

Supplementary Information

Dopant-Controlled Transition-Metal Ordering in High-Voltage Spinel Cathodes

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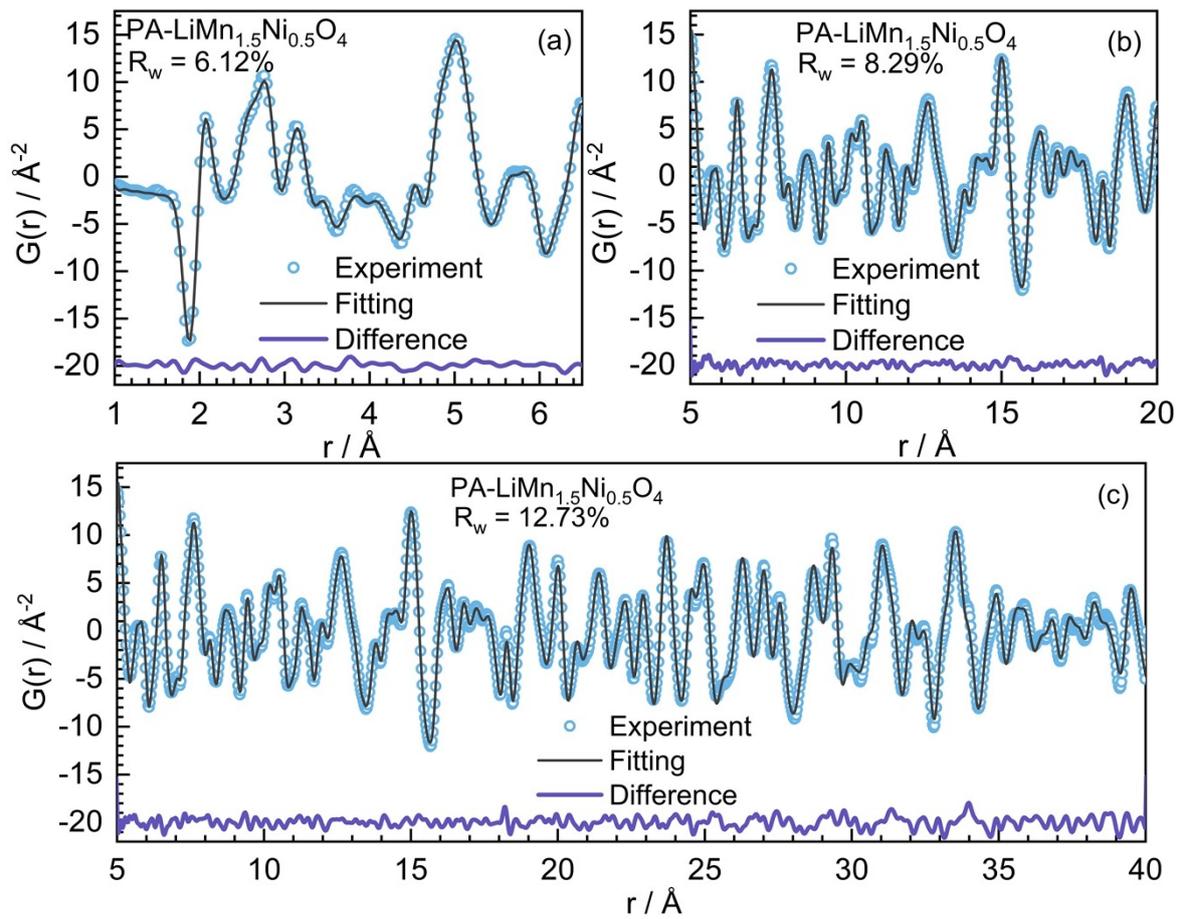


Figure S1. Experimental and fitted neutron pair distribution function profiles for post-annealed (PA) $\text{LiMn}_{1.5}\text{Ni}_{0.5}\text{O}_4$ over the real-space ranges 1 – 6.5 \AA (a), 5 – 20 \AA (b), and 5 – 40 \AA (c), using the $P4_332$ structural model.

