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# Supporting Information

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On the Elusive Crystallography of Lithium-Rich Layered Oxides: Novel Structural Models

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# On the Elusive Crystallography of Lithium-Rich Layered Oxides: Novel Structural Models

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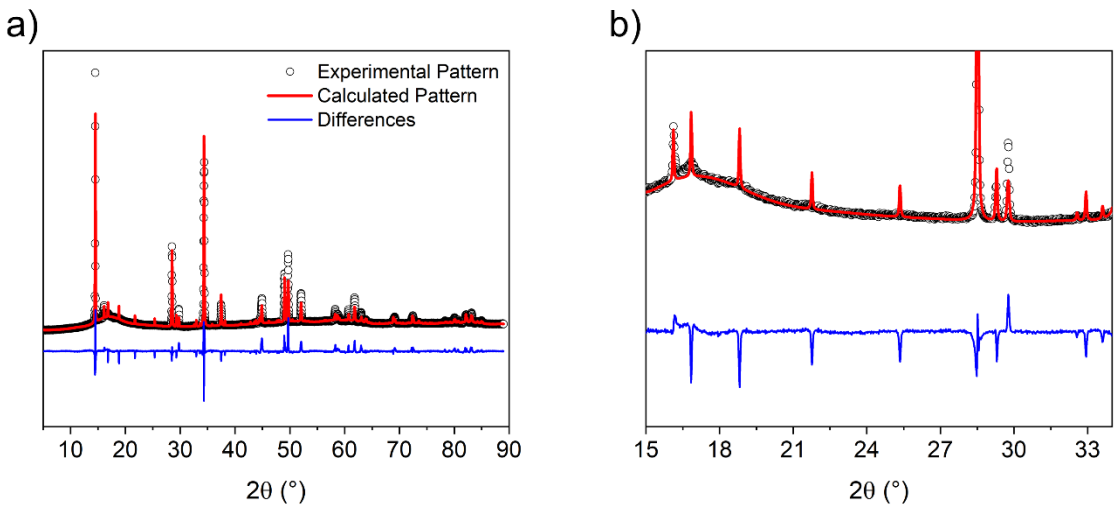


