Supporting Information

Metastable Layered Lithium-rich Niobium and Tantalum Oxides via Nearly Instantaneous Ion Exchange

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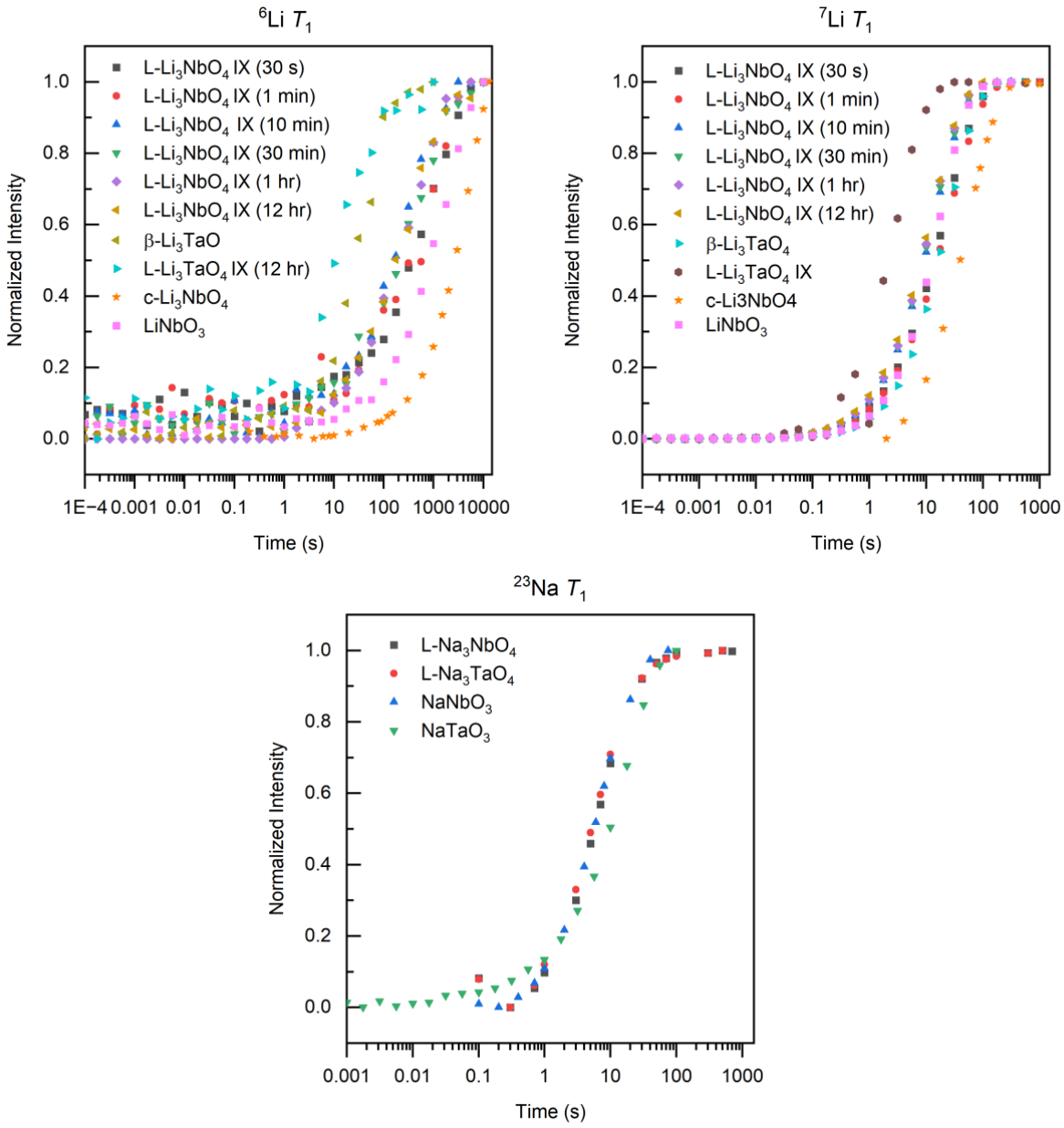
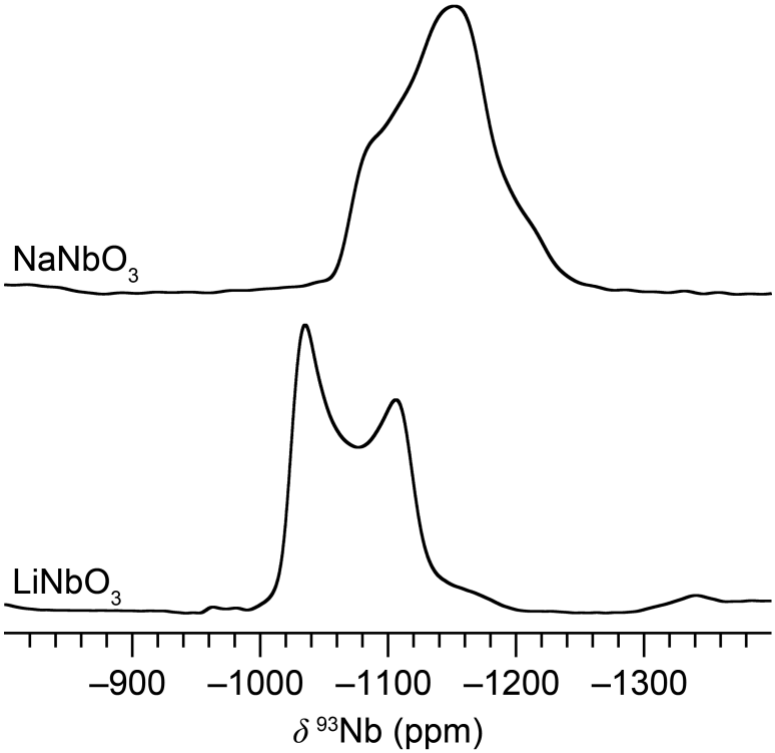
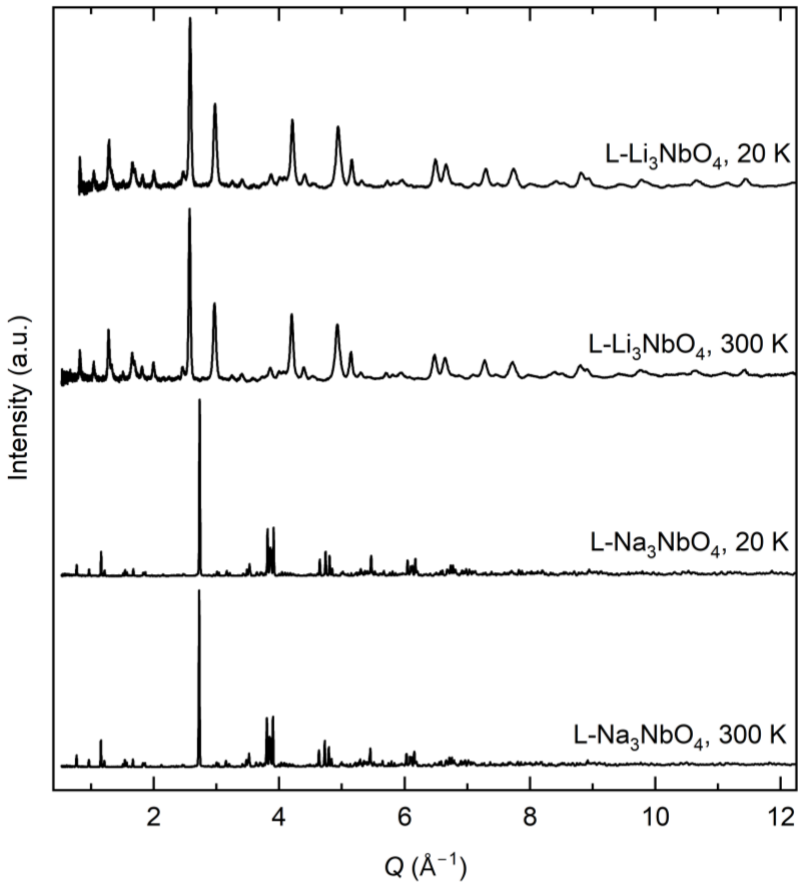