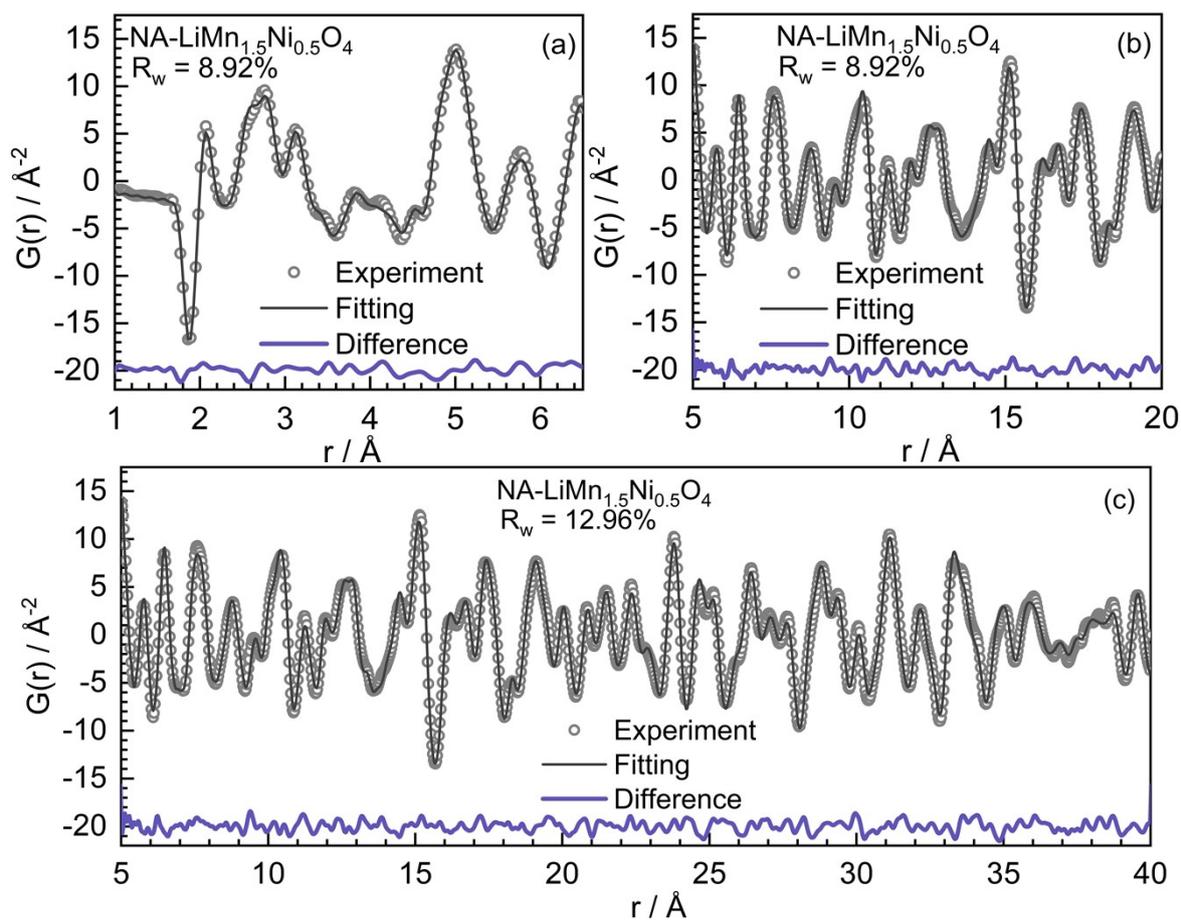


Figure S2. Experimental and fitted neutron pair distribution function profiles for non-annealed (NA) $\text{LiMn}_{1.5}\text{Ni}_{0.5}\text{O}_4$ over the real-space ranges 1 – 6.5 \AA (a), 5 – 20 \AA (b), and 5 – 40 \AA (c), using the $P4_332$ structural model.

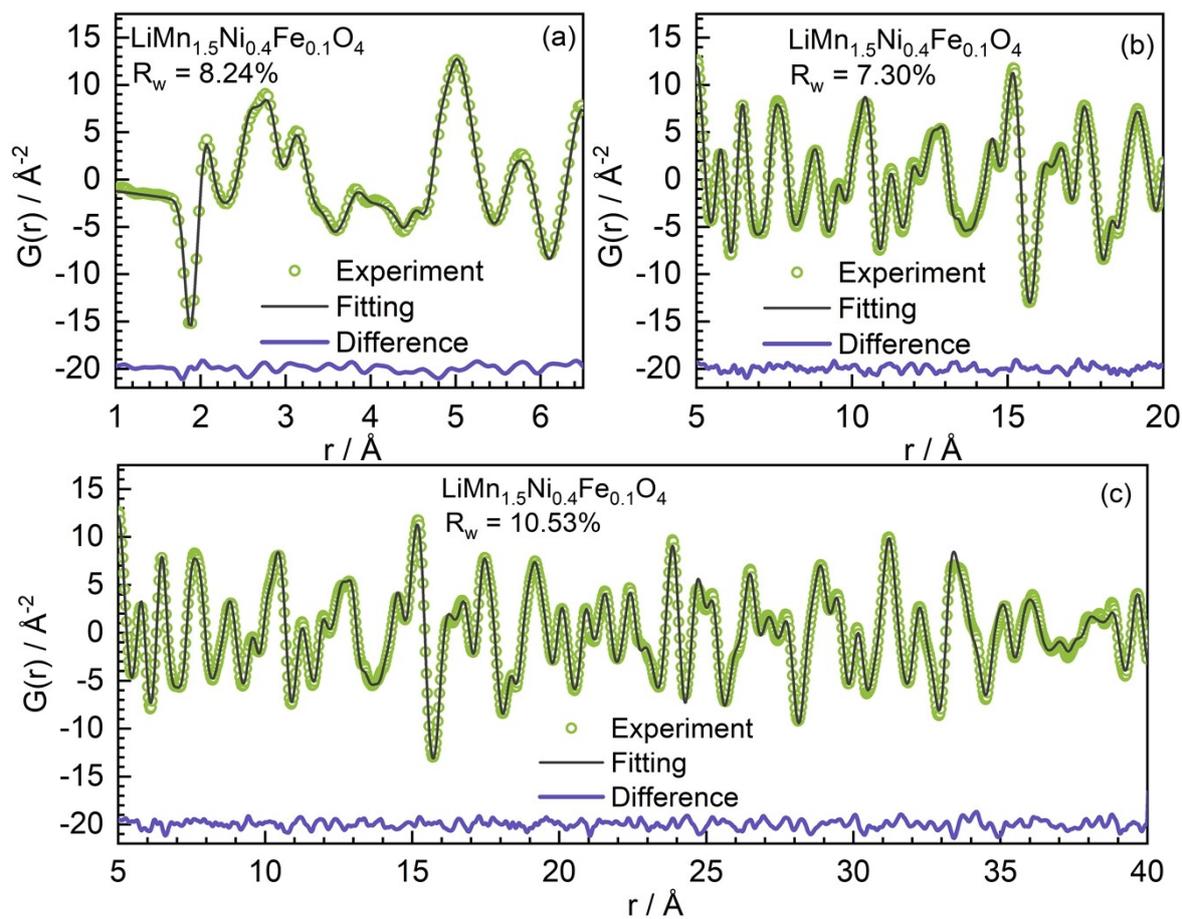


Figure S3. Experimental and fitted neutron pair distribution function profiles for $\text{LiMn}_{1.5}\text{Ni}_{0.4}\text{Fe}_{0.1}\text{O}_4$ over the real-space ranges 1 – 6.5 \AA (a), 5 – 20 \AA (b), and 5 – 40 \AA (c), using the $P4_332$ structural model.

