Supporting Information for

Chemical and structural evolution during synthesis of layered Li(Ni,Co,Mn)O_2 oxides

Weibo Hua[1,2,*], *Kai Wang*[3], *Michael Knapp*[1], *Björn Schwarz*[1,*], *Suning Wang*[4], *Hao Liu*[4], *Jing Lai*[4], *Marcus Müller*[1], *Alexander Schökel*[5], *Alexander Missyul*[6], *Dario Ferreira Sanchez*[7], *Xiaodong Guo*[3], *Joachim R. Binder*[1], *Jie Xiong*[2,*], *Sylvio Indris*[1,*], *and Helmut Ehrenberg*[1]

[1] Institute for Applied Materials (IAM), Karlsruhe Institute of Technology (KIT), Hermann-von-Helmholtz-Platz 1, 76344 Eggenstein-Leopoldshafen, Germany.

[2] State Key Laboratory of Electronic Thin Films and Integrated Devices, University of Electronic Science and Technology of China, Chengdu, 610054 China.

[3] Institute of Nanotechnology (INT), Karlsruhe Institute of Technology (KIT), 76344 Eggenstein-Leopoldshafen, Germany.

[4] College of Chemical Engineering, Sichuan University, No.24 South Section 1, Yihuan Road, Chengdu, 610065, China.

[5] Deutsches Elektronen-Synchrotron (DESY), Notkestr. 85, Hamburg 22607, Germany.

[6] CELLS-ALBA Synchrotron, Cerdanyola del Valles, E-08290 Barcelona, Spain.

[7] MicroXAS Beamline, Paul Scherrer Institut, Forschungsstrasse 111, 5232 Villigen PSI, Switzerland.

S1 Additional results

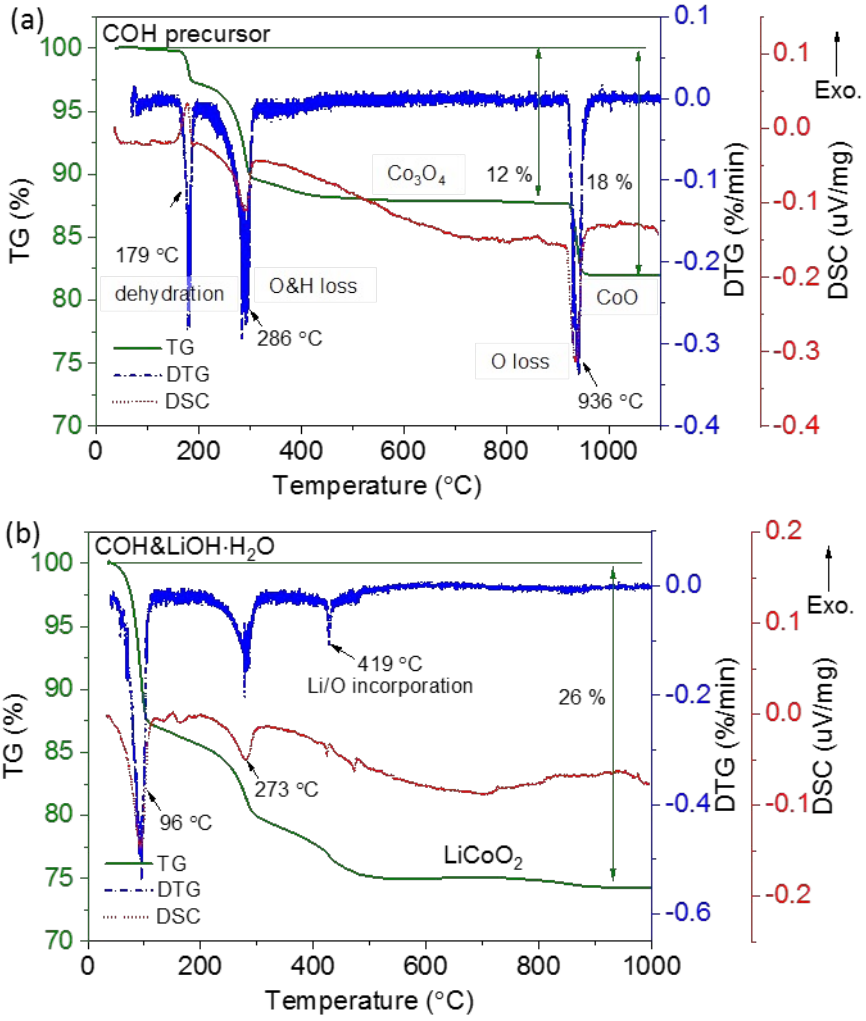

Figure S1. TG/DTG/DSC curves of (a) the COH precursor and (b) the mixture of COH and $LiOH{\cdot}H_2O$, respectively.

