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SUPPLEMENTARY INFORMATION

Structural, Mechanical, Spectroscopic and Thermodynamic Characterization of the Copper-Uranyl Tetrahydroxide Mineral Vandenbrandeite

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Table S.1. Interatomic distances in vandenbrandeite (in Å). The experimental and theoretical values correspond to room temperature and 0 K, respectively.

Bond	Exp. [this work]	Calc.
U-O		
U-O3	1.786(3)	1.806
U-O4	1.801(3)	1.819
U-O8	2.314(3)	2.273
U-O7	2.335(3)	2.338
U-O7#	2.403(2)	2.417
U-O5	2.417(2)	2.410
U-O6	2.454(2)	2.480
<U-Oeq>	2.38	2.38
CuO		
Cu-O8	1.886(3)	1.930
Cu-O5	1.956(3)	1.999
Cu-O6	1.972(3)	2.030
Cu-O6#	1.978(3)	2.036
Cu-O4	2.591(3)	2.667
Cu-O3	3.100(3)	3.132
<Cu1-O>	2.25	2.30
OH		
O5-H10	0.93(3)	0.994
O6-H12	0.94(3)	1.017
O7-H9	0.93(2)	0.985
O8-H11	0.937(15)	0.983
Hydrogen bonds (O-H···O)		
O5···O7	2.825(4)	2.771
H10···O7	1.91(4)	1.794
O6···O5	2.664(4)	2.651
H12···O5	1.73(3)	1.644
O7···O3	2.841(4)	2.792
H9···O3	1.92(2)	1.823
O8···O4	2.927(4)	2.774
H11···O4	2.11(3)	1.801

Table S.2. Interatomic angles in vandenbrandeite (in degrees). The experimental and theoretical values correspond to room temperature and 0 K, respectively.

Angle	Exp. [this work]	Calc.
O-U-O		
O3-U-O4	176.15	176.80
O3-U-O8	87.26	86.77
O3-U-O7	90.08	90.28
O3-U-O7#	93.99	94.57
O3-U-O5	85.54	86.55
O3-U-O6	88.96	90.51
O4-U-O8	94.63	95.45
O4-U-O7	90.51	89.38
O4-U-O7#	89.77	88.29
O4-U-O5	90.86	90.26
O4-U-O6	88.30	90.26
O-Cu-O		
O8-Cu-O5	96.34	100.14
O8-Cu-O6	174.98	175.00
O8-Cu-O6#	95.66	98.17
O8-Cu-O4	88.76	87.48
O8-Cu-O3	107.03	108.84
O5-Cu-O6	84.25	83.58
O5-Cu-O6#	162.18	156.97
O5-Cu-O4	92.70	94.55
O5-Cu-O3	65.25	65.18
O6-Cu-O6#	82.67	77.43
O6-Cu-O4	96.20	95.59
Hydrogen bonds (O-H···O)		
O5-H10···O7	166.84	166.77
O6-H12···O5	172.41	169.78
O7-H9···O3	170.30	166.80
O8-H11···O4	145.20	169.72

Figure. S.1. Frontier band functions in vandenbrandeite: (A) Highest occupied band function: (B) Lowest unoccupied band function. Color code: U-Blue, Cu-Orange-pink, O-Red, H-White.

