

Thermochemical measurements of alkali cation association to hexatantalate – Supplementary Information

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S1 Drop Solution Enthalpies

Table S1: Drop solution enthalpy of $\text{Li}_8\text{Ta}_6\text{O}_{19}$

Mass (mg)	ΔH_{ds} (kJ mol ⁻¹)
4.73	1860.21
3.85	1853.85
3.75	1839.61
3.47	1856.16
3.00	1855.44
3.69	1859.97
2.31	1862.38
3.22	1856.14
Average:	1855.47 ± 4.97
-18 H ₂ O	-1242.00
Final:	613.47 ± 4.97

Table S3: Drop solution enthalpy of $\text{Rb}_8\text{Ta}_6\text{O}_{19}$

Mass (mg)	ΔH_{ds} (kJ mol ⁻¹)
3.92	1406.56
5.74	1403.56
4.31	1388.76
5.38	1389.67
5.33	1379.51
7.61	1427.34
6.88	1401.91
4.40	1401.85
Average:	1399.89 ± 10.22
-14 H ₂ O	-966.00
Final:	433.89 ± 10.22

Table S2: Drop solution enthalpy of $\text{K}_8\text{Ta}_6\text{O}_{19}$

Mass (mg)	ΔH_{ds} (kJ mol ⁻¹)
4.65	1586.34
4.91	1672.26
5.41	1603.25
5.13	1586.34
7.87	1647.62
4.29	1635.12
5.39	1665.30
6.97	1627.86
Average	1628.01 ± 23.71
-16 H ₂ O	-1104.00
Final:	514.01 ± 23.71

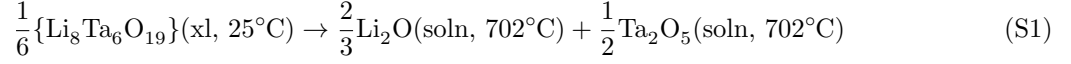
Table S4: Drop solution enthalpy of $\text{Cs}_8\text{Ta}_6\text{O}_{19}$

Mass (mg)	ΔH_{ds} (kJ mol ⁻¹)
4.95	1415.26
5.69	1421.01
4.58	1409.12
4.35	1427.62
5.70	1426.25
7.83	1413.61
4.20	1423.81
4.02	1422.82
Average:	1419.94 ± 4.65
-14 H ₂ O	-966.00
Final:	453.94 ± 4.65

S2 Thermochemical Cycles

Lithium Hexatantalate

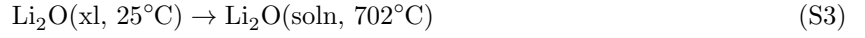
The formation enthalpy of $\text{Li}_8\text{Ta}_6\text{O}_{19}$ from constituent binary oxides is -117.2 kJ/mol Ta. The correction of 69 kJ/mol H_2O for lattice water has been applied as seen in Table S1.



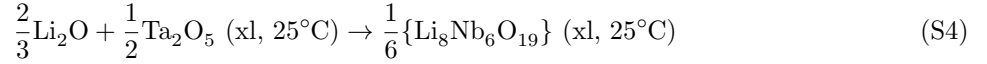
$$\Delta H_1 = \Delta H_{ds} = 102.25 \pm 0.83 \text{kJ/mol Ta}$$



$$\Delta H_2 = \Delta H_{ds}(\text{Ta}_2\text{O}_5) = 90.41 \pm 2.50 \text{kJ/mol Ta}$$



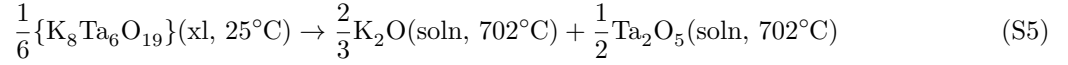
$$\Delta H_3 = \Delta H_{ds}(\text{Li}_2\text{O}) = -90.3 \pm 2.5 \text{kJ/mol Ta}$$



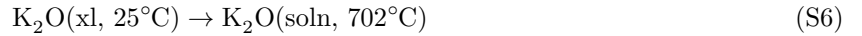
$$\Delta H_4 = \Delta H_f^{ox}(\text{Li}_8\text{Ta}_6\text{O}_{19}) = -\Delta H_1 + \frac{1}{2}\Delta H_2 + \frac{2}{3}\Delta H_3 = -117.2 \pm 2.1 \text{kJ/mol Ta}$$

Potassium Hexatantalate

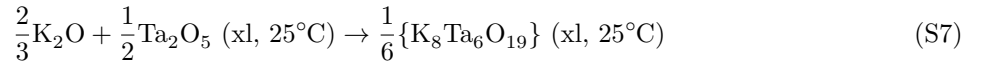
The formation enthalpy of $\text{K}_8\text{Ta}_6\text{O}_{19}$ from constituent binary oxides is -253.7 kJ/mol Ta. The correction of 69 kJ/mol H_2O for lattice water has been applied as seen in Table S2.