**Figure S1:** a) Rietveld refinement using two phases model, rhombohedral and monoclinic.

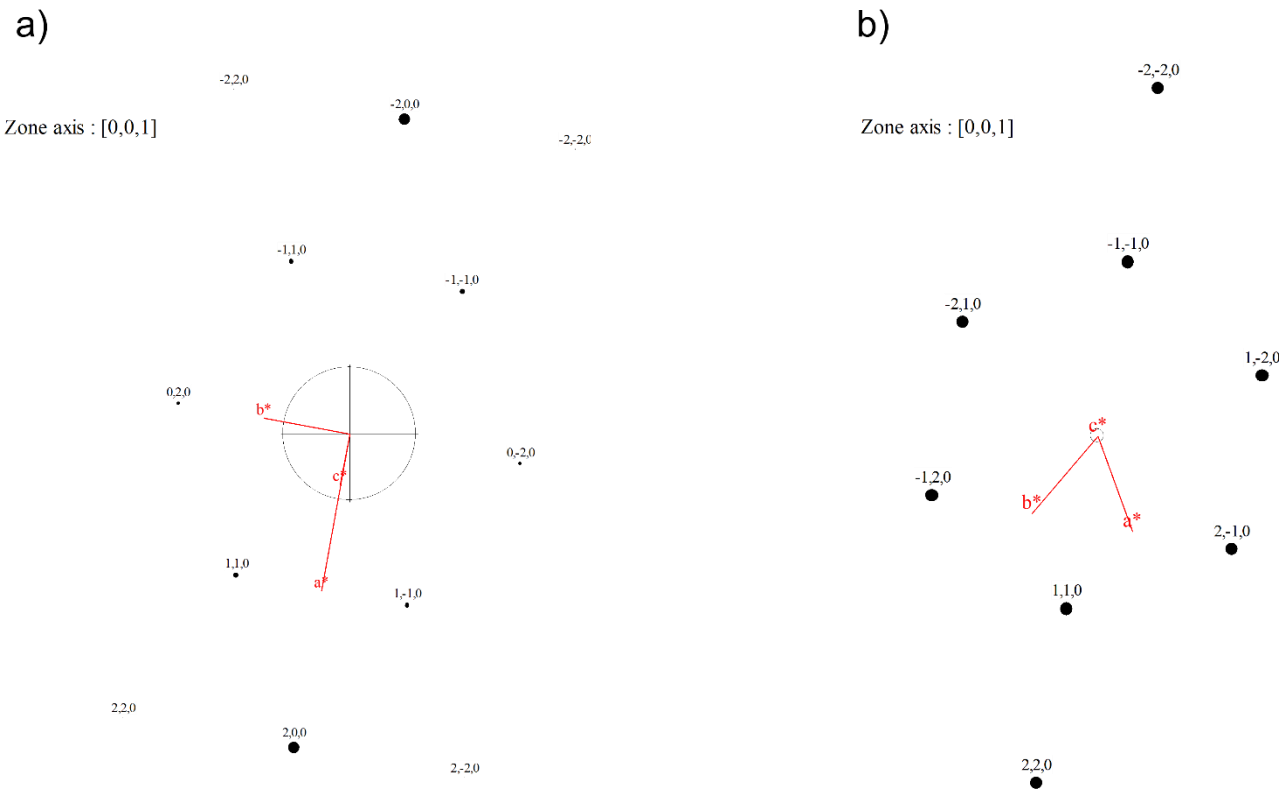


**Figure S2:** Single-crystal ED pattern calculated for the [001] axis zone for a) C2/m and b) R-3m (with lattice parameters a and b 3 times larger).

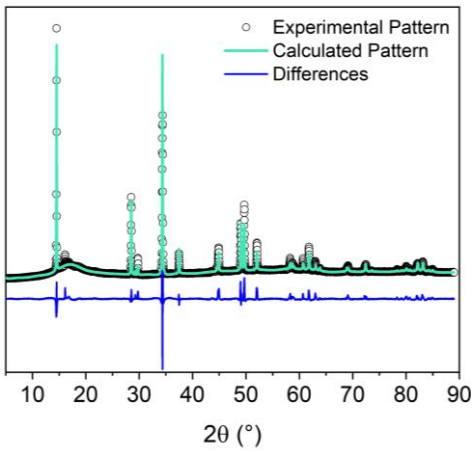


**Figure S3:** a) Rietveld refinement using R-3m with anti-site and oxygen defects.

| **Table S1:** Rietveld refined parameters for R-3m with anti-site and oxygen defects. | |
|---|---|
| **Space group** | R-3m (R=4.9%; Z=99) |
| **Lattice parameters** | a=b=2.855 c=14.247<br>α=β=90° γ=120° |
| **Atomic position and occupancies (Wycoff position; OF=occupancy fraction)** | |
| **Lithium ion layer** | (3b) ( 0 0 ½ )<br>OF(Li)=0.981 OF(TM)=0.019 |
| **Metal ions blend layer** | (3a) ( 0 0 0 )<br>OF(Li)=0.299 OF(TM)=0.701 |
| **Oxygen ions layers** | (6c) ( 0 0 0.746 )<br>OF=0.97 |

| **Table S2:** Rietveld refined parameters for C2/M with 2b-4g site mixing. | |
|---|---|
| **Space group** | C 2/m (R=4%; Z=83) |
| **Lattice parameters** | a=4.947 b=8.563 c=5.032<br>α=γ=90° β=109.3° |
| **Atomic position and occupancies (Wycoff position; OF=occupancy fraction)** | |
| **Lithium ion layer** | (2c) ( 0 0 ½ )<br>OF(Li)=1 |
| | (4h) ( 0 0.685 ½ )<br>OF(Li)=1 |
| **Metal ions blend layer** | (2b) ( 0 ½ 0 )<br>OF(Li)=0.466 OF(TM)=0.534 |
| | (4g) ( 0 0.169 0 )<br>OF(Li)=0.187 OF(TM)=0.813 |
| **Oxygen ions layers** | (4i) ( 0.252 0 0.231 )<br>OF(O)=1 |
| | (8j) ( 0.25 0.327 0.245 )<br>OF(O)=1 |