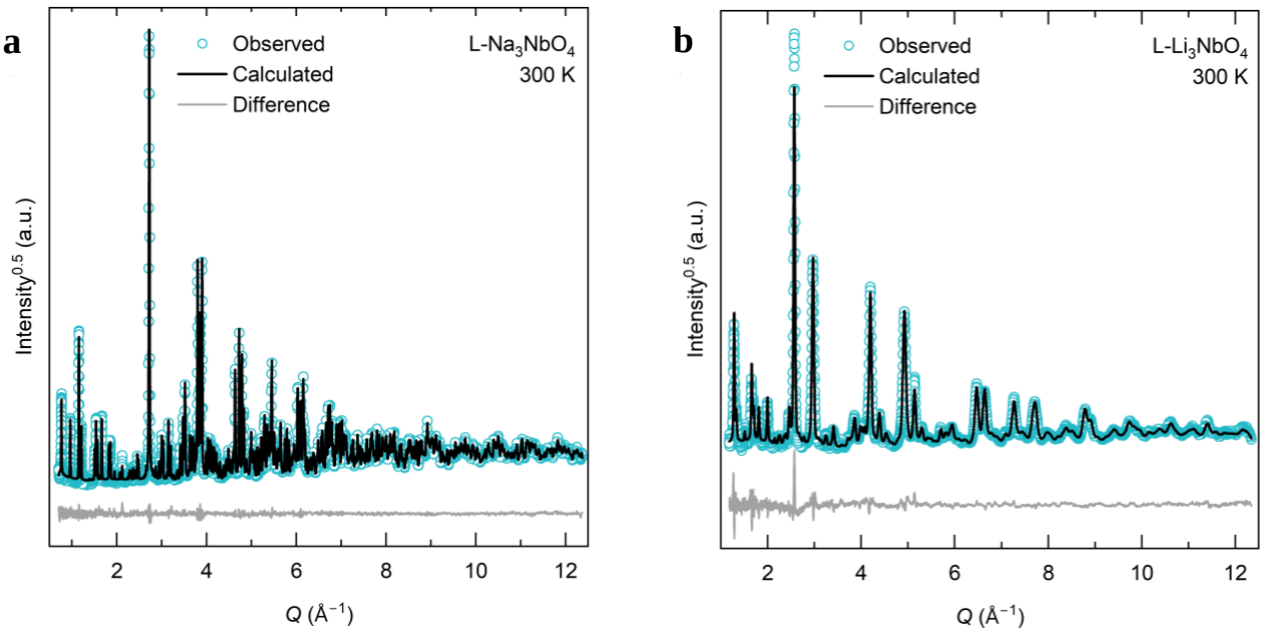
Supplementary Figure S1. T_1 magnetization saturation recovery curves of ^{6}Li, ^{7}Li, and ^{23}Na for A_3MO_4 (A = Li, Na; M = Nb, Ta).