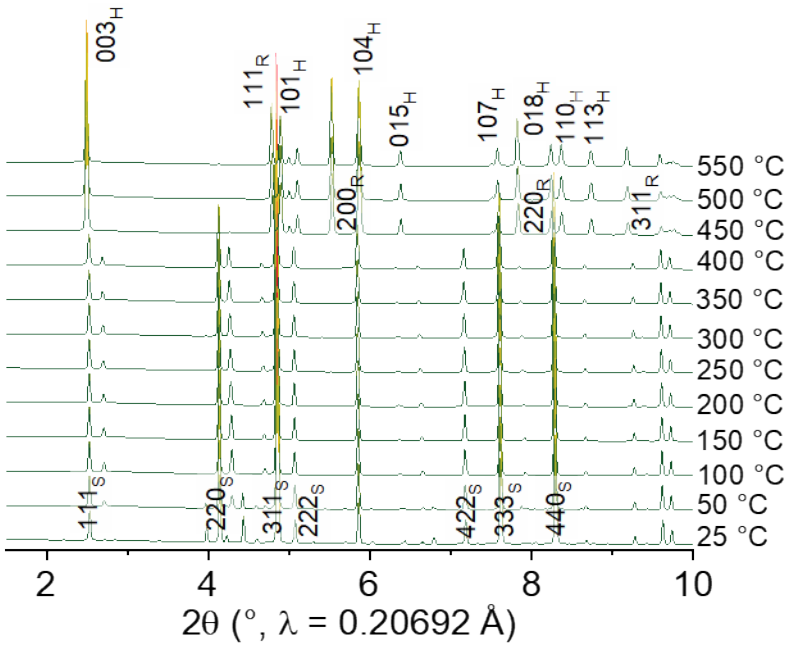

Figure S2. *In situ* HTSRD patterns of a mixture of the CO and $LiOH{\cdot}H_2O$. H, S, R represent the hexagonal layered phase ($R\bar{3}m$), spinel phase ($Fd\bar{3}m$) and rock-salt-type phase ($Fm\bar{3}m$), respectively. Note that the pure layered $LiCoO_2$ can be obtained by increasing the temperature to 800 °C.