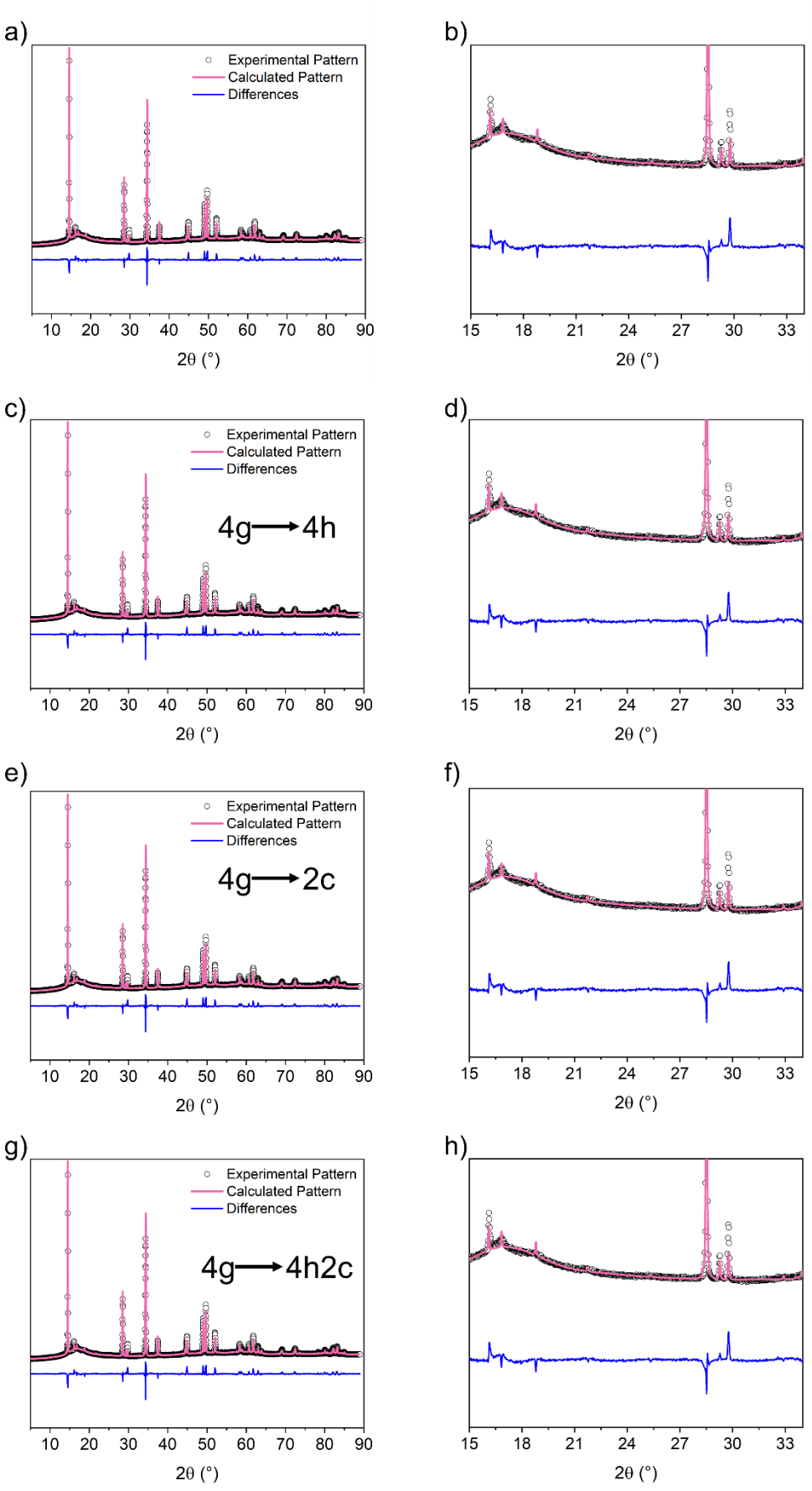


**Figure S4:** Rietveld refinement using C2/m with a-b) Li-TM mixing in TM layers, c-d) 4g-4h, e-f) 4g-2c and g-h) 4g-4h2c anti-site defects.

