Electronic Supplementary Material (ESI) for Dalton Transactions.

Supporting Information

Reductive Lithium Insertion into B-cation deficient Niobium Perovskite Oxides

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Cation	Anion	Bond length (Å)	BVS
Ba(1)	O(1)	2.959(4) × 3	Ba+2.06
	O(1)	2.906(2) × 6	
	O(2)	2.999(4) × 3	
Ba(2)	O(1)	2.773(4) × 3	Ba+2.42
	O(2)	2.905(1) × 6	
	O(3)	2.970(3) × 3	
Ba(3)	O(2)	2.849(3) × 6	Ba+2.47
	O(3)	2.901(1) × 6	
Nb(1)	O(1)	1.895(3) × 3	Nb+4.72
	O(2)	2.145(3) × 3	
Nb(2)	O(2)	2.011(9) × 3	Nb+4.33
	O(3)	2.053(2) × 3	
Li(1)	O(1)	2.177(2) × 6	Li+0.87

Table S1: Selected bond lengths from the refined structure of $Ba_5LiNb_4O_{15}$.

Cation	Anion	Bond length (Å)	BVS
Ba(1)	O(1)	2.825(11) × 3	Ba+2.36
	O(2)	2.923(13) × 6	
	O(3)	2.900(5) × 3	
Ba(2)	O(2)	2.950(6) × 3	Ba+2.05
	O(3)	2.910(18) × 6	
	O(3)	3.008(6) × 3	
Ba(3)	O(1)	2.828(22) × 3	Ba+2.37
	O(1)	2.903(9) × 6	
	O(2)	2.932(6) × 3	
Nb/Ti(1)	O(1)	1.966(13) × 3	Nb+4.54/Ti+3.50
	O(2)	2.069(3) × 3	
Nb/Ti(2)	O(2)	2.064(5) × 3	Nb+4.41/Ti+3.40
	O(3)	1.989(26) × 3	
Nb/Ti(3)	O(3)	2.108(24) × 6	Nb+3.52/Ti+2.71
Li(1)	O(1)	2.115(13) × 6	Li+1.03

Table S2: Selected bond lengths from the refined structure of $Ba_6LiTiNb_5O_{18}$.

Atom	*x*	*y*	*z*	Fraction	U_{iso} (Å^2)
Ba(1)	0	0	0.2418(4)	1	0.041(2)
Ba(2)	1/3	2/3	0.4195(5)	1	0.041(2)
Ba(3)	2/3	1/3	0.0783(6)	1	0.041(2)
Nb/Ti(1)	1/3	2/3	0.1657(8)	0.98(1)/0.02(1)	0.022(1)
Nb/Ti(2)	2/3	1/3	0.3359(6)	0.71(1)/0.29(1)	0.022(1)
Nb/Ti(3)	0	0	0.5	0.71(1)/0.29(1)	0.022(1)
Li(1)	0	0	0	1	0.022(1)
O(1)	0.734	0.3450	0.0854	1	0.093(1)
O(2)	0.4981	0.4927	0.2470	1	0.093(1)
O(3)	0.8321	0.1633	0.4089	1	0.093(1)
$Ba_6LiTiNb_4O_{18}$ – space group P-3 : *a* = 5.7782(1) Å, *c* = 14.2293(4) Å					
χ^2 = 1.323, wRp = 5.39%, Rp = 4.44%					

Table S3: Structural parameters of $Ba_6LiTiNb_4O_{18}$ refined from X-ray powder diffraction data collected at 298K.

Atom	*x*	*y*	*z*	Fraction	U_{iso} (Å^2)
Ba/La(1)	0	0	0.2838(2)	0.61(2)/ 0.39(2)	0.082(3)
Ba/La(2)	0	0	0.1336(1)	0.89(2)/ 0.11(2)	0.082(3)
Nb/Li(1)	0	0	0.4160(2)	0.77(1)/ 0.23(1)	0.0043(3)
Nb/Li(2)	0	0	0.5	0.46(2)/ 0.54(2)	0.0043(3)
Nb(3)	0	0	0	1	0.0043(3)
O(1)	0.1690	0.8309	0.6283	1	0.026(1)
O(2)	0.1639	0.8360	0.4529	1	0.026(1)
$Ba_3LaLiNb_3O_{12}$ – space group *R*-3*m* : *a* = 5.7968(1) Å, *c* = 28.477(1) Å Phase fraction: 88.2 weight percent					
$Ba_3LaNb_3O_{12}$ – space group *R*-3*m* : *a* = 5.765(1) Å, *c* = 28.161(4) Å Phase fraction: 11.8 weight percent					
χ^2 = 1.39, wRp = 2.04%, Rp = 1.93%					

Table S4: Structural parameters of $Ba_3LaliNb_3O_{12}$ refined from X-ray powder diffraction data collected at 298K. The positions of the oxide ions were not refined, but taken from the neutron diffraction refinement, as were the fractions of the two phases.

