Electronic Supplemental Information for

Structural Changes in the Alkaline Earth Uranyl Phosphites

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Section 1.1: $[(Ca^{2+})_{1.81}(UO_2^{2+})_{0.19}][(UO_2)_2(HPO_3)_4]\cdot 5H_2O$.

Table 1.1.1: Selected bond distances for $[(Ca^{2+})_{1.81}(UO_2^{2+})_{0.19}][(UO_2)_2(HPO_3)_4]\cdot 5H_2O$.

Bond Distances (Å) for $[(Ca^{2+})_{1.81}(UO_2^{2+})_{0.19}][(UO_2)_2(HPO_3)_4]\cdot 5H_2O$			
U(1)-O(2)	1.759(9)	P(2)-O(7)#4	1.520(10)
U(1)-O(1)	1.774(9)	P(2)-O(8)#5	1.528(14)
U(1)-O(4)	2.304(9)	P(2)-O(3)	1.532(9)
U(1)-O(3)	2.338(8)	Ca(1)-O(8)	2.270(14)
U(1)-O(7)	2.365(8)	Ca(1)-O(3W)	2.298(12)
U(1)-O(6)#1	2.474(9)	Ca(1)-O(6)#3	2.333(8)
U(1)-O(5)	2.487(10)	Ca(1)-O(5)	2.338(9)
P(1)-O(6)	1.520(9)	Ca(1)-O(2W)	2.367(13)
P(1)-O(5)#5	1.523(9)	Ca(1)-O(7)#4	2.468(11)
P(1)-O(4)	1.537(10)	Ca(1)-O(3)	2.491(10)

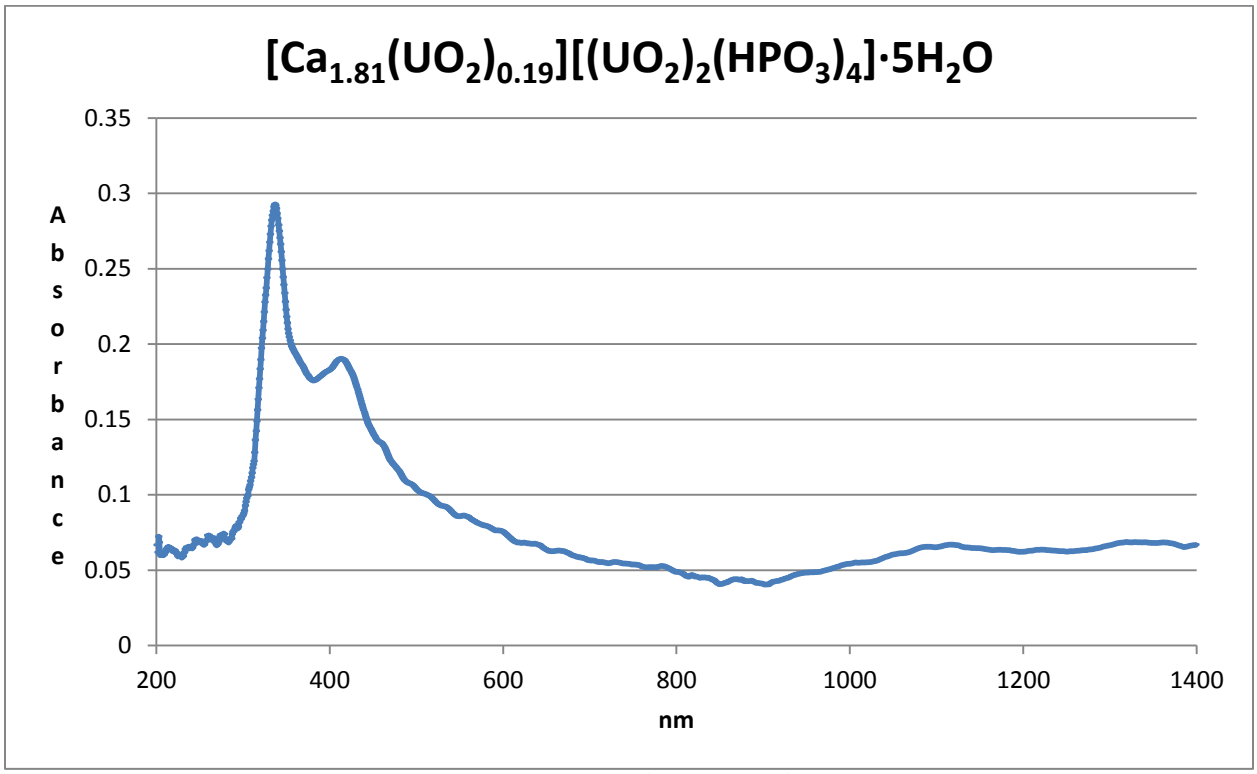


Figure 1.1.1: UV-vis-NIR absorbance for $[(Ca^{2+})_{1.81}(UO_2{}^{2+})_{0.19}][(UO_2)_2(HPO_3)_4]\cdot 5H_2O$. The characteristic U^{6+} transitions are seen between 370-500 nm.[1]

