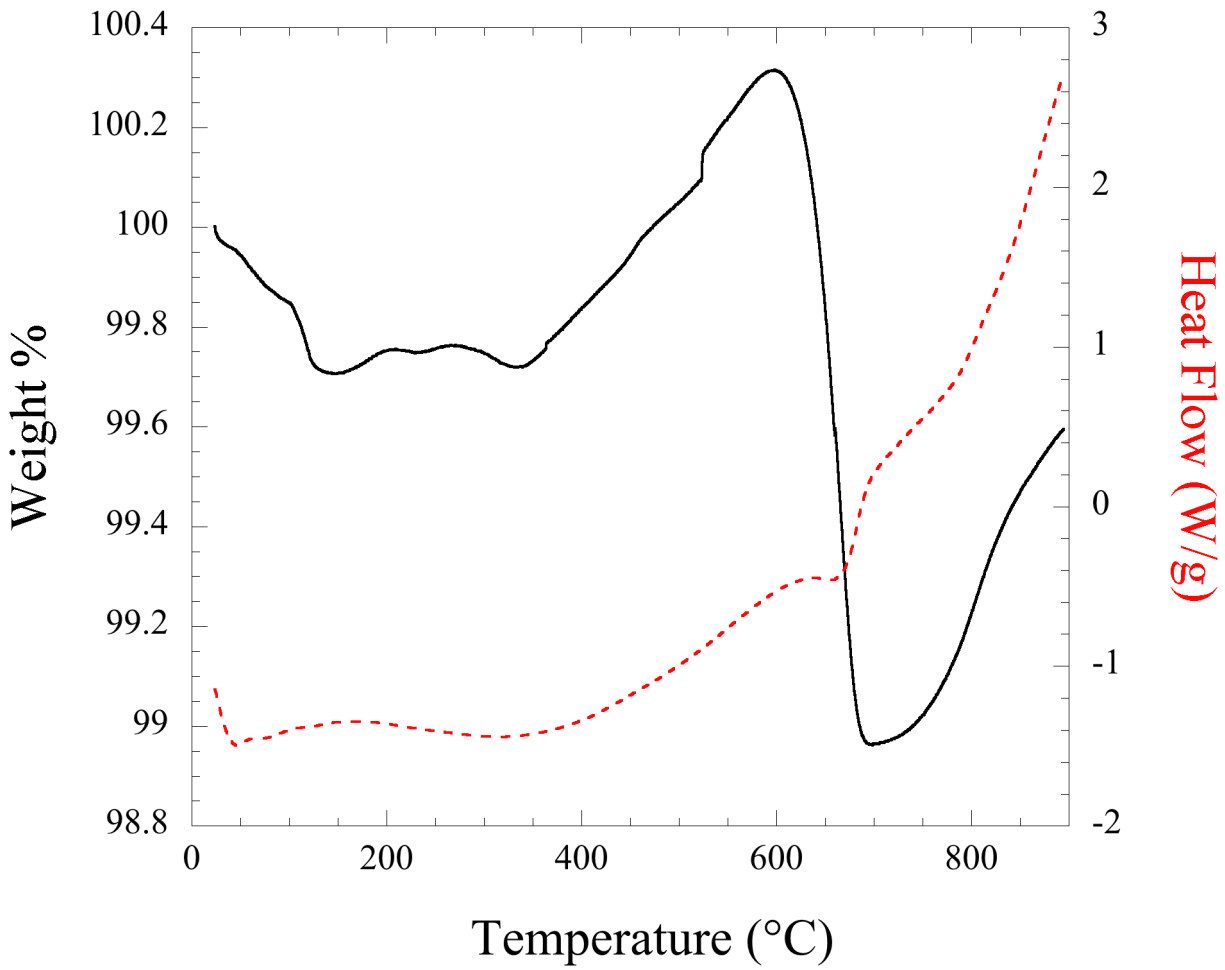

Figure S3 TGA-DTA thermogram of $K_2Na[(U^{IV,V}O)_2(Si_2O_6)_2]$ (**3**), heated in air from room temperature to 900°C at 10°C per minute.