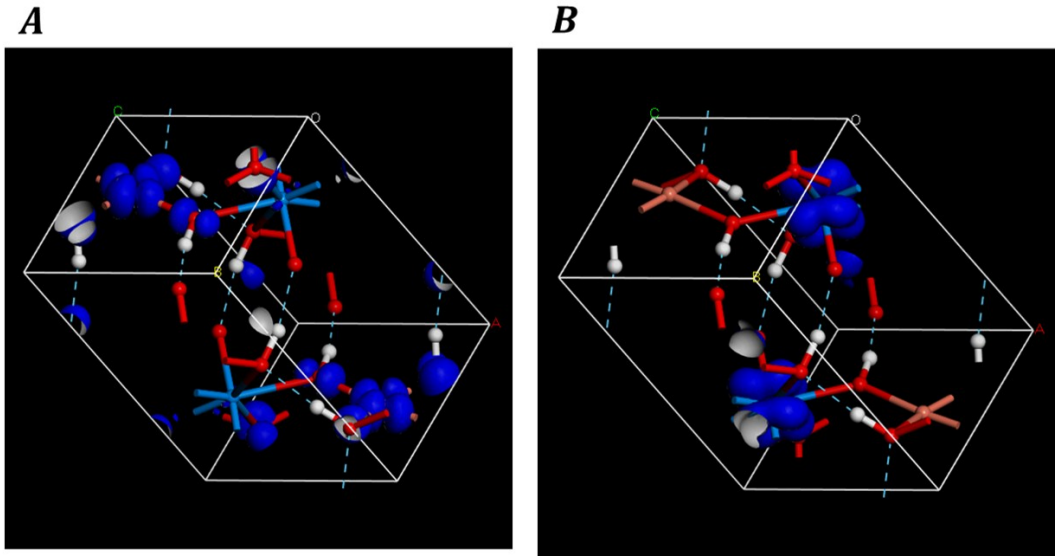


Table S.3. Computed elastic constants of vandenbrandeite. All the values are given in GPa.

ij	C_{ij}
11	62.32
22	85.75
33	80.00
44	20.62
55	25.08
66	28.50
12	25.67
13	24.88
14	-0.69
15	4.03
16	-14.88
23	20.25
24	-6.71
25	1.49
26	-5.92
34	1.20
35	-4.02
36	-5.53
45	-6.57
46	-2.02
56	1.34

Figure S.2. Calculated phonon density of states of vandenbrandeite.

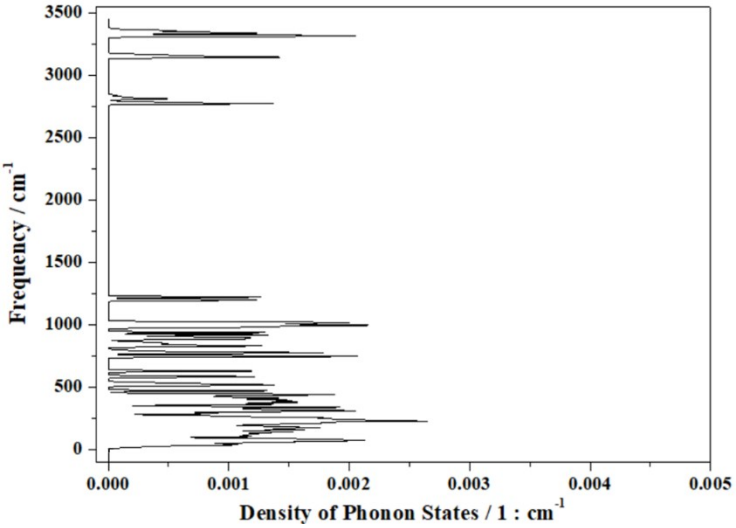


Figure S.3. Unit cell volume of vandenbrandeite as a function of the applied external pressure.

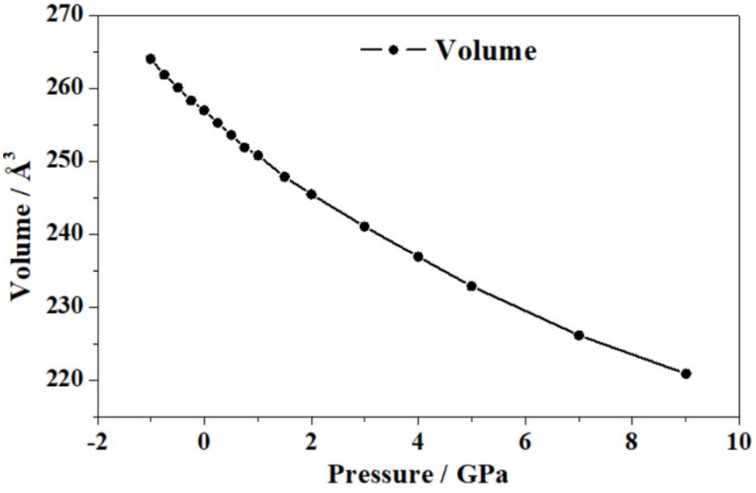


Table S.4. Calculated isobaric heat capacity function, C_P, of vandenbrandeite. Temperature and heat capacity values are given in K and $J \cdot K^{-1} \cdot mol^{-1}$ units, respectively.