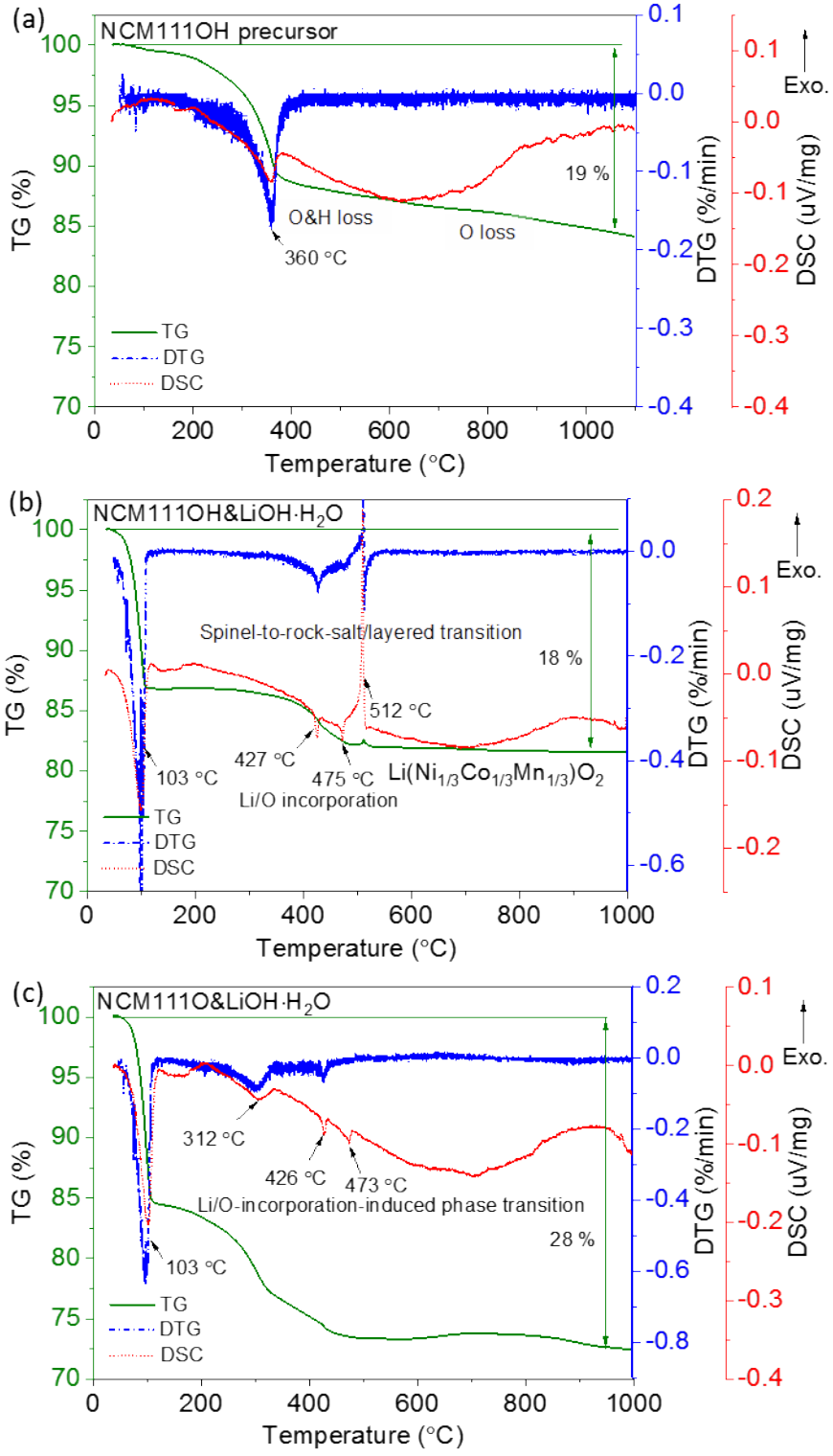

Figure S3. TG/DTG/DSC curves of (a) the NCM111OH precursor, (b) the mixture of NCM111OH and $LiOH{\cdot}H_2O$, (c) a mixture of NCM111O together with $LiOH{\cdot}H_2O$, respectively.

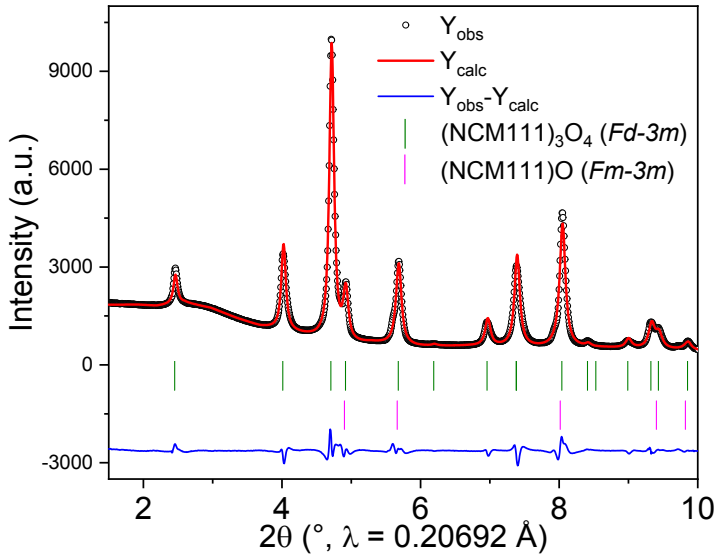

Figure S4. Rietveld refinement to the SRD pattern of NCM111OH precursor heated at 850 °C during in situ heating.