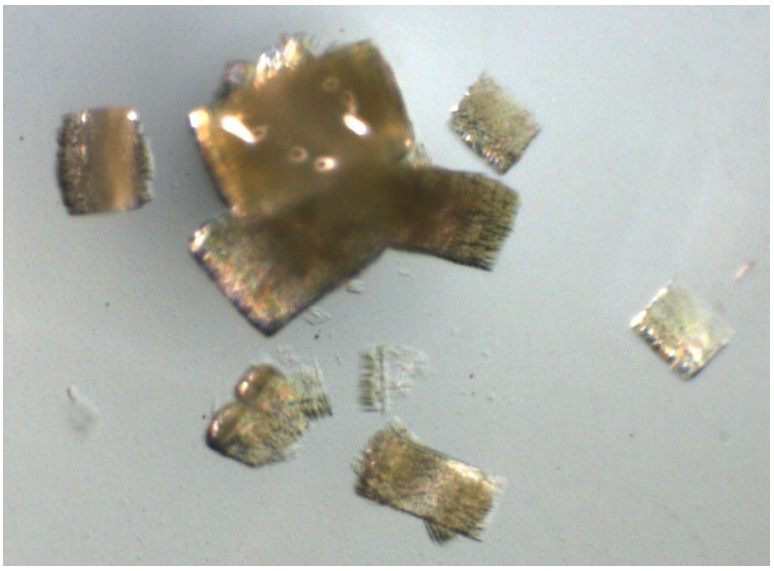


Figure 1.1.2: Picture of the crystals of $[(Ca^{2+})_{1.81}(UO_2{}^{2+})_{0.19}][(UO_2)_2(HPO_3)_4]\cdot 5H_2O$.

Table 1.1.2: Bond Valence Sum (BVS) calculations for $[(Ca^{2+})_{1.81}(UO_2^{2+})_{0.19}][(UO_2)_2(HPO_3)_4]\cdot 5H_2O$.[2]

O1,O2 are terminal uranyl oxo groups
vu = exp[(R0 – d)/b]. O8 is a terminal P-O unit

Phosphite			distance	vu
R(0) : P-O	1.626	O(1)		
b	0.37	O(2)		
		P(2)-O(3)	1.532	1.289
		P(1)-O(4)	1.537	1.272
		P(1)-O(5)	1.523	1.321
		P(1)-O(6)	1.52	1.332
		P(2)-O(7)	1.52	1.332
		P(2)-O(8)	1.528	1.303

U(VI)			distance	vu
R(0) : U-O	2.051	U(1)-O(1)	1.774	1.705
b	0.519	U(1)-O(2)	1.759	1.755
		U(1)-O(3)	2.338	0.575
		U(1)-O(4)	2.304	0.614
		U(1)-O(5)	2.487	0.432
		U(1)-O(6)	2.474	0.443
		U(1)-O(7)	2.365	0.546
		O(8)		

			distance	vu	Total
R(0) : Ca-O	1.967	O(1)			**1.705**
b	0.37	O(2)			**1.755**
		Ca(1)-O(3)	2.491	0.243	**2.107**
		O(4)			**1.886**
		Ca(1)-O(5)	2.338	0.367	**2.120**
		Ca(1)-O(6)	2.333	0.372	**2.146**
		Ca(1)-O(7)	2.468	0.258	**2.136**
		Ca(1)-O(8)	2.27	0.441	**1.744**
		Ca(1)-O2W	2.367	0.339	**0.339**
		Ca(1)-O3W	2.298	0.409	**0.409**

P1-O4,O5,O6
P2-O3,O7,O8

H(P1)= -0.152
H(P2)= 0.013

Zero Protons

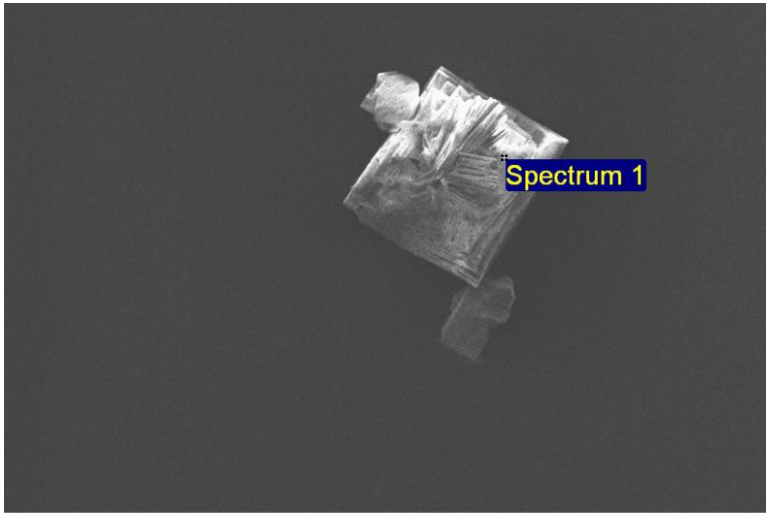
U(VI)			distance	vu
R(0) : U-O	2.051	U(1)-O(1)	1.774	1.705
b	0.519	U(1)-O(2)	1.759	1.755
		U(1)-O(3)	2.338	0.575
		U(1)-O(4)	2.304	0.614
		U(1)-O(5)	2.487	0.432
		U(1)-O(6)	2.474	0.443
		U(1)-O(7)	2.365	0.546
		U(1) BVS		6.070