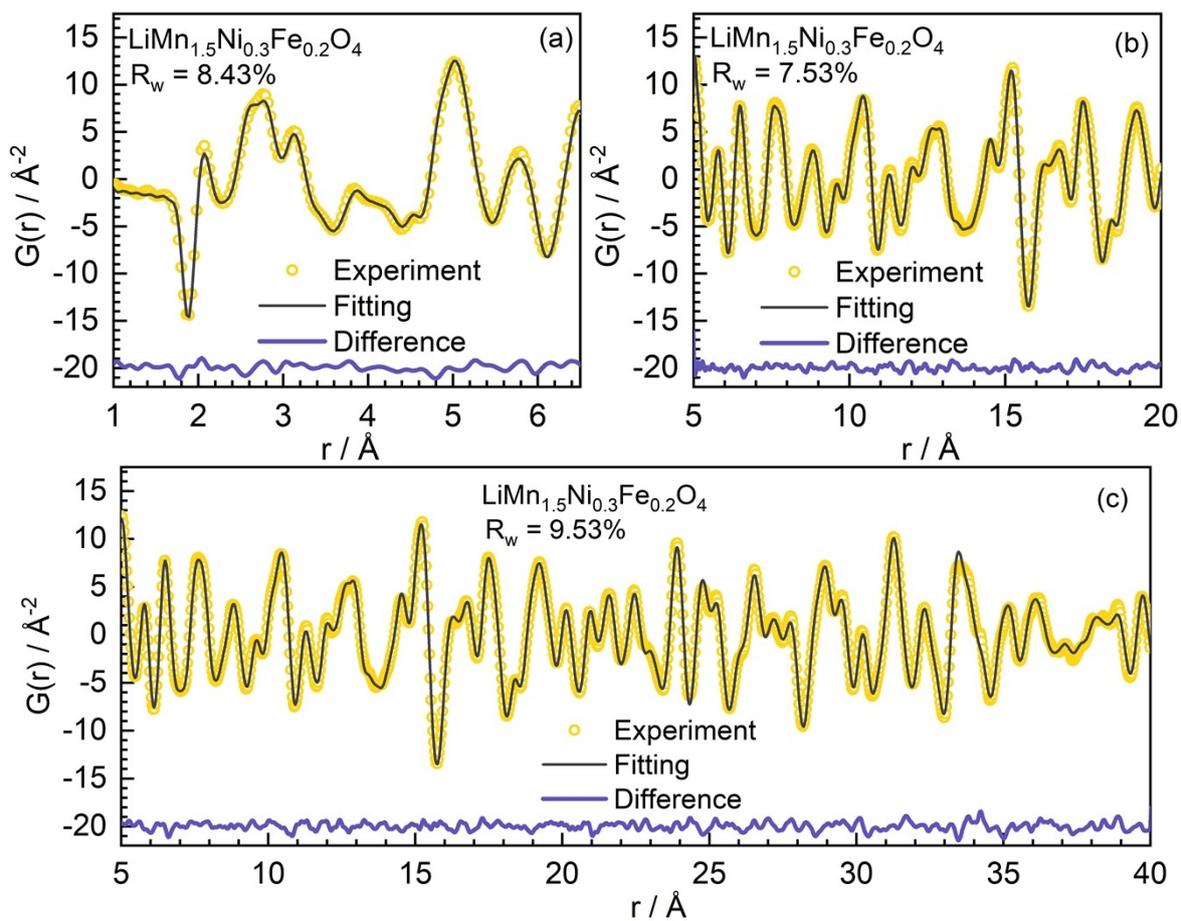


Figure S4. Experimental and fitted neutron pair distribution function profiles for $\text{LiMn}_{1.5}\text{Ni}_{0.3}\text{Fe}_{0.2}\text{O}_4$ over the real-space ranges 1 – 6.5 \AA (a), 5 – 20 \AA (b), and 5 – 40 \AA (c), using the $P4_332$ structural model.