T	C_P	T	C_P	T	C_P
10	1.3517	350	194.0970	690	241.5597
20	7.6831	360	196.5251	700	242.3337
30	16.2246	370	198.8549	710	243.0901
40	25.2779	380	201.0905	720	243.8295
50	34.5997	390	203.2361	730	244.5527
60	44.0545	400	205.2960	740	245.2605
70	53.4669	410	207.2738	750	245.9534
80	62.6764	420	209.1736	760	246.6320
90	71.5610	430	210.9990	770	247.2970
100	80.0397	440	212.7537	780	247.9487
110	88.0693	450	214.4411	790	248.5879
120	95.6370	460	216.0645	800	249.2148
130	102.7521	470	217.6272	810	249.8300
140	109.4387	480	219.1323	820	250.4339
150	115.7289	490	220.5826	830	251.0268
160	121.6576	500	221.9811	840	251.6092
170	127.2591	510	223.3304	850	252.1813
180	132.5654	520	224.6329	860	252.7435
190	137.6048	530	225.8913	870	253.2961
200	142.4017	540	227.1078	880	253.8393
210	146.9770	550	228.2845	890	254.3736
220	151.3481	560	229.4235	900	254.8990
230	155.5296	570	230.5268	910	255.4159
240	159.5337	580	231.5963	920	255.9245
250	163.3706	590	232.6337	930	256.4250
260	167.0492	600	233.6406	940	256.9176
270	170.5772	610	234.6186	950	257.4025
280	173.9615	620	235.5691	960	257.8799
290	177.2081	630	236.4935	970	258.3500
300	180.3229	640	237.3932	980	258.8130
310	183.3110	650	238.2693	990	259.2689
320	186.1777	660	239.1229	1000	259.7180
330	188.9278	670	239.9552	-	-
340	191.5660	680	240.7672	-	-

Table S.5. Calculated entropy function, S, of vandenbrandeite. Temperature and entropy values are given in K and $J \cdot K^{-1} \cdot mol^{-1}$ units, respectively.

T	S	T	S	T	S
10	0.4009	350	229.5601	690	378.7338
20	3.0505	360	235.0622	700	382.2151
30	7.7512	370	240.4788	710	385.6579
40	13.6510	380	245.8118	720	389.0630
50	20.2890	390	251.0632	730	392.4312
60	27.4323	400	256.2348	740	395.7633
70	34.9318	410	261.3286	750	399.0601
80	42.6755	420	266.3463	760	402.3223
90	50.5744	430	271.2898	770	405.5507
100	58.5567	440	276.1608	780	408.7459
110	66.5655	450	280.9610	790	411.9086
120	74.5564	460	285.6921	800	415.0394
130	82.4953	470	290.3556	810	418.1391
140	90.3573	480	294.9533	820	421.2083
150	98.1245	490	299.4867	830	424.2475
160	105.7846	500	303.9572	840	427.2573
170	113.3296	510	308.3664	850	430.2384
180	120.7551	520	312.7157	860	433.1912
190	128.0587	530	317.0066	870	436.1163
200	135.2399	540	321.2404	880	439.0142
210	142.2992	550	325.4184	890	441.8855
220	149.2383	560	329.5421	900	444.7307
230	156.0589	570	333.6125	910	447.5501
240	162.7634	580	337.6311	920	450.3444
250	169.3542	590	341.5990	930	453.1138
260	175.8339	600	345.5174	940	455.8590
270	182.2050	610	349.3874	950	458.5803
280	188.4701	620	353.2102	960	461.2782
290	194.6316	630	356.9868	970	463.9529
300	200.6921	640	360.7183	980	466.6051
310	206.6539	650	364.4056	990	469.2350
320	212.5194	660	368.0499	1000	471.8430
330	218.2908	670	371.6521	-	-
340	223.9703	680	375.2131	-	-

Table S.6. Calculated enthalpy function, ΔH ($\Delta H=H_T-H_{298}$), of vandenbrandeite. Temperature and enthalpy values are given in K and $J \cdot K^{-1} \cdot mol^{-1}$ units, respectively.