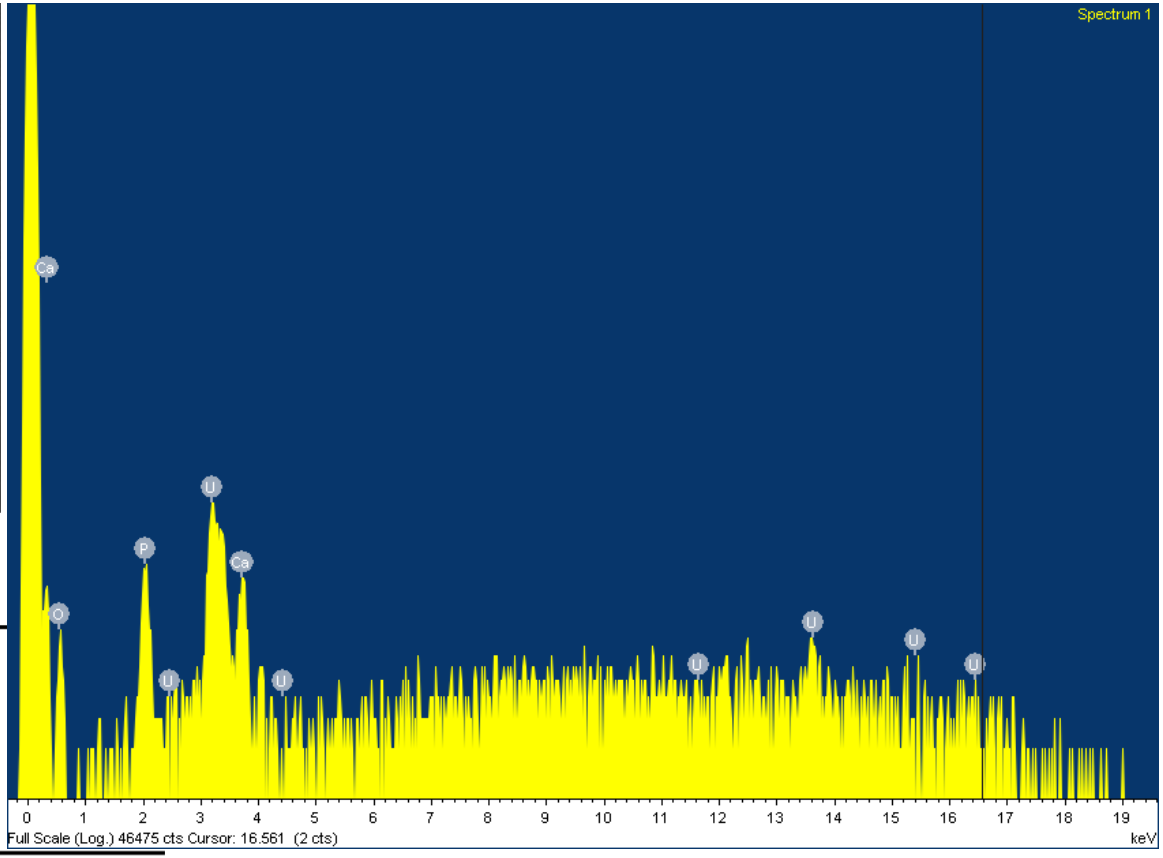
BVS for Phosphites
HP(3+)-O(2-)
Should Equal 4+ for PO3

P(1)BVS	3.925
P(2)BVS	3.924

Ca(1) BVS	2.428

Figure 1.1.3: EDS/SEM image and elemental analysis by weight % for $[(Ca^{2+})_{1.81}(UO_2^{2+})_{0.19}][(UO_2)_2(HPO_3)_4]\cdot 5H_2O$.





Processing option : All elements analysed (Normalised)

Spectrum	In stats.	O	P	Ca	U	Total
Spectrum 1	Yes	14.66	8.47	10.37	66.50	100.00
Mean		14.66	8.47	10.37	66.50	100.00
Std. deviation		0.00	0.00	0.00	0.00	
Max.		14.66	8.47	10.37	66.50	
Min.		14.66	8.47	10.37	66.50	

All results in weight%

Section 1.2: $Sr[(UO_2)(HPO_3)_2]\cdot 2H_2O$.

Table 1.2.1: Selected bond distances for $Sr[(UO_2)(HPO_3)_2]\cdot 2H_2O$.