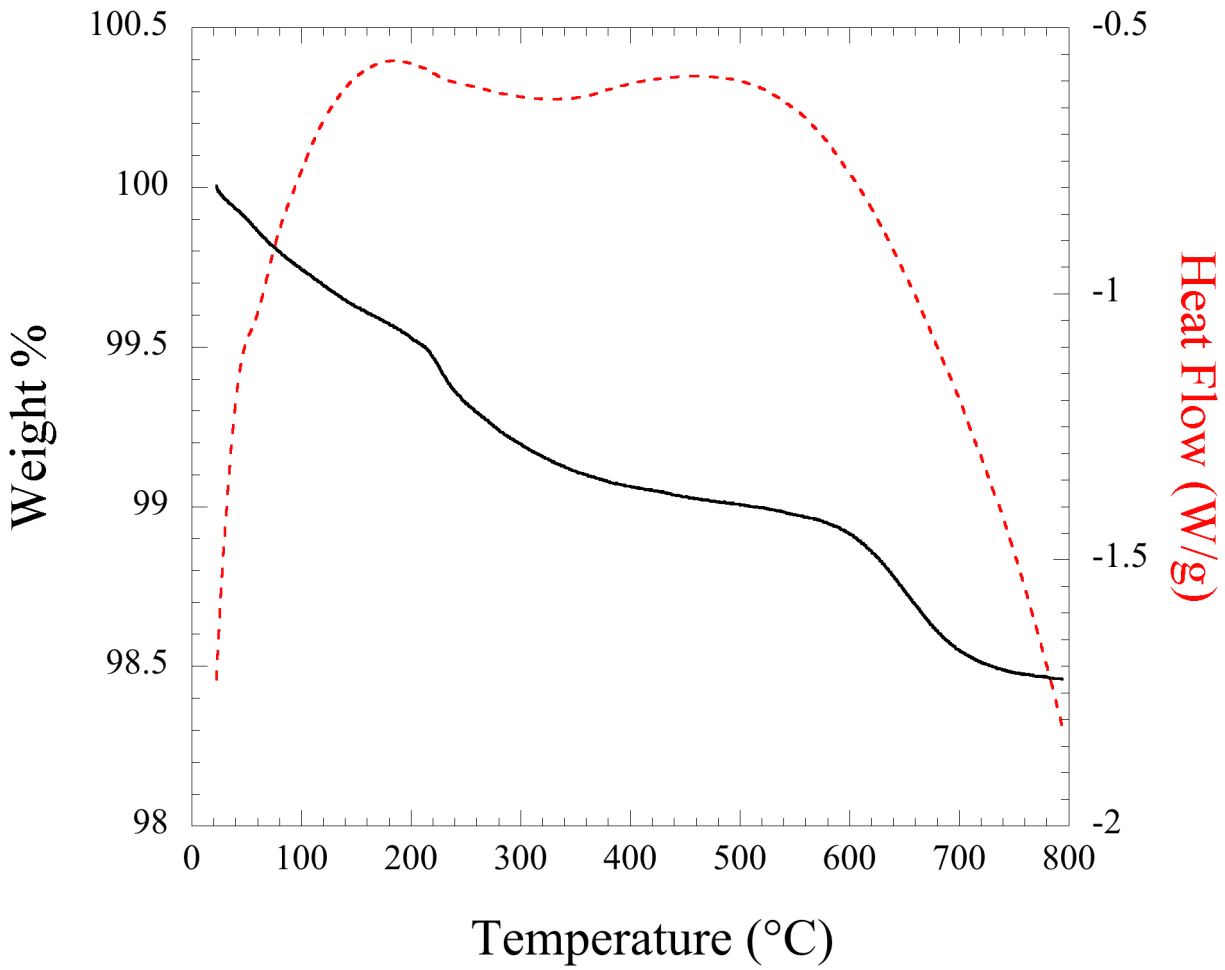

Figure S4 TGA-DTA thermogram of $Cs_2Na[(U^{V,VI}O_2)_2(Si_2O_7)]$ (**4**), heated in air from room temperature to 800°C at 10°C per minute.

