Electronic Supplementary Material (ESI) for Dalton Transactions.

Supplementary data:

Biphasic P2/O3-$Na_{2/3}Li_{0.18}Mn_{0.8}Fe_{0.2}O_2$: A Structural Investigation.

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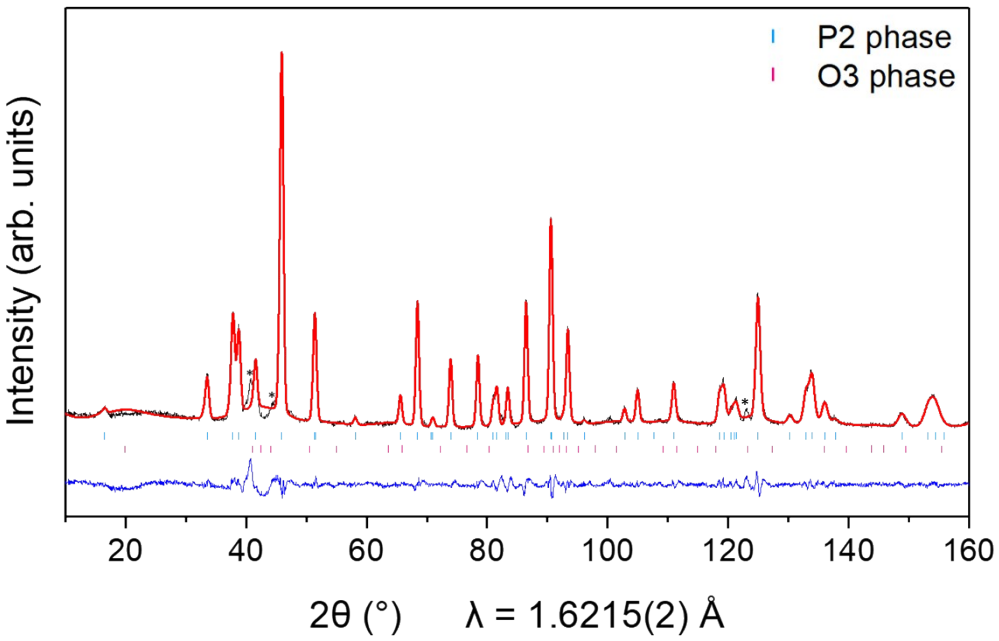

Figure S1. Neutron diffraction data collected at room temperature for the pristine P2/O3-$Na_{2/3}Li_{0.18}Mn_{0.8}Fe_{0.2}O_2$ powder, indexed with a P2 and O3 phase (Le Bail fit). Observed, calculated and difference are shown by a solid black, red and blue line, respectively. Asterisks indicate reflection intensity around 2θ = 40°, 43° and 125° which are not accounted for by the model. The peak around 2θ = 40° is later accounted for upon introducing Li to Rietveld-refined model, while the origin of the peaks around 2θ = 43° and 125° are unknown.

Table S1. Concentration (in ppm) of the experimental and theoretical molar ratio (fixing Mn content) of the elements detected in the sample by ICP-OES measurement.

Element	ICP Concentration (ppm)	Experimental molar ratio*	Theoretical molar ratio
Na	6.61	0.62(1)	0.67
Mn	20.4	0.80	0.8
Fe	4.82	0.19(1)	0.2
Li	0.574	0.18(2)	0.18

*Errors calculated based on a 10% variation in ICP concentrations. No error is given for Mn since the Mn content is fixed to perform the calculations.

Table S2. Crystallographic parameters for P2-$Na_{2/3}Mn_{0.8}Fe_{0.2}O_2$ as determined from Rietveld analysis of neutron powder diffraction data ($P6_3/mmc$), see also Figure 4.

Atom	Wyckoff	x	y	z	SOF [a]	Isotropic ADP [a] (×100/Å²)
Na_e	2b	0	0	0.25	0.30(1) *	7.2(3)
Na_f	2d	1/3	2/3	0.75	0.37(1) *	6.8(3)
Mn	2a	0	0	0	0.8	0.29(9)
Fe	2a	0	0	0	0.2	0.27(9)
O	4f	1/3	2/3	0.0909(1)	1	1.3(1)

[a] Atomic displacement parameter (ADP), site occupancy factor (SOF).* Total Na content constrained to be 0.67. Space group $P6_3/mmc$, R_p = 4.4%, wR_p = 5.6%, a = 2.8816(1) Å, c =11.2060(4) Å. Weight fraction = 93.83(2)%.

Table S3. Crystallographic parameters for O3-$LiMn_{0.8}Fe_{0.2}O_2$ as determined from Rietveld analysis of neutron powder diffraction data (R-3m), see also Figure 4.