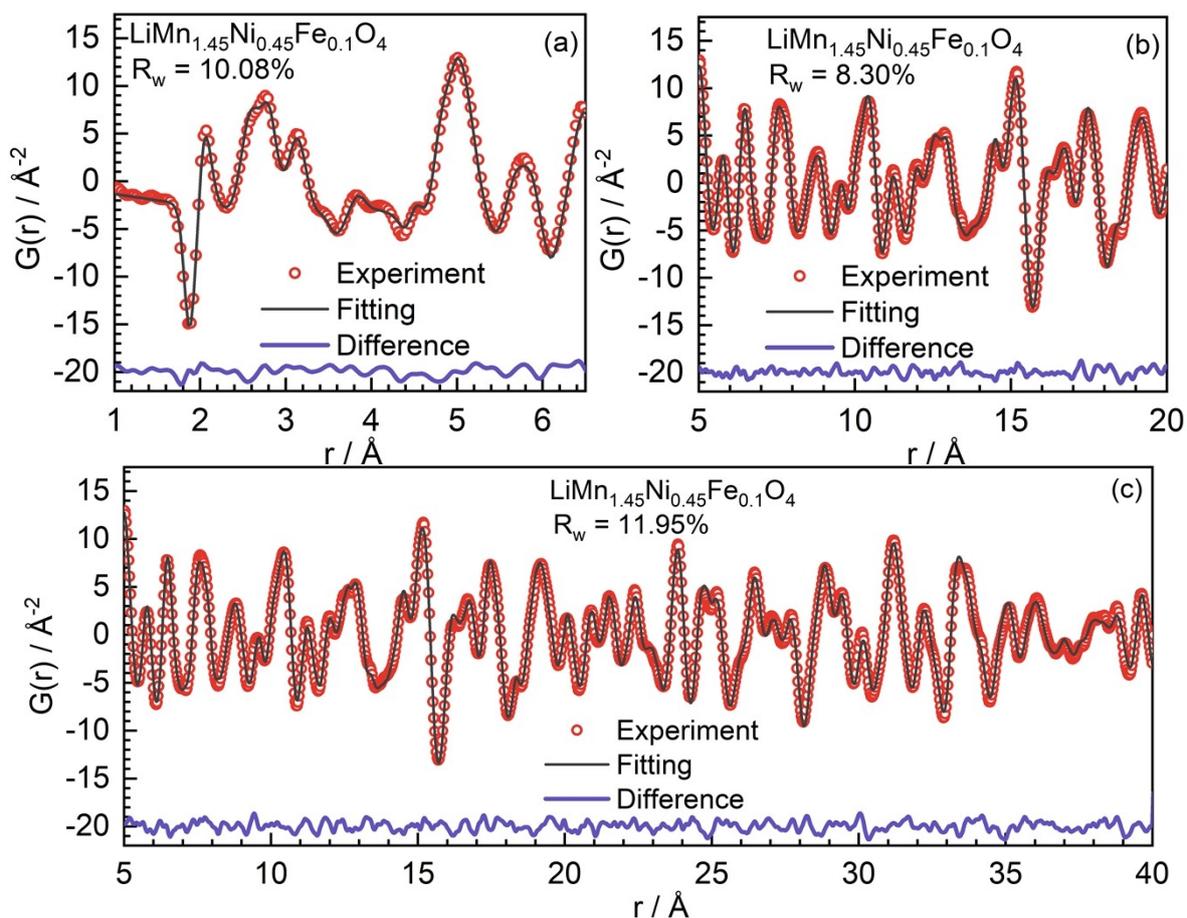


Figure S5. Experimental and fitted neutron pair distribution function profiles for $\text{LiMn}_{1.45}\text{Ni}_{0.45}\text{Fe}_{0.1}\text{O}_4$ over the real-space ranges 1 – 6.5 \AA (a), 5 – 20 \AA (b), and 5 – 40 \AA (c), using the $P4_332$ structural model.

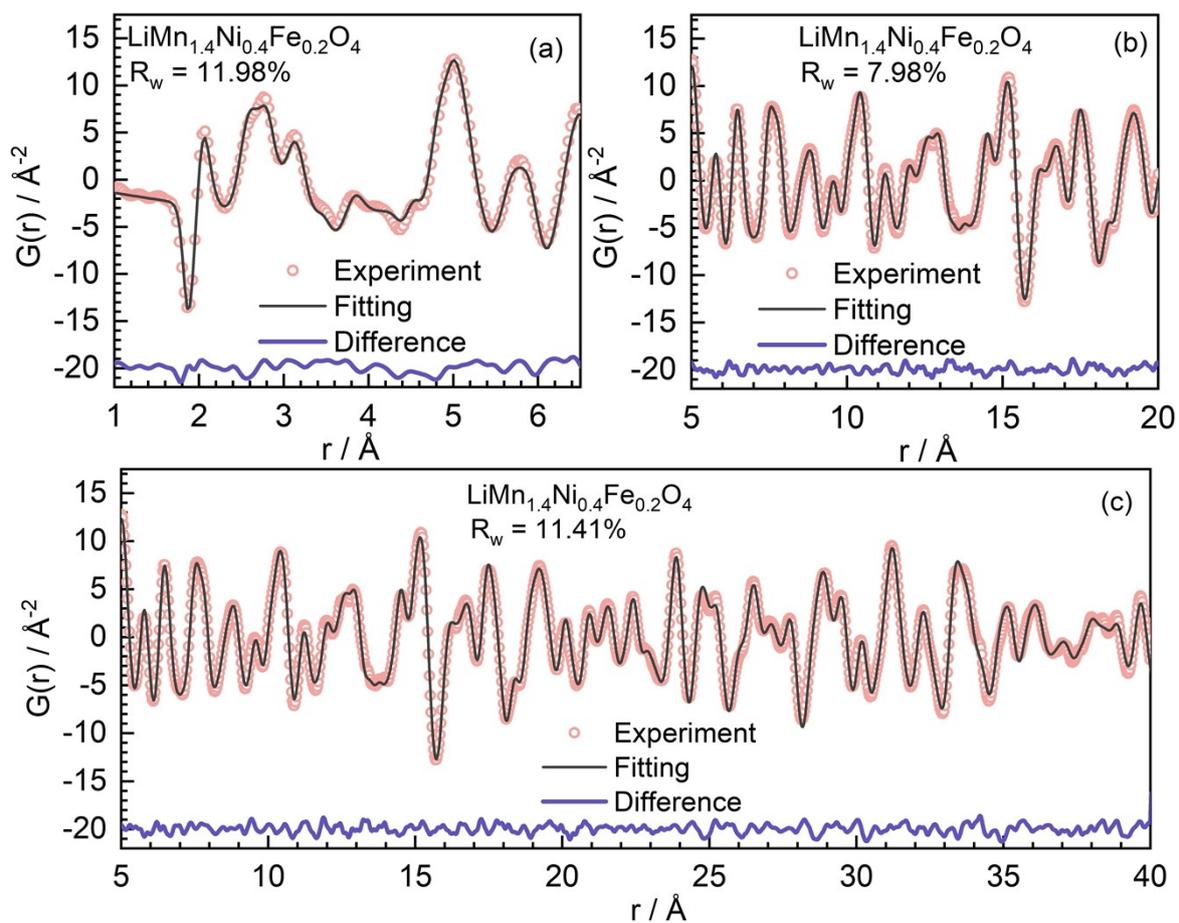


Figure S6. Experimental and fitted neutron pair distribution function profiles for $\text{LiMn}_{1.4}\text{Ni}_{0.4}\text{Fe}_{0.2}\text{O}_4$ over the real-space ranges 1 – 6.5 \AA (a), 5 – 20 \AA (b), and 5 – 40 \AA (c), using the $P4_332$ structural model.