T	H_T-H_{298}	T	H_T-H_{298}	T	H_T-H_{298}
10	-3091.8628	350	27.7294	690	123.6639
20	-1543.8392	360	32.3851	700	125.3535
30	-1025.2587	370	36.8530	710	127.0064
40	-763.7700	380	41.1455	720	128.6241
50	-605.0339	390	45.2747	730	130.2074
60	-497.6420	400	49.2493	740	131.7570
70	-419.5826	410	53.0795	750	133.2750
80	-359.8683	420	56.7743	760	134.7625
90	-312.4214	430	60.3400	770	136.2195
100	-273.5955	440	63.7841	780	137.6479
110	-241.0789	450	67.1127	790	139.0480
120	-213.3345	460	70.3332	800	140.4209
130	-189.2907	470	73.4506	810	141.7683
140	-168.1889	480	76.4703	820	143.0899
150	-149.4665	490	79.3972	830	144.3866
160	-132.7046	500	82.2341	840	145.6593
170	-117.5769	510	84.9881	850	146.9095
180	-103.8272	520	87.6612	860	148.1368
190	-91.2506	530	90.2572	870	149.3425
200	-79.6881	540	92.7802	880	150.5268
210	-69.0016	550	95.2333	890	151.6905
220	-59.0849	560	97.6196	900	152.8342
230	-49.8438	570	99.9416	910	153.9586
240	-41.2019	580	102.2026	920	155.0643
250	-33.0951	590	104.4042	930	156.1515
260	-25.4672	600	106.5501	940	157.2211
270	-18.2721	610	108.6414	950	158.2728
280	-11.4668	620	110.6809	960	159.3082
290	-5.0162	630	112.6709	970	160.3266
300	1.1106	640	114.6122	980	161.3292
310	6.9402	650	116.5080	990	162.3164
320	12.4958	660	118.3595	1000	163.2882
330	17.8010	670	120.1686	-	-
340	22.8736	680	121.9359	-	-

Table S.7. Calculated free-energy function, ΔG (ΔG = G_T-H_{298}), of vandenbrandeite. Temperature and free-energy values are given in K and $J \cdot K^{-1} \cdot mol^{-1}$ units, respectively.

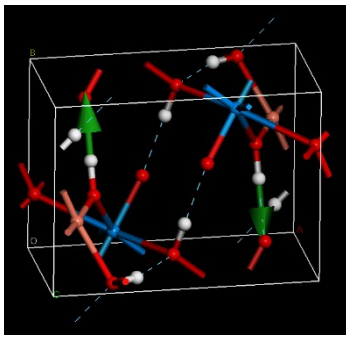
T	G_T-H_{298}	T	G_T-H_{298}	T	G_T-H_{298}
10	-3092.2637	350	-201.8299	690	-255.0697
20	-1546.8898	360	-202.6773	700	-256.8614
30	-1033.0097	370	-203.6262	710	-258.6516
40	-777.4227	380	-204.6661	720	-260.4389
50	-625.3151	390	-205.7888	730	-262.2242
60	-525.0679	400	-206.9856	740	-264.0063
70	-454.5103	410	-208.2487	750	-265.7851
80	-402.5449	420	-209.5723	760	-267.5604
90	-362.9958	430	-210.9499	770	-269.3315
100	-332.1524	440	-212.3767	780	-271.0980
110	-307.6450	450	-213.8483	790	-272.8607
120	-287.8895	460	-215.3588	800	-274.6186
130	-271.7856	470	-216.9045	810	-276.3711
140	-258.5440	480	-218.4833	820	-278.1186
150	-247.5921	490	-220.0903	830	-279.8611
160	-238.4917	500	-221.7227	840	-281.5978
170	-230.9074	510	-223.3781	850	-283.3288
180	-224.5813	520	-225.0542	860	-285.0543
190	-219.3095	530	-226.7490	870	-286.7740
200	-214.9267	540	-228.4597	880	-288.4875
210	-211.3014	550	-230.1854	890	-290.1950
220	-208.3236	560	-231.9226	900	-291.8962
230	-205.9025	570	-233.6708	910	-293.5913
240	-203.9667	580	-235.4287	920	-295.2799
250	-202.4501	590	-237.1948	930	-296.9623
260	-201.3024	600	-238.9671	940	-298.6382
270	-200.4775	610	-240.7462	950	-300.3072
280	-199.9372	620	-242.5294	960	-301.9701
290	-199.6470	630	-244.3157	970	-303.6261
300	-199.5821	640	-246.1057	980	-305.2758
310	-199.7143	650	-247.8970	990	-306.9185
320	-200.0222	660	-249.6904	1000	-308.5549
330	-200.4897	670	-251.4835	-	-
340	-201.0972	680	-253.2771	-	-