Bond Distances (Å) for $Sr[(UO_2)(HPO_3)_2]\cdot 2H_2O$			
U(1)-O(7)	1.789(7)	P(2)-O(3)	1.492(6)
U(1)-O(6)	1.800(6)	P(2)-O(8)#2	1.531(6)
U(1)-O(4)	2.295(5)	P(2)-O(4)	1.538(6)
U(1)-O(8)	2.300(6)	Sr(1)-O(1)#3	2.482(6)
U(1)-O(2)#1	2.341(6)	Sr(1)-O(5)#2	2.517(6)
U(1)-O(5)	2.413(5)	Sr(1)-O(3)#4	2.557(6)
U(1)-O(2)	2.535(6)	Sr(1)-O(3)	2.559(6)
P(1)-O(1)	1.488(7)	Sr(1)-O(1W)#4	2.604(7)
P(1)-O(5)	1.522(6)	Sr(1)-O(2W)	2.625(6)
P(1)-O(2)	1.569(6)	Sr(1)-O(6)#5	2.684(6)
		Sr(1)-O(8)#2	2.891(6)

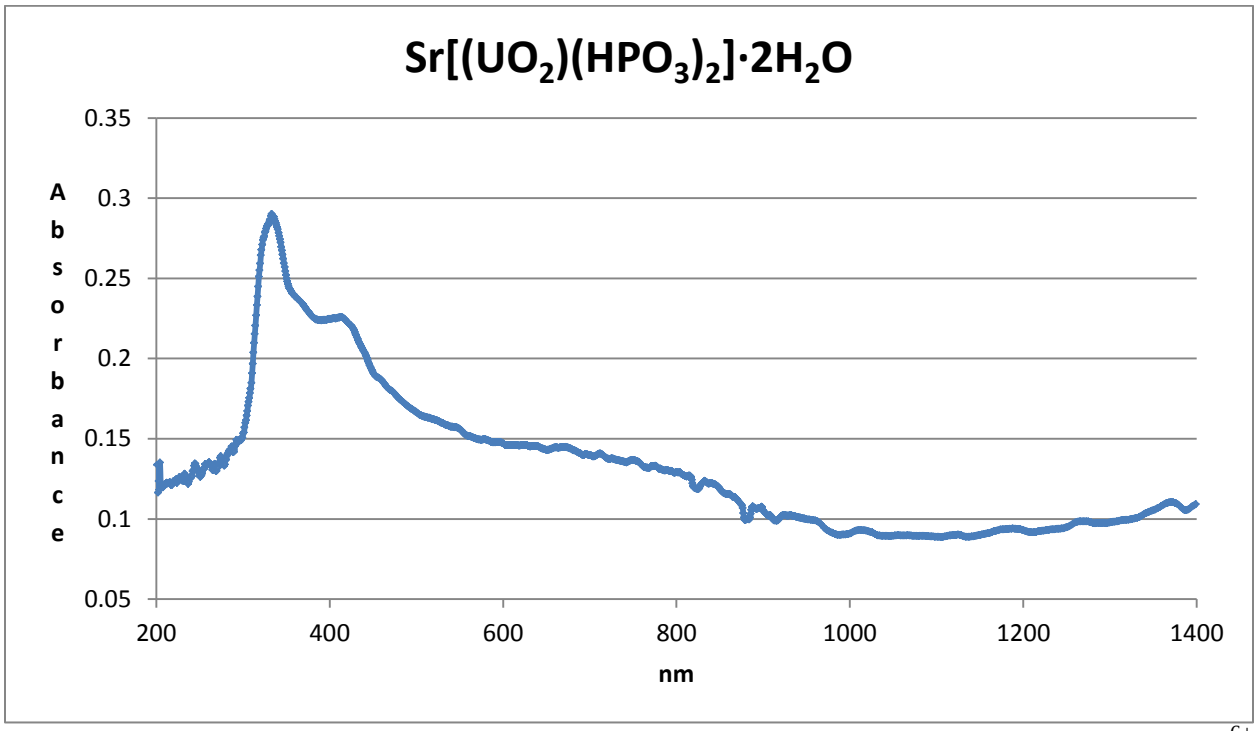


Figure 1.2.1: UV-vis-NIR absorbance for $Sr[(UO_2)(HPO_3)_2]\cdot 2H_2O$. The characteristic U^{6+} transitions are seen between 370-500 nm.[1]

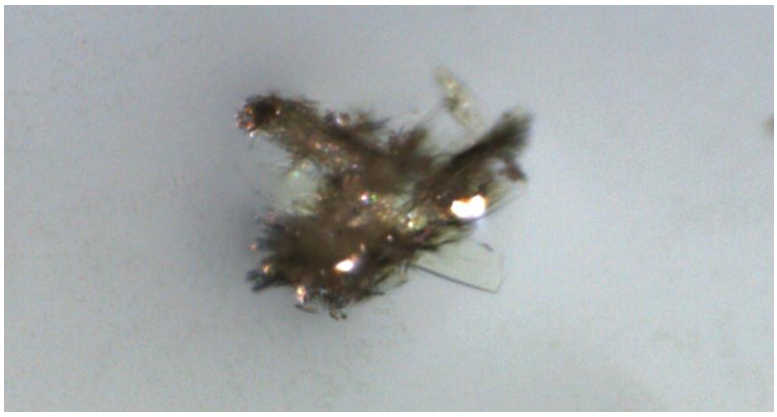


Figure 1.2.2: Picture of the crystals of $Sr[(UO_2)(HPO_3)_2]\cdot 2H_2O$.

