Electronic Supplementary Material (ESI) for Dalton Transactions.

Synthesis and characterisation of $Li_{11}RE_{18}M_4O_{39-\delta}$:

RE = Nd or Sm; M = Al, Co or Fe

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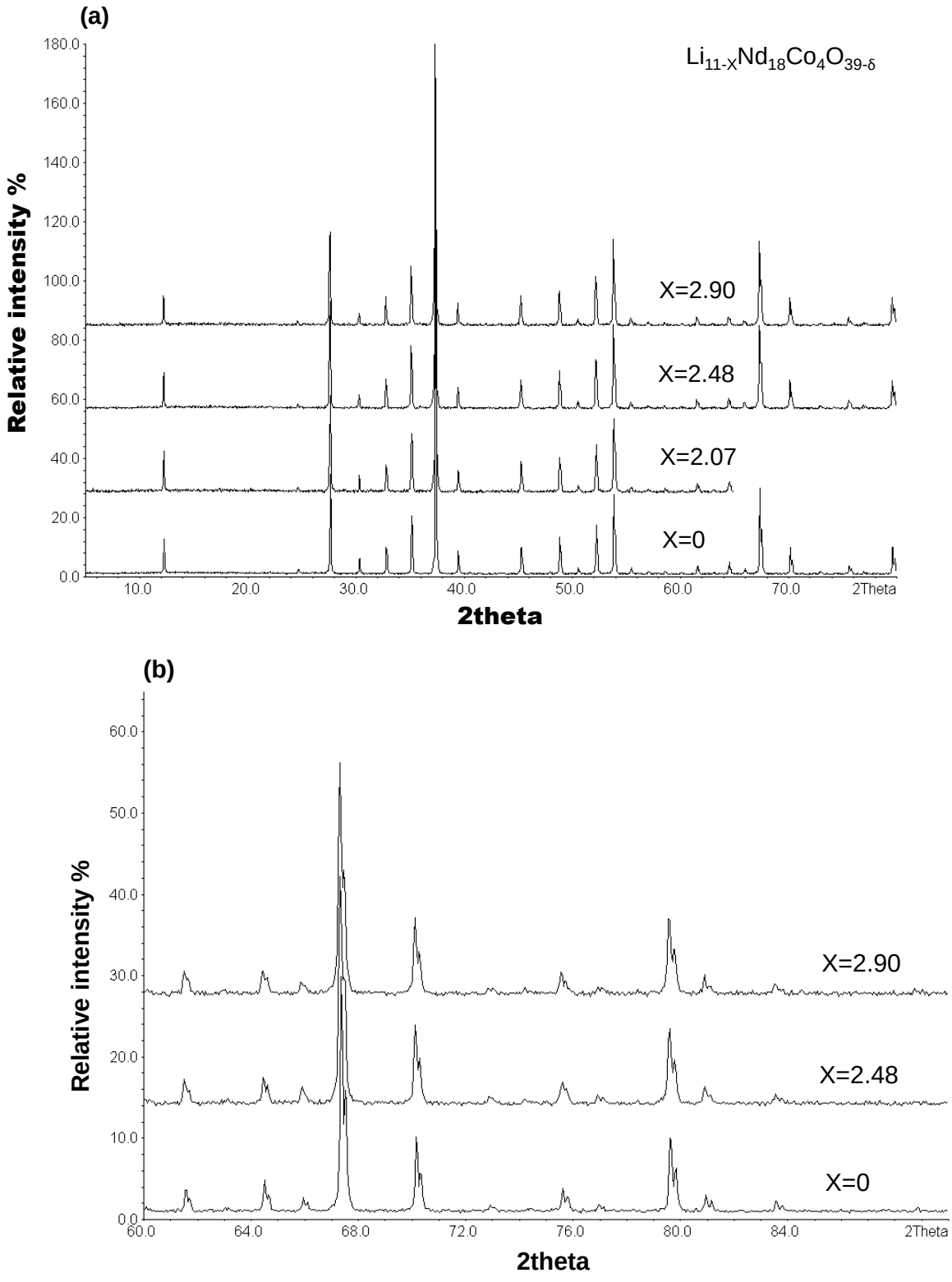
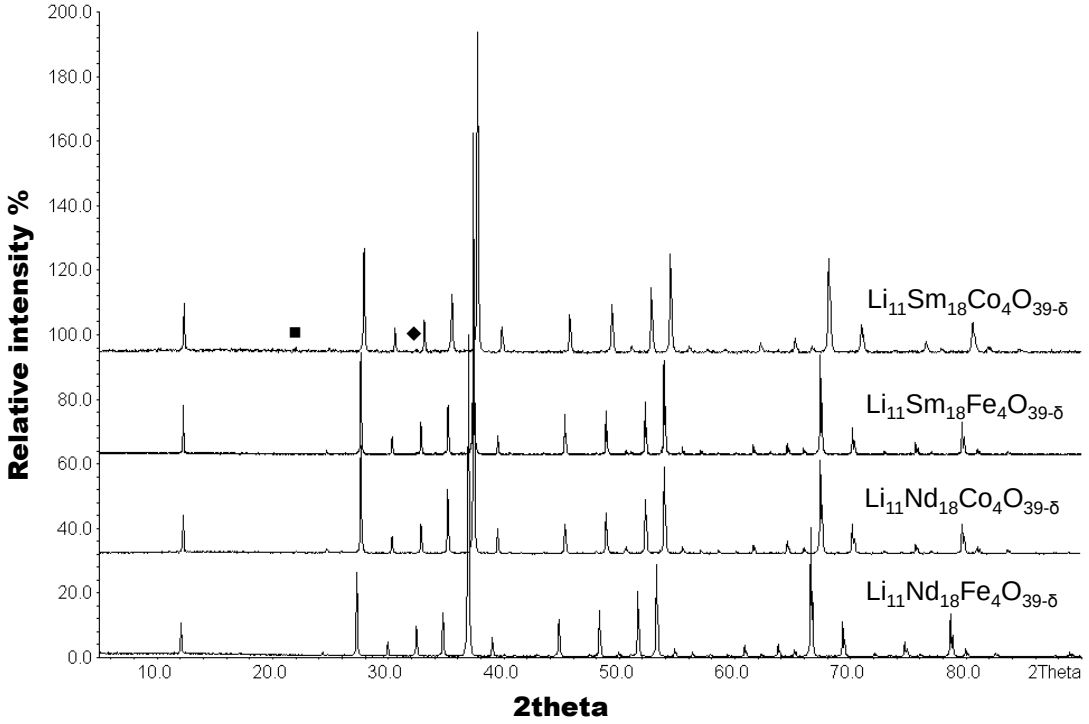
Supplementary Figure 1.

