



## Supporting Information

© Copyright Wiley-VCH Verlag GmbH & Co. KGaA, 69451 Weinheim, 2016

### **Distinctive Interactions of Cesium and Hexaniobate in Water**

Dylan J. Sures, Sulata K. Sahu, Pedro I. Molina, Alexandra Navrotsky, and May Nyman\*

## Contents

<b>S1 Drop Solution Enthalpies</b>	<b>S2</b>
<b>S2 Thermochemical Cycles</b>	<b>S3</b>
<b>S3 Room Temperature Dissolution Enthalpies</b>	<b>S4</b>
S3.1 Tables of Aqueous Dissolution Enthalpies . . . . .	S5
S3.2 Tables of 1M Parent Hydroxide Dissolution Enthalpies . . . . .	S8
S3.3 Dissolution Enthalpy Plots Uncorrected for Lattice Water . . . . .	S10
<b>S4 Supplementary Characterization</b>	<b>S11</b>
S4.1 Synthesis . . . . .	S11
S4.2 Thermogravimetric Analysis (TGA) . . . . .	S12
S4.3 Elemental Analysis . . . . .	S13

## S1 Drop Solution Enthalpies

$\Delta H_{ds}$  was measured in a custom-made isoperibol Tian-Calvet twin microcalorimeter.<sup>1,2</sup> Pellets of about 5 mg were loosely pressed, weighed, and dropped from room temperature into  $3\text{Na}_2\text{O}\cdot 4\text{MoO}_3$  molten solvent at  $702\text{ }^\circ\text{C}$ . The calorimeter assembly was washed with oxygen at  $43\text{ mL min}^{-1}$ . Oxygen was bubbled through the solvent at  $4.5\text{ mL min}^{-1}$  to aid dissolution, evolve water vapor, and to maintain oxidizing conditions. The calorimeter was calibrated against the heat content of 5 mg pellets of high-purity  $\text{Al}_2\text{O}_3$  (99.997%, Alfa Aesar) dropped into an empty crucible.

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

Mass (mg)	$\Delta H_{ds}$ ( $\text{kJ mol}^{-1}$ )
3.961	2329.54
4.997	2337.22
4.397	2384.57
4.677	2345.47
4.753	2362.28
4.857	2401.55
4.181	2380.88
4.073	2379.58
Average:	$2365.13 \pm 18.13$
-23.5 $\text{H}_2\text{O}$	-1621.50
<b>Final:</b>	<b><math>743.63 \pm 18.13</math></b>

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

Mass (mg)	$\Delta H_{ds}$ ( $\text{kJ mol}^{-1}$ )
5.745	1616.96
6.927	1618.01
5.718	1606.60
5.366	1597.92
5.908	1594.62
5.234	1606.34
5.563	1580.90
5.344	1580.31
Average:	$1600.21 \pm 10.28$
-14.1 $\text{H}_2\text{O}$	-927.90
<b>Final:</b>	<b><math>627.31 \pm 10.28</math></b>

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

Mass (mg)	$\Delta H_{ds}$ ( $\text{kJ mol}^{-1}$ )
4.992	1703.17
5.340	1701.07
6.863	1726.15
7.137	1701.78
6.918	1669.54
4.923	1687.22
8.214	1692.57
6.703	1688.89
Average	$1696.30 \pm 11.52$
-16.0 $\text{H}_2\text{O}$	-1104.00
<b>Final:</b>	<b><math>592.30 \pm 11.52</math></b>

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

Mass (mg)	$\Delta H_{ds}$ ( $\text{kJ mol}^{-1}$ )
5.304	1698.86
4.847	1700.79
8.326	1699.83
5.316	1693.16
6.698	1707.05
5.132	1700.20
5.039	1703.34
6.210	1700.20
Average:	$1700.43 \pm 3.93$
-14.8 $\text{H}_2\text{O}$	-1021.20
<b>Final:</b>	<b><math>679.23 \pm 3.93</math></b>

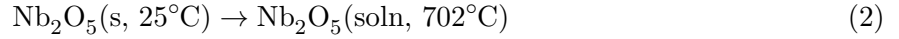
## S2 Thermochemical Cycles

### Lithium Hexaniobate

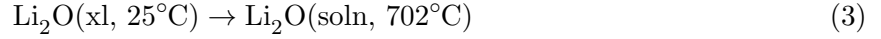
The formation enthalpy of  $\text{Li}_8\text{Nb}_6\text{O}_{19}$  from constituent binary oxides is -137.2 kJ/mol Nb. The correction of 69 kJ/mol  $\text{H}_2\text{O}$  for lattice water has been applied as seen in Table S1.



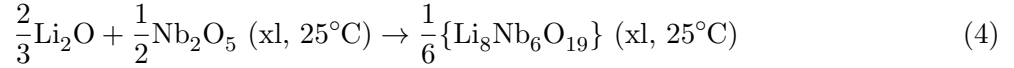
$$\Delta H_1 = \Delta H_{ds} = 123.94 \pm 3.02 \text{kJ/mol Nb}$$



$$\Delta H_2 = \Delta H_{ds}(\text{Nb}_2\text{O}_5) = 93.97 \pm 1.60 \text{kJ/mol Nb}$$



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



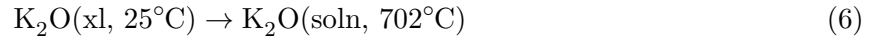
$$\Delta H_4 = \Delta H_f^{ox}(\text{Li}_8\text{Nb}_6\text{O}_{19}) = -\Delta H_1 + \frac{1}{2}\Delta H_2 + \frac{2}{3}\Delta H_3 = -137.2 \pm 4.8 \text{kJ/mol Nb}$$

### Potassium Hexaniobate

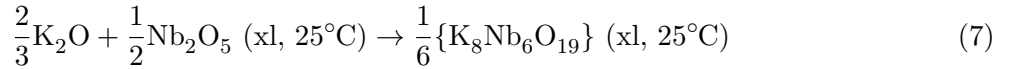
The formation enthalpy of  $\text{K}_8\text{Nb}_6\text{O}_{19}$  from constituent binary oxides is -262.7 kJ/mol Nb. The correction of 69 kJ/mol  $\text{H}_2\text{O}$  for lattice water has been applied as seen in Table S2.



