Electronic Supplementary Material (ESI) for Journal of Materials Chemistry A.

Atomic scale drivers of ordering transitions in $LiNi_{0.5}Mn_{1.5}O_4$ and relationship with electrochemical properties

Montse Casas-Cabanas *[,†], Chunjoong Kim [‡,§,¶], Juan Rodríguez-Carvajal [‖], Jordi Cabana *[,‡,§]

[†] CIC energiGUNE, Parque Tecnológico de Álava, Albert Einstein 48, ED.CIC, 01510, Miñano, Spain.

[‡] University of Illinois at Chicago, 845 West Taylor Street, Chicago, IL 60607, United States.

[§] Environmental Energy Technologies Division, Lawrence Berkeley National Laboratory, 1 Cyclotron Rd., Berkeley, CA 94720, United States.

[¶] Chungnam National University, School of Materials Science and Engineering, Daejeon, 305-764, Republic of Korea.

[‖] Institute Laue-Langevin, 71 avenue des Martyrs, CS 20156, 38042 Grenoble Cedex 9, France.

*Correspondance - JCabana@uic.edu

Supplementary material

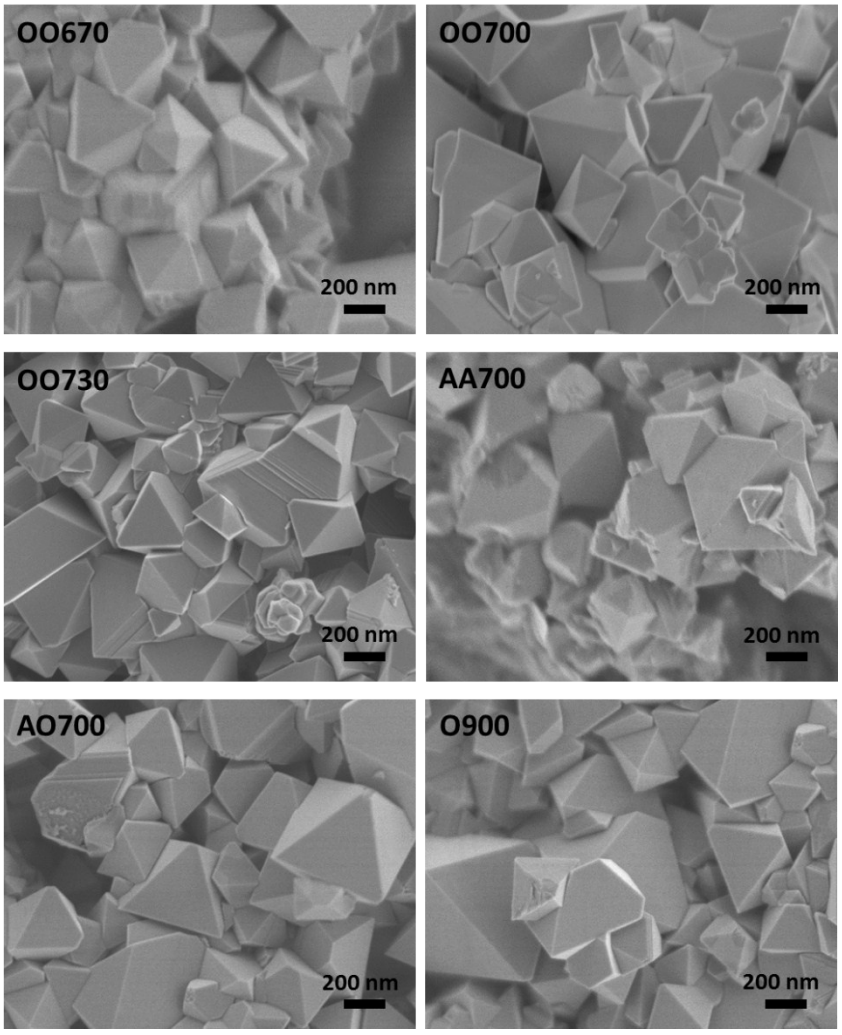

Figure S1. SEM images of prepared spinel samples. Similar morphologies among samples are confirmed.