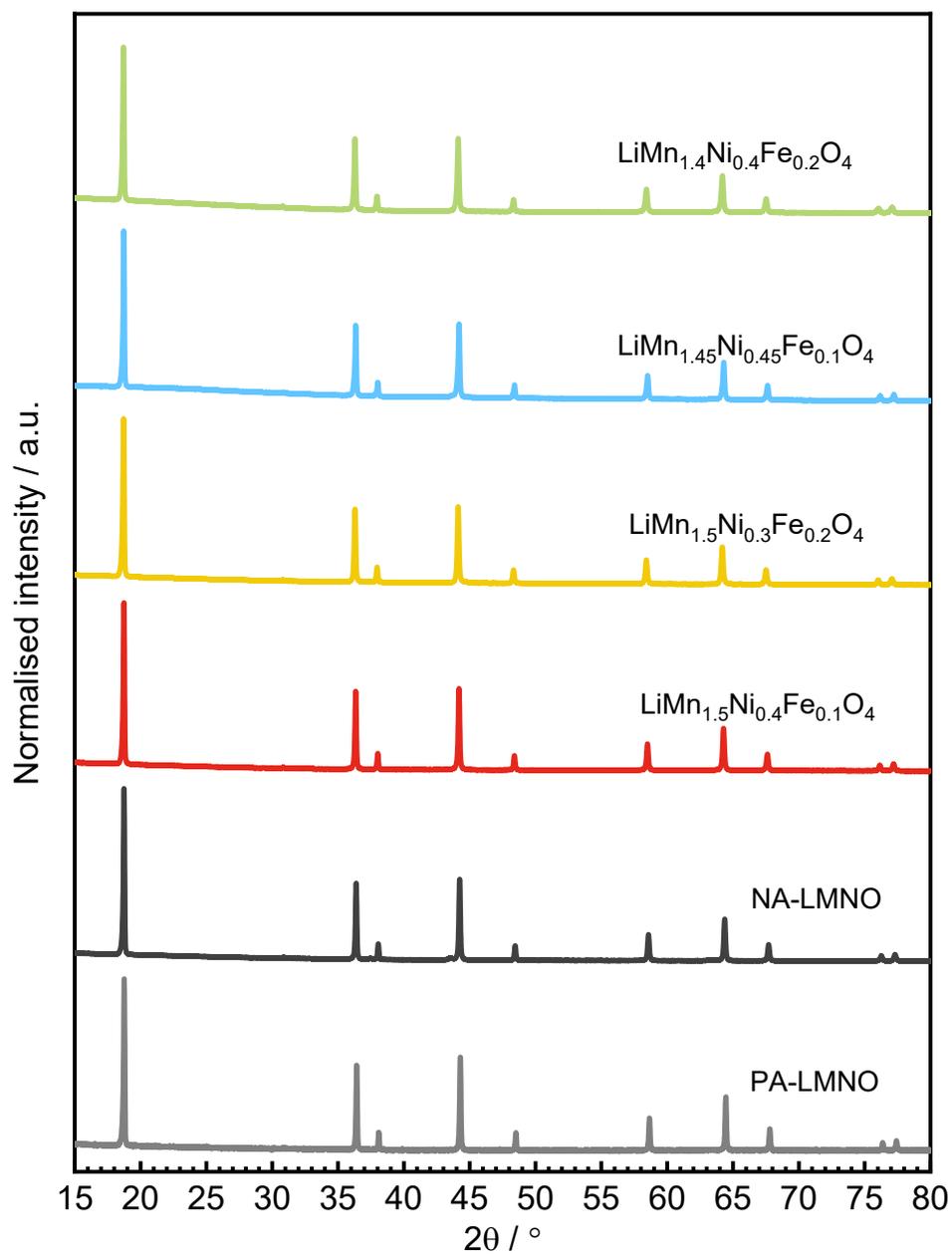


Figure S7. Powder X-ray diffraction patterns of post-annealed (PA) LiMn_{1.5}Ni_{0.5}O₄, non-annealed (NA) LiMn_{1.5}Ni_{0.5}O₄, and Fe-substituted LiMn_{1.5}Ni_{0.5-2x}Fe_{2x}O₄ and LiMn_{1.5-x}Ni_{0.5-x}Fe_{2x}O₄ (x = 0.05 and 0.1).

Table S1. Site-occupancy constraints used for Mn and Ni atoms at the $4b$ and $12d$ sites during PDF refinement of post-annealed LMNO and non-annealed LMNO using the $P4_32$ space group. These constraints ensure chemically consistent Mn/Ni distributions and enable direct comparison of cation ordering between annealed and non-annealed samples.

	Post-annealed $\text{LiMn}_{1.5}\text{Ni}_{0.5}\text{O}_4$	Non-annealed $\text{LiMn}_{1.5}\text{Ni}_{0.5}\text{O}_4$
Mn in $4b$ site	$1-x$	$1-x$
Ni in $4b$ site	x	x
Mn in $12d$ site	$(2+x)/3$	$(2+x)/3$
Ni in $12d$ site	$(1-x)/3$	$(1-x)/3$

Table S2. Site-occupancy constraints used for Mn, Ni, and Fe atoms at the $4b$ and $12d$ sites during PDF refinement of Fe-substituted spinel samples $\text{LiMn}_{1.5}\text{Ni}_{0.4}\text{Fe}_{0.1}\text{O}_4$ and $\text{LiMn}_{1.5}\text{Ni}_{0.3}\text{Fe}_{0.2}\text{O}_4$ using the $P4_32$ space group. These constraints were implemented to maintain charge balance and structural consistency, while evaluating Fe-induced cation redistribution.