XRD patterns of the solid solution $Li_{11-x}Nd_{18}Co_4O_{39-\delta}$: x = 0-~ 2.9

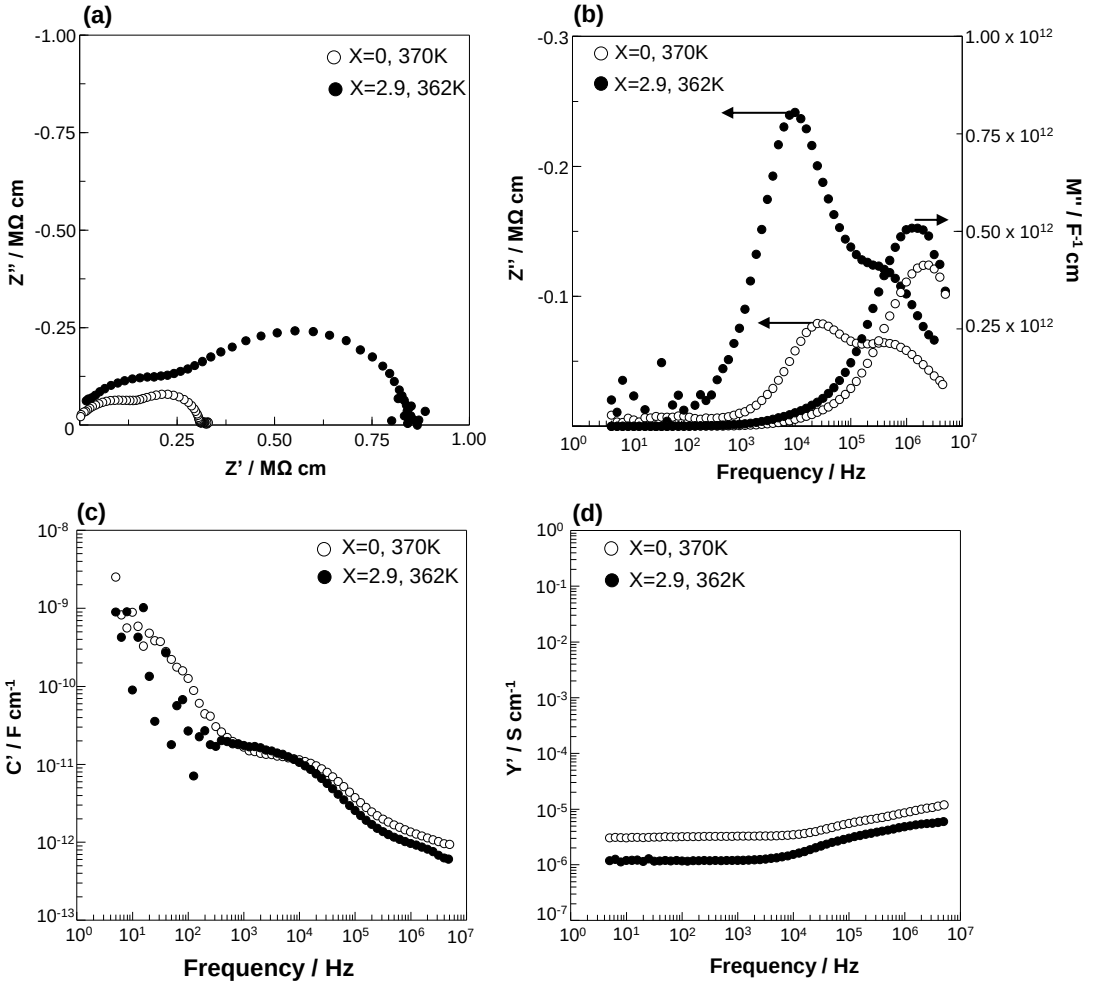


Supplementary Figure 2. XRD patterns of $Li_{11}RE_{18}M_4O_{39-\delta}$:RE = Nd, Sm;

M=Co,Fe: ■ $LiCoO_2$ and ◆: Sm_2O_3



Supplementary Figure 3. IS data for the solid solution, $Li_{11-x}Nd_{18}Co_4O_{39-x/2}$:$x$ = 0 and 2.9.



Supplementary Table 1. Results of Rietveld refinement of $Li_{11}Nd_{18}Al_4O_{38.5}$.

Nd(1) 24k : 0, y, z	y	0.30637(7)
	z	0.30499(8)
	U_{iso}/Å^2	0.0061(1)
Nd(2) 12f : x, 0, 0	x	0.34739(7)
	U_{iso}/Å^2	0.0066(2)
Al(1) 2a : 0, 0, 0	U_{iso}/Å^2	0.0164(10)
Al,Li(2) 8e : ¼,¼,¼	occupancy Al,Li	0.65 , 0.35
	U_{iso}/Å^2	0.0066(6)
Al,Li(1) 16i : x, x, x	x	0.36671(18)
	occupancy Al,Li	0.05 , 0.95
	U_{iso}/Å^2	0.0149(6)
O(1) 48l : x, y, z	x	0.86303(7)
	y	0.85850(8)
	z	0.69523(5)
	U_{iso}/Å^2	0.0113(1)
O(2) 6d : ¼, ½, 0	U_{iso}/Å^2	0.0097(3)
O(3) 12g : x, 0, ½	x	0.63110(11)
	U_{iso}/Å^2	0.0079(2)
O(4) 48l : x, y, z	x	0.1405(5)
	y	0.0269(9)
	z	0.0158(34)
	occupancy	0.23
	U_{ij}/Å^2	0.042(2), 0.144(11),0.199(22)