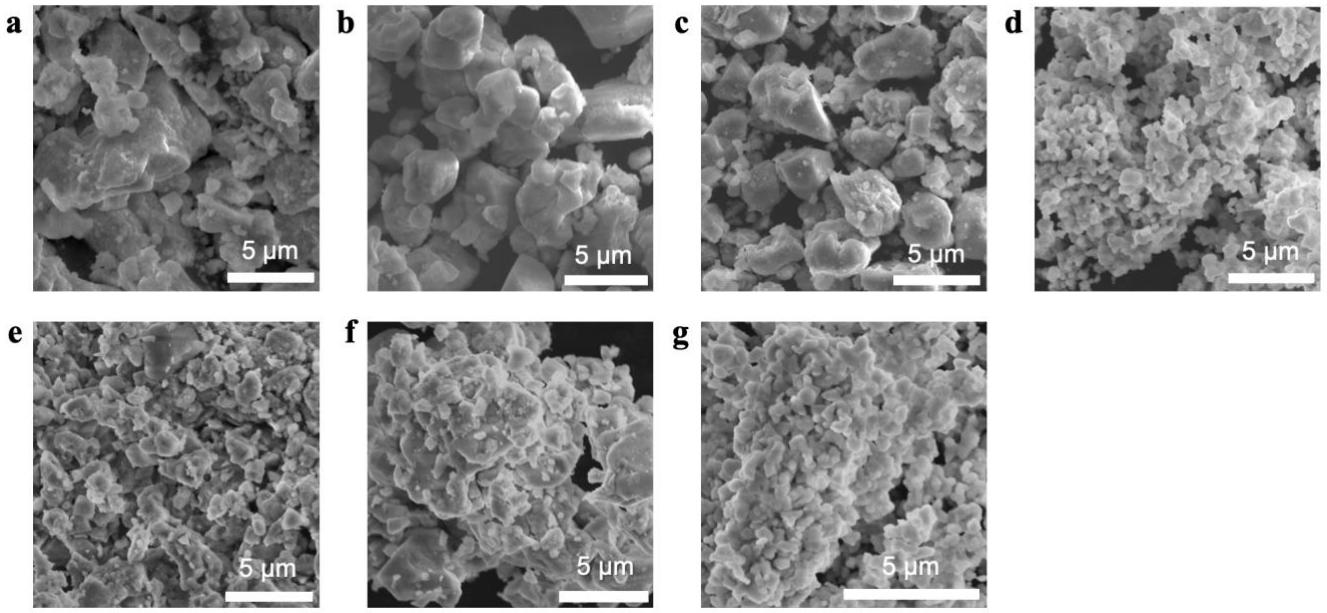
Supplementary Figure S2. ^{93}Nb NMR spectra of $LiNbO_3$ and $NaNbO_3$ at 30 kHz MAS and 9.4 T.