| **Table S3:** Rietveld refined parameters for C2/M with different anti-site defects. | | | |
|---|---|---|---|
| **Space group** | **4g-4h (R=3.99%; Z=83)** | **4g-4h2c (R=3.98%; Z=83)** | **4g-2c (R=3.97%; Z=83)** |
| **Lattice parameters** | a=4.947 b=8.563 c=5.032<br>α=γ=90° β=109.3° | a=4.947 b=8.563 c=5.032<br>α=γ=90° β=109.3° | a=4.947 b=8.563 c=5.032<br>α=γ=90° β=109.3° |
| **Atomic position and occupancies (Wycoff position; OF=occupancy fraction)** | | | |
| **Lithium ion layer** | (2c) ( 0 0 ½)<br>OF(Li)=1 | (2c) ( 0 0 ½)<br>OF(Li)=0.9970<br>OF(Mn)=0.0030 | (2c) ( 0 0 ½)<br>OF(Li)=0.9899<br>OF(Mn)=0.0101 |
| | (4h) ( 0 0.688 ½ )<br>OF(Li)=0.9989<br>OF(Mn)=0.0011 | (4h) ( 0 0.686 ½ )<br>OF(Li)=0.9985<br>OF(Mn)=0.0015 | (4h) ( 0 0.687 ½ )<br>OF(Li)=1 |
| **Metal ions blend layer** | (2b) ( 0 ½ 0)<br>OF(Li)=0.466<br>OF(Mn)=0.534 | (2b) ( 0 ½ 0)<br>OF(Li)=0.466<br>OF(Mn)=0.534 | (2b) ( 0 ½ 0)<br>OF(Li)=0.460<br>OF(Mn)=0.540 |
| | (4g) ( 0 0.169 0)<br>OF(Mn)=0.812<br>OF(Li)=0.188 | (4g) ( 0 0.168 0)<br>OF(Mn)=0.811<br>OF(Li)=0.188 | (4g) ( 0 0.169 0)<br>OF(Mn)=0.808<br>OF(Li)=0.192 |
| **Oxygen ions layers** | (4i) ( 0.252 0 0.231)<br>OF (O) = 1 | (4i) ( 0.252 0 0.231)<br>OF (O) = 1 | (4i) ( 0.254 0 0.232)<br>OF (O) = 1 |
| | (8j) ( 0.25 0.327 0.246)<br>OF (O) = 1 | (8j) ( 0.25 0.327 0.245)<br>OF (O) = 1 | (8j) ( 0.249 0.326 0.245)<br>OF (O) = 1 |