$$\Delta H_5 = \Delta H_{ds} = 98.72 \pm 1.22 \text{kJ/mol Nb}$$



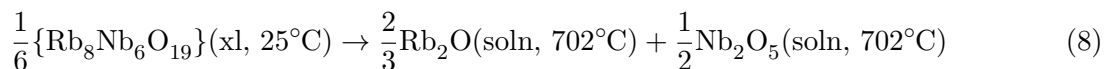
$$\Delta H_6 = \Delta H_{ds}(\text{K}_2\text{O}) = -318.0 \pm 3.1 \text{kJ/mol Nb}$$



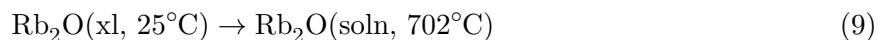
$$\Delta H_7 = \Delta H_f^{ox}(\text{K}_8\text{Nb}_6\text{O}_{19}) = -\Delta H_5 + \frac{1}{2}\Delta H_2 + \frac{2}{3}\Delta H_6 = -262.7 \pm 5.0 \text{kJ/mol Nb}$$

## Rubidium Hexaniobate

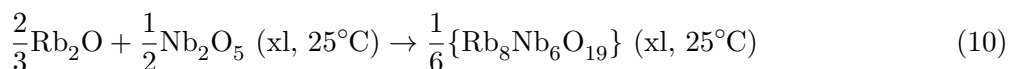
The formation enthalpy of  $\text{Rb}_8\text{Nb}_6\text{O}_{19}$  from constituent binary oxides is  $-279.3$  kJ/molNb. The correction of  $69$  kJ/mol  $\text{H}_2\text{O}$  for lattice water has been applied as seen in Table S3.



$$\Delta H_8 = \Delta H_{ds} = 104.55 \pm 1.71 \text{kJ/mol Nb}$$



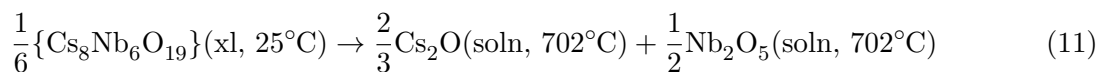
$$\Delta H_9 = \Delta H_{ds}(\text{Rb}_2\text{O}) = -332.6 \pm 2.2 \text{kJ/mol Nb}$$



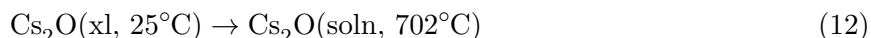
$$\Delta H_{10} = \Delta H_f^{ox}(\text{Rb}_8\text{Nb}_6\text{O}_{19}) = -\Delta H_8 + \frac{1}{2}\Delta H_2 + \frac{2}{3}\Delta H_9 = -279.3 \pm 5.9 \text{kJ/mol Nb}$$

## Cesium Hexaniobate

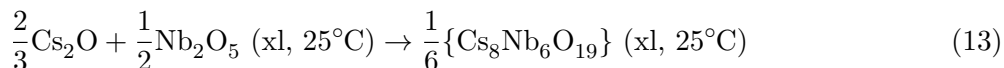
The formation enthalpy of  $\text{Cs}_8\text{Nb}_6\text{O}_{19}$  from constituent binary oxides is  $-298.7$  kJ/molNb. The correction of  $69$  kJ/mol  $\text{H}_2\text{O}$  for lattice water has been applied as seen in Table S4.



$$\Delta H_{11} = \Delta H_{ds} = 113.21 \pm 0.66 \text{kJ/mol Nb}$$



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



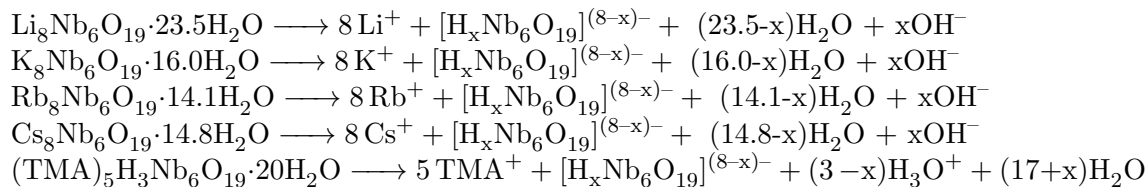
$$\Delta H_{13} = \Delta H_f^{ox}(\text{Cs}_8\text{Nb}_6\text{O}_{19}) = -\Delta H_{11} + \frac{1}{2}\Delta H_2 + \frac{2}{3}\Delta H_{12} = -298.7 \pm 4.2 \text{kJ/mol Nb}$$

Where  $\Delta H_{ds}$  are drop solution enthalpies under oxygen bubbling.

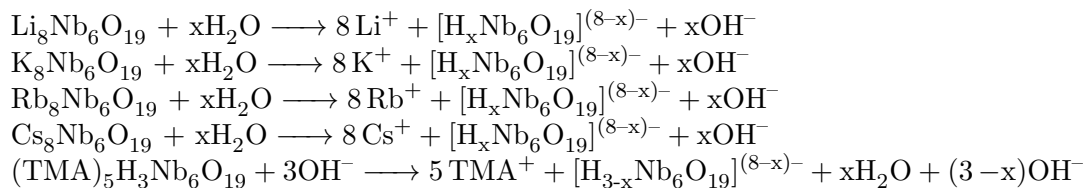
## S3 Room Temperature Dissolution Enthalpies

$\Delta H_{dis}$  was measured using a CSC 4400 isothermal microcalorimeter operated at  $25^\circ\text{C}$ . About  $5$  mg of each sample was hand pressed into a pellet and dropped one at a time into  $25.0$  g of  $\text{H}_2\text{O}$ . Each experiment was repeated in  $1\text{M}$  AOH ( $A = \text{K}, \text{Rb}, \text{Cs}, \text{TMA}$ ) for the respective clusters.

## Dissolution enthalpies of hydrated hexaniobate clusters in water



## Dissolution enthalpies of anhydrous hexaniobate clusters in water



Enthalpies of anhydrous clusters were found by subtracting the enthalpy of dissolution of lattice water ( $0.4 \text{ kJ mol}^{-1}$ )<sup>3</sup> and then adjusting for the relative molar weights of the hydrated and anhydrous clusters, namely:

$$\Delta H_{dis,anhydrous} = (\Delta H_{dis,hydrated} - (0.4 \text{ kJ mol}^{-1})(n_{\text{H}_2\text{O}})) \frac{\text{MW}(\text{Anhydrous Cluster})}{\text{MW}(\text{Hydrated Cluster})} \quad (14)$$

The calorimeter was calibrated by dissolving 15 mg pellets of KCl in water with stirring at 25 °C. Hydrated and anhydrous cluster dissolution enthalpy values in water are reported in Tables S5-S9.