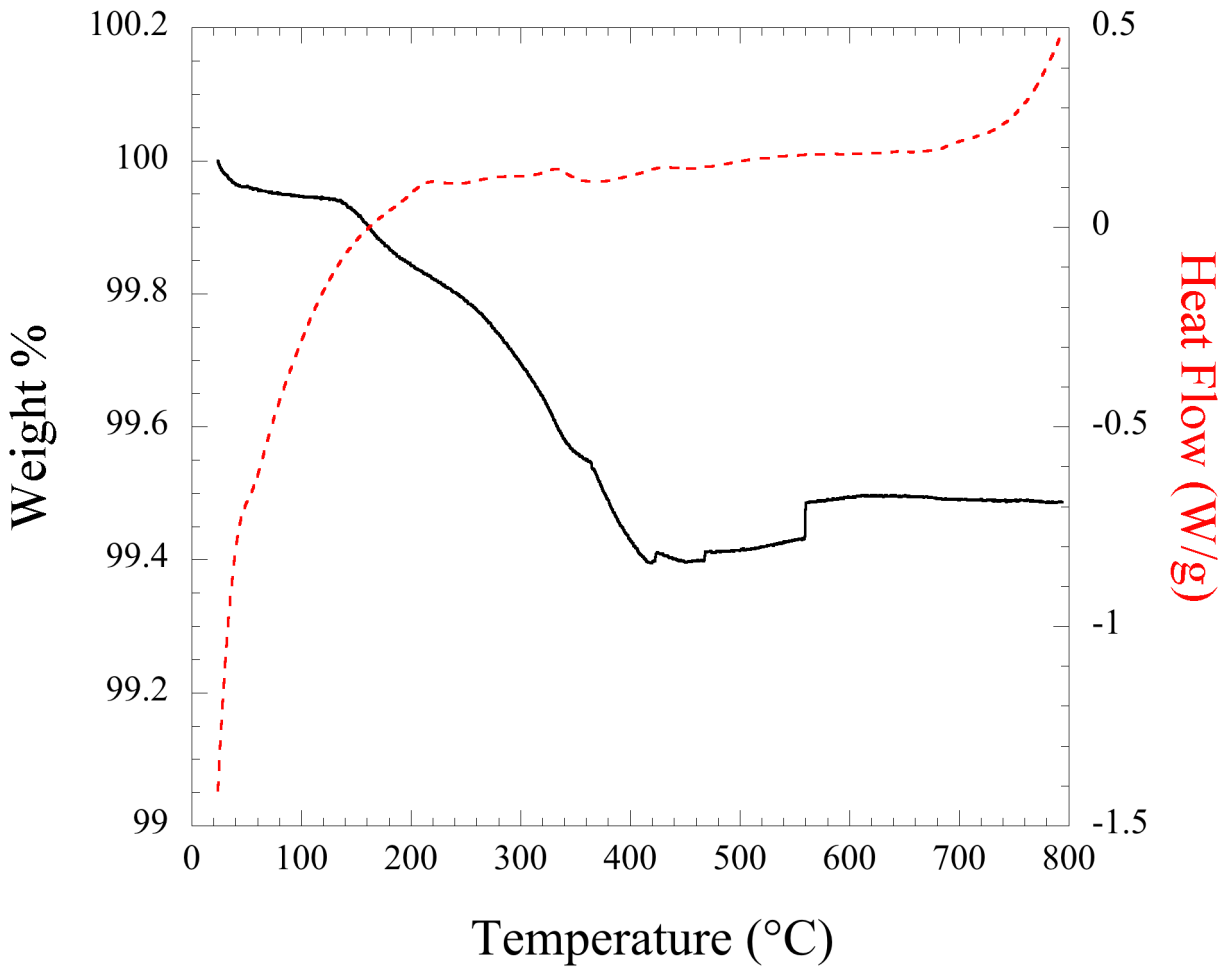

Figure S5 TGA-DTA thermogram of $Rb_2Na[(U^{V,VI}O_2)_2(Si_2O_7)]$ (**5**), heated in air from room temperature to 800°C at 10°C per minute.