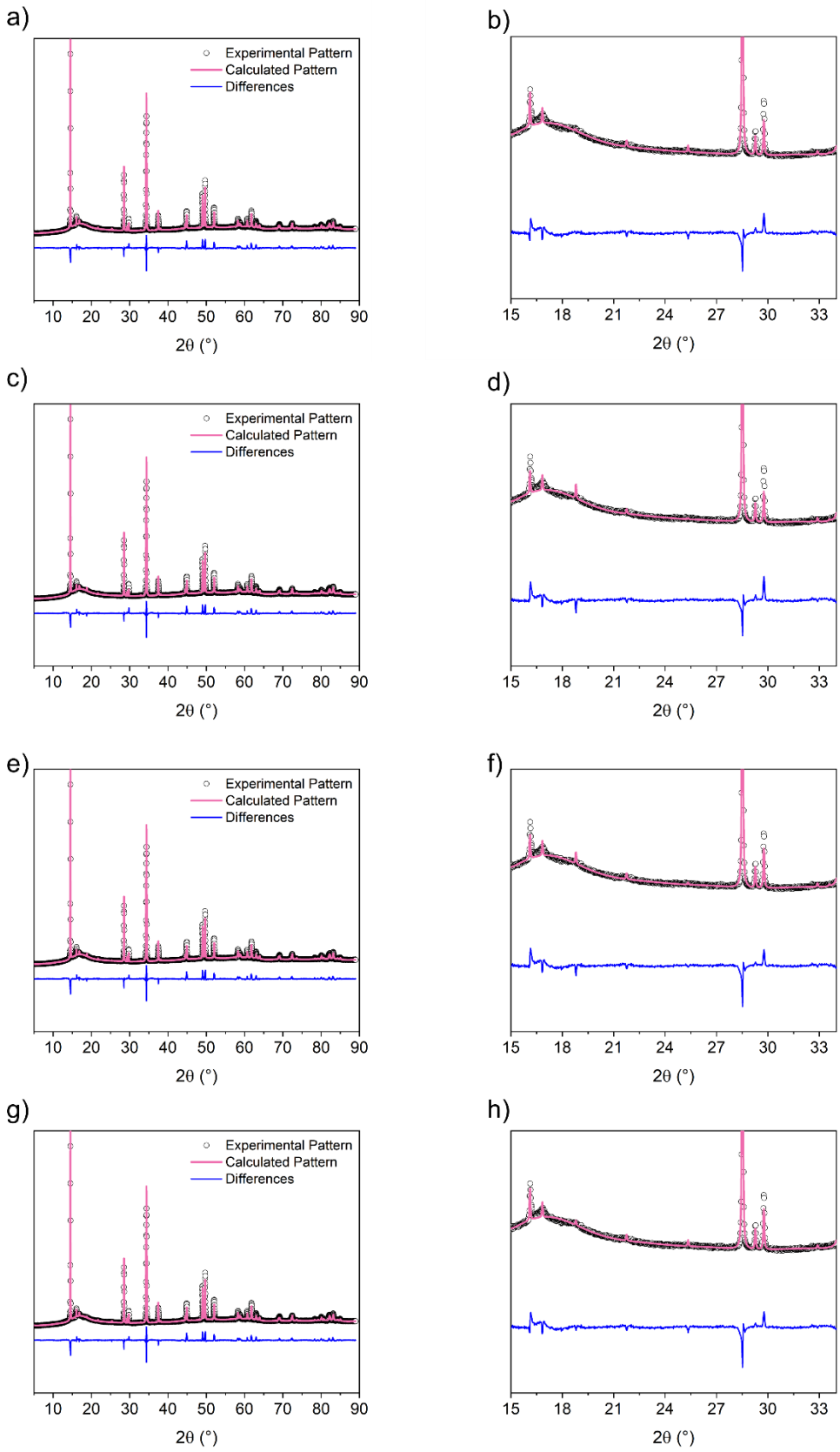


**Figure S5:** Calculated patterns vs experimental pattern using C2/M with anti-site defects and oxygen vacancies. a-b) oxygen vacancies in 4i site, c-d) oxygen vacancies in 8j site, e-f) oxygen vacancies in 4i and 8j sites with a constrain in the atomic fraction and g-h) oxygen vacancies in 4i and 8j sites.

| **Table S4:** Rietveld refined parameters for C2/M with anti-site defects and oxygen vacancies. | | | | |
|---|---|---|---|---|
| **Space group** | 8j (R=3.97%; Z=77) | 4i8j equal fraction (R=3.95%; Z=76) | 4i8j (R=3.93%; Z=73) | 4i (R=3.94%; ; Z=73) |
| **Lattice parameters** | a=4.947 b=8.563 c=5.032 α=γ=90° β=109.3° | a=4.947 b=8.563 c=5.032 α=γ=90° β=109.3° | a=4.947 b=8.563 c=5.032 α=γ=90° β=109.3° | a=4.947 b=8.563 c=5.032 α=γ=90° β=109.3° |
| **Atomic position and occupancies (Wycoff position; OF=occupancy fraction)** | | | | |
| **Lithium ion layer** | (2c) ( 0 0 ½ ) OF(Li)=0.9899 OF(Mn)=0.0101 | (2c) ( 0 0 ½ ) OF(Li)=0.9899 OF(Mn)=0.0101 | (2c) ( 0 0 ½ ) OF(Li)=0.9899 OF(Mn)=0.0101 | (2c) ( 0 0 ½) OF(Li)=0.9899 OF(Mn)=0.0101 |
| | (4h) ( 0 0.685 ½ ) OF(Li)=1 | (4h) ( 0 0.685 ½ ) OF(Li)=1 | (4h) ( 0 0.685 ½ ) OF(Li)=1 | (4h) ( 0 0.682 ½ ) OF(Li)=1 |
| **Metal ions blend layer** | (2b) ( 0 ½ 0 ) OF(Li)=0.466 OF(TM)=0.534 | (2b) ( 0 ½ 0 ) OF(Li)=0.466 OF(TM)=0.534 | (2b) ( 0 ½ 0 ) OF(Li)=0.466 OF(TM)=0.534 | (2b) ( 0 ½ 0) OF(Li)=0.460 OF(Mn)=0.540 |
| | (4g) ( 0 0.169 0 ) OF(Li)=0.187 OF(TM)=0.813 | (4g) ( 0 0.169 0 ) OF(Li)=0.187 OF(TM)=0.813 | (4g) ( 0 0.169 0 ) OF(Li)=0.187 OF(TM)=0.813 | (4g) ( 0 0.169 0) OF(Mn)=0.808 OF(Li)=0.192 |
| **Oxygen ions layers** | (4i) ( 0.252 0 0.232) OF (O) = 1 | (4i) ( 0.253 0 0.235) OF (O) = 0.9324 | (4i) ( 0.253 0 0.235) OF (O) = 0.8441 | (4i) ( 0.252 0 0.234) OF (O) = 0.8503 |
| | (8j) ( 0.25 0.326 0.245) OF (O) = 0.9659 | (8j) ( 0.249 0.327 0.244) OF (O) = 0.9324 | (8j) ( 0.249 0.327 0.244) OF (O) = 0.9722 | (8j) ( 0.249 0.326 0.245) OF (O) = 1 |