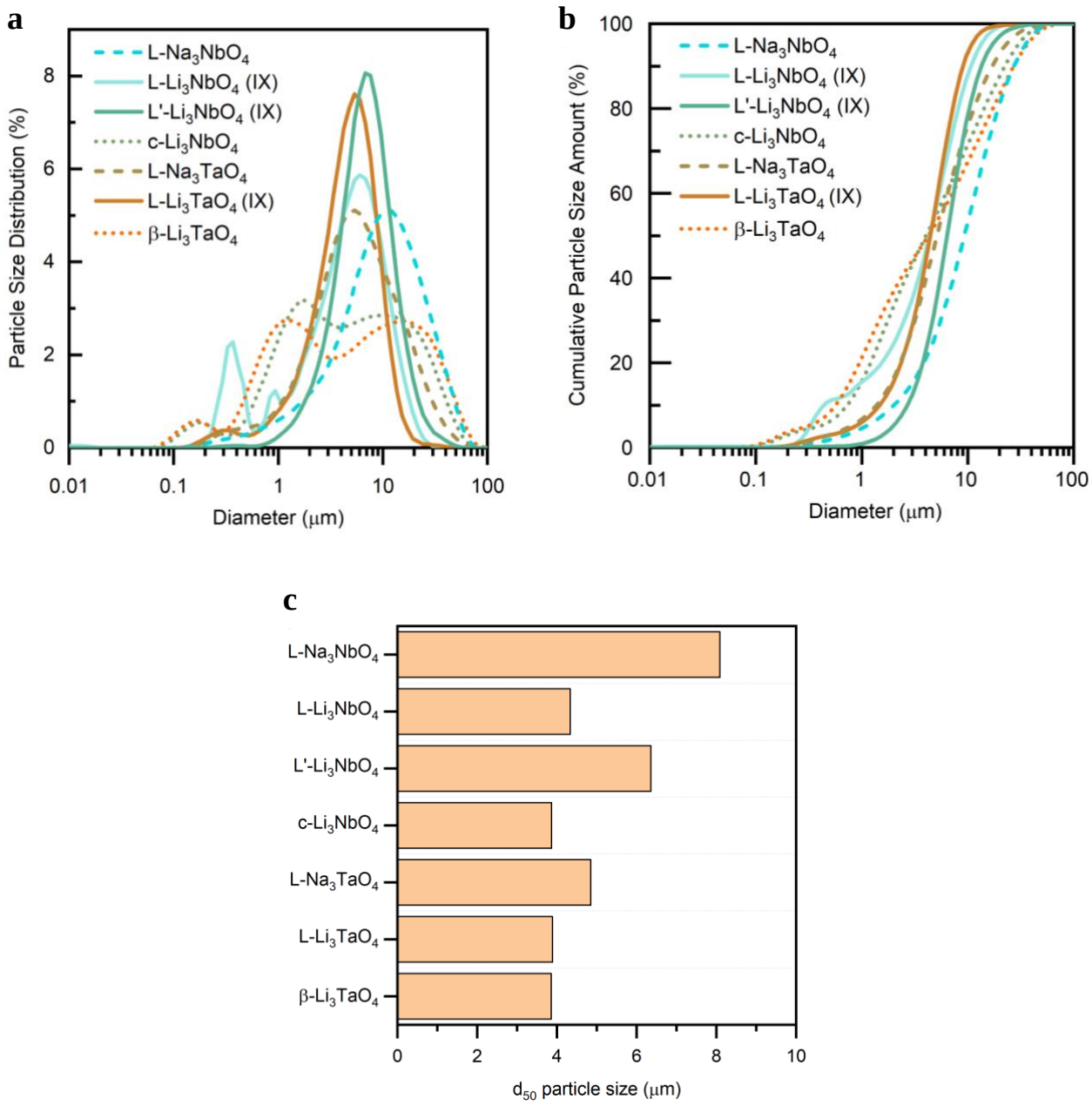
Supplementary Figure S3. Neutron powder diffraction patterns of L-Na_3NbO_4 and L-Li_3NbO4 at 20 K and 300 K.