Cation	Anion	Bond length (Å)	BVS
Ba/La(1)	O(1)	3.030(3) × 3	Ba+2.77/La+2.01
	O(1)	2.915(3) × 6	
	O(2)	2.610(3) × 3	
Ba/La(2)	O(1)	3.168(5) × 3	Ba+2.02/La+1.47
	O(2)	2.924(2) × 6	
	O(2)	2.846(5) × 3	
Nb/Li(1)	O(1)	2.121(4)) × 3	Nb+4.44/Li+1.33
	O(2)	1.944(2) × 3	
Nb/Li(2)	O(2)	2.121(2) × 6	Nb+3.40/Li+1.02
Nb(3)	O(1)	1.977(2) × 6	Nb+5.01

Table S5: Selected bond lengths from the refined structure of $Ba_3LaLiNb_3O_{12}$.

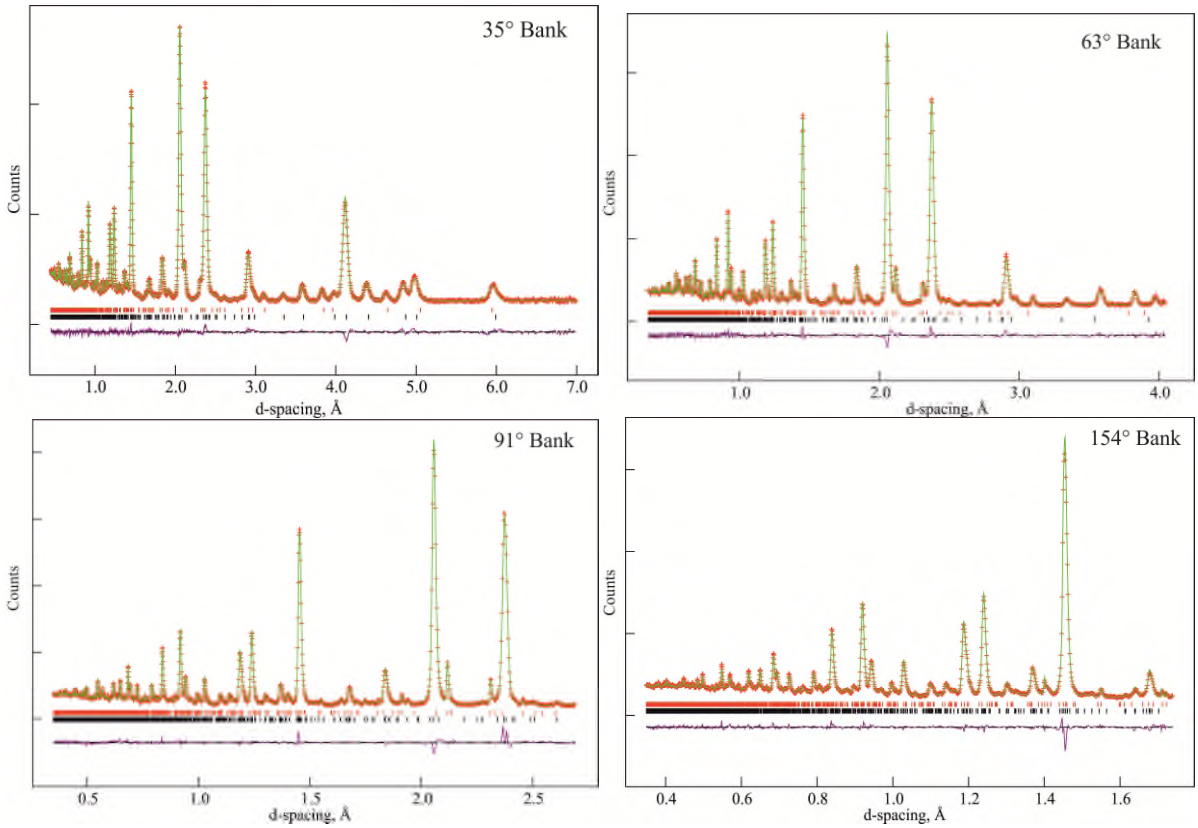

Figure S1: Observed, calculated and difference plots from the structural refinement of $Ba_5LiNb_4O_{15}$ against neutron powder diffraction data. Lower tick marks indicate peak positions for the majority phase, upper tick marks for the secondary phase $Ba_5Nb_4O_{15}$.