$$\Delta H_5 = \Delta H_{ds} = 72.32 \pm 3.95 \text{kJ/mol Ta}$$



$$\Delta H_6 = \Delta H_{ds}(\text{K}_2\text{O}) = -318.0 \pm 3.1 \text{kJ/mol Ta}$$



$$\Delta H_7 = \Delta H_f^{ox}(\text{K}_8\text{Ta}_6\text{O}_{19}) = -\Delta H_5 + \frac{1}{2}\Delta H_2 + \frac{2}{3}\Delta H_6 = -253.7 \pm 4.4 \text{kJ/mol Ta}$$

Rubidium Hexatantalate

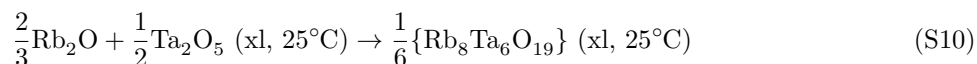
The formation enthalpy of $\text{Rb}_8\text{Ta}_6\text{O}_{19}$ from constituent binary oxides is -248.9 kJ/mol Ta. The correction of 69 kJ/mol H_2O for lattice water has been applied as seen in Table S3.



$$\Delta H_8 = \Delta H_{ds} = 85.67 \pm 1.70 \text{ kJ/mol Ta}$$



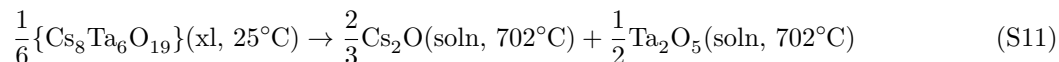
$$\Delta H_9 = \Delta H_{ds}(\text{Rb}_2\text{O}) = -332.6 \pm 2.2 \text{ kJ/mol Ta}$$



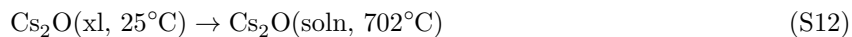
$$\Delta H_{10} = \Delta H_f^{ox}(\text{Rb}_8\text{Ta}_6\text{O}_{19}) = -\Delta H_8 + \frac{1}{2}\Delta H_2 + \frac{2}{3}\Delta H_9 = -248.9 \pm 2.7 \text{ kJ/mol Ta}$$

Cesium Hexatantalate

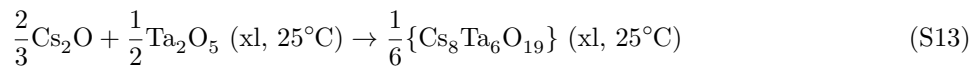
The formation enthalpy of $\text{Cs}_8\text{Ta}_6\text{O}_{19}$ from constituent binary oxides is -263.1 kJ/mol Ta. The correction of 69 kJ/mol H_2O for lattice water has been applied as seen in Table S4.



$$\Delta H_{11} = \Delta H_{ds} = 75.66 \pm 0.81 \text{ kJ/mol Ta}$$



$$\Delta H_{12} = \Delta H_{ds}(\text{Cs}_2\text{O}) = -348.9 \pm 1.7 \text{ kJ/mol Ta}$$

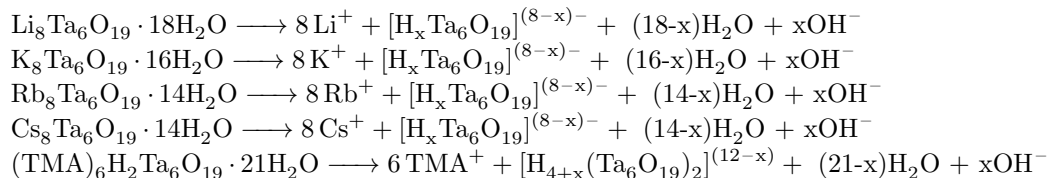


$$\Delta H_{13} = \Delta H_f^{ox}(\text{Cs}_8\text{Ta}_6\text{O}_{19}) = -\Delta H_{11} + \frac{1}{2}\Delta H_2 + \frac{2}{3}\Delta H_{12} = -263.1 \pm 1.9 \text{ kJ/mol Ta}$$

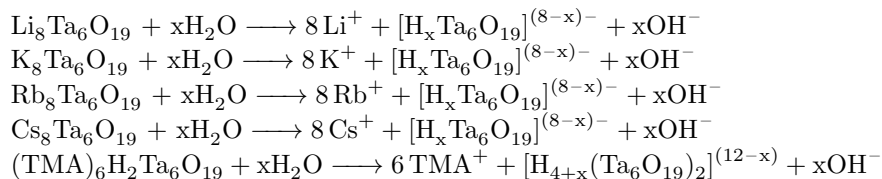
Where ΔH_{ds} are drop solution enthalpies under oxygen bubbling.