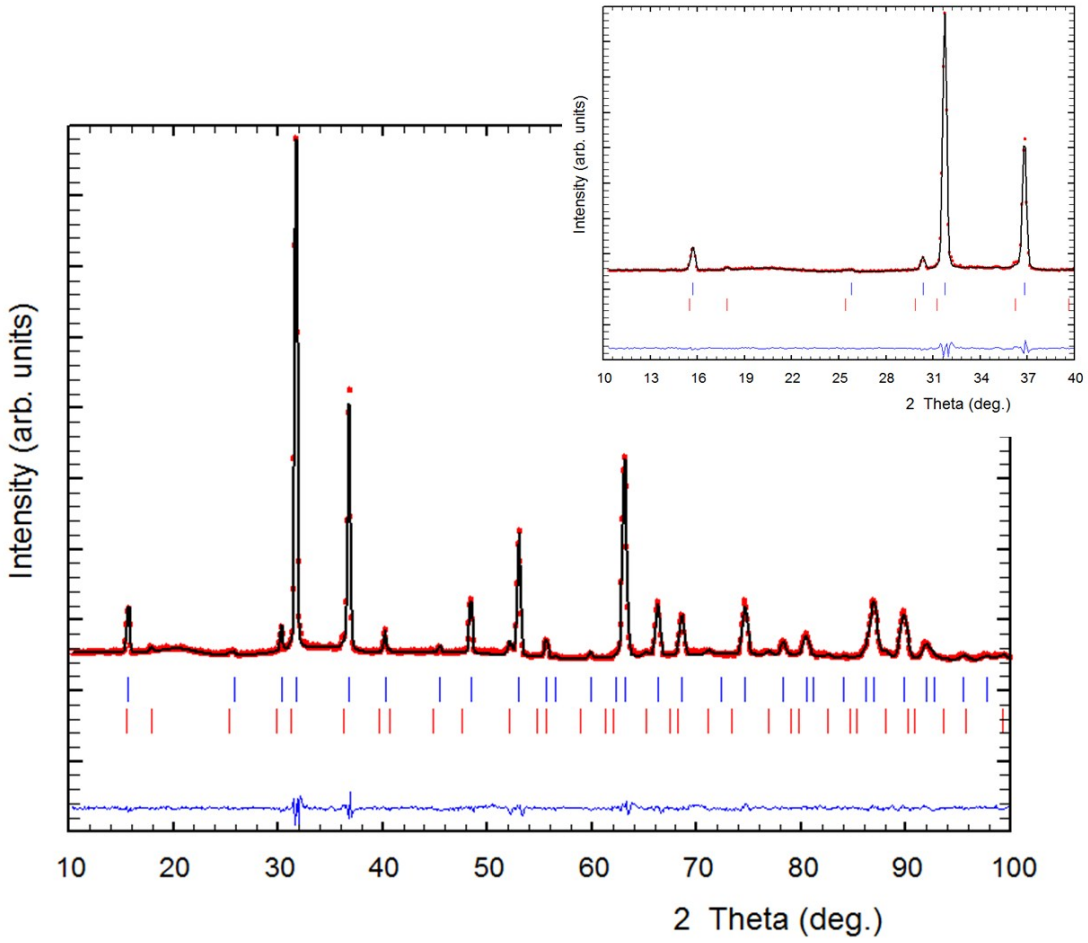

Figure S2. Neutron powder diffraction pattern of O900 (small circles), together with the final Rietveld fit (solid line) and difference plot (blue line below). Vertical bars: spinel Bragg reflections (blue) and rock salt reflections (red).