		-0.075(5), 0.057(15), 0.007(7)
Li(3) 24k : x, 0, z	x	0.1427(22)
	z	0.2092(19)
	occupancy	1/6
	U_{iso}/Å^2	0.0234(44)
a(Å)		11.88383(10)
χ^2 = 1.648	R_{wp} = 1.57%	R_p = 3.73%
Space group		P m$\bar{3}$n

Supplementary Table 2. Selected bond lengths (Å) in $Li_{11}Nd_{18}Al_4O_{38.5}$.

Nd1-O1	2.611(1) × 2	Al1-O4	1.710(8) × 6
Nd1-O1	2.547(1) × 2	8*i*-O1	1.9724(5) × 6
Nd1-O1	2.498(1) × 2	16*i*-O1	2.041(2) × 3
Nd1-O2	2.412(1)	16*i*-O4	1.89(3) × 3
Nd1-O3	2.423(1)	Li3-O1	2.65(2) × 2
Nd1-O3	3.093(1)	Li3-O1	2.03(1) × 2
Nd2-O1	2.3946(6) × 4	Li3-O4	2.18(2)
Nd2-O3	2.3909(11) × 2	Li3-O4	1.61(3)
Nd2-O4	2.487(7)	Li3-Li1	1.83(1)

Supplementary Table 3. Results of sample heat treatment in the Li_2O-Nd_2O_3-'CoO' system

Number (target formula)	Molar ratio Li :Nd: Co	Phases present
1 ($Li_{11}Nd_{18}Co_4O_\delta$)	0.333 : 0.546 : 0.121	Y
2 ($LiCoNd_4O_8$)	0.166 : 0.667 : 0.166	LCN4+NC
3 ($Li_8Nd_{18}Co_4O_\delta$)	0.267 : 0.600 : 0.133	Y+ LCN4+N
4	0.60 : 0.20 : 0.20	Y+LC+L
5	0.50 : 0.40 : 0.10	Y+ LC+L
6	0.400 : 0.514 : 0.086	Y+LN+L
7	0.33 : 0.58 : 0.09	Y+LN+ N
8	0.20 : 0.70 : 0.10	Y+LCN4+N
9	0.30 : 0.50 : 0.20	Y+LCN4+LC
10	0.10: 0.70 : 0.20	LCN4+ NC+ Nd
11	0.20 : 0.40 : 0.40	LC+NC+LCN4
12	0.30 : 0.20 : 0.50	LC+ NC
13	0.258 : 0.581 : 0.161	Y+LCN4+LC
14	0.20 : 0.20 : 0.60	LC+NC+C
15	0.70 : 0.10 : 0.20	Y+LC+L

16	0.364 : 0.546 : 0.09	Y+LN+N
17	0.30 : 0.55 : 0.05	Y+LC
18	0.183 : 0.667 : 0.15	Y+LC+N
19 $Li_{8.1}Nd_{18}Co_4O_{37.55}$	0.269 : 0.598 : 0.133	Y solid solution
20 $Li_{8.52}Nd_{18}Co_4O_{37.76}$	0.279 : 0.590 : 0.131	Y solid solution
21 $Li_{8.93}Nd_{18}Co_4O_{37.97}$	0.289 : 0.582 : 0.129	Y solidsolution
Y: $Li_{11}Nd_{18}Co_4O_{39-\delta}$, LCN4: $LiCoNd_4O_8$, NC: $NdCoO_3$, LC: $LiCoO_2$, LN: $LiNdO_2$, N: Nd_2O_3, C: 'CoO', L: Li_2O, Y solid solution: $Li_{11-X}Nd_{18}Co_4O_{39-0.5X}$ (x=0 - ~2.9).		