Table 1.2.2: Bond Valence Sum (BVS) calculations for $Sr[(UO_2)(HPO_3)_2]\cdot 2H_2O$.[2]

O6,O7 are terminal uranyl oxo groups
vu = exp[(R0 – d)/b]. O1,O3 are terminal P-O units

Phosphite			distance	vu	U(VI)			distance	vu		distance	vu
R(0) : P-O	1.626	P(1)-O(1)	1.488	1.452	R(0) : U-O	2.051	O(1)					
b	0.37	P(1)-O(2)	1.569	1.167	b	0.519	U(1)-O(2)	2.535	0.394	O(2)-U(1)	2.341	0.572
		P(2)-O(3)	1.492	1.436			O(3)					
		P(2)-O(4)	1.538	1.269			U(1)-O(4)	2.295	0.625			
		P(1)-O(5)	1.522	1.325			U(1)-O(5)	2.413	0.498			
		O(6)					U(1)-O(6)	1.8	1.622			
		O(7)					U(1)-O(7)	1.789	1.657			
		P(2)-O(8)	1.531	1.293			U(1)-O(8)	2.3	0.619			

			distance	vu		distance	vu	**Total**
R(0) : Sr-O	2.118	Sr(1)-O(1)	2.482	0.374				**1.826**
b	0.37	O(2)						**2.132**
		Sr(1)-O(3)	2.557	0.305	Sr(1)-O(3)	2.559	0.304	**2.045**
		O(4)						**1.893**
		Sr(1)-O(5)	2.517	0.340				**2.163**
		Sr(1)-O(6)	2.684	0.217				**1.839**
		O(7)						**1.657**
		Sr(1)-O(8)	2.891	0.124				**2.035**
		Sr(1)-O1W	2.604	0.269				**0.269**
		Sr(1)-O2W	2.625	0.254				**0.254**

	P1-O1,O2,O5
	P2-O3,O4,O8
H(P1)=	-0.120
H(P2)=	0.026
	Zero Protons

R(0) : U-O	2.051	U(1)-O(2)	2.535	0.394
b	0.519	O(2)-U(1)	2.341	0.572
		U(1)-O(4)	2.295	0.625
		U(1)-O(5)	2.413	0.498
		U(1)-O(6)	1.8	1.622
		U(1)-O(7)	1.789	1.657
		U(1)-O(8)	2.3	0.619
		U(1) BVS		5.986

BVS for Phosphites
HP(3+)-O(2-)
Should Equal 4+ for PO3

P(1)BVS	3.943
P(2)BVS	3.998

Sr(1) BVS	2.186

Section 1.3: $Ba_2[(UO_2)_2(HPO_3)_4]\cdot 5H_2O$.

Table 1.3.1: Selected bond distances for $Ba_2[(UO_2)_2(HPO_3)_4]\cdot 5H_2O$.

U(1)-O(12)	1.775(6)	P(4)-O(4)	1.511(5)
U(1)-O(7)	1.788(5)	P(4)-O(9)#8	1.534(6)
U(1)-O(16)#1	2.296(6)	P(4)-O(8)#9	1.547(5)
U(1)-O(8)	2.318(5)	Ba(1)-O(14)#2	2.723(5)
U(1)-O(13)#2	2.341(5)	Ba(1)-O(10)#5	2.726(4)
U(1)-O(2)#2	2.494(6)	Ba(1)-O(2W)	2.760(7)
U(1)-O(14)#2	2.515(5)	Ba(1)-O(5)	2.832(5)
U(2)-O(11)	1.765(6)	Ba(1)-O(1)#4	2.846(6)
U(2)-O(3)	1.791(5)	Ba(1)-O(4)#4	2.860(5)
U(2)-O(15)#4	2.275(7)	Ba(1)-O(1W)	2.935(6)
U(2)-O(9)	2.316(5)	Ba(1)-O(8)	3.076(5)
U(2)-O(5)	2.339(5)	Ba(1)-O(15)#4	3.122(7)
U(2)-O(2)	2.514(6)	Ba(1)-O(10)	3.217(6)
U(2)-O(6)	2.529(5)	Ba(2)-O(1)	2.728(5)
P(1)-O(1)	1.508(5)	Ba(2)-O(6)	2.777(6)
P(1)-O(16)	1.526(6)	Ba(2)-O(13)#6	2.805(5)
P(1)-O(15)	1.546(7)	Ba(2)-O(4W)	2.827(8)
P(2)-O(10)	1.515(5)	Ba(2)-O(1W)#7	2.914(6)
P(2)-O(5)	1.534(6)	Ba(2)-O(1)#8	2.928(6)
P(2)-O(13)	1.544(5)	Ba(2)-O(4)	2.928(5)
P(3)-O(14)	1.515(6)	Ba(2)-O(16)#8	2.975(6)
P(3)-O(6)	1.524(6)	Ba(2)-O(4)#8	2.976(6)
P(3)-O(2)	1.559(5)	Ba(2)-O(9)	3.001(5)
		Ba(2)-O(10)#6	3.098(6)