### S3.1 Tables of Aqueous Dissolution Enthalpies

Table S5: Lithium Hexaniobate Dissolution Enthalpies in Water

Concentration (M $\times 10^5$ )	Dissolution Enthalpy ( $\Delta H_{dis}$ / $\text{kJ mol}^{-1}$ )	Anhydrous Dissolution Enthalpy ( $\Delta H_{dis}$ / $\text{kJ mol}^{-1}$ )
Run #1		
6.97	100.12	59.12
22.23	95.53	55.97
39.86	93.49	54.58
56.35	83.98	48.07
70.75	81.83	47.02
Run #2		
5.28	100.81	59.58
21.91	96.32	56.51
42.46	91.71	53.36
61.29	85.74	49.27
77.04	81.28	46.22

Table S6: Potassium Hexaniobate Dissolution Enthalpies in Water

Concentration (M $\times 10^5$ )	Dissolution Enthalpy ( $\Delta H_{dis}$ / kJ mol $^{-1}$ )	Anhydrous Dissolution Enthalpy ( $\Delta H_{dis}$ / kJ mol $^{-1}$ )
Run #1		
10.40	125.61	91.47
28.06	119.77	86.78
43.67	115.34	83.22
65.46	111.28	79.96
87.03	108.11	77.42
106.97	106.42	76.06
Run #2		
3.90	127.91	96.315
20.15	119.57	89.62
41.92	117.67	88.09
59.68	111.06	82.79
75.02	106.82	79.38

Table S7: Rubidium Hexaniobate Dissolution Enthalpies in Water

Concentration (M $\times 10^5$ )	Dissolution Enthalpy ( $\Delta H_{dis}$ / kJ mol $^{-1}$ )	Anhydrous Dissolution Enthalpy ( $\Delta H_{dis}$ / kJ mol $^{-1}$ )
Run #1		
8.05	111.89	90.04
34.08	105.07	84.19
65.08	101.49	81.11
89.90	101.75	81.33
120.13	94.32	74.95
159.55	91.41	72.45
Run #2		
12.50	112.57	91.19
43.61	108.54	87.72
76.37	101.64	81.79
105.65	95.08	76.15
135.25	93.17	74.51

Table S8: Cesium Hexaniobate Dissolution Enthalpies in Water

Concentration (M $\times 10^5$ )	Dissolution Enthalpy ( $\Delta H_{dis}$ / kJ mol $^{-1}$ )	Anhydrous Dissolution Enthalpy ( $\Delta H_{dis}$ / kJ mol $^{-1}$ )
Run #1		
3.99	118.38	98.07
12.27	114.30	94.48
24.09	106.55	87.67
37.78	104.16	85.57
47.58	97.25	79.51
55.81	93.22	75.96
64.28	87.48	70.92
87.62	87.03	69.19
101.64	80.36	63.33
113.91	75.75	59.28
135.96	75.14	58.75
Run #2		
7.25	117.19	97.03
25.52	104.55	85.92
58.66	90.88	73.91
76.24	82.71	66.73
134.52	74.00	59.09

Table S9: TMA Hexaniobate Dissolution Enthalpies in Water

Concentration (M $\times 10^5$ )	Dissolution Enthalpy $\Delta H_{dis}$ / kJ mol $^{-1}$	Anhydrous Dissolution Enthalpy $\Delta H_{dis}$ / kJ mol $^{-1}$
Run #1		
4.88	-47.16	-44.52
33.72	-44.74	-42.65
61.103	-43.68	-41.82
82.60	-43.04	-41.33
106.62	-41.15	-39.86
126.62	-40.17	-39.11
Run #2		
7.93	-46.68	-44.15
38.11	-43.72	-41.85
81.43	-42.37	-40.91



### S3.2 Tables of 1M Parent Hydroxide Dissolution Enthalpies

Each experiment was repeated in 1M AOH, (A = K, Rb, Cs, TMA) for the respective clusters. Enthalpies are reported in tables S10-S13. Lithium was omitted due to its insolubility.

Table S10: Potassium Hexaniobate Dissolution Enthalpies in 1M KOH

Concentration (M $\times 10^5$ )	Dissolution Enthalpy ( $\Delta H_{dis}$ / kJ mol $^{-1}$ )	Anhydrous Dissolution Enthalpy ( $\Delta H_{dis}$ / kJ mol $^{-1}$ )
Run #1		
9.31	10.29	-1.14
36.41	8.95	-2.21
62.19	12.78	0.86
80.68	11.63	-0.06
98.17	13.16	1.16
Run #2		
14.09	9.84	-1.15
60.42	9.31	-1.92

Table S11: Rubidium Hexaniobate Dissolution Enthalpies in 1M RbOH

Concentration (M $\times 10^5$ )	Dissolution Enthalpy ( $\Delta H_{dis}$ / kJ mol $^{-1}$ )	Anhydrous Dissolution Enthalpy ( $\Delta H_{dis}$ / kJ mol $^{-1}$ )
Run #1		
15.27	56.97	43.38
49.98	57.79	44.09
84.87	57.77	44.07
122.68	53.41	40.32
Run #2		
15.19	55.43	49.83
59.00	53.67	48.07
131.79	59.10	50.62

Table S12: Cesium Hexaniobate Dissolution Enthalpies in 1M CsOH

Concentration (M $\times 10^5$ )	Dissolution Enthalpy ( $\Delta H_{dis}$ / kJ mol $^{-1}$ )	Anhydrous Dissolution Enthalpy ( $\Delta H_{dis}$ / kJ mol $^{-1}$ )
Run #1		
5.73	35.62	25.37
26.08	37.37	26.90
57.41	34.13	24.06
73.45	32.28	22.43
96.24	30.35	20.74
Run #2		
12.66	34.71	24.57
48.34	33.90	23.86
106.05	31.94	22.14

Table S13: TMA Hexaniobate Dissolution Enthalpies in 1M TMAOH

Concentration (M $\times 10^5$ )	Dissolution Enthalpy $\Delta H_{dis}$ / kJ mol $^{-1}$	Anhydrous Dissolution Enthalpy $\Delta H_{dis}$ / kJ mol $^{-1}$
Run #1		
8.52	-196.79	-160.31
36.08	-191.05	-155.93
69.96	-188.11	-153.66
96.52	-186.23	-152.20
118.58	-182.55	-149.35
Run #2		
40.97	-191.50	-156.28
82.99	-185.48	-151.62
137.76	-180.05	-147.42