S3 Room Temperature Dissolution Enthalpies

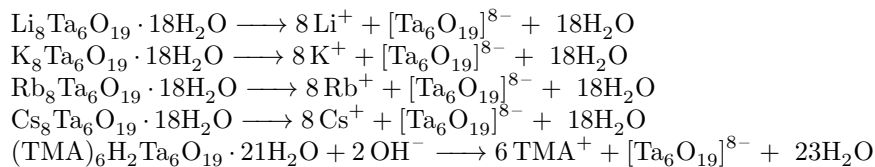
Dissolution enthalpies of hydrated hexatantalate clusters in water



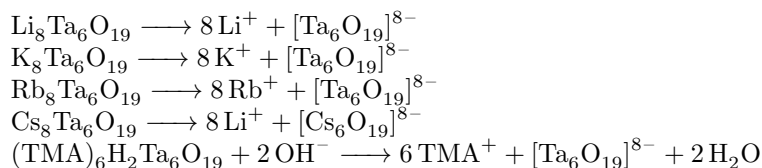
Dissolution enthalpies of anhydrous hexatantalate clusters in water



Dissolution enthalpies of hydrated hexatantalate clusters in 1M parent hydroxide



Dissolution enthalpies of anhydrous hexatantalate clusters in 1M parent hydroxide



S3.1 Tables of Aqueous Dissolution Enthalpies

Table S5: Lithium Hexatantalate Dissolution Enthalpies in Water

Concentration (M $\times 10^5$)	Dissolution Enthalpy (ΔH_{dis} / kJ mol $^{-1}$)	Anhydrous Dissolution Enthalpy (ΔH_{dis} / kJ mol $^{-1}$)
22.59	73.61	54.24
27.27	72.90	53.67
39.49	71.06	52.17
51.54	66.91	48.77
63.29	64.77	47.02
69.94	61.39	44.27

Table S6: Potassium Hexatantalate Dissolution Enthalpies in Water

Concentration (M $\times 10^5$)	Dissolution Enthalpy (ΔH_{dis} / kJ mol $^{-1}$)	Anhydrous Dissolution Enthalpy (ΔH_{dis} / kJ mol $^{-1}$)
16.56	130.46	106.10
35.20	122.37	99.18
50.19	118.60	95.94
55.29	110.35	88.91
79.44	111.50	89.89
95.57	106.98	86.02
104.90	106.52	85.63
122.31	104.02	83.49
126.64	101.47	81.31

Table S7: Rubidium Hexatantalate Dissolution Enthalpies in Water

Concentration (M $\times 10^5$)	Dissolution Enthalpy (ΔH_{dis} / kJ mol $^{-1}$)	Anhydrous Dissolution Enthalpy (ΔH_{dis} / kJ mol $^{-1}$)
10.25	107.69	91.02
25.29	114.87	97.42
31.49	107.27	90.64
44.00	105.64	89.20
65.45	102.88	86.73
80.98	88.78	74.16
89.57	89.69	74.97
104.87	87.23	72.78
114.09	87.66	73.16
128.03	84.66	70.49

Table S8: Cesium Hexatantalate Dissolution Enthalpies in Water

Concentration (M $\times 10^5$)	Dissolution Enthalpy (ΔH_{dis} / kJ mol $^{-1}$)	Anhydrous Dissolution Enthalpy (ΔH_{dis} / kJ mol $^{-1}$)
14.14	109.64	94.34
26.14	114.21	98.48
31.09	105.95	91.00
43.84	93.33	79.56
54.10	93.60	79.79
61.43	86.61	73.46
78.12	85.84	72.76
96.32	82.94	70.13
122.55	79.77	67.25

Table S9: Tetramethylammonium Hexatantalate Dissolution Enthalpies in Water

Concentration (M $\times 10^5$)	Dissolution Enthalpy (ΔH_{dis} / kJ mol $^{-1}$)	Anhydrous Dissolution Enthalpy (ΔH_{dis} / kJ mol $^{-1}$)
30.32	-5.02	-12.04
59.36	-4.17	-11.20
93.65	-2.53	-9.55
117.01	-5.87	-12.89
139.70	-3.65	-10.68

S3.2 Tables of 1M Parent Hydroxide Dissolution Enthalpies

Table S10: Potassium Hexatantalate Dissolution Enthalpies in 1M KOH

Concentration (M $\times 10^5$)	Dissolution Enthalpy (ΔH_{dis} / kJ mol $^{-1}$)	Anhydrous Dissolution Enthalpy (ΔH_{dis} / kJ mol $^{-1}$)
16.34	56.329	42.70
45.57	61.43	47.06
72.78	56.17	42.56
105.07	59.23	45.18
133.24	61.68	47.28

Table S11: Rubidium Hexatantalate Dissolution Enthalpies in 1M RbOH

Concentration (M $\times 10^5$)	Dissolution Enthalpy (ΔH_{dis} / kJ mol $^{-1}$)	Anhydrous Dissolution Enthalpy (ΔH_{dis} / kJ mol $^{-1}$)
13.57	41.31	31.84
38.66	40.82	31.40
64.17	40.81	35.41
92.30	46.66	31.39
121.00	46.02	36.61

Table S12: Cesium Hexatantalate Dissolution Enthalpies in 1M CsOH

Concentration (M $\times 10^5$)	Dissolution Enthalpy (ΔH_{dis} / kJ mol $^{-1}$)	Anhydrous Dissolution Enthalpy (ΔH_{dis} / kJ mol $^{-1}$)
11.99	24.82	17.43
31.28	27.32	19.70
49.15	30.80	22.85
68.96	25.71	18.24
93.97	29.01	21.23
110.76	21.05	14.01
123.02	30.99	23.02
136.68	31.66	23.63