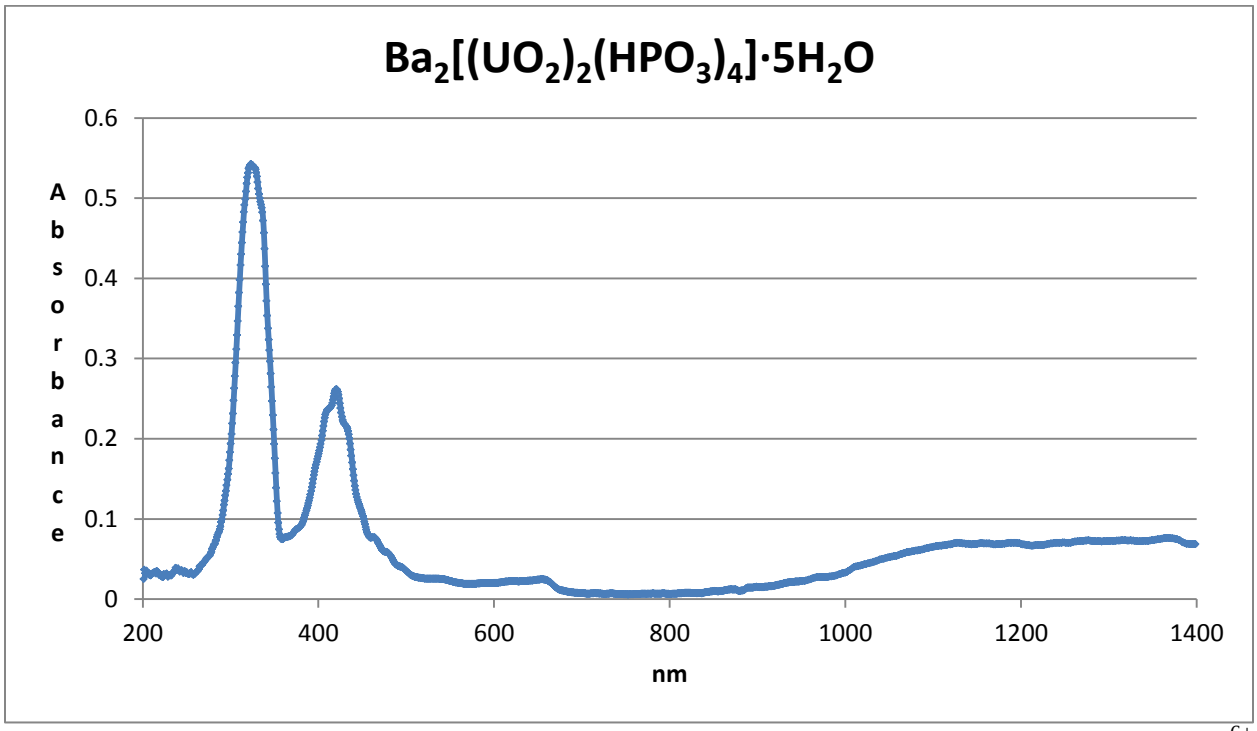


Figure 1.3.1: UV-vis-NIR absorbance for $Ba_2[(UO_2)_2(HPO_3)_4]\cdot 5H_2O$. The characteristic U^{6+} transitions are seen between 370-500 nm.[1]

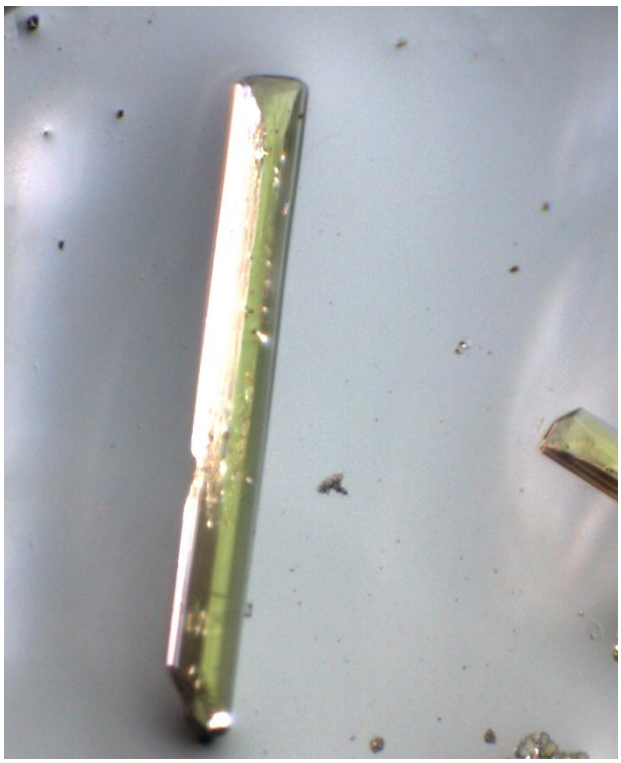


Figure 1.3.2: Picture of the crystals of $Ba_2[(UO_2)_2(HPO_3)_4]\cdot 5H_2O$.

Table 1.3.2: Bond Valence Sum (BVS) calculations for $Ba_2[(UO_2)_2(HPO_3)_4]\cdot 5H_2O$.[2]

vu = exp[(R0 – d)/b].