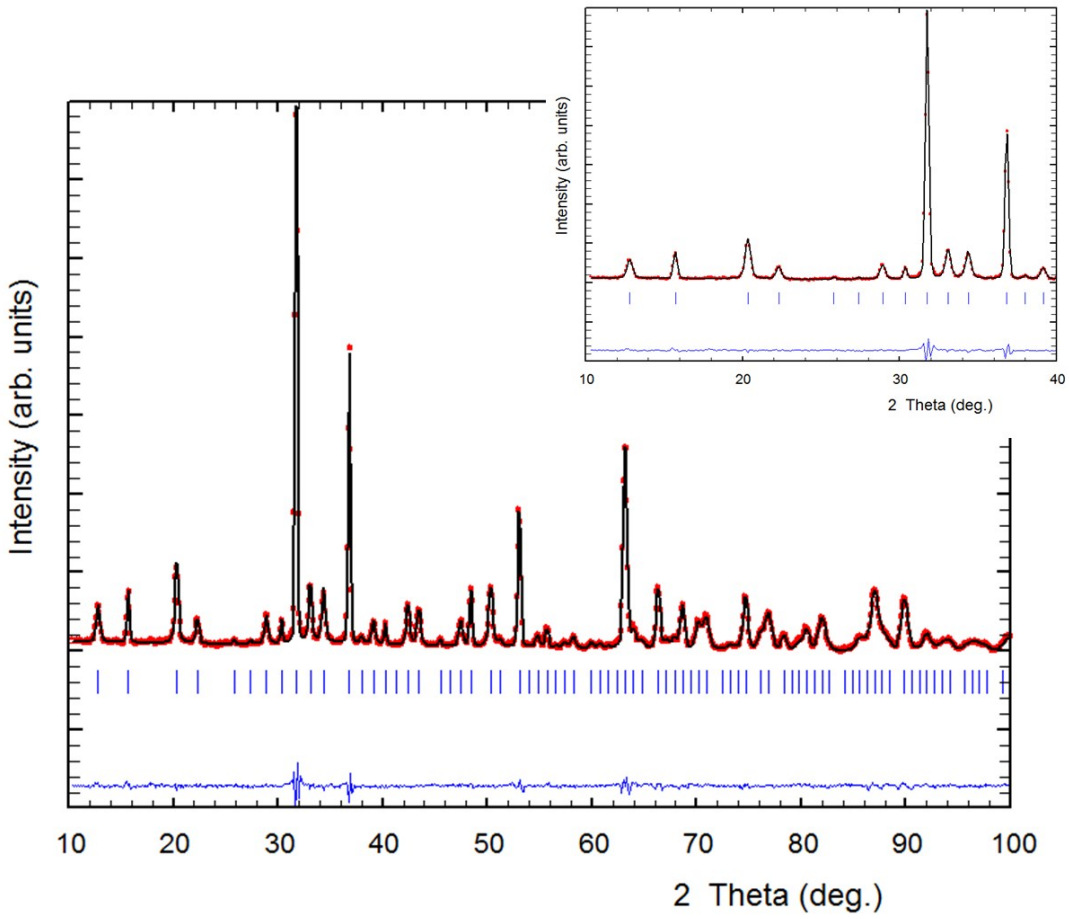

Figure S3. Neutron powder diffraction pattern of OO700 (small circles), together with the final Rietveld fit (solid line) and difference plot (blue line below). Vertical bars: spinel Bragg reflections.