Table S.8. Calculated enthalpies ($^{\Delta_r H}$) and free-energies ($^{\Delta_r G}$) of reaction and associated reaction constants (Log K) of reactions (A)-(E). The values of $^{\Delta_r H}$ and $^{\Delta_r G}$ are in units of $kJ{\cdot}mol^{-1}$.

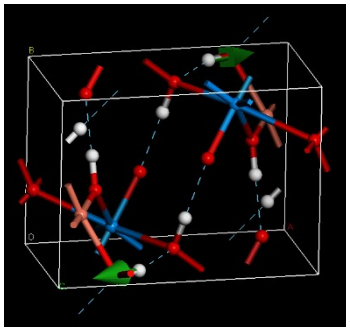
T(K)	$\Delta_r H$	$\Delta_r G$	$Log\ K$	$\Delta_r H$	$\Delta_r G$	$Log\ K$
	Reaction (A)			**Reaction (B)**		
298.15	-46.54	-23.92	4.19	-21.65	-10.28	1.80
300	-46.26	-23.33	4.06	-21.43	-9.90	1.72
320	-43.64	-17.35	2.83	-19.31	-6.07	0.99
340	-41.58	-11.87	1.82	-17.61	-2.62	0.40
360	-39.80	-6.62	0.96	-16.17	0.59	-0.09
380	-38.84	-2.14	0.29	-15.23	3.34	-0.46
400	-38.07	2.21	-0.29	-14.47	5.95	-0.78
420	-37.64	6.28	-0.78	-13.95	8.34	-1.04
440	-37.54	10.10	-1.20	-13.65	10.55	-1.25
460	-37.74	13.68	-1.55	-13.57	12.59	-1.43
480	-38.24	17.06	-1.86	-13.69	14.48	-1.58
500	-39.03	20.25	-2.12	-14.00	16.22	-1.69
T(K)	**Reaction (C)**			**Reaction (D)**		
298.15	40.26	14.08	-2.47	12.13	26.08	-4.57
300	40.37	14.20	-2.47	11.20	26.36	-4.59
320	41.32	15.27	-2.49	11.95	29.20	-4.77
340	41.94	16.07	-2.47	12.50	31.87	-4.90
360	42.47	16.84	-2.44	12.96	34.47	-5.00
380	42.34	17.02	-2.34	13.06	36.76	-5.05
400	42.17	17.24	-2.25	13.12	39.03	-5.10
420	41.77	17.30	-2.15	13.04	41.20	-5.12
440	41.16	17.23	-2.05	12.85	43.27	-5.14
460	40.33	17.03	-1.93	12.53	45.27	-5.14
480	39.29	16.73	-1.82	12.09	47.18	-5.13
500	38.03	16.33	-1.71	11.53	49.03	-5.12
T(K)	**Reaction (E)**			**Reaction (F)**		
298.15	-8.82	-9.46	1.66	-127.11	-114.749	20.10
300	-8.97	-9.60	1.67	-127.10	-114.50	19.94
320	-10.32	-10.88	1.78	-126.97	-111.90	18.27
340	-11.50	-11.98	1.84	-126.96	-109.37	16.80
360	-12.53	-12.92	1.87	-127.06	-106.94	15.52
380	-13.45	-13.75	1.89	-127.28	-104.60	14.38
400	-14.24	-14.43	1.88	-127.60	-102.36	13.37
420	-14.92	-15.00	1.87	-128.02	-100.21	12.46
440	-15.50	-15.47	1.84	-128.54	-98.13	11.65
460	-15.99	-15.83	1.80	-129.13	-96.12	10.91
480	-16.40	-16.11	1.75	-129.82	-94.17	10.25
500	-16.74	-16.30	1.70	-130.61	-92.27	9.64