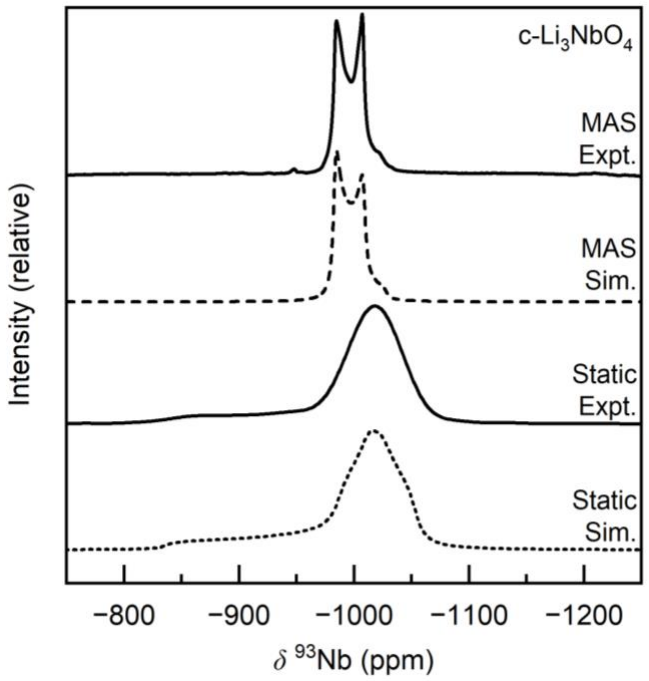
Supplementary Figure S4. Rietveld refinement of L-Li_3NbO_4 and L-Na_3NbO_4 with neutron powder diffraction data measured at 300 K. Square-root intensity is shown to better depict data to high *Q*.



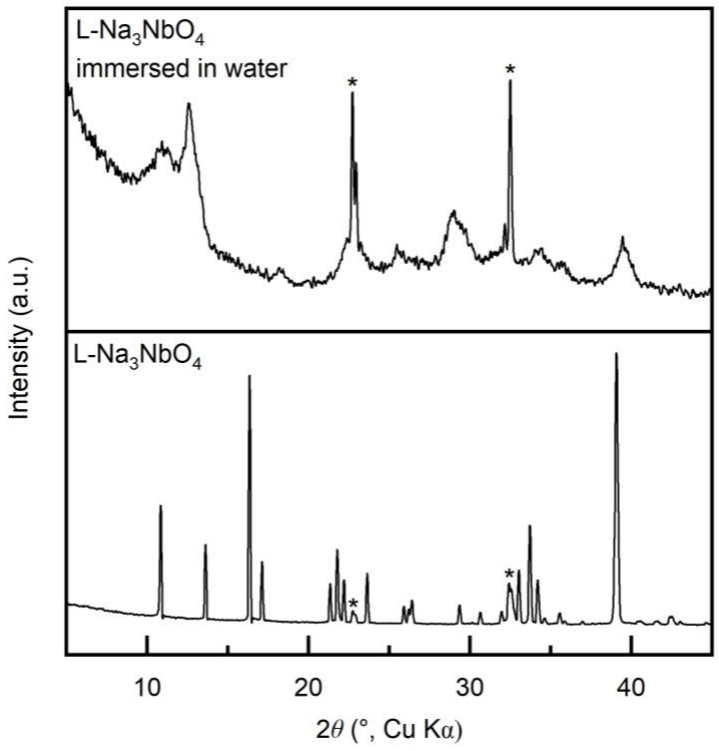
Supplementary Figure S5. Scanning electron microscopy images of A_3MO_4 (*A* = Li, Na; *M* = Nb, Ta). (a) L-Na_3NbO_4, (b) L'-Li_3NbO_4 (1 min IX), (c) L-Li_3NbO_4 (12 hours IX), (d) c-Li_3NbO_4, (e) L-Na_3TaO_4, (f) L-Li_3TaO_4, (g) β-Li_3TaO4.



Supplementary Figure S6. Particle size distributions of A_3MO_4 (A = Li, Na; M = Nb, Ta). Particle size distribution by (a) volume percentage, (b) cumulative distribution, and (c) d_{50}.



Supplementary Figure S7. ^{93}Nb NMR spectra of c-Li_3NbO_4 under static and 30 kHz MAS conditions at 9.4 T. Spectra are intensity normalized. Simulations are fit with the parameters listed in Table 3.



Supplementary Figure S8. Water instability of L-Na_3NbO_4. X-ray diffraction patterns of L-Na_3NbO_4 before and after immersion in water for 1 hr. The water-immersed sample was dried overnight in air at 80 °C prior to XRD. Asterisks denote observed $NaNbO_3$ reflections. The $NaNbO_3$ impurity is water stable.