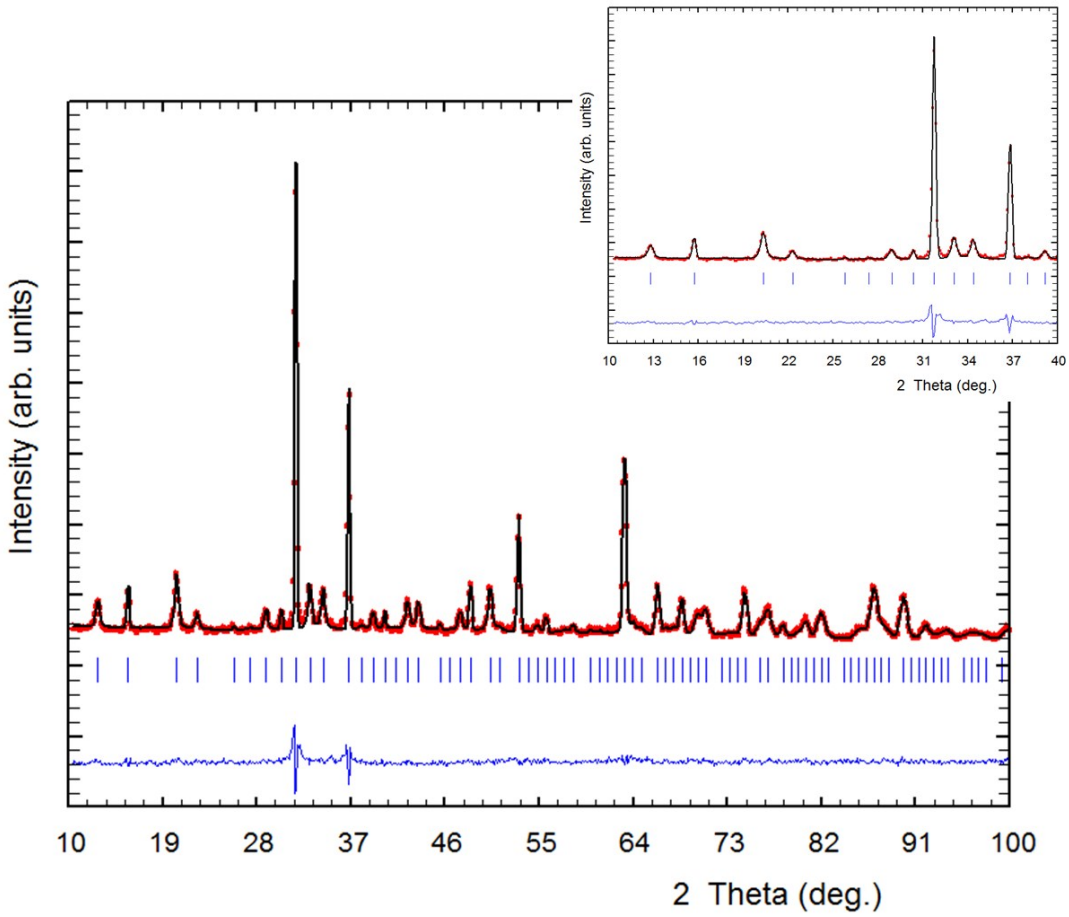

Figure S4. Neutron powder diffraction pattern of AO700 (small circles), together with the final Rietveld fit (solid line) and difference plot (blue line below). Vertical bars: spinel Bragg reflections.