Figure S.4. The atomic motions associated to some Raman active vibrational normal modes of vandenbrandeite. Color code: U-blue; Cu-pink-orange; O-red; H-white.

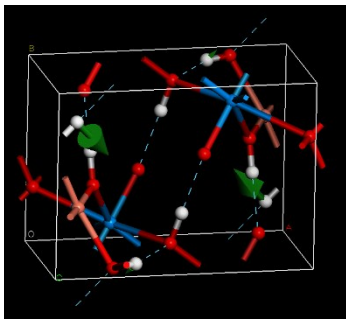
- Mode $\nu =$ 3331 cm^{-1} – $\nu(OH)$ – OH bond stretching vibrations.



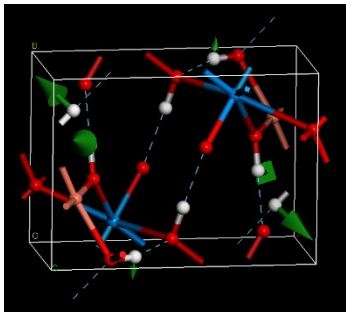
- Mode $\nu =$ 3146 cm^{-1} – $\nu(OH)$ – OH bond stretching vibrations.



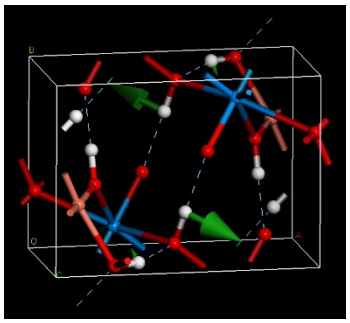
- Mode $\nu =$ 1224 cm^{-1} – $\delta(UOH)$ – UOH bending vibrations.



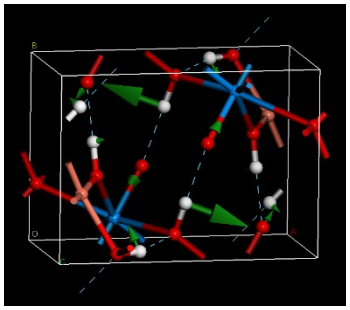
- Mode $\nu =$ 1014 cm^{-1} – $\delta(UOH)$ – UOH bending vibrations.



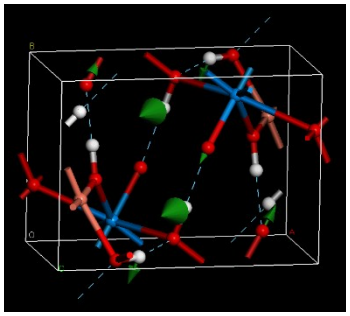
- Mode $\nu =$ 894 cm^{-1} – $\delta(UOH)$ – UOH bending vibrations.



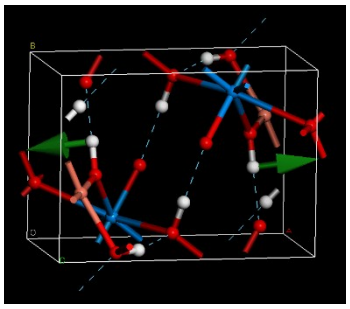
- Mode $\nu =$ 834 cm^{-1} – $\nu^{a}\left(UO^{2+}_{2}\right) + \delta(UOH)$ – Uranyl antisymmetric stretching and UOH bending vibrations.