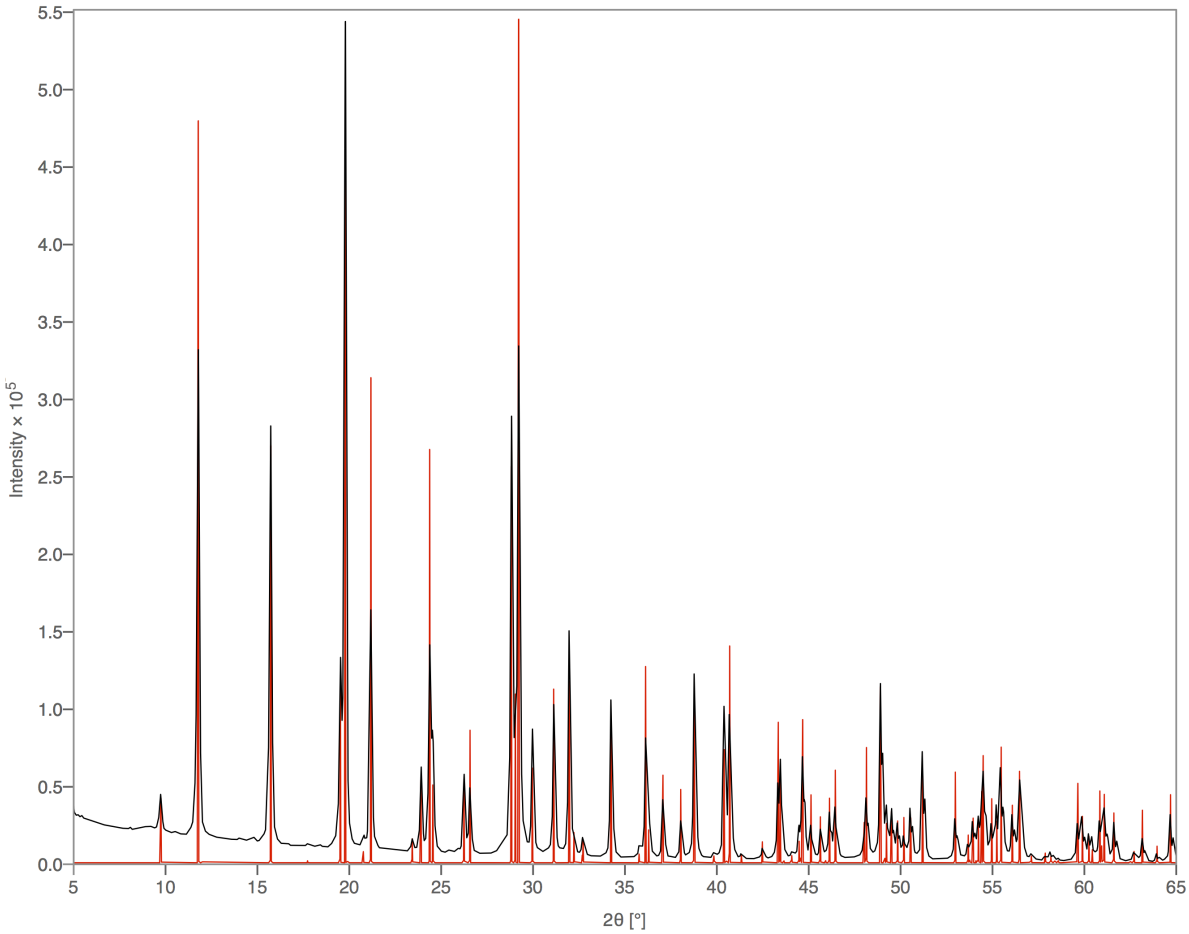

Figure S6 PXRD pattern of $K_2Na[(UO)_2(Si_2O_6)_2]$ (**3**) in black, compared to the calculated pattern derived from the .cif in red.