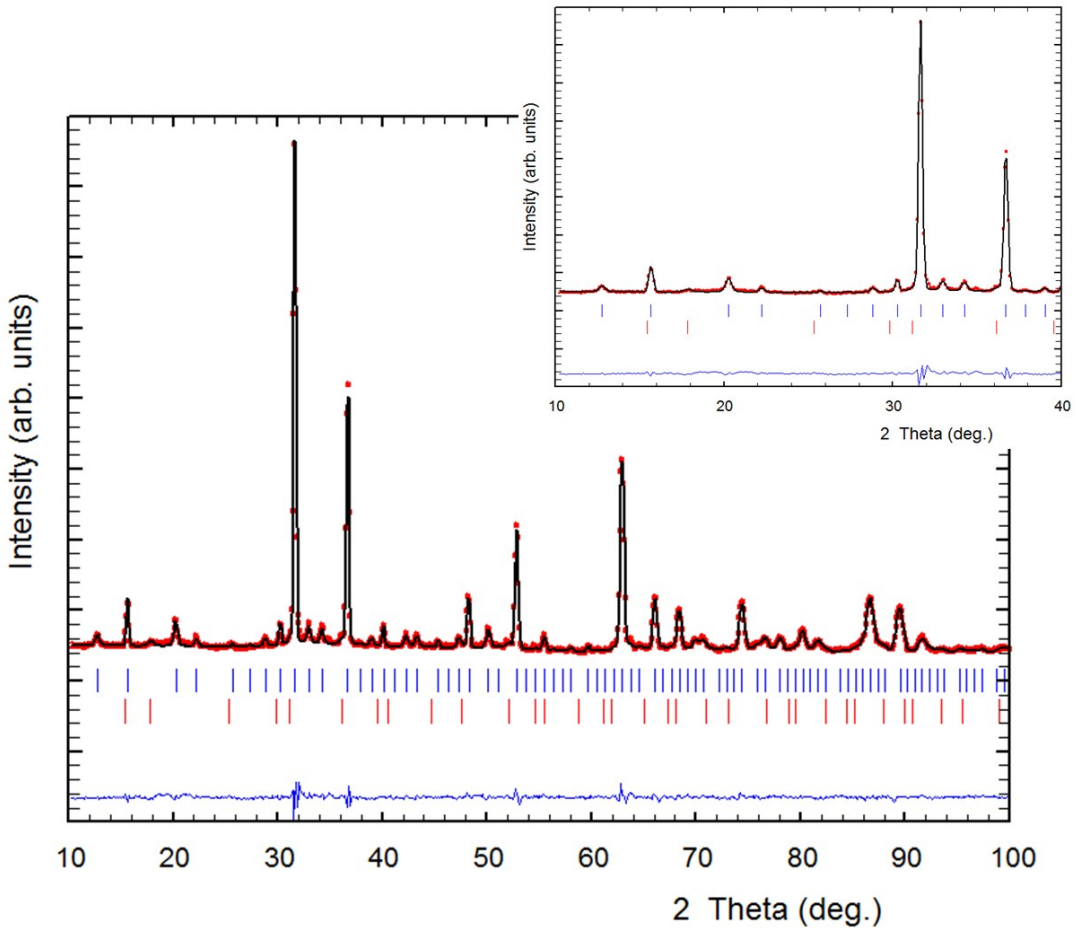

Figure S5. Neutron powder diffraction pattern of OO670 (small circles), together with the final Rietveld fit (solid line) and difference plot (blue line below). Vertical bars: spinel Bragg reflections (blue) and rock salt reflections (red).