O3,O7,O11,O12 are terminal uranyl oxo groups
O4,O10 are terminal P-O units

Phosphite			distance	vu
R(0) : P-O	1.626	P(1)-O(1)	1.508	1.376
b	0.37	P(3)-O(2)	1.559	1.199
		O(3)		
		P(4)-O(4)	1.511	1.365
		P(2)-O(5)	1.534	1.282
		P(3)-O(6)	1.524	1.317
		O(7)		
		P(4)-O(8)	1.547	1.238
		P(4)-O(9)	1.534	1.282
		P(2)-O(10)	1.515	1.350
		O(11)		
		O(12)		
		P(2)-O(13)	1.544	1.248
		P(3)-O(14)	1.515	1.350
		P(1)-O(15)	1.546	1.241
		P(1)-O(16)	1.526	1.310

U(VI)			distance	vu		distance	vu
R(0) : U-O	2.051	O(1)					
b	0.519	U(2)-O(2)	2.514	0.410	U(1)-O(2)	2.494	0.426
		U(2)-O(3)	1.791	1.650			
		O(4)					
		U(2)-O(5)	2.339	0.574			
		U(2)-O(6)	2.529	0.398			
		U(1)-O(7)	1.788	1.660			
		U(1)-O(8)	2.318	0.598			
		U(2)-O(9)	2.316	0.600			
		O(10)					
		U(2)-O(11)	1.765	1.735			
		U(1)-O(12)	1.775	1.702			
		U(1)-O(13)	2.341	0.572			
		U(1)-O(14)	2.515	0.409			
		U(2)-O(15)	2.275	0.649			
		U(1)-O(16)	2.296	0.624			

			distance	vu		distance	vu		distance	vu	Total
R(0) : Ba-O	2.29	Ba(1)-O(1)	2.846	0.223	Ba(2)-O(1)	2.728	0.223	Ba(2)-O(1)	2.928	0.306	**2.127**
b	0.37	O(2)									**2.034**
		O(3)									**1.650**
		Ba(1)-O(4)	2.86	0.214	Ba(2)-O(4)	2.928	0.214	Ba(2)-O(4)	2.976	0.178	**1.971**
		Ba(1)-O(5)	2.832	0.231							**2.088**
		Ba(2)-O(6)	2.777	0.268							**1.984**
		O(7)									**1.660**
		Ba(1)-O(8)	3.076	0.120							**1.955**
		Ba(2)-O(9)	3.001	0.146							**2.029**
		Ba(1)-O(10)	2.726	0.308	Ba(1)-O(10)	3.217	0.082	Ba(2)-O(10)	3.098	0.082	**1.821**
		O(11)									**1.735**
		O(12)									**1.702**
		Ba(2)-O(13)	2.805	0.249							**2.069**
		Ba(1)-O(14)	2.723	0.310							**2.069**
		Ba(1)-O(15)	3.122	0.106							**1.996**
		Ba(2)-O(16)	2.975	0.157							**2.091**
		Ba(1)-O1W	2.935	0.175	Ba(2)-O1W	2.915	0.185				**0.360**
		Ba(1)-O2W	2.761	0.280							**0.280**
		Ba(2)-O4W	2.827	0.234							**0.234**

P1-O1,O15,O16
P2-O5,O10,O13
P3-O2,O6,O14
P4-O4,O8,O9

H(P1)= -0.214
H(P2)= 0.023
H(P3)= -0.087
H(P4)= 0.044

Zero Protons

R(0) : U-O	2.051	U(1)-O(7)	1.788	1.660	2.051	U(2)-O(2)	2.514	0.410
b	0.519	U(1)-O(8)	2.318	0.598	0.519	U(2)-O(3)	1.791	1.650
		U(1)-O(12)	1.775	1.702		U(2)-O(5)	2.339	0.574
		U(1)-O(13)	2.341	0.572		U(2)-O(6)	2.529	0.398
		U(1)-O(14)	2.515	0.409		U(2)-O(9)	2.316	0.600
		U(1)-O(16)	2.296	0.624		U(2)-O(11)	1.765	1.735
		U(1)-O(30)	2.35	0.562		U(2)-O(15)	2.275	0.649
		U(1) BVS		6.126		**U(2) BVS**		6.017

BVS for Phosphites
HP(3+)-O(2-)
Should Equal 4+ for PO3

P(1)BVS	3.927
P(2)BVS	3.880
P(3)BVS	3.866
P(4)BVS	3.885

Ba(1) BVS	2.048
Ba(2) BVS	2.242

Section 1.4: $Ba[U^{IV}(PO_4)_2]$.

Table 1.4.1: Selected bond distances for $Ba[U^{IV}(PO_4)_2]$.

Bond Distances (Å) for $Ba[U^{IV}(PO_4)_2]$			
U(1)-O(2)#1	2.230(15)	Ba(1A)-O(1W)#9	2.7845(4)
U(1)-O(2)#2	2.230(15)	Ba(1A)-O(1W)	2.7845(4)
U(1)-O(2)#3	2.230(15)	Ba(1A)-O(1)#10	2.826(14)
U(1)-O(2)#4	2.230(15)	Ba(1A)-O(1)#11	2.826(14)
U(1)-O(1)#5	2.456(15)	Ba(1A)-O(1)#12	2.826(14)
U(1)-O(1)#6	2.456(15)	Ba(1A)-O(1)#13	2.826(14)
U(1)-O(1)#7	2.456(15)	Ba(1A)-O(2)	3.296(13)
U(1)-O(1)	2.456(15)	Ba(1A)-O(2)#14	3.296(13)
P(1)-O(2)#7	1.517(14)	Ba(1A)-O(2)#7	3.296(13)
P(1)-O(2)	1.517(14)	Ba(1A)-O(2)#9	3.296(13)
P(1)-O(1)	1.541(17)		
P(1)-O(1)#7	1.541(17)		