Atom	Wyckoff	x	y	z	SOF [a]	Isotropic ADP [a] (×100/Å²)
Li	3a	0	0	0	1	5.2(11)
Mn	3b	0	0	0.5	0.8	1.0*
Fe	3b	0	0	0.5	0.2	1.0*
O	6c	0	0	0.2358(5)	1	0.42(9)

[a] Atomic displacement parameter (ADP), site occupancy factor (SOF). * Values fixed. Space group R-3m, R_p = 4.4%, wR_p = 5.6%, a = 2.8419(6) Å, c =14.198(6) Å. Weight fraction = 6.17(1)%.

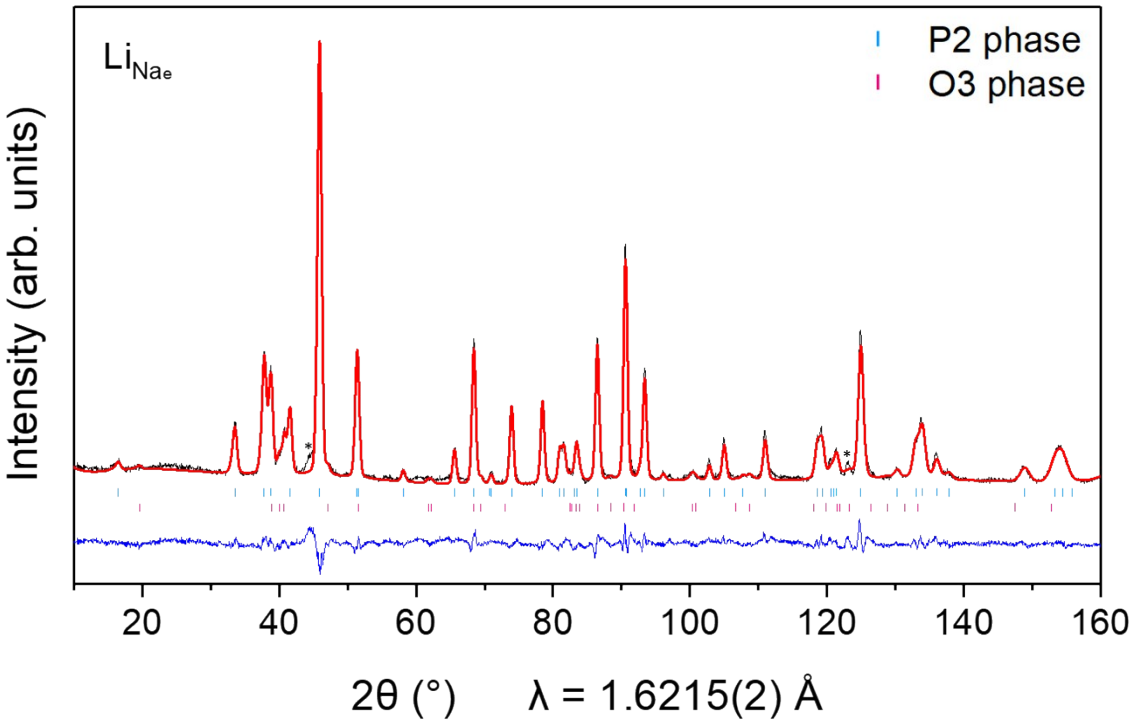

Figure S2. Rietveld analysis of neutron diffraction data collected at room temperature for the pristine P2/O3-$Na_{2/3}Li_{0.18}Mn_{0.8}Fe_{0.2}O_2$ powder, indexed with O3-$LiMn_{0.8}Fe_{0.2}O_2$ and P2-$Na_{2/3}Li_{0.12}Mn_{0.8}Fe_{0.2}O_2$ whereby Li is introduced onto the Na_e site. Observed, calculated and difference are shown by a solid black, red and blue line, respectively. The asterisks indicate small peaks around 2θ = 43° and 125° which are not accounted for by the model; the origin of these reflections is unknown.

Table S4. Crystallographic parameters for P2-$Na_{0.71}Li_{0.12}Mn_{0.8}Fe_{0.2}O_2$ with Li on the Na_e site (model 1) as determined from Rietveld analysis of neutron powder diffraction data ($P6_3/mmc$).

Atom	Wyckoff	x	y	z	SOF [a]	Isotropic ADP [a] (×100/Å^2)
Na_e	2b	0	0	0.25	0.32(1) *	4.6(2)
Na_f	2d	1/3	2/3	0.75	0.39(1) *	7.4(3)
Li	2b	0	0	0.25	0.12	3.5(7)
Mn	2a	0	0	0	0.8	0.71(4)
Fe	2a	0	0	0	0.2	0.78(6)
O	4f	1/3	2/3	0.0907(1)	1	1.4(1)

[a] Atomic displacement parameter (ADP), site occupancy factor (SOF).* Total Na content constrained to be 0.71. Space group $P6_3/mmc$, R_p = 4.4%, wR_p = 5.5%, a = 2.8816(1) Å, c =11.2057(4) Å.