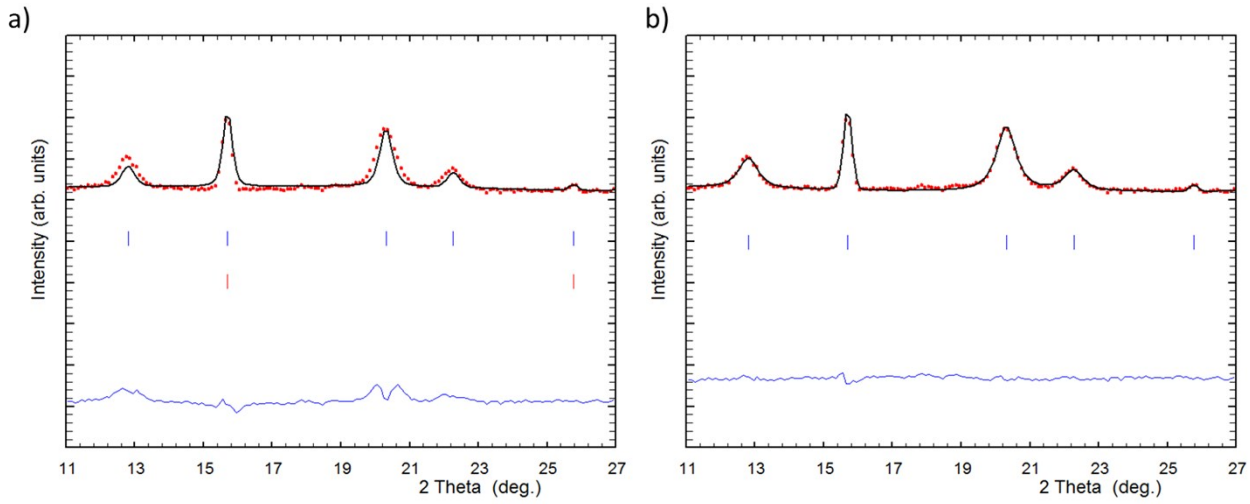

Figure S6. Comparison of the Rietveld fit of sample OO730 using a)2 phase model and b) antiphase boundaries model. Experimental data (small circles), final Rietveld fit (solid line) and difference plot (blue line below). Vertical bars: ordered spinel Bragg reflections (blue) and disordered spinel reflections (red).