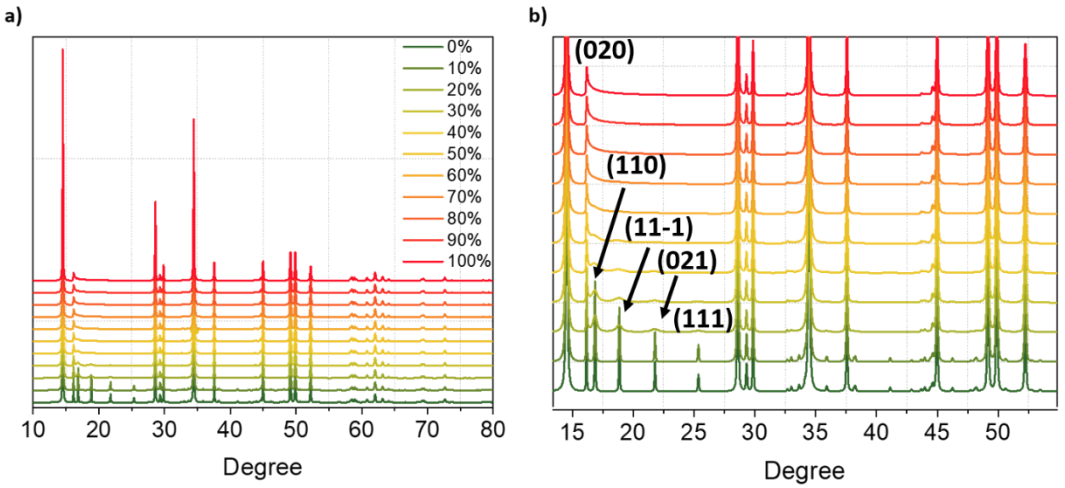

**Figure S6:** a) DIFFaX simulated XRD patterns with varying stacking fault probabilities. b) Enlarged view in the superstructure region.