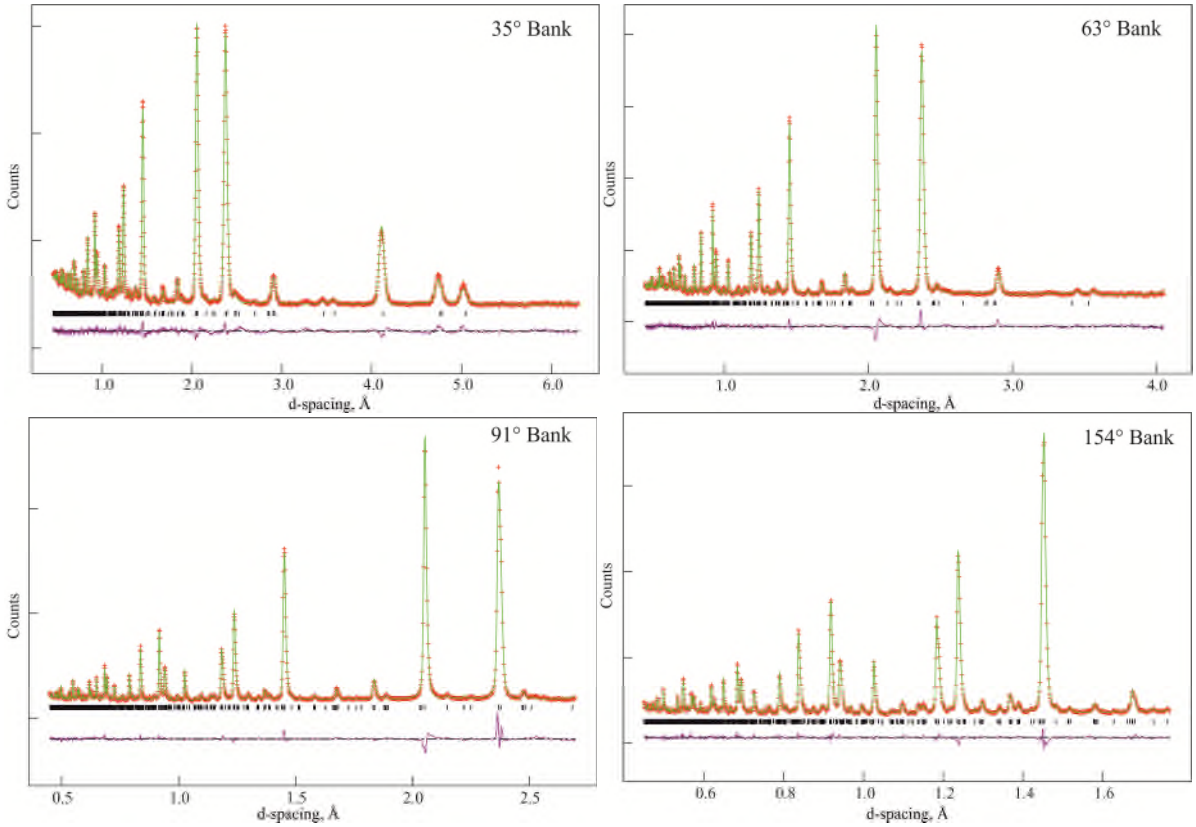

Figure S2: Observed, calculated and difference plots from the structural refinement of $Ba_6LiTiNb_4O_{18}$ against neutron powder diffraction data.

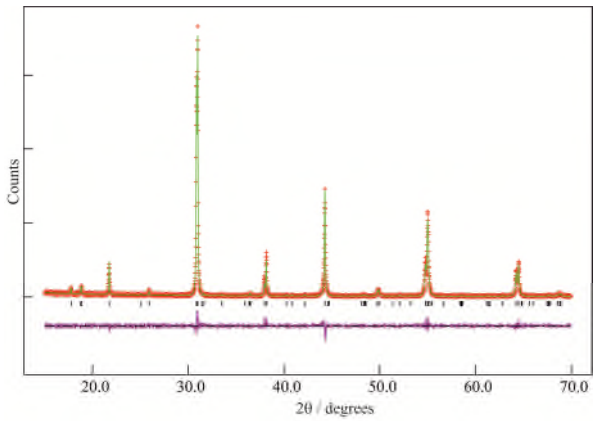

Figure S3: Observed, calculated and difference plots from the structural refinement of $Ba_6LiTiNb_4O_{18}$ against X-ray powder diffraction data.