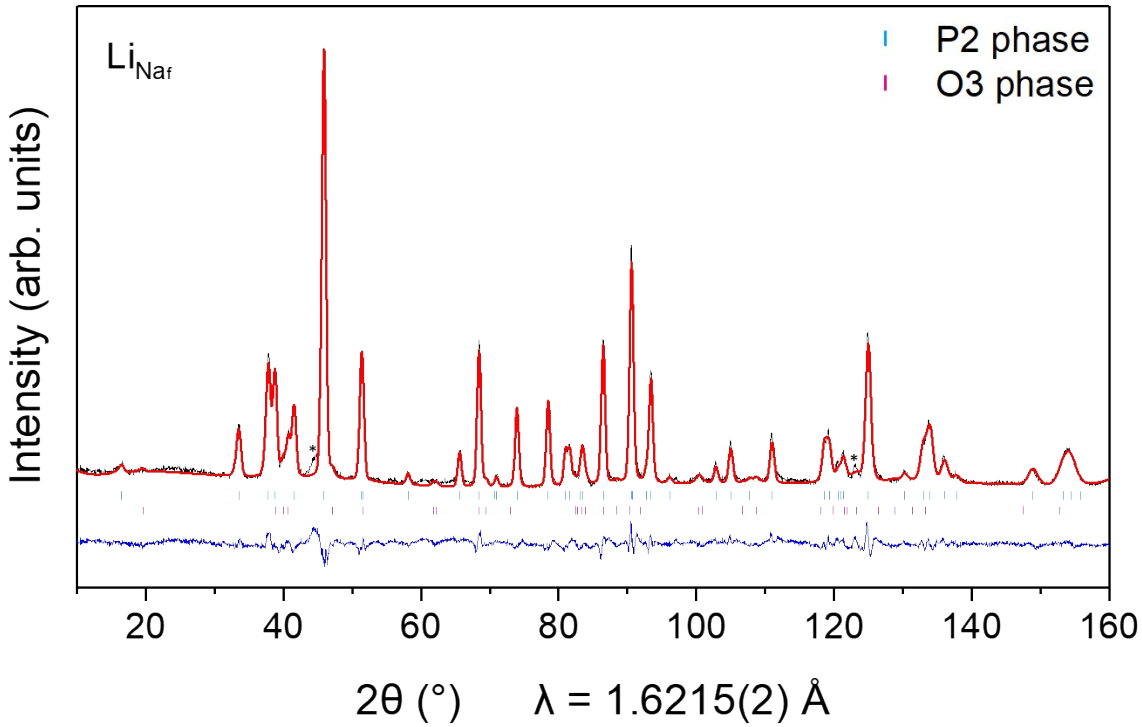

Figure S3. Rietveld analysis of neutron diffraction data collected at room temperature for the pristine P2/O3-$Na_{2/3}Li_{0.18}Mn_{0.8}Fe_{0.2}O_2$ powder, indexed with O3-$LiMn_{0.8}Fe_{0.2}O_2$ and P2-$Na_{2/3}Li_{0.12}Mn_{0.8}Fe_{0.2}O_2$ whereby Li is introduced onto the Na_f site. Observed, calculated and difference are shown by a solid black, red and blue line, respectively. The asterisks indicate small peaks around 2θ = 43° and 125° which are not accounted for by the model; the origin of these reflections is unknown.

Table S5. Crystallographic parameters for P2-$Na_{0.71}Li_{0.12}Mn_{0.8}Fe_{0.2}O_2$ with Li on the Na_f site (model 2) as determined from Rietveld analysis of neutron powder diffraction data ($P6_3/mmc$).

Atom	Wyckoff	x	y	z	SOF [a]	Isotropic ADP [a] (×100/Å^2)
Na_e	2b	0	0	0.25	0.32(1) *	7.7(3)
Na_f	2d	1/3	2/3	0.75	0.39(1) *	5.8(2)
Li_f	2d	1/3	2/3	0.75	0.12	2.5(9)
Mn	2a	0	0	0	0.8	0.26(3)
Fe	2a	0	0	0	0.2	0.17(5)
O	4f	1/3	2/3	0.0908(1)	1	1.4(1)

[a] Atomic displacement parameter (ADP), site occupancy factor (SOF). * Total Na content constrained to be 0.71. Space group $P6_3/mmc$, R_p = 4.4%, wR_p = 5.5%, a = 2.8816(1) Å, c =11.2057(4) Å.