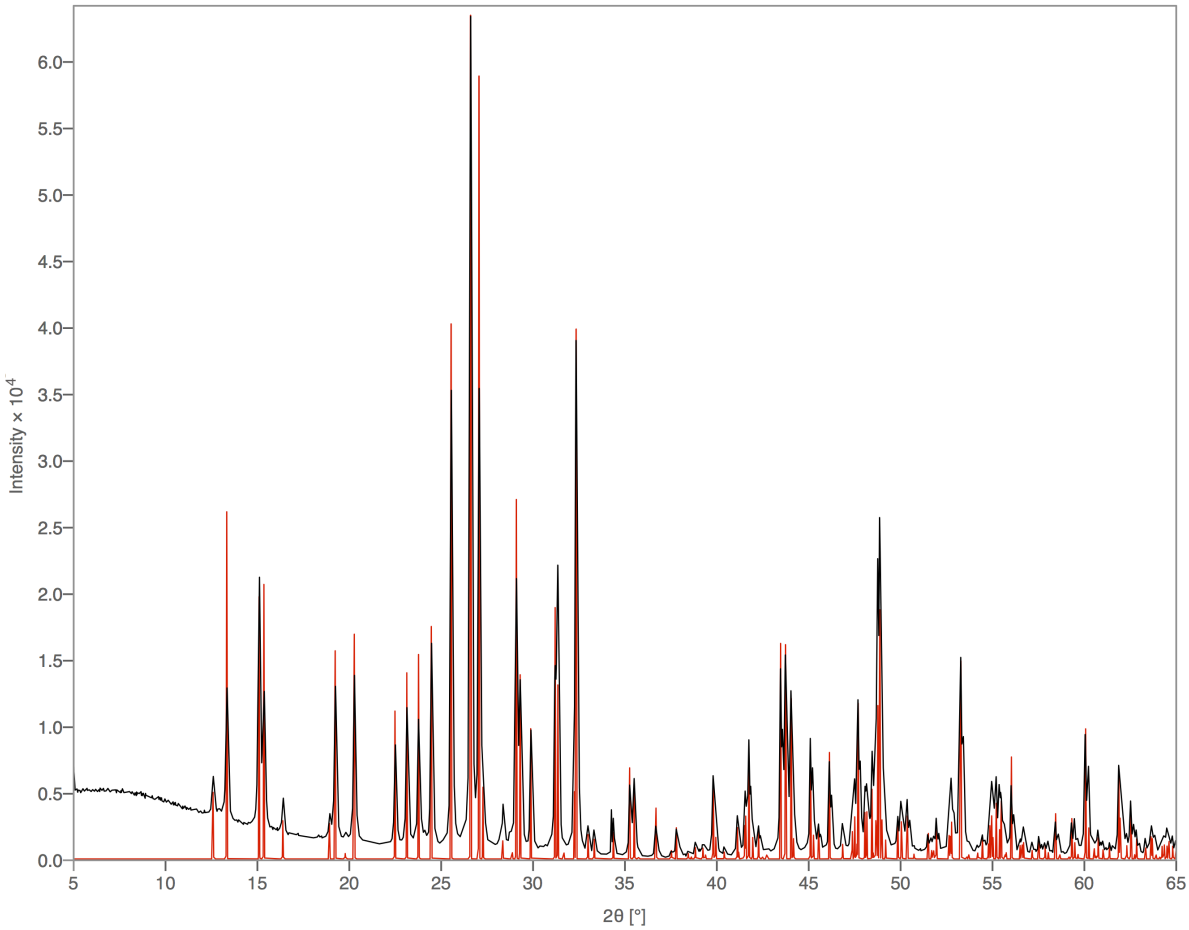

Figure S7 PXRD pattern of $Cs_2Na[(UO_2)_2(Si_2O_7)]$ (**4**) in black, compared to the calculated pattern derived from the .cif in red.