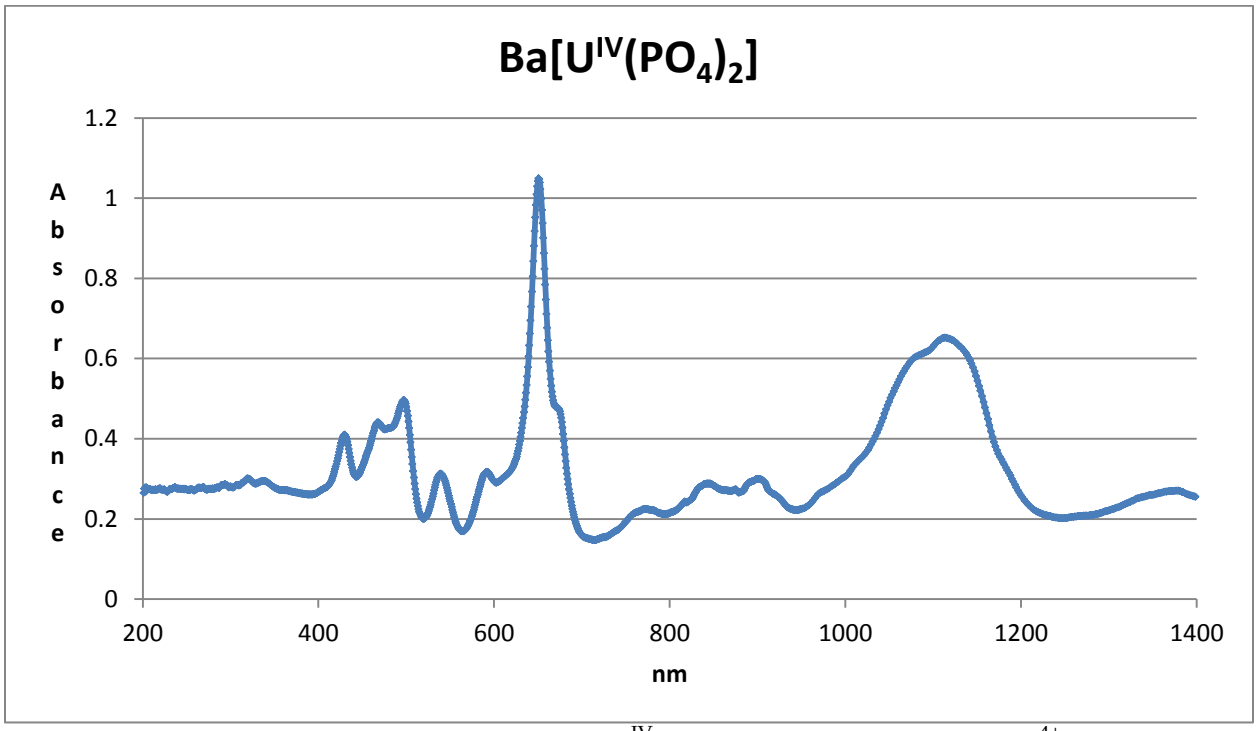


Figure 1.4.1: UV-vis-NIR absorbance for $Ba[U^{IV}(PO_4)_2]$. The characteristic U^{4+} transitions are observed at approximately 429, 486, 495, 549, 649, 672, 880, 1070 and 1133, with the transitions at 649, 1070 and 1133 being the largest observed.[3]

Figure 1.4.2: Picture of the crystals of $Ba[U^{IV}(PO_4)_2]$.

Table 1.4.2: Bond Valence Sum (BVS) calculations for $Ba[U^{IV}(PO_4)_2].^2$

vu = exp[(R0 – d)/b].

Phosphate			distance	vu	U(IV)			distance	vu				distance	vu	**Total**
R(0) : P-O	1.604	P(1)-O(1)	1.541	1.186	R(0) : U-O	2.112	U(1)-O(1)	2.456	0.395	R(0) : Ba-O	2.29	Ba(1A)-O(1)	2.826	0.235	**1.815**
b	0.37	P(1)-O(2)	1.517	1.265	b	0.37	U(1)-O(2)	2.23	0.727	b	0.37	Ba(1A)-O(2)	3.296	0.066	**2.058**

R(0) : U-O	2.051	U(1)-O(1)	2.456	0.395
b	0.519	U(1)-O(1)	2.456	0.395
		U(1)-O(1)	2.456	0.395
		U(1)-O(1)	2.456	0.395
		U(1)-O(2)	2.23	0.727
		U(1)-O(2)	2.23	0.727
		U(1)-O(2)	2.23	0.727
		U(1)-O(2)	2.23	0.727
		U(1) BVS		4.486

P1-O1,O1,O2,O2

H(P1)=	0.254

Zero Protons

BVS for Phosphate
Should Equal 5+ for PO4

P(1)BVS	4.901

Table 1.6.3: Shape8 calculations for U1 in $Ba[U^{IV}(PO_4)_2].^4$

	D4d	**C2v**	**D2d**
U1	20.0243	14.6568	10.5861

Section 2: References.

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