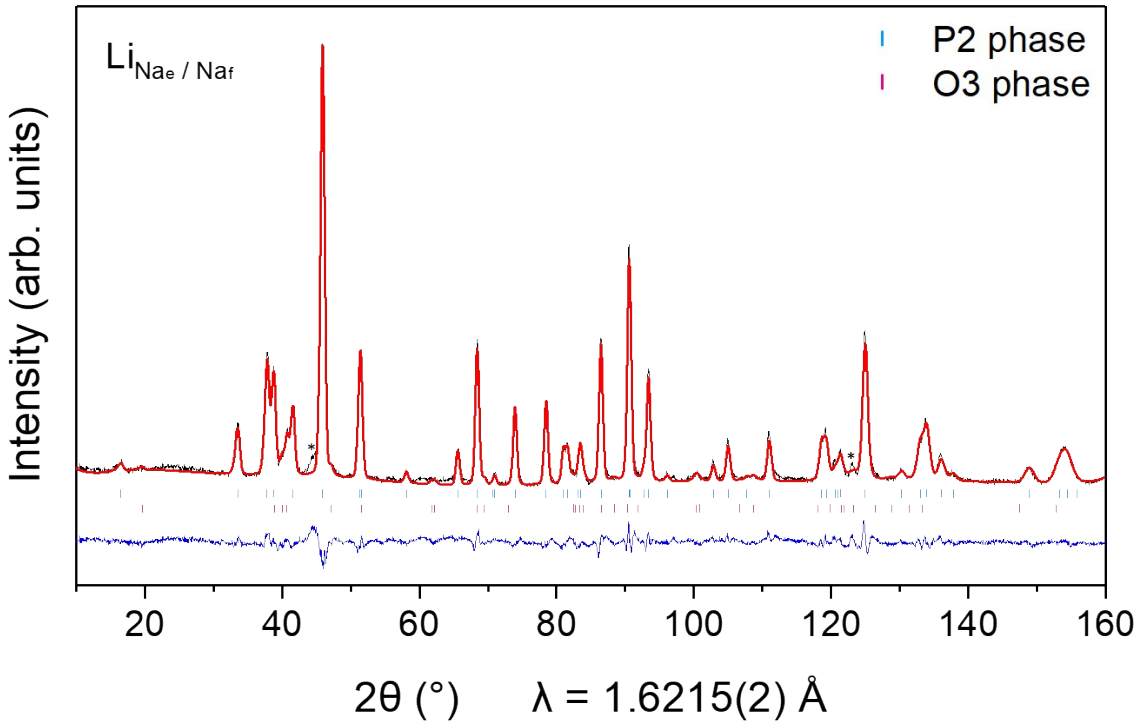

Figure S4. Rietveld analysis of neutron diffraction data collected at room temperature for the pristine P2/O3-$Na_{2/3}Li_{0.18}Mn_{0.8}Fe_{0.2}O_2$ powder, indexed with O3-$LiMn_{0.8}Fe_{0.2}O_2$ and P2-$Na_{2/3}Li_{0.12}Mn_{0.8}Fe_{0.2}O_2$ whereby Li is introduced onto both the Na_e and Na_f site. Observed, calculated and difference are shown by a solid black, red and blue line, respectively. The asterisks indicate small peaks around 2θ = 43° and 125° which are not accounted for by the model; the origin of these reflections is unknown.

Table S6. Crystallographic parameters for P2-$Na_{0.71}Li_{0.12}Mn_{0.8}Fe_{0.2}O_2$ with Li on both the Na_e and Na_f site (model 3) as determined from Rietveld analysis of neutron powder diffraction data ($P6_3/mmc$).

Atom	Wyckoff	x	y	z	SOF [a]	Isotropic ADP [a] (×100/Å^2)
Na_e	2b	0	0	0.25	0.32(1) *	6.3(2)
Na_f	2d	1/3	2/3	0.75	0.39(1) *	6.5(2)
Li_e	2b	0	0	0.25	0.06	5.3(2)
Li_f	2d	1/3	2/3	0.75	0.06	3.2(2)
Mn	2a	0	0	0	0.8	0.48(3)
Fe	2a	0	0	0	0.2	0.47(5)
O	4f	1/3	2/3	0.0908(1)	1	1.4(1)

[a] Atomic displacement parameter (ADP), site occupancy factor (SOF). * Total Na content constrained to be 0.71. Space group $P6_3/mmc$, R_p = 4.4%, wR_p = 5.5%, a = 2.8816(1) Å, c =11.2057(4) Å.

Calculation for the distribution of alkali ions in the P2 phase:

Overall composition: P2/O3-$Na_{2/3}Li_{0.18}Mn_{0.8}Fe_{0.2}O_2$

Composition of O3 phase: $LiMn_{0.8}Fe_{0.2}O_2$

Relative phase fractions: P2 = 93.83 %; O3 = 6.17 %

Remaining Li that must occupy the P2 phase: 0.18 – 1*6.17%/100 = 0.12

Na present in P2 phase: 0.67/0.9383 = 0.71