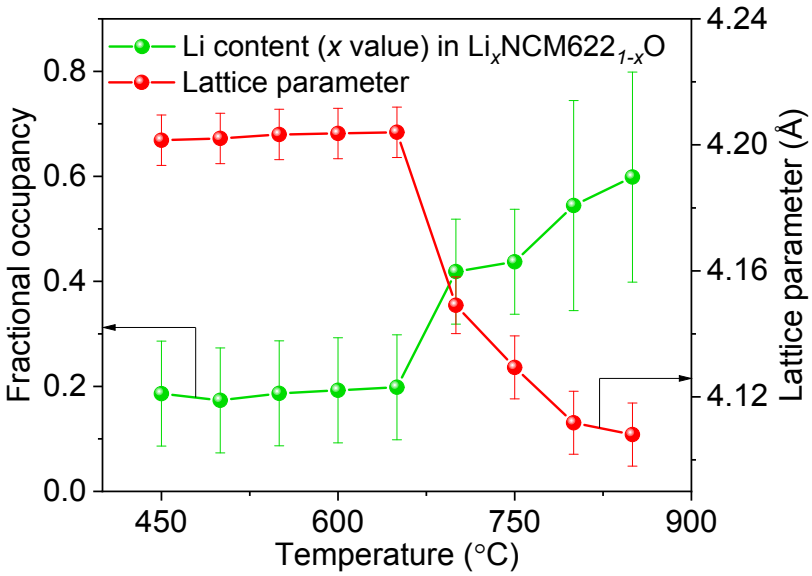

Figure S5. Evolution of lattice parameters in the fully disordered Li-containing rock-salt-type structure (*Fm-3m*) as a function of temperature during synthesis of LNCM622O.

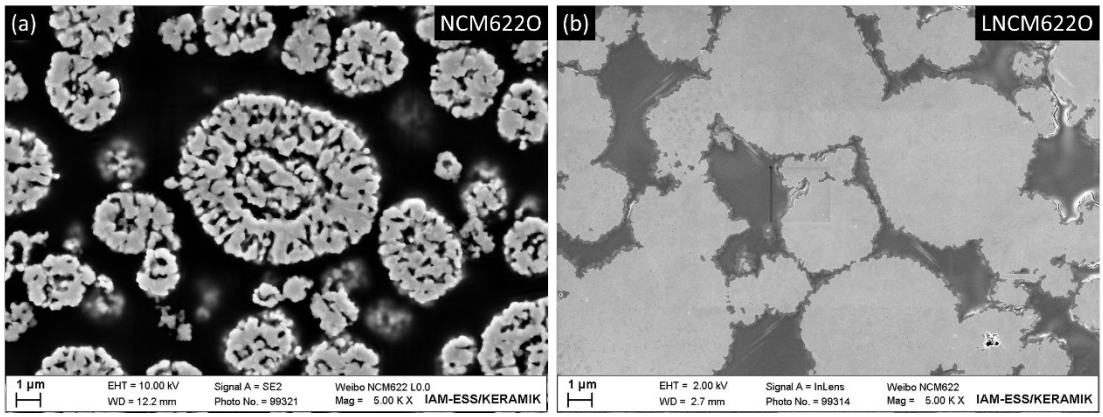

Figure S6. Cross section SEM images of (a) NCM622O and (b) LNCM622O.