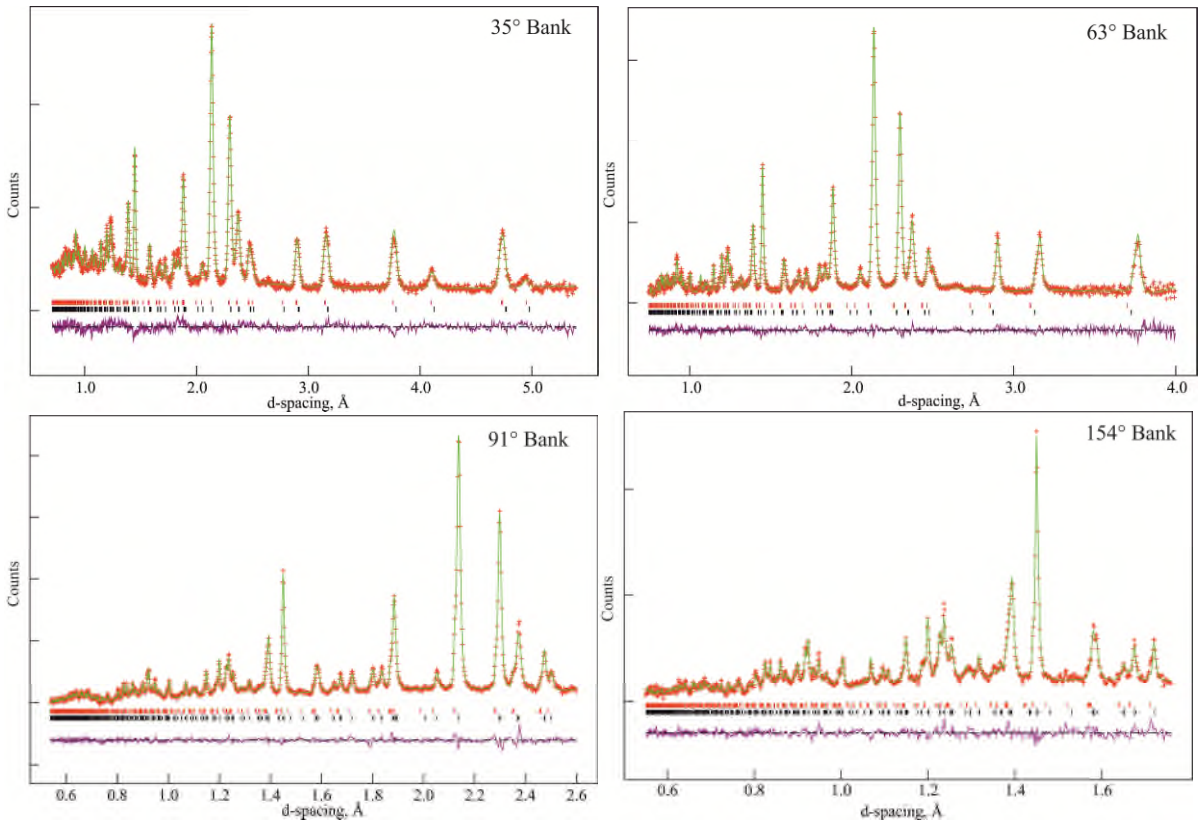

Figure S4: Observed, calculated and difference plots from the structural refinement of $Ba_3LaLiNb_3O_{12}$ against neutron powder diffraction data. Lower tick marks indicate peak positions for the majority phase, upper tick marks for the secondary phase $Ba_3LaNb_3O_{12}$.

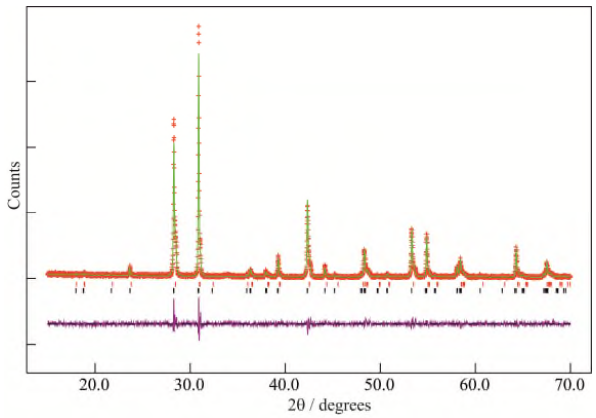

Figure S5: Observed, calculated and difference plots from the structural refinement of $Ba_3LaLiNb_3O_{12}$ against X-ray powder diffraction data.