	$\text{LiMn}_{1.5}\text{Ni}_{0.4}\text{Fe}_{0.1}\text{O}_4$		$\text{LiMn}_{1.5}\text{Ni}_{0.3}\text{Fe}_{0.2}\text{O}_4$	
	Model 1	Model 2	Model 1	Model 2
Mn in $4b$ site	$1-x$	$(14-11x)/15$	$1-x$	$(13-7x)/15$
Ni in $4b$ site	$4x/5$	$4x/5$	$3x/5$	$3x/5$
Fe in $4b$ site	$x/5$	$(1-x)/15$	$2x/5$	$2(1-x)/15$
Mn in $12d$ site	$(2+x)/3$	$(31+11x)/45$	$(2+x)/3$	$(32+7x)/45$
Ni in $12d$ site	$4 \times (1-x)/15$	$4 \times (1-x)/15$	$(1-x)/5$	$(1-x)/5$
Fe in $12d$ site	$(1-x)/15$	$(2+x)/45$	$2(1-x)/15$	$2 \times (2+x)/45$

Table S3. Site-occupancy constraints used for Mn, Ni, and Fe atoms at the $4b$ and $12d$ sites during PDF refinement of Fe-substituted spinel samples $\text{LiMn}_{1.45}\text{Ni}_{0.45}\text{Fe}_{0.1}\text{O}_4$ and $\text{LiMn}_{1.4}\text{Ni}_{0.4}\text{Fe}_{0.2}\text{O}_4$ using the $P4_32$ space group. These constraints were implemented to maintain charge balance and structural consistency, while evaluating Fe-induced cation redistribution.

	$\text{LiMn}_{1.45}\text{Ni}_{0.45}\text{Fe}_{0.1}\text{O}_4$		$\text{LiMn}_{1.4}\text{Ni}_{0.4}\text{Fe}_{0.2}\text{O}_4$	
	Model 1 $\sqrt{\quad}$	Model 2 \times	Model 1 $\sqrt{\quad}$	Model 2 \times
Mn in $4b$ site	$29 \times (1-x)/30$	$(28-25x)/30$	$14 \times (1-x)/15$	$(13-10x)/15$
Ni in $4b$ site	$(1+23x)/30$	$9x/10$	$(8x+1)/15$	$4x/5$
Fe in $4b$ site	$x/5$	$(1-x)/15$	$2x/5$	$2 \times (1-x)/15$
Mn in $12d$ site	$29 \times (2+x)/90$	$(59+25x)/90$	$14 \times (2+x)/45$	$(29+10x)/45$
Ni in $12d$ site	$(26-23x)/90$	$3 \times (1-x)/10$	$(11-8x)/45$	$4 \times (1-x)/15$
Fe in $12d$ site	$(1-x)/15$	$(2+x)/45$	$2(1-x)/15$	$2 \times (2+x)/45$

Table S4. Refined structural parameters for post-annealed $\text{LiMn}_{1.5}\text{Ni}_{0.5}\text{O}_4$ obtained from PDF analysis over the real-space ranges 1 – 6.5 Å, 5 – 20 Å, and 5 – 40 Å, corresponding to the fits shown in Figure S1. Parameters include lattice constants, atomic positions, and Mn/Ni occupancies, capturing the evolution of short-, intermediate-, and long-range structural ordering.

	Atom	Wyckoff site	x	y	z	occ.
Fitting range 1 – 6.5 Å $a = 8.14916 \text{ Å}$	Li	8c	0.00092	0.00092	0.00092	1.0
	Mn	4b	0.625	0.625	0.625	0.01255
	Ni	4b	0.625	0.625	0.625	0.98745
	Mn	12d	0.125	0.37843	-0.12843	0.99582
	Ni	12d	0.125	0.37843	-0.12843	0.00418
	O1	8c	0.38380	0.38380	0.38380	1.0
	O2	24e	0.09986	0.12428	0.39348	1.0
Fitting range 5 – 20 Å $a = 8.16749 \text{ Å}$	Li	8c	0.00858	0.00858	0.00858	1.0
	Mn	4b	0.625	0.625	0.625	0.05986
	Ni	4b	0.625	0.625	0.625	0.94014
	Mn	12d	0.125	0.37991	-0.12991	0.98005
	Ni	12d	0.125	0.37991	-0.12991	0.01995
	O1	8c	0.38381	0.38381	0.38381	1.0
	O2	24e	0.10004	0.12452	0.39182	1.0
Fitting range 5 – 40 Å $a = 8.17054 \text{ Å}$	Li	8c	0.00453	0.00453	0.00453	1.0
	Mn	4b	0.625	0.625	0.625	0.12892
	Ni	4b	0.625	0.625	0.625	0.87108
	Mn	12d	0.125	0.38019	-0.13019	0.95703
	Ni	12d	0.125	0.38019	-0.13019	0.04297
	O1	8c	0.38372	0.38372	0.38372	1.0
	O2	24e	0.10049	0.12468	0.39229	1.0

Table S5. Refined structural parameters for non-annealed $\text{LiMn}_{1.5}\text{Ni}_{0.5}\text{O}_4$ obtained from PDF analysis over the real-space ranges 1 – 6.5 Å, 5 – 20 Å, and 5 – 40 Å, corresponding to the fits shown in Figure S2. Parameters include lattice constants, atomic positions, and Mn/Ni occupancies, capturing the evolution of short-, intermediate-, and long-range structural ordering.