### S3.3 Dissolution Enthalpy Plots Uncorrected for Lattice Water

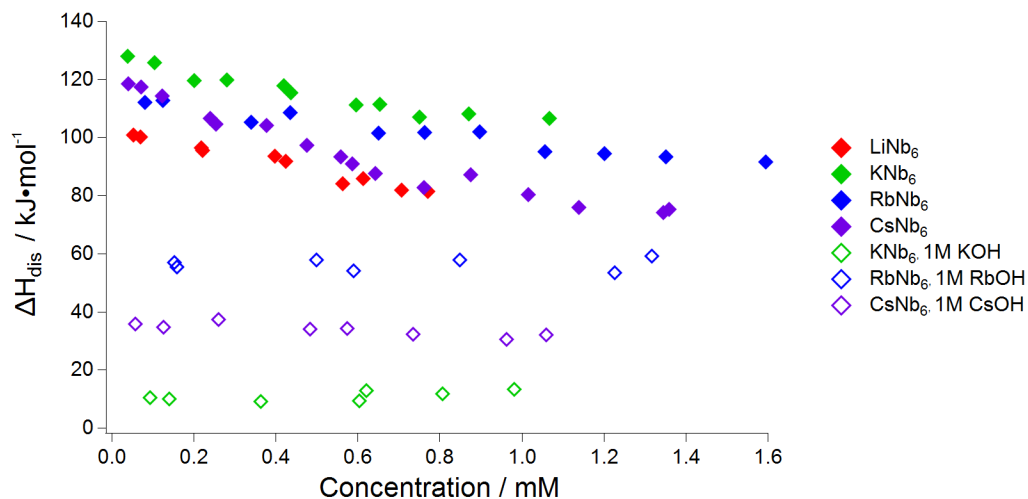


Figure S1: Enthalpies of dissolution for hydrated alkali metal salts of hexaniobate in water and in 1M solutions of their parent hydroxide, uncorrected for lattice water.

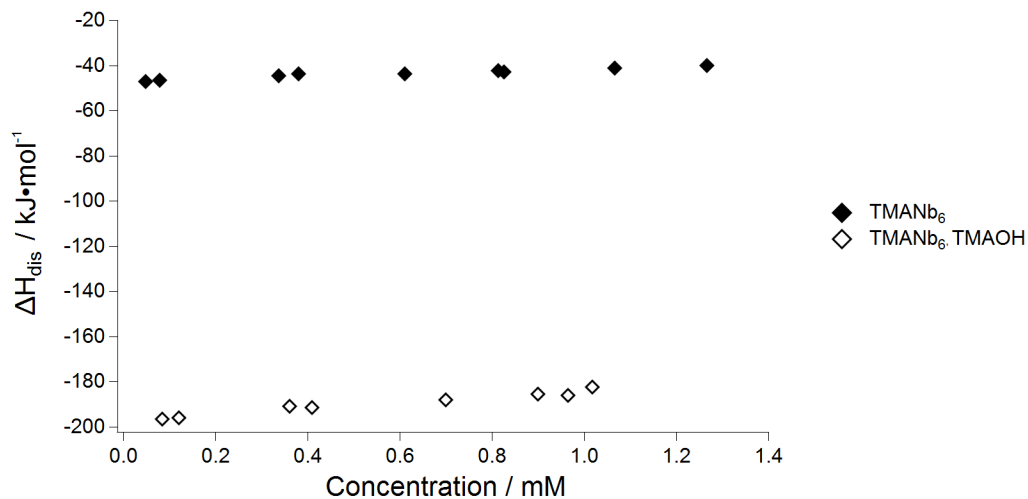


Figure S2: Enthalpies of dissolution for hydrated TMA hexaniobate in water and in 1M solutions of their parent hydroxide, uncorrected for lattice water.

## S4 Supplementary Characterization

### S4.1 Synthesis

#### Potassium Hexaniobate ( $\text{K}_8\text{Nb}_6\text{O}_{19}\cdot 16.0\text{H}_2\text{O}$ )<sup>4</sup>

2.13 g of  $\text{Nb}_2\text{O}_5 \cdot x\text{H}_2\text{O}$  were slowly added to 10 mL of 3M KOH at 90 °C and stirred such that the solution was allowed to become fully transparent after each aliquot. After the all of the solid had dissolved, the solution was microfiltered and allowed to crystallize at room temperature. Well-formed crystals formed after 2 days. These crystals were filtered under vacuum, washed with 2-propanol, and dried in air.

Full formula:  $\text{K}_8\text{Nb}_6\text{O}_{35}\text{H}_{32}$ .  $M_W = 1461.86 \text{ g mol}^{-1}$ . Atomic ratios, calculated (found): K/Nb: 1.33 (1.39). Water content (%), crystallographic (TGA 22-600°C in air): 16.0 (19.76).

#### Rubidium Hexaniobate ( $\text{Rb}_8\text{Nb}_6\text{O}_{19}\cdot 14.1\text{H}_2\text{O}$ )<sup>4</sup>

2.10 g of  $\text{Nb}_2\text{O}_5 \cdot x\text{H}_2\text{O}$  were slowly added to 5.0 g of 50 wt% RbOH solution at 90 °C and stirred such that the solution was allowed to become fully transparent after each aliquot. After all of the solid had dissolved, the solution was microfiltered and allowed to crystallize at room temperature. Well-formed crystals formed after 2 days. These crystals were filtered under vacuum, washed with 2-propanol, and dried in air.

Full formula:  $\text{Rb}_8\text{Nb}_6\text{O}_{33.1}\text{H}_{28.2}$ .  $M_W = 1799.18 \text{ g mol}^{-1}$ . Atomic ratios, calculated (found): Rb/Nb: 1.33 (1.33). Water content (%), crystallographic (TGA 22-600°C in air): 14.1 (14.13).

#### Cesium Hexaniobate ( $\text{Cs}_8\text{Nb}_6\text{O}_{19}\cdot 14.8\text{H}_2\text{O}$ )<sup>4</sup>

3.42 g of  $\text{Nb}_2\text{O}_5 \cdot x\text{H}_2\text{O}$  were slowly added to 10.0 g of 50 wt% CsOH solution at 90 °C and stirred such that the solution was allowed to become fully transparent after each aliquot. After all of the solid had dissolved, the solution was microfiltered and allowed to crystallize at room temperature. Well-formed crystals formed after 2 days. These crystals were filtered under vacuum, washed with 2-propanol, and dried in air.