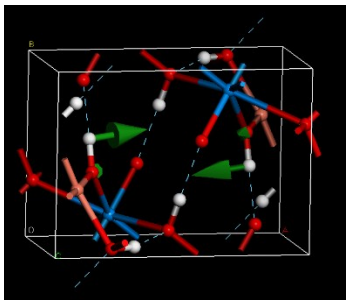
- Mode $\nu =$ 772 cm^{-1} – $\nu^{s}\left(UO^{2+}_{2}\right) + \delta(UOH)$ – Uranyl symmetric stretching and UOH bending vibrations.



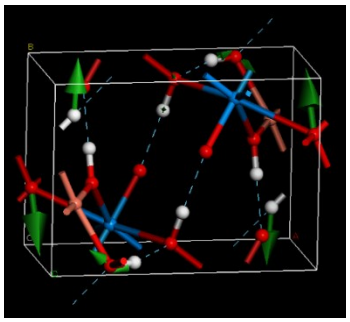
- Mode $\nu =$ 631 cm^{-1} – $\delta(UOH)$ – UOH bending vibrations.



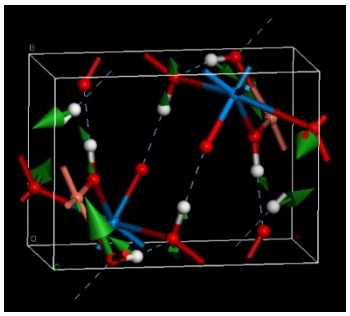
- Mode $\nu =$ 516 cm^{-1} – $\nu(CuO) + \delta(UOH)$ – CuO bond stretching and UOH bending vibrations.



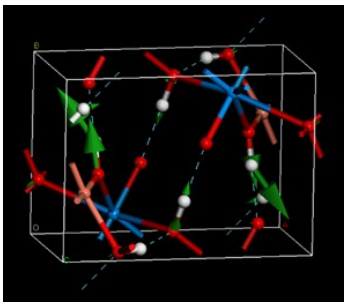
- Mode $\nu =$ 474 cm^{-1} – $\delta(UOCu) + \delta(UOH)$ – $UOCu$ and UOH bending vibrations.



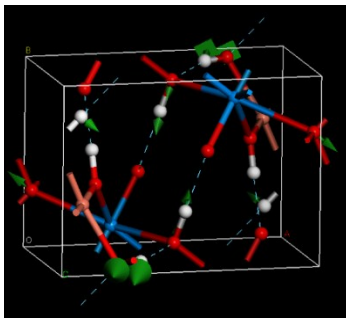
- Mode $\nu =$ 440 cm^{-1} – $\delta(UOCu) + T(OH)$ – $UOCu$ bending and hydroxyl translations.



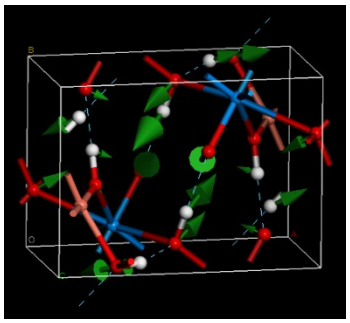
- Mode $\nu =$ 394 cm^{-1} – $\nu(OH) + \delta(UOH)$ – OH bond stretching and UOH bending vibrations.



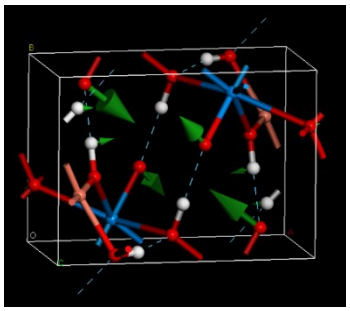
- Mode $\nu =$ 348 cm^{-1} – $\nu(UO_{eq}) + T(OH)$ – Equatorial UO bond stretching and hydroxyl translations.



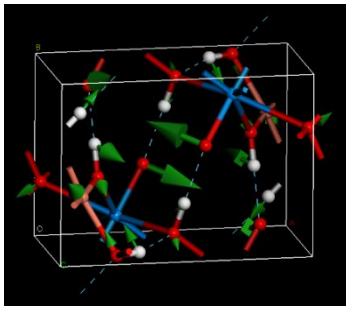
- Mode $\nu =$ 271 cm^{-1} – $\gamma\left(UO_2^{2+}\right) + \delta(UOCu) + T(OH)$ – Uranyl deformation, $UOCu$ bending and hydroxyl translations.