	Atom	Wyckoff site	x	y	z	occ.
Fitting range 1 – 6.5 Å $a = 8.14442 \text{ Å}$	Li	8c	-0.00384	-0.00384	-0.00384	1.0
	Mn	4b	0.625	0.625	0.625	0.08605
	Ni	4b	0.625	0.625	0.625	0.91395
	Mn	12d	0.125	0.37579	-0.12579	0.97132
	Ni	12d	0.125	0.37579	-0.12579	0.02868
	O1	8c	0.38285	0.38285	0.38285	1.0
	O2	24e	0.09986	0.12339	0.39496	1.0
Fitting range 5 – 20 Å $a = 8.17857 \text{ Å}$	Li	8c	0.01189	0.01189	0.01189	1.0
	Mn	4b	0.625	0.625	0.625	0.57230
	Ni	4b	0.625	0.625	0.625	0.42770
	Mn	12d	0.125	0.38332	-0.13332	0.80923
	Ni	12d	0.125	0.38332	-0.13332	0.19077
	O1	8c	0.38943	0.38943	0.38943	1.0
	O2	24e	0.10756	0.11960	0.38772	1.0
Fitting range 5 – 40 Å $a = 8.17765 \text{ Å}$	Li	8c	0.01231	0.01231	0.01231	1.0
	Mn	4b	0.625	0.625	0.625	0.67868
	Ni	4b	0.625	0.625	0.625	0.32132
	Mn	12d	0.125	0.38155	-0.13155	0.77377
	Ni	12d	0.125	0.38155	-0.13155	0.22623
	O1	8c	0.38874	0.38874	0.38874	1.0
	O2	24e	0.10861	0.12123	0.39169	1.0

Table S6. Refined structural parameters for $\text{LiMn}_{1.5}\text{Ni}_{0.4}\text{Fe}_{0.1}\text{O}_4$ obtained from PDF analysis over the real-space ranges 1 – 6.5 Å, 5 – 20 Å, and 5 – 40 Å, corresponding to the fits shown in Figure S3. Parameters include lattice constants, atomic positions, and Mn/Ni occupancies, capturing the evolution of short-, intermediate-, and long-range structural ordering.

	Atom	Wyckoff site	x	y	z	occ.
Fitting range 1 – 6.5 Å $a = 8.16240 \text{ Å}$	Li	8c	-0.00486	-0.00486	-0.00486	1.0
	Mn	4b	0.625	0.625	0.625	0.12978
	Ni	4b	0.625	0.625	0.625	0.69618
	Fe	4b	0.625	0.625	0.625	0.17404
	Mn	12d	0.125	0.37552	-0.12552	0.95674
	Ni	12d	0.125	0.37552	-0.12552	0.03461
	Fe	12d	0.125	0.37552	-0.12552	0.00865
	O1	8c	0.38300	0.38300	0.38300	1.0
	O2	24e	0.10223	0.12289	0.39518	1.0
Fitting range 5 – 20 Å $a = 8.19565 \text{ Å}$	Li	8c	0.01056	0.01056	0.01056	1.0
	Mn	4b	0.625	0.625	0.625	0.76691
	Ni	4b	0.625	0.625	0.625	0.18647
	Fe	4b	0.625	0.625	0.625	0.04662
	Mn	12d	0.125	0.38278	-0.13278	0.74436
	Ni	12d	0.125	0.38278	-0.13278	0.20451
	Fe	12d	0.125	0.38278	-0.13278	0.05113
	O1	8c	0.38756	0.38756	0.38756	1.0
	O2	24e	0.11336	0.11894	0.39582	1.0
Fitting range 5 – 40 Å $a = 8.19671 \text{ Å}$	Li	8c	0.01199	0.01199	0.01199	1.0
	Mn	4b	0.625	0.625	0.625	0.71494
	Ni	4b	0.625	0.625	0.625	0.22805
	Fe	4b	0.625	0.625	0.625	0.05701
	Mn	12d	0.125	0.38148	-0.13148	0.76169
	Ni	12d	0.125	0.38148	-0.13148	0.19065
	Fe	12d	0.125	0.38148	-0.13148	0.04766
	O1	8c	0.38933	0.38933	0.38933	1.0
	O2	24e	0.10982	0.12102	0.39278	1.0

Table S7. Refined structural parameters for $\text{LiMn}_{1.5}\text{Ni}_{0.3}\text{Fe}_{0.2}\text{O}_4$ obtained from PDF analysis over the real-space ranges 1 – 6.5 Å, 5 – 20 Å, and 5 – 40 Å, corresponding to the fits shown in Figure S4. Parameters include lattice constants, atomic positions, and Mn/Ni occupancies, capturing the evolution of short-, intermediate-, and long-range structural ordering.

	Atom	Wyckoff site	x	y	z	occ.
Fitting range 1 – 6.5 Å $a = 8.17741 \text{ Å}$	Li	8c	-0.00548	-0.00548	-0.00548	1.0
	Mn	4b	0.625	0.625	0.625	0.17237
	Ni	4b	0.625	0.625	0.625	0.49658
	Fe	4b	0.625	0.625	0.625	0.33105
	Mn	12d	0.125	0.37462	-0.12462	0.94254
	Ni	12d	0.125	0.37462	-0.12462	0.03447
	Fe	12d	0.125	0.37462	-0.12462	0.02298
	O1	8c	0.38289	0.38289	0.38289	1.0
	O2	24e	0.10299	0.12255	0.39554	1.0
Fitting range 5 – 20 Å $a = 8.21039 \text{ Å}$	Li	8c	0.00256	0.00256	0.00256	1.0
	Mn	4b	0.625	0.625	0.625	0.81855
	Ni	4b	0.625	0.625	0.625	0.10887
	Fe	4b	0.625	0.625	0.625	0.07258
	Mn	12d	0.125	0.37446	-0.12446	0.72715
	Ni	12d	0.125	0.37446	-0.12446	0.16371
	Fe	12d	0.125	0.37446	-0.12446	0.10914
	O1	8c	0.38748	0.38748	0.38748	1.0
	O2	24e	0.11478	0.11711	0.39562	1.0
Fitting range 5 – 40 Å $a = 8.21198 \text{ Å}$	Li	8c	0.01232	0.01232	0.01232	1.0
	Mn	4b	0.625	0.625	0.625	0.78020
	Ni	4b	0.625	0.625	0.625	0.13188
	Fe	4b	0.625	0.625	0.625	0.08792
	Mn	12d	0.125	0.38464	-0.13464	0.73993
	Ni	12d	0.125	0.38464	-0.13464	0.15604
	Fe	12d	0.125	0.38464	-0.13464	0.10403
	O1	8c	0.38979	0.38979	0.38979	1.0
	O2	24e	0.11085	0.12032	0.39290	1.0