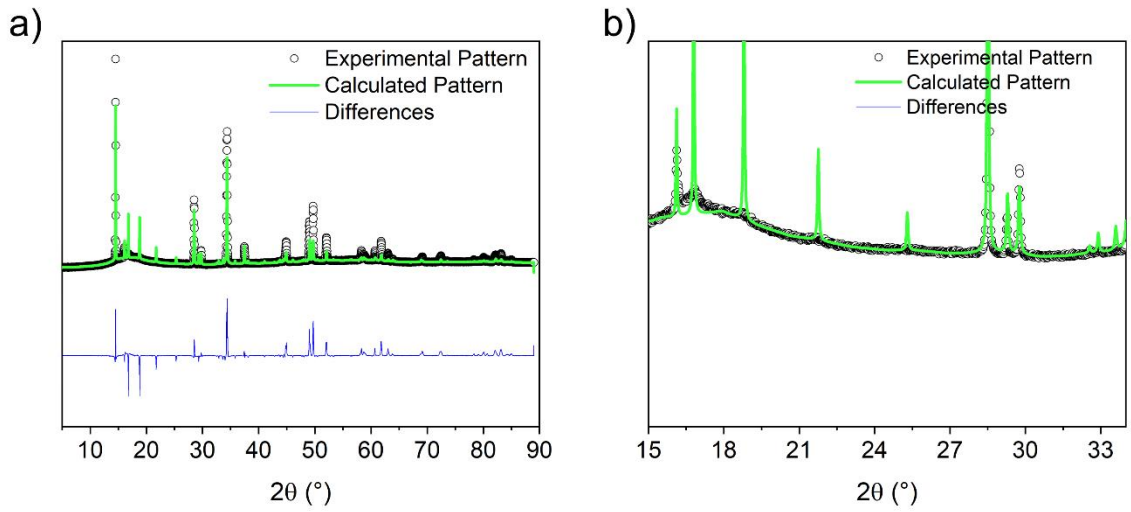


**Figure S7:** a) FAULTS refinement pattern without stacking faults. R-factor=8.4% and Z=95.

| **Table S5:** Values from the FAULTS refinement without stacking faults. | | | | | |
|---|---|---|---|---|---|
| **Unit cell parameters** | | | | | |
| **a, b (Å)** | | **c (Å)** | | **γ (°)** | |
| 4.939 | | 4.743 | | 60.09 | |
| **Layer compositions** | | | | | |
| **Layer** | Atom | x/a | y/b | z/c | Occupancy |
| **L1** | Li | 0 | 0 | 0 | 1 |
| | Li | 1/3 | 1/3 | 0 | 1 |
| | Li | 2/3 | 2/3 | 0 | 1 |
| **L2=L3=L4** | Li | 0 | 0 | 0 | 0.84 |
| | TM | 0 | 0 | 0 | 0.16 |
| | TM | 0.334 | 0.334 | 0 | 1 |
| | TM | 0.663 | 0.663 | 0 | 1 |
| | O | 0.354 | -0.0089 | 0.249 | 1 |
| | O | 0.643 | 0.0063 | -0.246 | 1 |
| | O | -0.0092 | 0.354 | -0.246 | 1 |
| | O | 0.337 | 0.660 | -0.225 | 1 |
| | O | 0.660 | 0.337 | 0.242 | 1 |
| | O | 0.0064 | 0.644 | 0.248 | 1 |

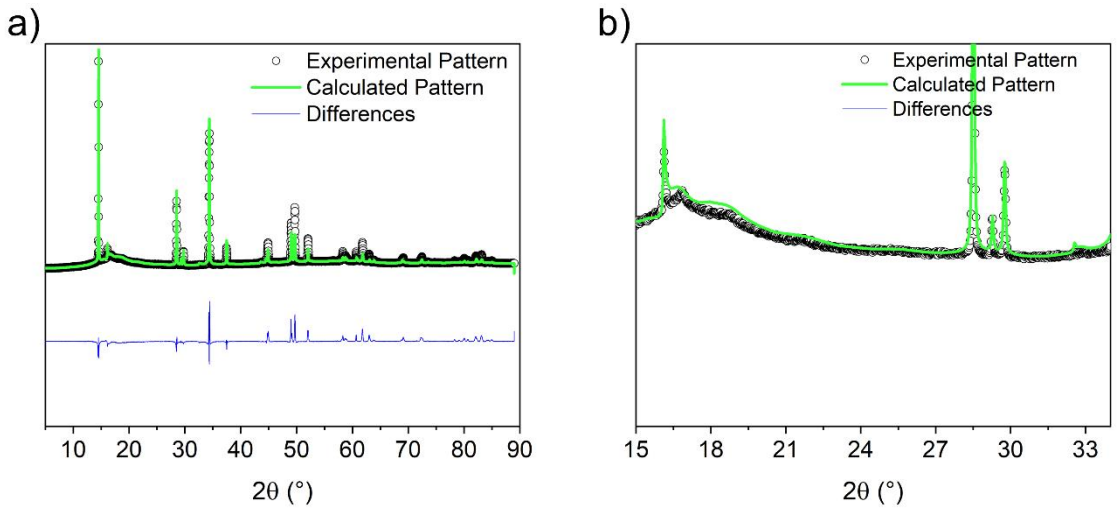


**Figure S8:** a) FAULTS refinement pattern. Magnified view of the refined data in the 15−25° 2θ range. R-factor=6.7% and Z=90.

| **Table S6:** Values from the FAULTS refinement with staking faults (around 48%). | | | | | |
|---|---|---|---|---|---|
| **Unit cell parameters** | | | | | |
| **a, b (Å)** | | **c (Å)** | | **γ (°)** | |
| 4.939 | | 4.743 | | 60.09 | |
| **Layer compositions** | | | | | |
| **Layer** | Atom | x/a | y/b | z/c | Occupancy |
| **L1** | Li | 0 | 0 | 0 | 1 |
| | Li | 1/3 | 1/3 | 0 | 1 |
| | Li | 2/3 | 2/3 | 0 | 1 |
| **L2=L3=L4** | Li | 0 | 0 | 0 | 0.84 |
| | TM | 0 | 0 | 0 | 0.16 |
| | TM | 0.337 | 0.337 | 0 | 1 |
| | Li | 0.337 | 0.337 | 0 | 1 |
| | TM | 0.662 | 0.662 | 0 | 1 |
| | Li | 0.662 | 0.662 | 0 | 1 |
| | O | 0.355 | -0.0055 | 0.252 | 1 |
| | O | 0.644 | 0.0023 | -0.251 | 1 |
| | O | -0.0021 | 0.360 | -0.252 | 1 |
| | O | 0.331 | 0.667 | -0.244 | 1 |
| | O | 0.668 | 0.330 | 0.245 | 1 |
| | O | 0.020 | 0.636 | 0.253 | 1 |