Supplementary Table S1. T_1 relaxation times of ^{6}Li, ^{7}Li, and ^{23}Na for A_3MO_4 (A = Li, Na; M = Nb, Ta).

		^{6}Li T_1 (s)	**^{7}Li T_1 (s)**
L-Li_3NbO_4 (IX)	30 s	>800	19.9
	1 min	>600	22.7
	10 min	237	13.3
	30 min	305	12.7
	1 hr	340	12.2
	12 hr	456	11.7
c-Li_3NbO_4		4040	59
$LiNbO_3$		1236	17.6
L-Li_3TaO_4 (IX)		15.5	3.2
β-Li_3TaO_4		43.0	23.7
		^{23}Na T_1 (s)	
L-Na_3NbO_4		8.4	
$NaNbO_3$		7.9	
L-Na_3TaO_4		7.6	
$NaTaO_3$		13.5	

Supplementary Table S2. Experimental ^{6}Li, ^{7}Li, ^{23}Na, and ^{93}Nb NMR measurement times.

	^{6}Li		**^{7}Li**		**^{23}Na**		**^{93}Nb**	
	d1 (s)	No. FIDs	d1 (s)	No. FIDs	d1 (s)	No. FIDs	d1 (s)	No. FIDs
L-Li_3NbO_4 (IX) 30 s	4000	36	100	8	40	120	0.5	8192
L-Li_3NbO_4 (IX) 1 min	3000	24	115	4	40	120	0.5	8192
L-Li_3NbO_4 (IX) 10 min	1190	44	67	8	40	120	0.5	8192
L-Li_3NbO_4 (IX) 30 min	2500	36	65	8	40	120	0.5	8192
L-Li_3NbO_4 (IX) 1 hr	1750	40	65	4	40	120	0.5	8192
L-Li_3NbO_4 (IX) 12 hr	2110	20	60	4	40	120	0.5	8192
L-Li_3NbO_4 (IX) 1 min unwashed	n/r	n/r	n/r	n/r	40	1320	0.5	8192
L-Li_3NbO_4 (IX) 12 hr unwashed	n/r	n/r	n/r	n/r	40	1320	0.5	16,384
c-Li_3NbO_4	13,000	1	300	1	n/a	n/a	2	192
L-Li_3TaO_4 (IX)	80	184	16	16	40	1472	n/a	n/a
β-Li_3TaO_4	200	284	80	16	n/a	n/a	n/a	n/a
L-Na_3NbO_4	n/a	n/a	n/a	n/a	15	1024	4	592
$NaNbO_3$	n/a	n/a	n/a	n/a	40	60	0.5	256
L-Na_3TaO_4	n/a	n/a	n/a	n/a	40	128	n/a	n/a
$NaTaO_3$	n/a	n/a	n/a	n/a	40	60	n/a	n/a

n/a = not applicable; n/r = not recorded

Supplementary Table S3. DFT calculated lattice and NMR parameters for layered A_3MO_4 (A = Li, Na; M = Nb, Ta).

Layered *C*2/*m*	**Na_3NbO_4**	**Li_3NbO_4**	**Na_3TaO_4**	**Li_3TaO_4**
a (Å)	11.2122	10.3770	11.2571	10.4328
b (Å)	13.1336	12.0303	13.1432	12.0683
c (Å)	5.8035	5.1865	5.8262	5.2108
β (°)	109.33	109.23	109.66	109.55
Volume ($Å^3$)	806.397	611.337	811.741	618.229

Supplementary Table S4. Calculated lattice and NMR parameters for L-Li_3NbO_4 containing residual Na^+.