Table S13: TMA Hexaniobate Dissolution Enthalpies in 1M TMAOH

Concentration (M $\times 10^5$)	Dissolution Enthalpy ΔH_{dis} / kJ mol $^{-1}$	Anhydrous Dissolution Enthalpy ΔH_{dis} / kJ mol $^{-1}$
12.62	-40.39	-38.37
43.26	-38.26	-36.69
74.52	-33.63	-33.05
101.71	-35.31	-34.37
130.60	-40.72	-38.63

S4 Supplementary Characterization

S4.1 Energy Dispersive X-ray Analysis (EDX)

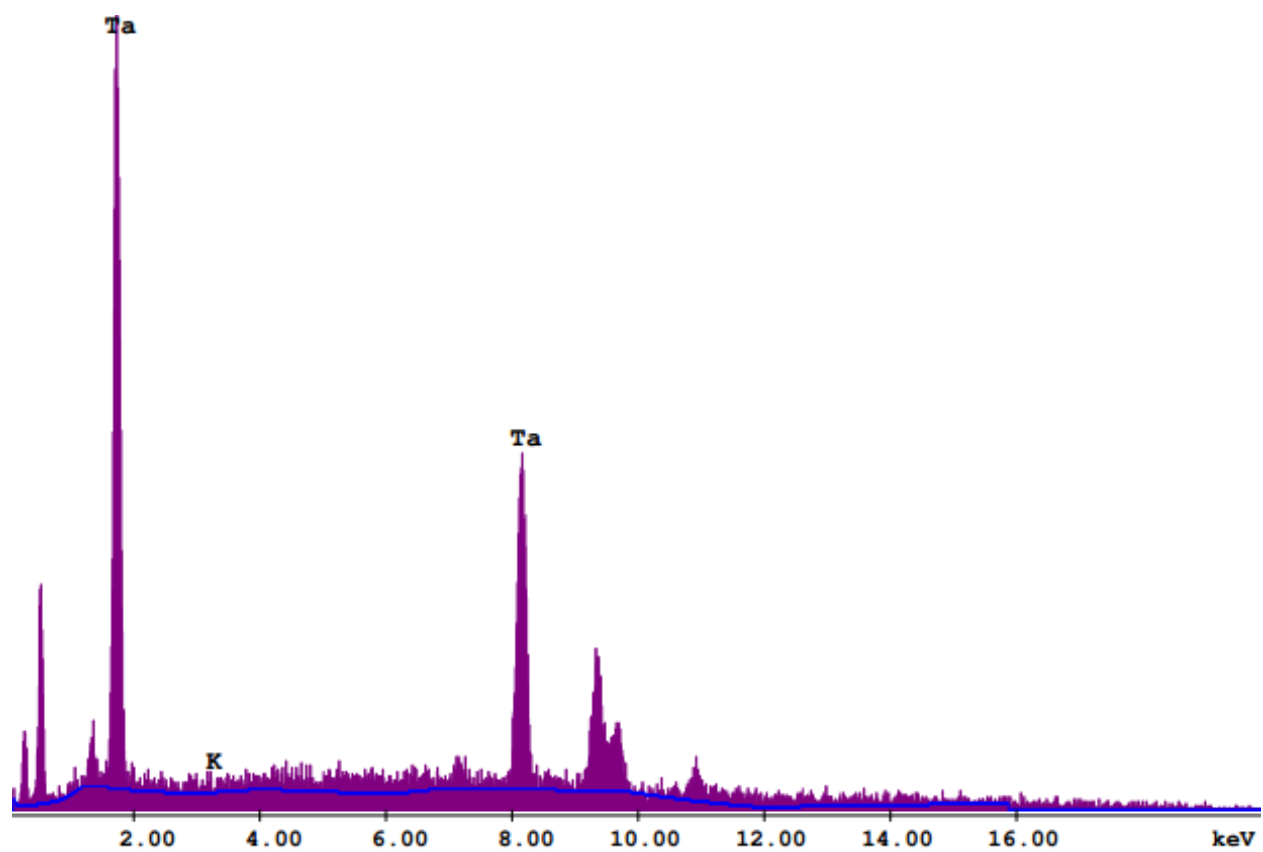


Figure S1: Sample EDX spectrum of $\text{Li}_8\text{Ta}_6\text{O}_{19}$, indicating the complete replacement of K^+ counterions (indistinguishable from background) by metathesis in 1M LiOH.