Full formula:  $\text{Cs}_8\text{Nb}_6\text{O}_{33.8}\text{H}_{29.6}$ .  $M_W = 2191.29 \text{ g mol}^{-1}$ . Atomic ratios, calculated (found): Cs/Nb: 1.33 (1.34). Water content (%), crystallographic (TGA 22-600°C in air): 14.8 (12.19).

#### Lithium Hexaniobate ( $\text{Li}_8\text{Nb}_6\text{O}_{19}\cdot 23.5\text{H}_2\text{O}$ )<sup>4</sup>

1.00 g of  $\text{Cs}_8\text{Nb}_6\text{O}_{19} \cdot 14\text{H}_2\text{O}$  was dissolved in 1.0 mL of  $\text{H}_2\text{O}$  at room temperature. This solution was then added dropwise to 25.0 mL of 1M LiOH solution and stirred. A precipitate began to form almost immediately. The solution was further stirred for 30 minutes to allow for more precipitate to form. The solution was then filtered under vacuum, washed with 2-propanol, and dried in air.

Full formula:  $\text{Li}_8\text{Nb}_6\text{O}_{42.5}\text{H}_{47}$ .  $M_W = 1340.32 \text{ g mol}^{-1}$ . Water content (%), crystallographic (TGA 22-600°C in air): 23.5 (31.59).

#### Tetramethylammonium Hexaniobate ( $[(\text{CH}_3)_4\text{N}]_5\text{H}_3\text{Nb}_6\text{O}_{19}\cdot 20\text{H}_2\text{O}$ )<sup>5</sup>

2.0 g of  $\text{Nb}_2\text{O}_5 \cdot x\text{H}_2\text{O}$  were slowly added to 10.0 mL of 25 wt% tetramethylammonium hydroxide (TMAOH) solution at 90 °C and stirred such that the solution was allowed to become fully transparent after each aliquot. After all of the solid had dissolved, the solution was microfiltered. 40 mL

of 2-propanol was added to the microfiltered solution. The resultant suspension was centrifuged, the supernatant was removed, and 40 mL of 2-propanol was again added. The solution was then filtered under vacuum, and dried at 60 °C under vacuum.

Full formula:  $C_{20}N_5Nb_6O_{39}H_{100}$ .  $M_W = 1595.48 \text{ g mol}^{-1}$ . Water content, 20.0 (from crystal structure).

## S4.2 Thermogravimetric Analysis (TGA)

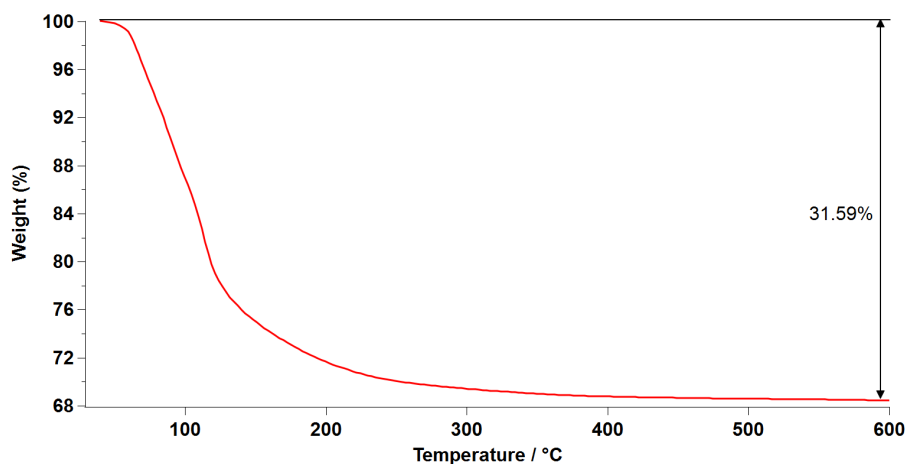


Figure S3: Thermogravimetric Analysis curve for LiNb<sub>6</sub>

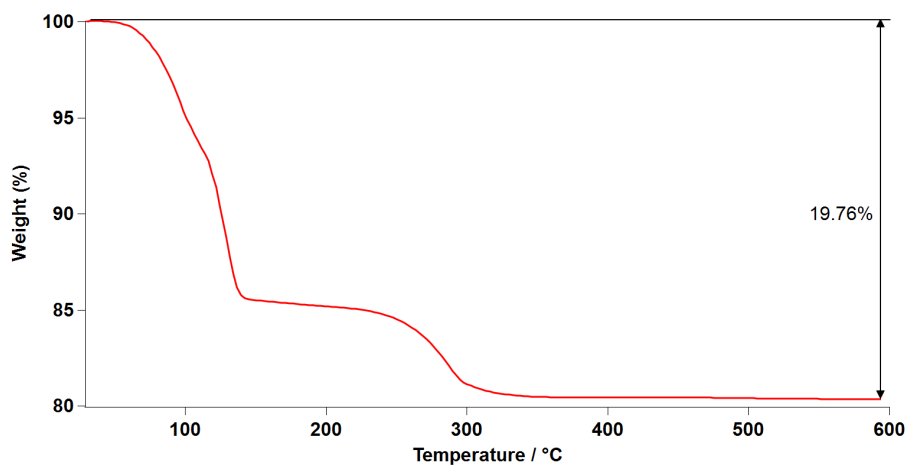


Figure S4: Thermogravimetric Analysis curve for K<sub>8</sub>Nb<sub>6</sub>O<sub>19</sub>.