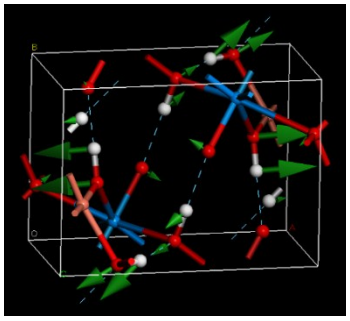
- Mode $\nu =$ 249 cm^{-1} – $\delta\left(UO_2^{2+}\right) + \delta(UOH)$ – Uranyl bending and UOH bending vibrations.



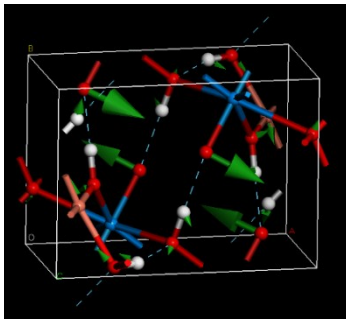
- Mode $\nu =$ 232 cm^{-1} – $\gamma\left(UO_2^{2+}\right) + \delta(UOCu) + \delta(UOH)$ – Uranyl deformation, $UOCu$ and UOH bending vibrations.



- Mode $\nu =$ 213 cm^{-1} – $\gamma\left(UO_2^{2+}\right) + T(OH)$ – Uranyl deformation and hydroxyl translations.



- Mode $\nu =$ 171 cm^{-1} – $T(Cu) + \rho\left(UO_2^{2+}\right) + \delta(UOCu) + \delta(UOH)$ – Copper translation, uranyl rocking, $UOCu$ and UOH bending vibrations.



- Mode $\nu =$ 72 cm^{-1} – $T(Cu) + T\left(UO_2^{2+}\right) + \delta(UOCu) + \delta(UOH)$ – Copper and uranyl translations, $UOCu$ and UOH bending vibrations.

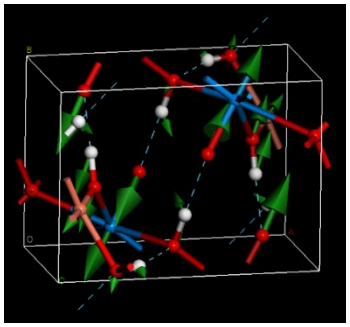


Figure S.5. Resolution of some composite bands in the experimental Raman spectrum of vandenbrandeite mineral into single band contributions: (A) Band β; (B) Bands δ and ε.

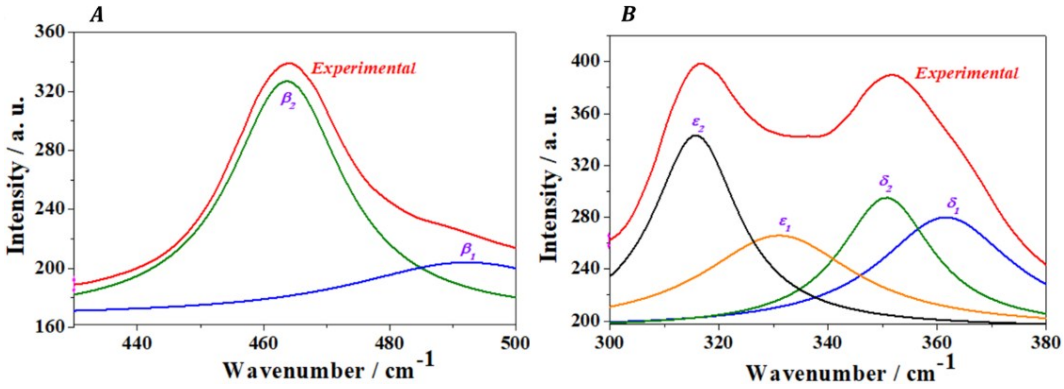


Figure S.6. Calculated free energies of formation and associated reaction constants of vandenbrandeite as a function of temperature.