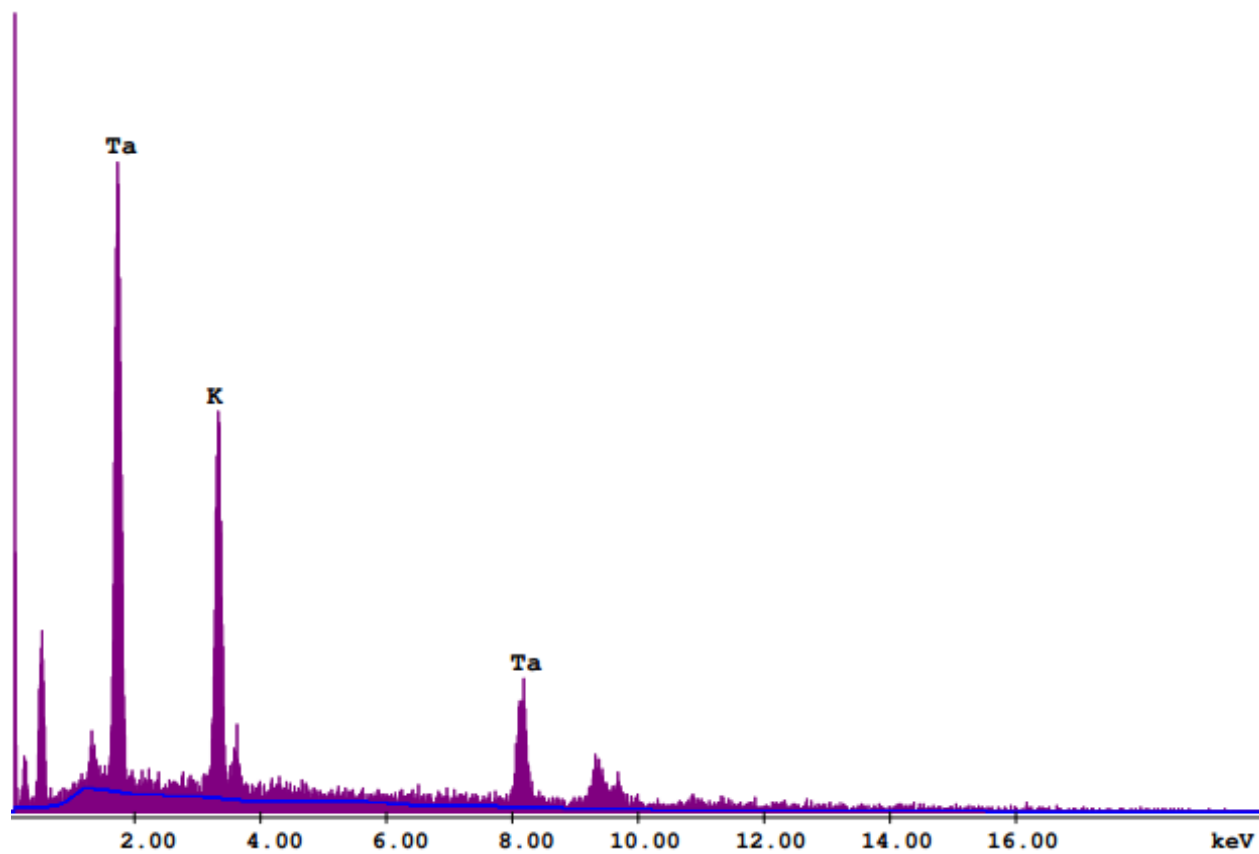


Figure S2: Sample EDX spectrum of $K_8Ta_6O_{19}$.

Table S14: Atom % values for K and Ta in $K_8Ta_6O_{19}$

Measurement #	at% K	at% Ta
1	59.97	40.03
2	55.59	44.41
3	60.14	39.86
4	52.85	47.15
5	58.72	41.28
Average	57.45	42.55
Expected	57.14	42.86