Thermogravimetric analysis could not be performed for TMANb<sub>6</sub>, due to TMA<sup>+</sup> being unstable at 600 °C

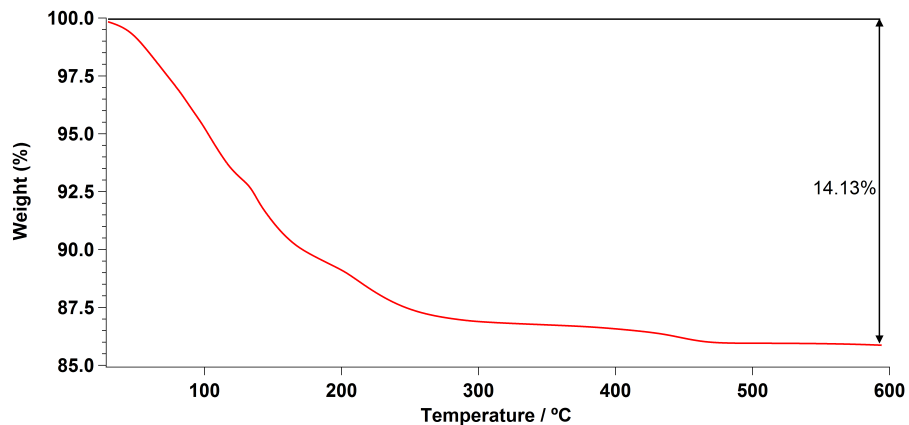


Figure S5: Thermogravimetric Analysis curve for  $\text{RbNb}_6$

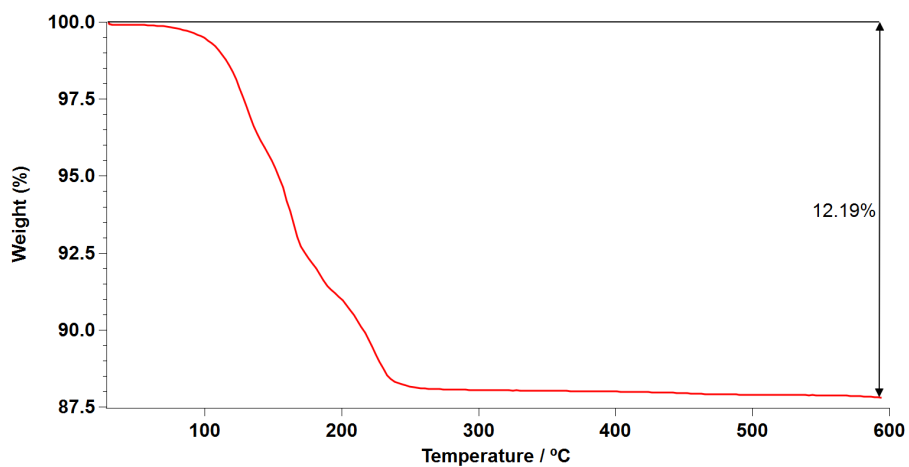
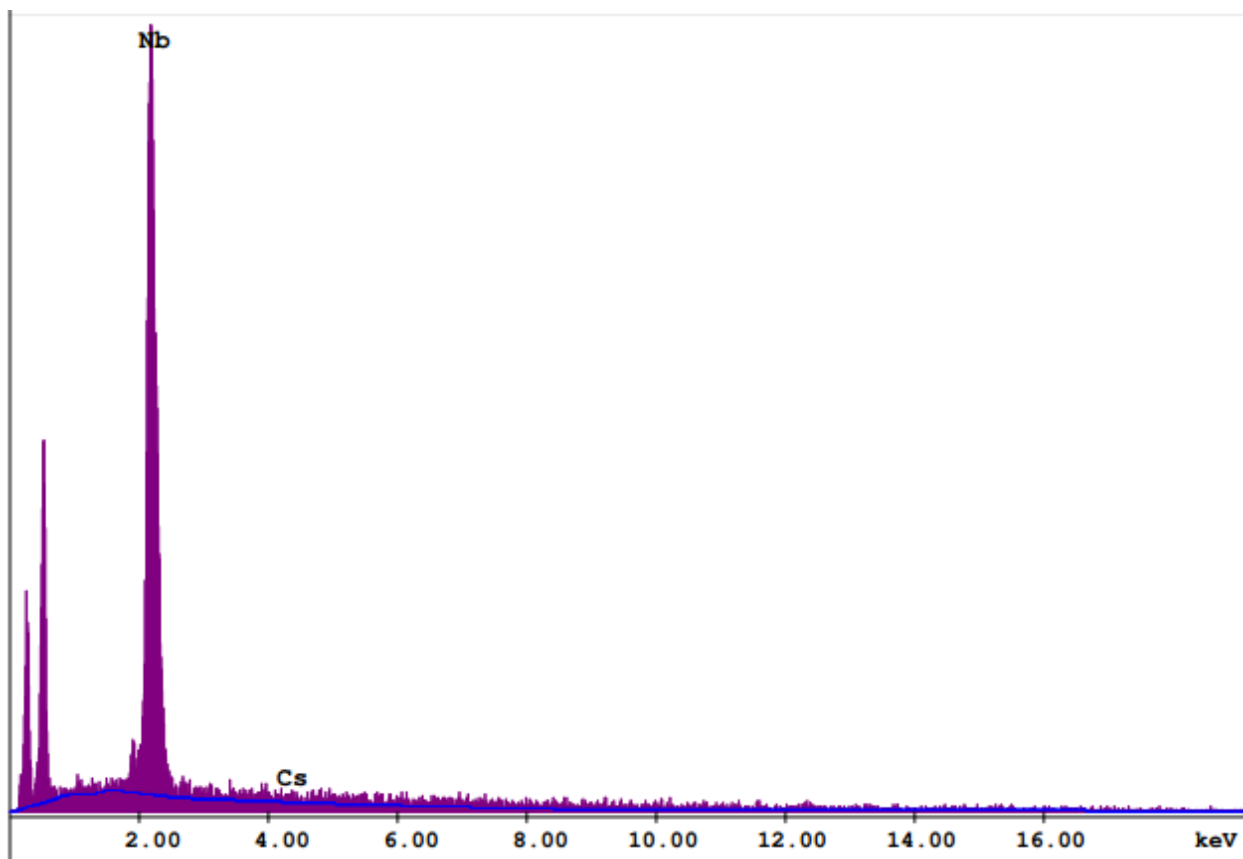


Figure S6: Thermogravimetric Analysis curve for  $\text{Cs}_8\text{Nb}_6\text{O}_{19}$

### S4.3 Elemental Analysis

Elemental analysis was not performed on tetramethylammonium hexaniobate, due to the lack of reliability in measuring the lighter elements in the  $\text{TMA}^+$  counter-cations.