Table S8. Refined structural parameters for $\text{LiMn}_{1.45}\text{Ni}_{0.45}\text{Fe}_{0.1}\text{O}_4$ obtained from PDF analysis over the real-space ranges 1 – 6.5 Å, 5 – 20 Å, and 5 – 40 Å, corresponding to the fits shown in Figure S5. Parameters include lattice constants, atomic positions, and Mn/Ni occupancies, capturing the evolution of short-, intermediate-, and long-range structural ordering.

	Atom	Wyckoff site	x	y	z	occ.
Fitting range 1 – 6.5 Å $a = 8.15952 \text{ \AA}$	Li	8c	-0.00505	-0.00505	-0.00505	1.0
	Mn	4b	0.625	0.625	0.625	0.06231
	Ni	4b	0.625	0.625	0.625	0.75058
	Fe	4b	0.625	0.625	0.625	0.18711
	Mn	12d	0.125	0.27551	-0.12551	0.94589
	Ni	12d	0.125	0.27551	-0.12551	0.04981
	Fe	12d	0.125	0.27551	-0.12551	0.00430
	O1	8c	0.38270	0.38270	0.38270	1.0
	O2	24e	0.10230	0.12290	0.39514	1.0
Fitting range 5 – 20 Å $a = 8.19336 \text{ \AA}$	Li	8c	0.01129	0.01129	0.01129	1.0
	Mn	4b	0.625	0.625	0.625	0.61507
	Ni	4b	0.625	0.625	0.625	0.31219
	Fe	4b	0.625	0.625	0.625	0.07274
	Mn	12d	0.125	0.37516	-0.12516	0.76164
	Ni	12d	0.125	0.37516	-0.12516	0.19594
	Fe	12d	0.125	0.37516	-0.12516	0.04242
	O1	8c	0.38935	0.38935	0.38935	1.0
	O2	24e	0.10797	0.11328	0.38154	1.0
Fitting range 5 – 40 Å $a = 8.19416 \text{ \AA}$	Li	8c	0.01242	0.01242	0.01242	1.0
	Mn	4b	0.625	0.625	0.625	0.59152
	Ni	4b	0.625	0.625	0.625	0.33086
	Fe	4b	0.625	0.625	0.625	0.07762
	Mn	12d	0.125	0.37456	-0.12456	0.76949
	Ni	12d	0.125	0.37456	-0.12456	0.18971
	Fe	12d	0.125	0.37456	-0.12456	0.04080
	O1	8c	0.38704	0.38704	0.38704	1.0
	O2	24e	0.10739	0.11542	0.38722	1.0

Table S9. Refined structural parameters for $\text{LiMn}_{1.4}\text{Ni}_{0.4}\text{Fe}_{0.2}\text{O}_4$ obtained from PDF analysis over the real-space ranges 1 – 6.5 Å, 5 – 20 Å, and 5 – 40 Å, corresponding to the fits shown in Figure S6. Parameters include lattice constants, atomic positions, and Mn/Ni occupancies, capturing the evolution of short-, intermediate-, and long-range structural ordering.

	Atom	Wyckoff site	x	y	z	occ.
Fitting range 1 – 6.5 Å $a = 8.16945 \text{ \AA}$	Li	8c	-0.00554	-0.00554	-0.00554	1.0
	Mn	4b	0.625	0.625	0.625	0.03511
	Ni	4b	0.625	0.625	0.625	0.57994
	Fe	4b	0.625	0.625	0.625	0.38495
	Mn	12d	0.125	0.37473	-0.12473	0.92163
	Ni	12d	0.125	0.37473	-0.12473	0.07335
	Fe	12d	0.125	0.37473	-0.12473	0.00502
	O1	8c	0.38221	0.38221	0.38221	1.0
	O2	24e	0.10243	0.12255	0.39506	1.0
Fitting range 5 – 20 Å $a = 8.20006 \text{ \AA}$	Li	8c	0.01149	0.01149	0.01149	1.0
	Mn	4b	0.625	0.625	0.625	0.49948
	Ni	4b	0.625	0.625	0.625	0.31458
	Fe	4b	0.625	0.625	0.625	0.18594
	Mn	12d	0.125	0.39968	-0.14968	0.76684
	Ni	12d	0.125	0.39968	-0.14968	0.16181
	Fe	12d	0.125	0.39968	-0.14968	0.07135
	O1	8c	0.38701	0.38701	0.38701	1.0
	O2	24e	0.11561	0.11654	0.39476	1.0
Fitting range 5 – 40 Å $a = 8.20109 \text{ \AA}$	Li	8c	0.01311	0.01311	0.01311	1.0
	Mn	4b	0.625	0.625	0.625	0.56066
	Ni	4b	0.625	0.625	0.625	0.27962
	Fe	4b	0.625	0.625	0.625	0.15972
	Mn	12d	0.125	0.36972	-0.11972	0.74645
	Ni	12d	0.125	0.36972	-0.11972	0.17346
	Fe	12d	0.125	0.36972	-0.11972	0.08009
	O1	8c	0.38651	0.38651	0.38651	1.0
	O2	24e	0.11558	0.11478	0.39401	1.0