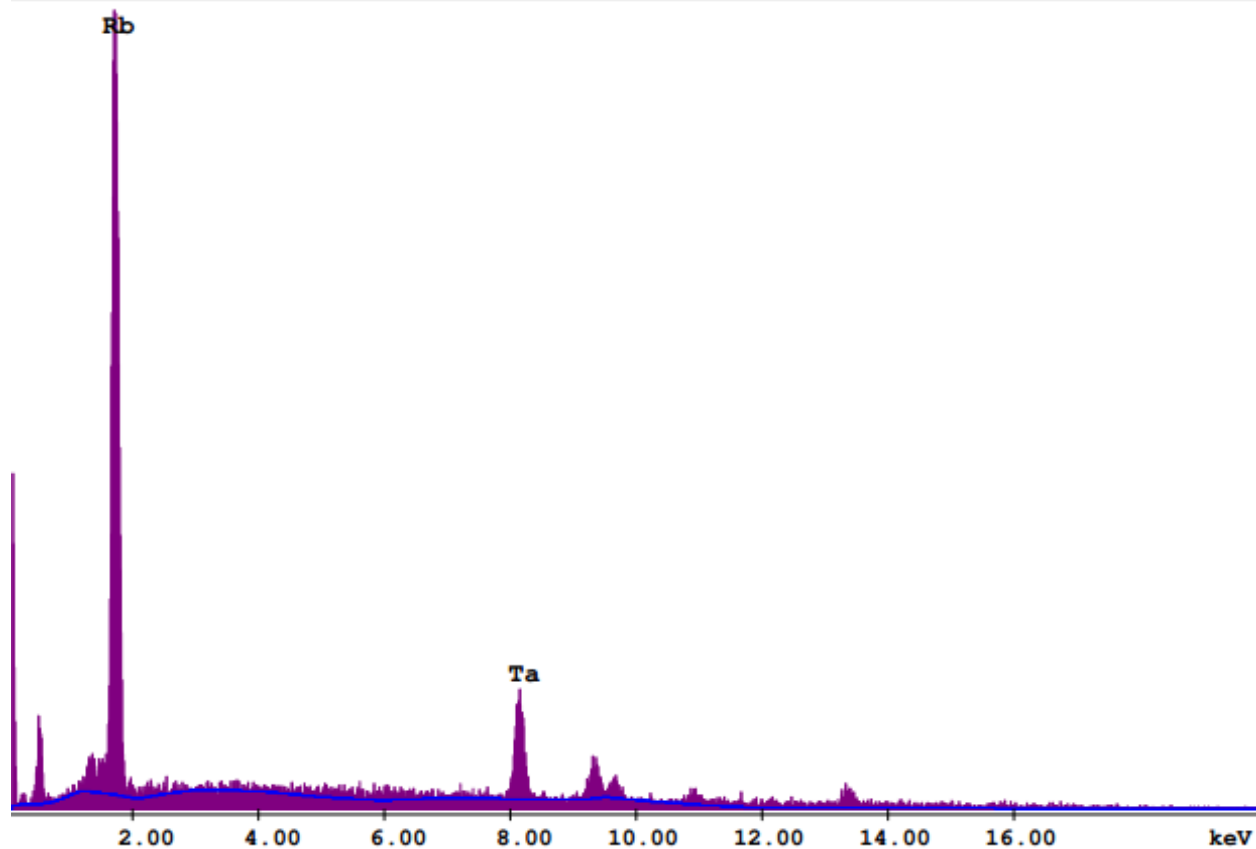


Figure S3: Sample EDX spectrum of $\text{Rb}_8\text{Ta}_6\text{O}_{19}$.

Table S15: Atom % values for Rb and Ta in $\text{Rb}_8\text{Ta}_6\text{O}_{19}$

Measurement #	at% Rb	at% Ta
1	58.42	41.58
2	56.38	43.62
3	56.82	43.18
4	57.93	42.07
5	56.39	43.61
Average	57.19	42.81
Expected	57.14	42.86