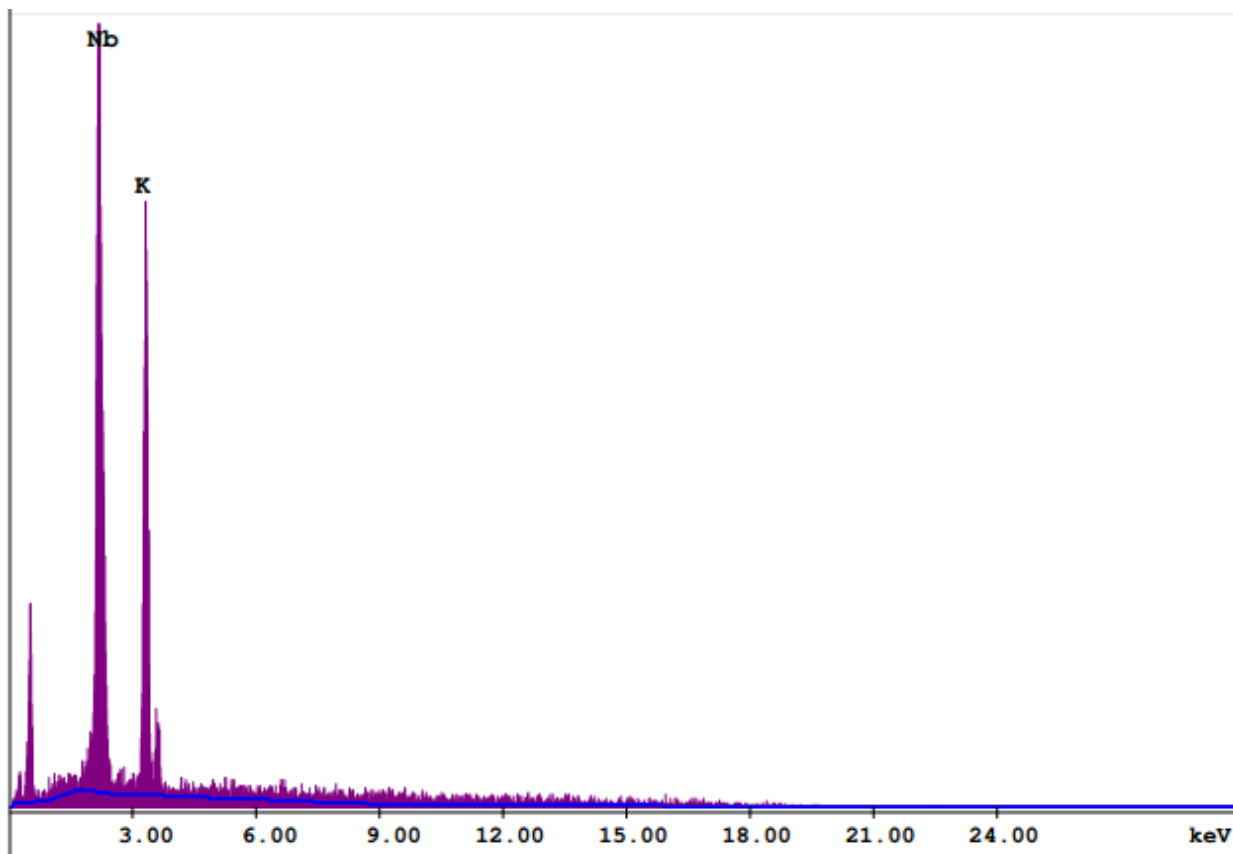
**EDAX ZAF Quantification (Standardless)**

**Element Normalized**  
**SEC Table : Default**

Element	Wt %	At %	K-Ratio	Z	A	F
NbL	97.77	98.43	0.9694	1.0018	0.9896	1.0002
CsL	2.23	1.57	0.0177	0.9280	0.8559	1.0000
Total	100.00	100.00				

Element	Net Inte.	Bkqd Inte.	Inte. Error	P/B
NbL	974.68	25.32	1.65	38.50
CsL	8.86	16.46	36.70	0.54

Figure S7: Sample Elemental Analysis spectrum for  $\text{LiNb}_6$ . Due to Li being too small for reliable measurement, it is instead demonstrated that the amount of remaining Cs from the starting material is indistinguishable from the background ( $P/B = 0.54$ ).



**EDAX ZAF Quantification (Standardless)**

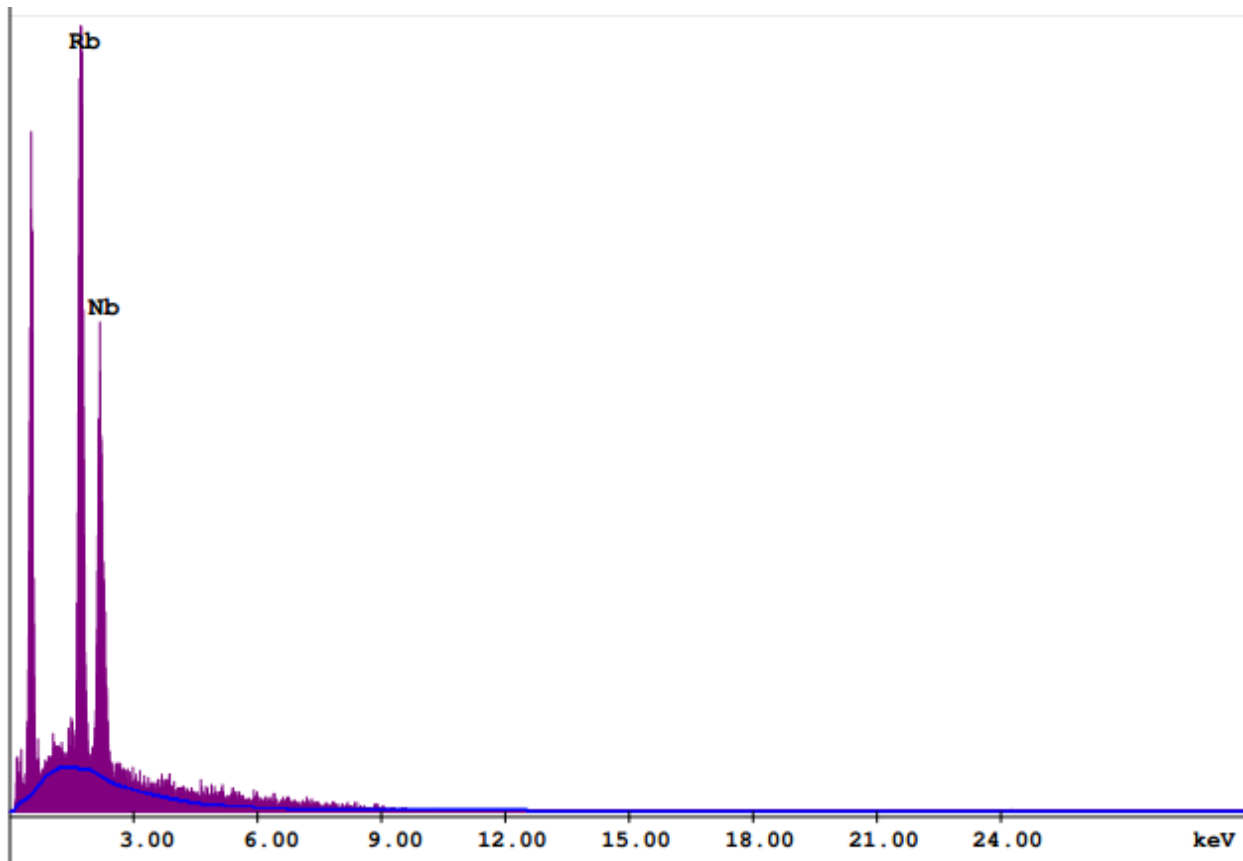
Element Normalized  
SEC Table : Default