	Site	σ_{iso} (ppm)	δ_{aniso} (ppm)	η_{CS}	C_Q (kHz)[a]	η_Q
L-$(Na_{1/6}Li_{5/6})_3NbO_4$ a = 10.8887 Å b = 12.1952 Å c = 5.3497 Å β = 112.6°	Na1	530.98	13.47	0.71	1.7	0.71
	Li2	90.42	–2.61	0.35	–0.12	0.34
	Li3	89.92	–1.77	0.32	0.14	0.40
	Li4	91.20	2.13	0.45	–0.13	0.25
	Li5	90.55	1.18	0.29	–0.065	0.62
	Li6	89.01	–2.53	0.59	–0.28	0.15
	Nb1	277.98	–179.76	0.43	–28.0	0.47
	Nb2	302.91	120.83	0.89	–17.2	0.84
L-$(Na_{1/6}Li_{5/6})_3NbO_4$ a = 10.4812 Å b = 12.6983 Å c = 5.1770 Å β = 107.7°	Li1	89.26	–1.65	0.11	0.054	0.88
	Na2	531.10	19.25	0.34	–1.9	0.40
	Li3	90.07	–0.91	0.49	–0.12	0.54
	Li4	90.98	–0.67	0.68	0.03	0.84
	Li5	89.72	–0.75	0.28	0.094	0.06
	Li6	89.75	–3.44	0.41	–0.092	0.29
	Nb1	248.59	–92.87	0.27	46.7	0.13
	Nb2	299.71	121.24	0.35	12.7	0.76
L-$(Na_{1/3}Li_{2/3})_3NbO_4$ a = 10.6024 Å b = 12.3521 Å c = 5.5097 Å β = 108.6°	Li1	89.24	–0.75	0.27	–0.054	0.62
	Li2	90.28	–1.51	0.81	0.095	0.78
	Na3	531.69	–4.31	0.58	1.8	0.84
	Li4	90.99	–1.01	0.54	0.10	0.29
	Li5	90.15	–1.23	0.11	–0.081	0.85
	Li6	89.63	–2.77	0.48	–0.15	0.01
	Nb1	280.00	–89.77	0.50	38.8	0.32
	Nb2	293.59	93.28	0.64	–10.1	0.05
L-$(Na_{1/12}Li_{11/12})_3NbO_4$ a = 10.4278 Å b = 12.0855 Å c = 5.3098 Å β = 109.1°	Li1	88.87	–0.56	0.30	0.031	0.34
	Li2	90.19	–1.21	0.91	0.12	0.63
	Li3	90.19	0.59	0.69	0.058	0.19
	Na4	524.95	–7.97	0.55	–1.4	0.04
	Li5	90.09	0.77	0.63	–0.048	0.75
	Li6	89.44	–3.27	0.42	–0.13	0.44
	Nb1	280.81	–151.84	0.08	44.1	0.42
	Nb2	327.43	118.91	0.92	20.8	0.75
L-$(Na_{1/6}Li_{5/6})_3NbO_4$ a = 10.5787 Å b = 12.1957 Å c = 5.4092 Å	Li1	89.21	–0.81	0.27	–0.026	0.50
	Li2	90.36	3.25	0.80	–0.058	0.69
	Li3	90.00	–0.77	0.14	0.11	0.43
	Li4	90.72	1.97	0.61	–0.13	0.09
	Na5	531.55	10.47	0.26	0.40	0.54

β = 111.2°	Li6	89.97	–3.16	0.43	–0.12	0.12
	Nb1	277.17	–124.57	0.38	25.3	0.03
	Nb2	339.57	104.35	0.73	–40.2	0.10
L-$(Na_{1/12}Li_{11/12})_3NbO_4$ a = 10.5282 Å b = 12.0242 Å c = 5.2459 Å β = 108.5°	Li1	89.00	–0.65	0.64	0.044	0.27
	Li2	90.12	–3.30	0.74	0.13	0.51
	Li3	90.15	–0.56	0.32	0.052	0.96
	Li4	91.09	1.39	0.27	–0.057	0.21
	Li5	90.30	–0.39	0.46	0.11	0.37
	Na6	526.45	–27.90	0.38	1.8	0.93
	Nb1	290.94	–138.17	0.28	22.5	0.74
	Nb2	318.52	149.82	0.21	–22.0	0.47
L-$(Na_{1/3}Li_{2/3})_3NbO_4$ a = 10.7688 Å b = 13.0701 Å c = 5.2191 Å β = 108.4°	Na1	546.22	14.14	0.72	1.2	0.21
	Na2	544.21	18.27	0.56	–2.8	0.18
	Li3	89.87	–0.71	0.65	–0.14	0.49
	Li4	90.96	–1.09	0.45	–0.042	0.50
	Li5	89.83	–1.06	0.53	0.13	0.73
	Li6	89.42	–2.82	0.49	–0.20	0.01
	Nb1	234.97	–115.37	0.25	50.5	0.35
	Nb2	264.38	145.14	0.54	21.6	0.73

[a]C_Q for ^{7}Li nucleus. ^{6}Li C_Qs are scaled by $Q(^6Li)/Q(^7Li)$ = 0.808/40.1.

Supplementary Table S5. Calculated lattice and NMR parameters for L-Li_3NbO_4 containing residual H^+.