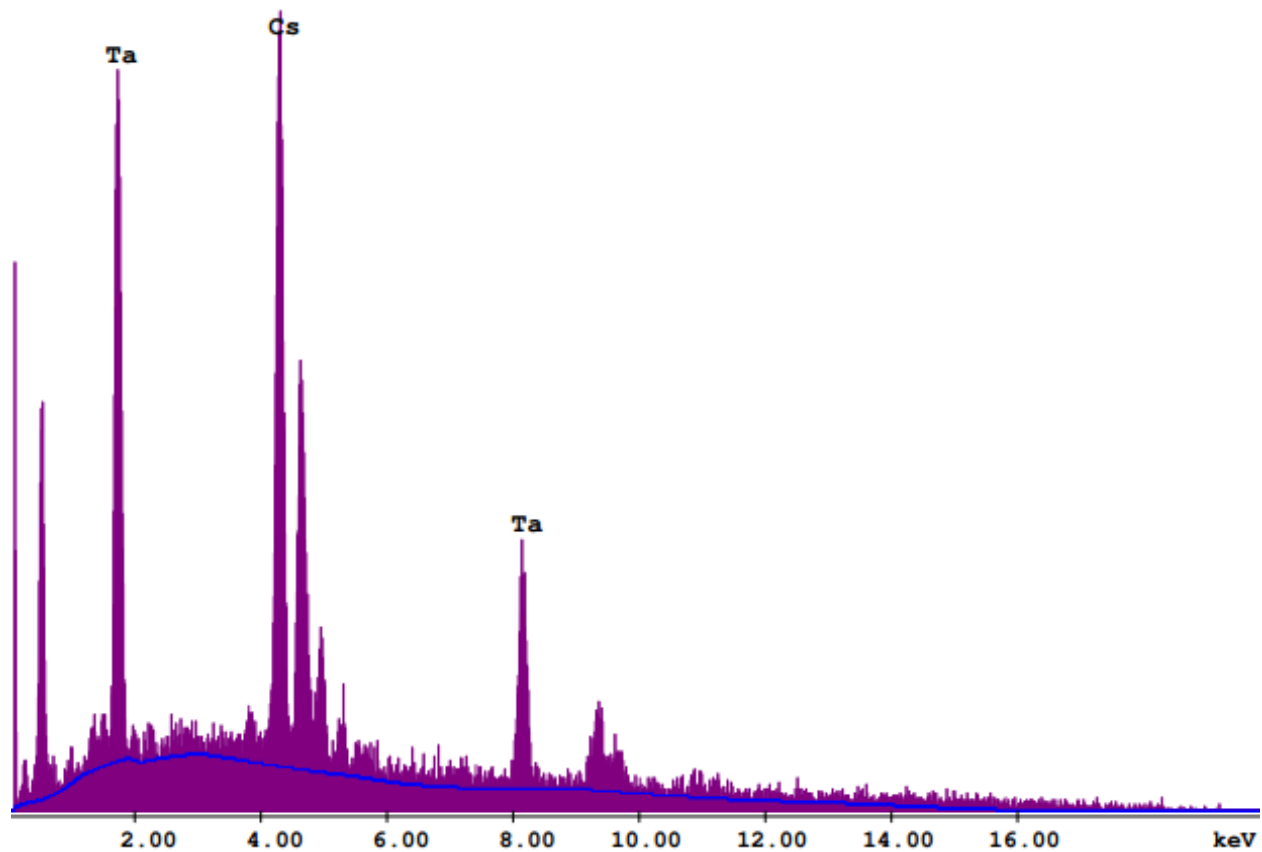


Figure S4: Sample EDX spectrum of $\text{Cs}_8\text{Ta}_6\text{O}_{19}$.

Table S16: Atom % values for Cs and Ta in $\text{Cs}_8\text{Ta}_6\text{O}_{19}$

Measurement #	at% Cs	at% Ta
1	58.56	41.44
2	56.82	43.18
3	59.72	40.28
4	59.65	40.35
5	59.71	40.29
Average	58.89	41.11
Expected	57.14	42.86

S4.2 Thermogravimetric Analysis

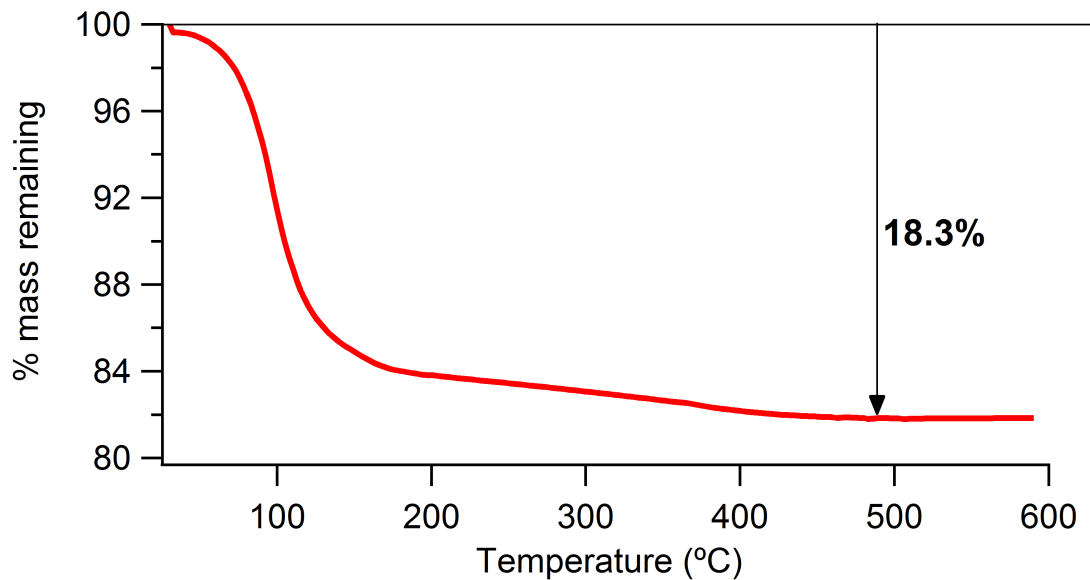


Figure S5: Thermogravimetric analysis of $\text{Li}_8\text{Ta}_6\text{O}_{19}$. All mass loss is due to lattice water, corresponding to 18 H_2O molecules per formula unit.

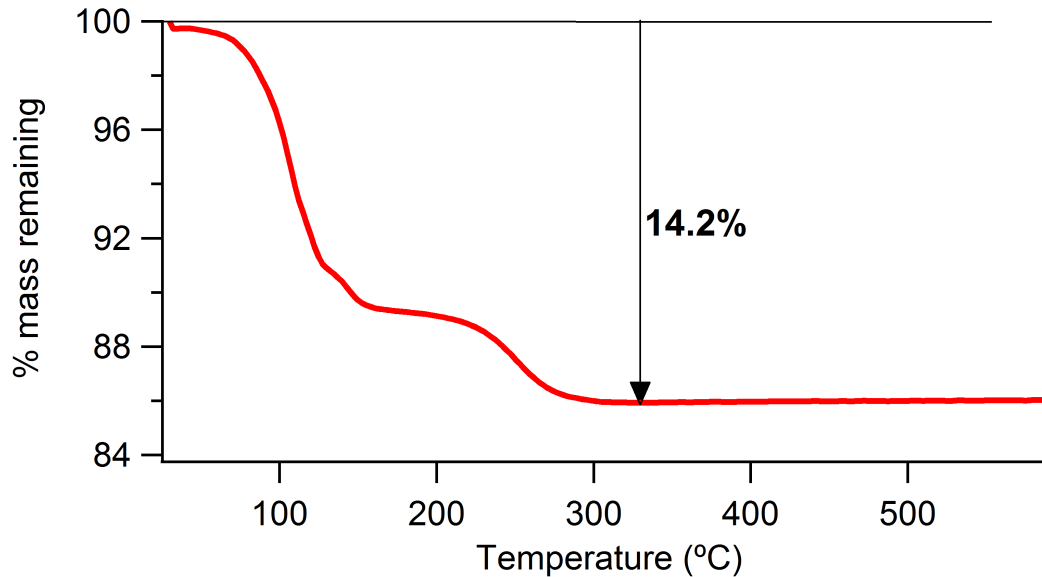


Figure S6: Thermogravimetric analysis of $\text{K}_8\text{Ta}_6\text{O}_{19}$. All mass loss is due to lattice water, corresponding to 16 H_2O molecules per formula unit.