Element	Wt %	At %	K-Ratio	Z	A	F
NbL	63.38	42.15	0.6100	0.9335	1.0229	1.0078
K K	36.62	57.85	0.2892	1.0924	0.7230	1.0000
Total	100.00	100.00				

Element	Net Inte.	Bkqd Inte.	Inte. Error	P/B
NbL	207.62	4.72	1.84	43.97
K K	156.69	4.86	2.14	32.26

Figure S8: Sample Elemental Analysis spectrum for  $\text{KNb}_6$ .





**EDAX ZAF Quantification (Standardless)**

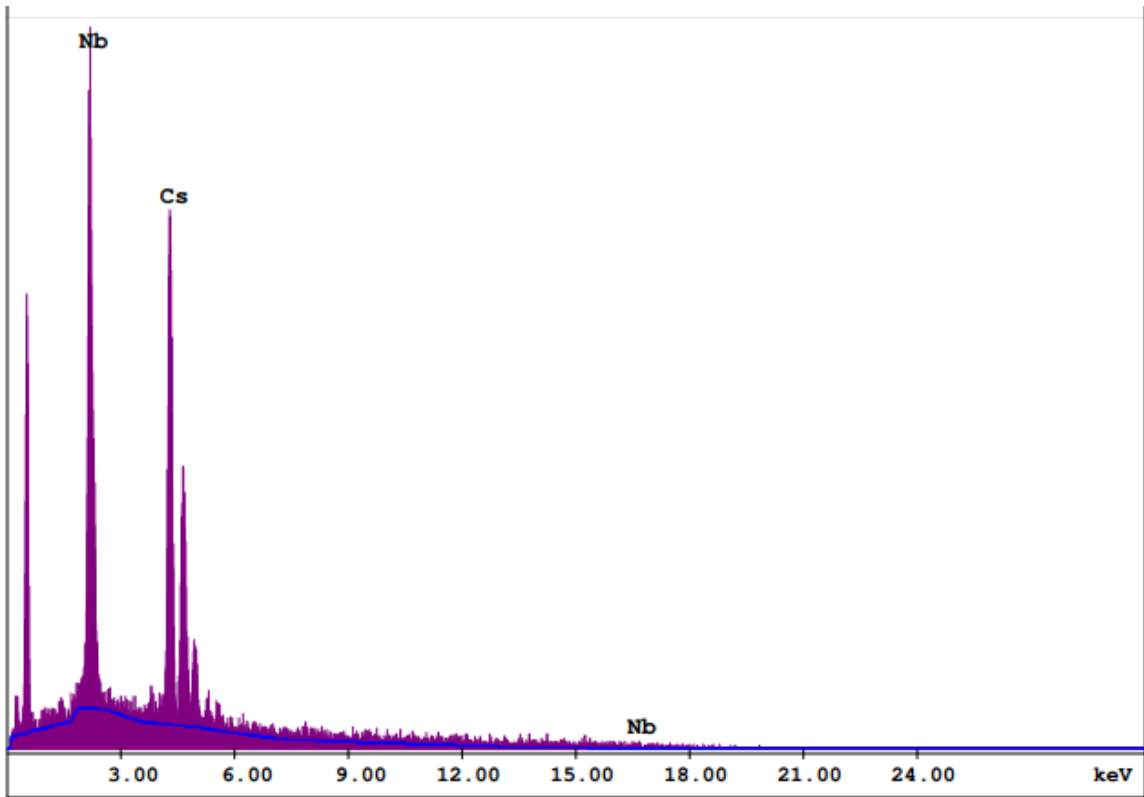
**Element Normalized**

**SEC Table : Default**

Element	Wt %	At %	K-Ratio	Z	A	F
RbL	54.51	56.57	0.5347	0.9969	0.9783	1.0057
NbL	45.49	43.43	0.3857	1.0041	0.8444	1.0000
Total	100.00	100.00				

Element	Net Inte.	Bkqd Inte.	Inte. Error	P/B
RbL	290.89	19.96	1.80	14.58
NbL	156.26	16.96	2.55	9.21

Figure S9: Sample Elemental Analysis spectrum for RbNb<sub>6</sub>.



**EDAX ZAF Quantification (Standardless)**  
**Element Normalized**  
**SEC Table : Default**

Element	Wt %	At %	K-Ratio	Z	A	F
NbL	35.43	43.98	0.2817	1.0561	0.7489	1.0054
CsL	64.57	56.02	0.5921	0.9715	0.9438	1.0000
Total	100.00	100.00				

Element	Net Inte.	Bkgd Inte.	Inte. Error	P/B
NbL	176.38	14.54	1.85	12.13
CsL	184.37	11.16	1.78	16.52

Figure S10: Sample Elemental Analysis spectrum for CsNb<sub>6</sub>.

## References

- [1] Alexandra Navrotsky. *Physics and Chemistry of Minerals*, 24(3):222–241, 1997.
- [2] Alexandra Navrotsky. *MRS Bulletin*, 22(05):35–41, 1997.
- [3] Richard A Robie, BS Hemmingway, and James Russell Fisher. *Geol. Surv. Bull.*, 1:1452–1452, 1978.
- [4] May Nyman, Todd M Alam, Francois Bonhomme, Mark A Rodriguez, Colleen S Frazer, and Margaret E Welk. *Journal of Cluster Science*, 17(2):197–219, 2006.
- [5] Lauren B Fullmer, Ryan H Mansergh, Lev N Zakharov, Douglas A Keszler, and May Nyman. *Crystal Growth & Design*, 15(8):3885–3892, 2015.