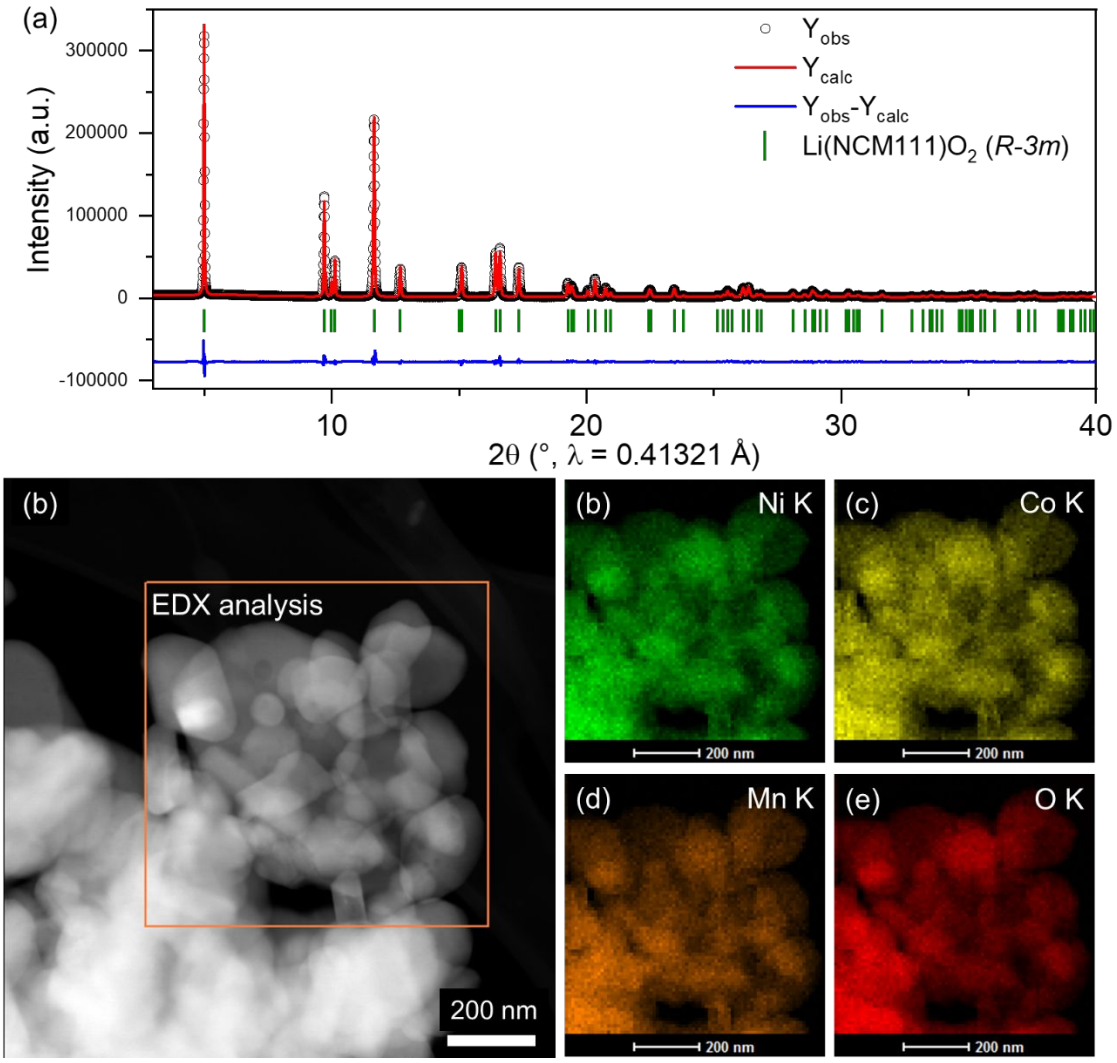

Figure S7. (a) Rietveld refinement against SRD patterns, (b) HAADF-STEM, (c-f) HAADF-STEM-EDX mapping images of LNCM111O.