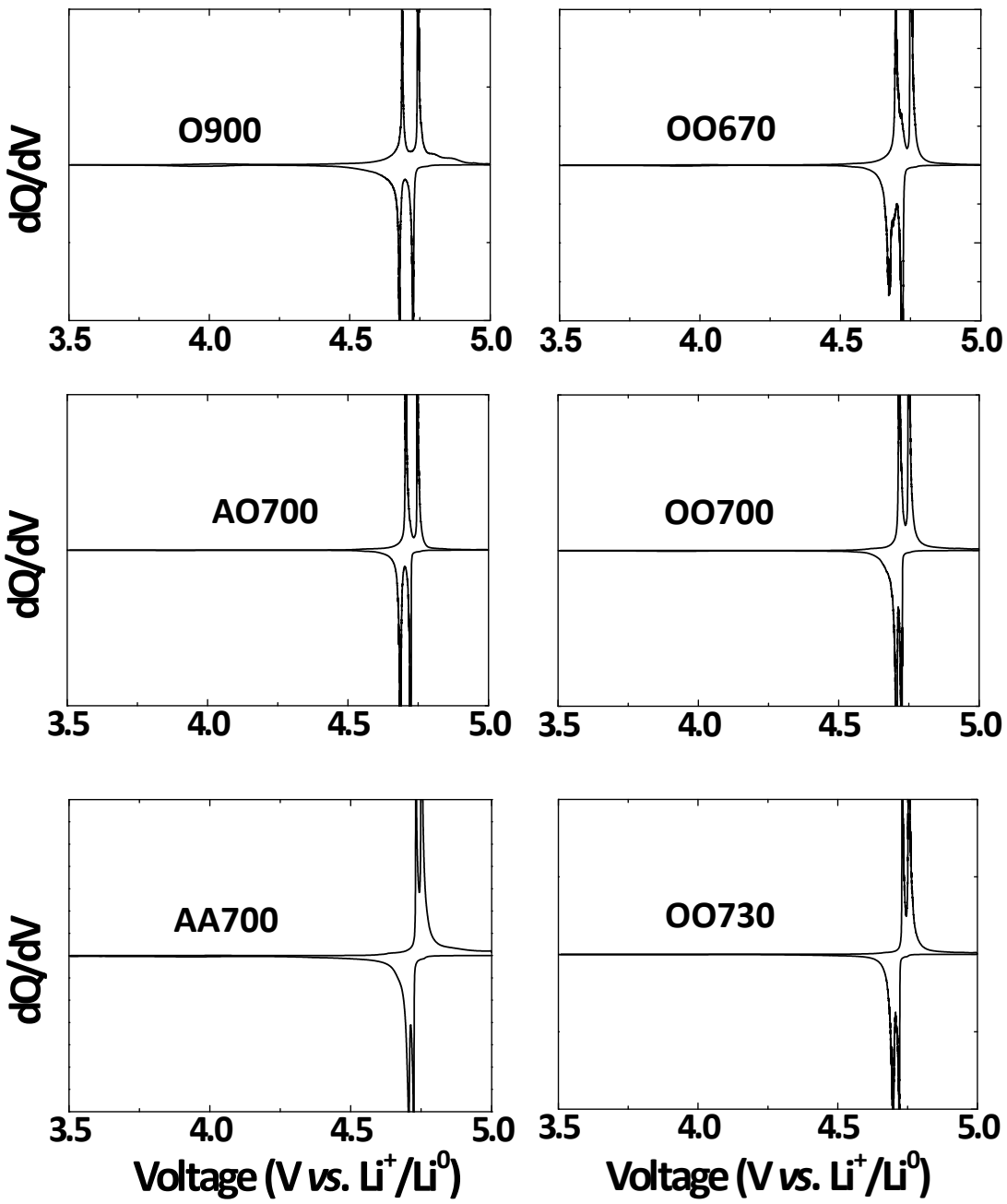

Figure S7. Differential-capacity curves for spinel samples with different Ni/Mn ordering. Differential-capacity curves are derived from the capacity-voltage curves, Figure 4a.

Table S1 Rietveld refinement details for sample AO700 refined as a single ordered phase: cell parameters, atomic coordinates, atomic occupancies, thermal factors and agreement factors.

AO700

Lattice parameter	a (Å)	8.1586(4)
Fractional coordinates	Mn/Ni x (*12d*)	0.125
	Mn/Ni y (*12d*)	0.382(3)
	Mn/Ni z (*12d*)	0.868(3)
	Ni/Mn x,y,z (*4b*)	0.625
	Li x,y,z (*8c*)	0.007(3)
	O1 x,y,z (*8c*)	0.3856(9)
	O2 x (*24e*)	0.1477(9)
	O2 y (*24e*)	0.8594(7)
	O2 z (*24e*)	0.1264(9)
Occupancies	Mn/Ni (*12d*)	1.425(3)/0.075(3)
	Ni/Mn (*4b*)	0.405(2)/0.095(2)
Biso (Å^2)	Mn/Ni (12d)	0.0(2)
	Ni/Mn (4b)	0.1(2)
	Li (8c)	0.6(4)
	O1 (8c)	0.2(1)
	O2 (24e)	0.61(9)
Agreement factors	Rp	18.0
	wRp	15.3
	Rexp	6.93
	x^2	4.871

Table S2 Rietveld refinement details for sample OO670 refined using the alternative model of coexistence of a ordered spinel phase and a disordered spinel phase of different domain size: : cell parameters, atomic coordinates, atomic occupancies, thermal factors and agreement factors. The rock salt phase was added in profile matching mode. Note: some thermal factors were left fixed as could not be refined.

OO670

Space group		P 4_3 3 2
Lattice parameter	a (Å)	8.1838(5)
Fractional coordinates	Mn/Ni x (12d)	0.125
	Mn/Ni y (12d)	0.374(2)
	Mn/Ni z (12d)	0.876(2)
	Ni/Mn x,y,z (4b)	0.625
	Li x,y,z (8c)	0.020(5)
	O1 x,y,z (8c)	0.386(2)
	O2 x (24e)	0.154(2)
	O2 y (24e)	0.855(1)
	O2 z (24e)	0.122(2)
Occupancies	Mn/Ni (12d)	1.5(-)/0
	Ni/Mn (4b)	0.46(1)/0.04(1)
Biso (Å2)	Mn/Ni (12d)	0.0(3)
	Ni/Mn (4b)	0.6(2)
	Li (8c)	1.0(3)
	O1 (8c)	2(1)
	O2 (24e)	0.1(4)
Domain size(Å)		389
Space group		Fd-3m
Lattice parameter	a (Å)	8.1854(2)
Fractional coordinates	Mn/Ni x,y,z (16d)	0.5
	Li x,y,z (8a)	0.125
	O x,y,z (32e)	0.2622(3)

Occupancies	Mn/Ni	(16d)	1.52(3)/0.48(3)
Biso (Å2)	Mn/Ni	(16d)	1
	Li	(8a)	0.0
	O	(32e)	0.61(7)
Rock salt			
Lattice parameter	a (Å)		8.312(1)
Agreement factors	Rp		8.21
	wRp		7.95
	Rexp		4.14
	×2		3.686