	Site	σ_{iso} (ppm)	δ_{aniso} (ppm)	η_{CS}	C_Q (kHz)[a]	η_Q
L-$(H_{1/6}Li_{5/6})_3NbO_4$ a = 10.3078 Å b = 12.3012 Å c = 5.1978 Å β = 108.0°	H1	12.24	–16.81	0.49		
	Li2	89.73	1.06	0.69	0.10	0.48
	Li3	90.28	–1.83	0.63	0.10	0.56
	Li4	90.94	–1.62	0.35	0.082	0.69
	Li5	89.98	1.36	0.03	0.087	0.24
	Li6	87.61	–4.13	0.62	–0.14	0.74
	Nb1	350.15	–274.93	0.46	–45.9	0.57
	Nb2	294.50	215.25	0.33	–30.9	0.36
L-$(H_{1/6}Li_{5/6})_3NbO_4$ a = 10.8488 Å b = 11.3108 Å c = 5.3523 Å β = 111.5°	Li1	88.08	–1.34	0.02	0.17	0.59
	H2	11.77	–8.65	0.33		
	Li3	89.88	–1.05	0.06	0.091	0.62
	Li4	88.92	3.59	0.36	–0.33	0.11
	Li5	89.10	–0.91	0.02	0.14	0.85
	Li6	90.61	–6.29	0.34	0.23	0.13
	Nb1	340.58	254.21	0.74	78.5	0.70
	Nb2	143.93	172.14	0.29	119	0.94
L-$(H_{1/3}Li_{2/3})_3NbO_4$ a = 10.9188 Å b = 12.3626 Å c = 5.7249 Å β = 122.1°	Li1	87.83	–1.54	0.93	0.23	0.95
	Li2	90.61	1.91	0.82	–0.28	0.50
	H3	18.95	–3.32	0.34		
	Li4	91.12	4.58	0.97	–0.31	0.84
	Li5	90.89	2.85	0.48	0.16	0.86
	Li6	88.18	2.63	0.12	0.30	0.99
	Nb1	175.82	–430.60	0.01	–197	0.68
	Nb2	316.66	165.63	0.15	–79.0	0.60
L-$(H_{1/12}Li_{11/12})_3NbO_4$ a = 10.6543 Å b = 11.7842 Å c = 5.3082 Å β = 114.1°	Li1	88.60	–0.75	0.62	–0.077	0.30
	Li2	90.08	–3.87	0.56	0.15	0.16
	Li3	89.51	1.47	0.46	–0.11	0.94
	H4	11.02	3.44	0.62		
	Li5	90.85	1.89	0.49	–0.084	0.82
	Li6	89.57	–2.90	0.56	–0.18	0.60
	Nb1	313.50	130.89	0.93	–27.1	0.17
	Nb2	329.66	103.11	0.38	–12.5	0.15
L-$(H_{1/6}Li_{5/6})_3NbO_4$ a = 10.6073 Å b = 12.1838 Å c = 5.0354 Å β = 89.1°	Li1	89.59	–1.51	0.03	0.073	0.52
	Li2	89.16	–1.61	0.97	–0.27	0.38
	Li3	88.81	–2.99	0.93	0.14	0.86
	Li4	89.18	–12.35	0.13	0.53	0.11
	H5	11.20	–13.05	0.01		

	Li6	89.01	–15.52	0.12	0.51	0.16
	Nb1	266.55	157.49	0.38	111	0.07
	Nb2	325.79	178.39	0.63	–50.4	0.01
L-$(H_{1/12}Li_{11/12})_3NbO_4$ a = 10.5857 Å b = 11.8977 Å c = 5.3371 Å β = 113.9°	Li1	88.72	2.09	0.35	–0.13	0.11
	Li2	90.09	–1.75	0.38	0.12	0.63
	Li3	89.81	1.67	0.84	0.10	0.99
	Li4	91.32	1.33	0.44	–0.12	0.19
	Li5	90.62	1.88	0.34	-0.10	0.32
	H6	8.09	–3.38	0.21		
	Nb1	312.43	–110.10	0.55	16.7	0.21
	Nb2	308.39	117.45	0.59	–17.5	0.01
L-$(H_{1/3}Li_{2/3})_3NbO_4$ a = 10.2121 Å b = 11.7563 Å c = 5.9172 Å β = 99.4°	H1	12.93	–19.45	0.39		
	H2	13.78	–16.22	0.01		
	Li3	89.27	–3.32	0.35	0.22	0.62
	Li4	90.30	–9.71	0.10	0.51	0.07
	Li5	89.56	–4.97	0.33	0.24	0.97
	Li6	86.07	–4.37	0.87	–0.35	0.46
	Nb1	377.60	–298.56	0.54	52.6	0.47
	Nb2	239.54	296.45	0.42	17.8	0.40

[a]C_Q for ^{7}Li nucleus. ^{6}Li C_Qs are scaled by $Q(^6Li)/Q(^7Li)$ = 0.808/40.1.