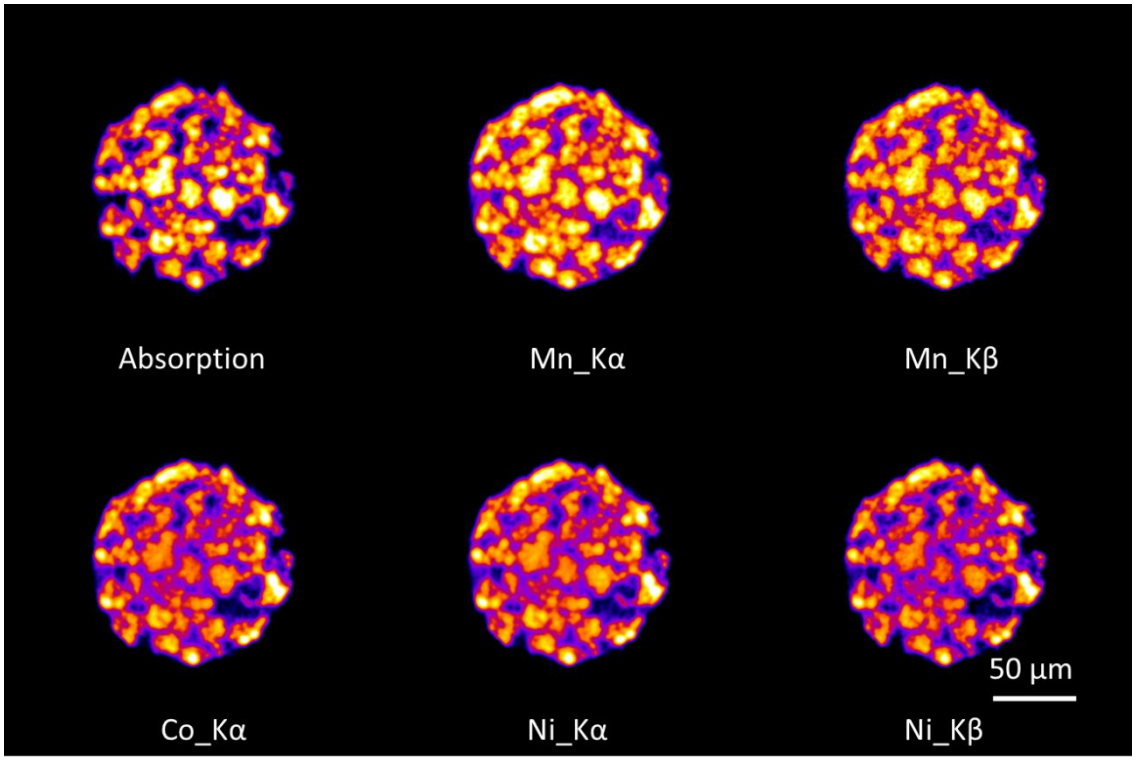

Figure S8. A virtual slice obtained from micro-XRF combined with absorption contrast computed scanning tomography projection slices of the sample LNCM622O, showing homogeneous spatial distributions of transition metals, i.e. Ni, Co, and Mn.

Table S1. Crystallographic parameters of NCM622OH.

Cell parameters

Space group: *P-3m1*, a = 3.1087 Å, b = 3.1087 Å, c = 4.6131 Å , V = 38.6081 Å^3, gamma = 120°, Z = 2

Atomic positions

Name	site	*x*	*y*	*z*	Fract
Ni1	1*c*	0.000	0.000	0.000	0.600
Co1	1*c*	0.000	0.000	0.000	0.200
Mn1	1*c*	0.000	0.000	0.000	0.200
O1	2*d*	0.333	0.667	0.205	1.000
H1	2*d*	0.333	0.333	0.453	1.000

Refinement parameters

R_{wp}= 6.38 %, R_p= 5.35 %, χ^2: 2.68

Note: Fract is the fractional occupancy of the atom on this site. Considering that synchrotron diffraction technique is not sensitive to distinguish Ni, Co and Mn, the ratio of Ni:Co:Mn is fixed according to their chemical composition.

Table S2. Crystallographic parameters of the NCM622O.

Cell parameters (Spinel phase, 56 wt%)					
Space group: *Fd-3m*, $a = b = c = 8.2876$ Å, $V = 569.2296$ Å^3, $Z = 8$, formula: AB2O4					
Atomic positions					
Name	site	*x*	*y*	*z*	Fract
Ni1	8*a*	0.125	0.125	0.125	0.600
Co1	8*a*	0.125	0.125	0.125	0.200
Mn1	8*a*	0.125	0.125	0.125	0.200
Ni2	16*d*	0.500	0.500	0.500	0.600
Co2	16*d*	0.500	0.500	0.500	0.200
Mn2	16*d*	0.500	0.500	0.500	0.200
O1	32*e*	0.261	0.261	0.261	1.000
Cell parameters (rock-salt-type phase, 44 wt%)					
Space group: *Fm-3m*, $a = b = c = 4.1834$ Å, $V = 73.2113$ Å^3, $Z = 4$, formula: AB					
Atomic positions					
Name	site	*x*	*y*	*z*	Fract
Ni1	4*a*	0.000	0.000	0.000	0.600
Co1	4*a*	0.000	0.000	0.000	0.200
Mn1	4*a*	0.000	0.000	0.000	0.200
O1	4*b*	0.500	0.500	0.500	1.000
Refinement parameters					
R_{wp}= 9.08 %, R_p= 7.40 %, χ^2: 23.93					

Table S3. Crystallographic parameters of LNCM622O.

Cell parameters

Space group: *R-3m*, $a = b = 2.8653$ Å, $c = 14.2117$ Å, $V = 101.0479$ Å^3, , gamma = 120°, $Z = 3$, formula: ABO2

Atomic positions

Name	site	*x*	*y*	*z*	Fract
Li1	3*a*	0.000	0.000	0.000	0.981
Ni2	3*a*	0.000	0.000	0.000	0.019
Li2	3*b*	0.000	0.000	0.500	0.019
Ni1	3*b*	0.000	0.000	0.500	0.581
Co1	3*b*	0.000	0.000	0.500	0.200
Mn1	3*b*	0.000	0.000	0.500	0.200
O1	6*c*	0.241	0.241	0.241	1.000

Refinement parameters

R_{wp}= 10.80 %, R_p= 8.73 %, χ^2: 37.70