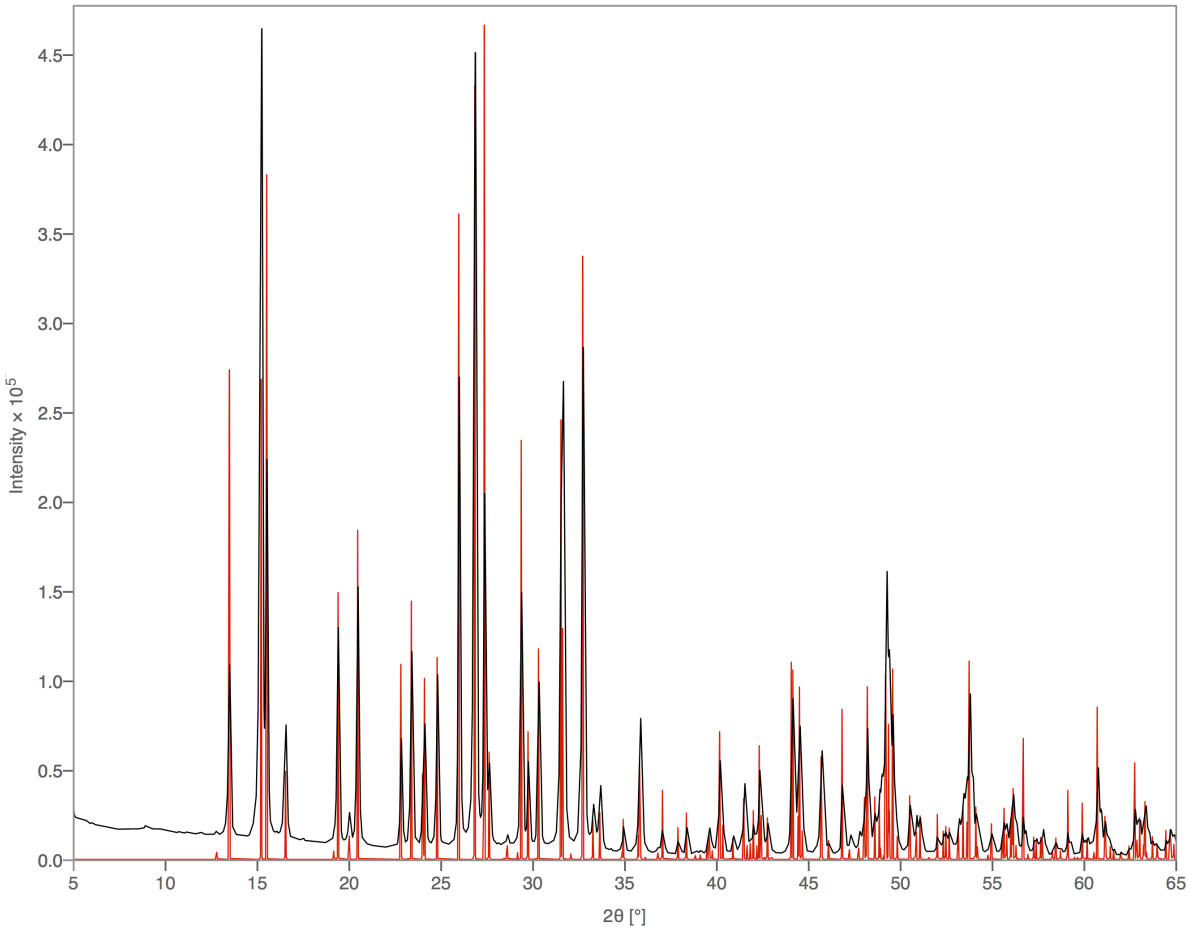

Figure S8 PXRD pattern of $Rb_2Na[(UO_2)_2(Si_2O_7)]$ (**5**) in black, compared to the calculated pattern derived from the .cif in red.