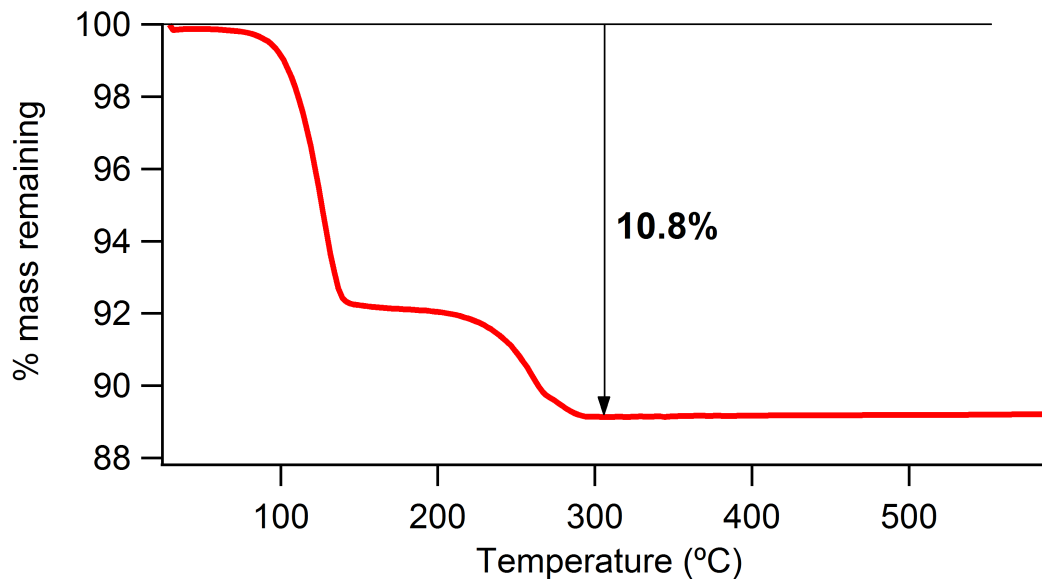


Figure S7: Thermogravimetric analysis of $\text{Rb}_8\text{Ta}_6\text{O}_{19}$. All mass loss is due to lattice water, corresponding to 14 H_2O molecules per formula unit.

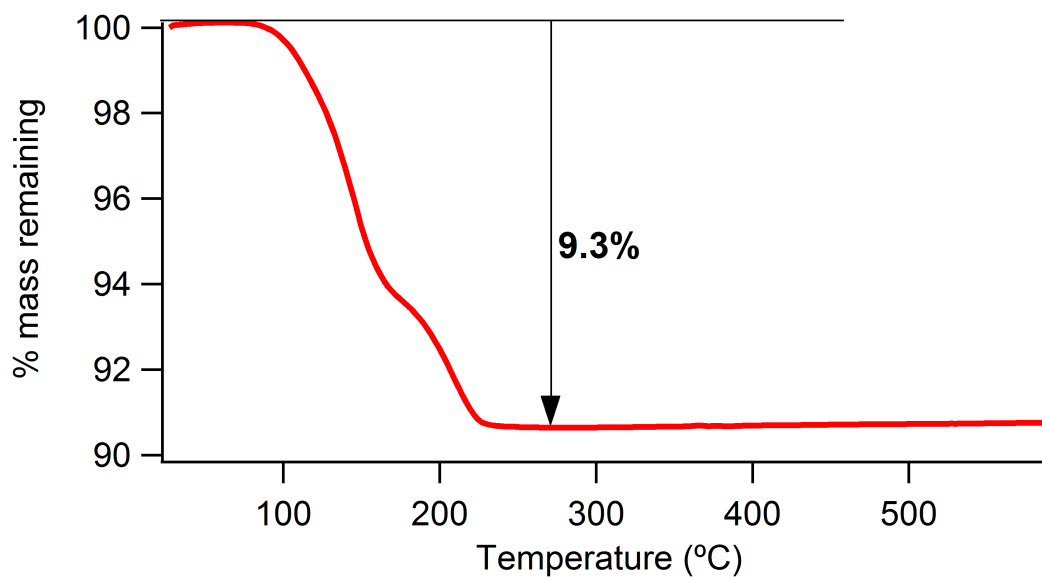


Figure S8: Thermogravimetric analysis of $\text{Cs}_8\text{Ta}_6\text{O}_{19}$. All mass loss is due to lattice water, corresponding to 14 H_2O molecules per formula unit.