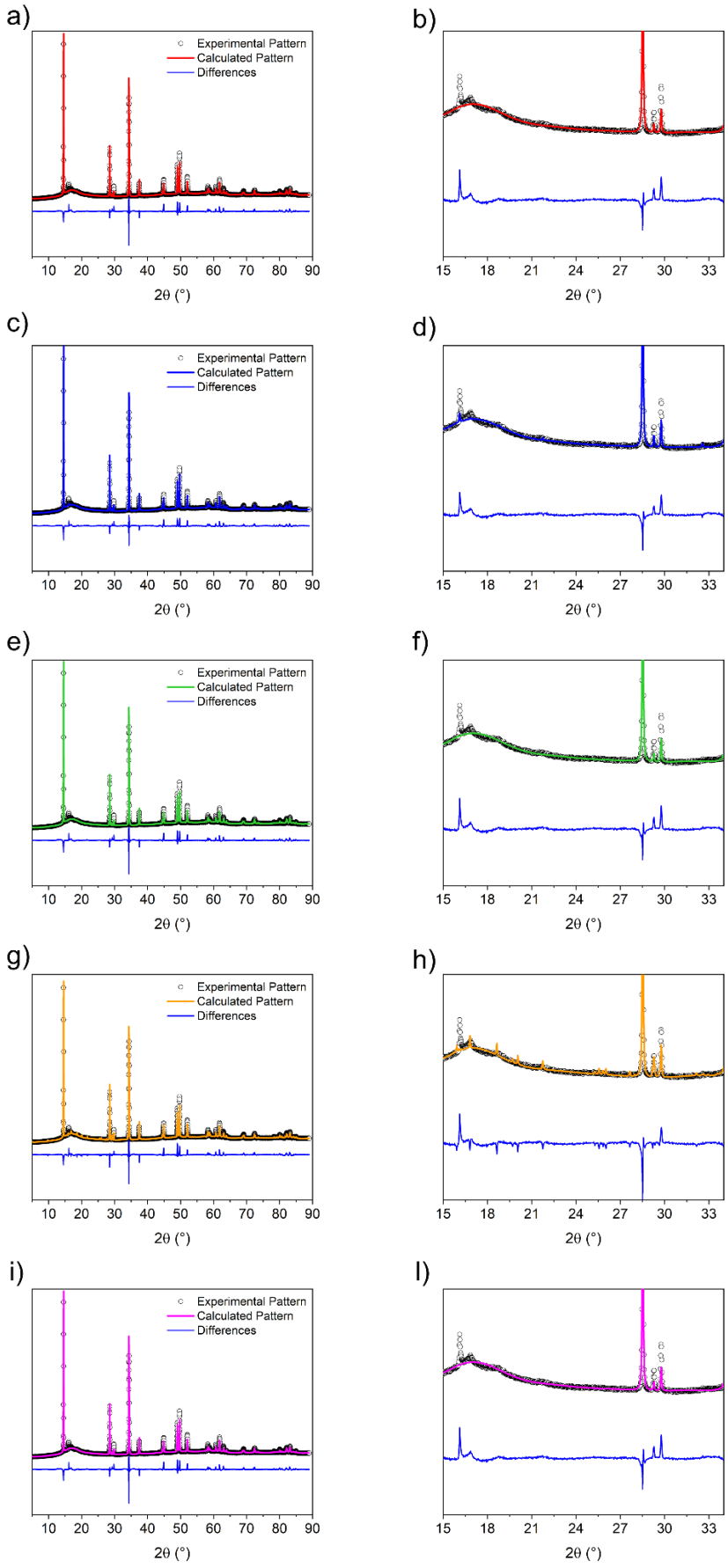


**Figure S9:** Comparison of Rietveld refinements results using a-b) RC_3a, c-d) RC_3b, e-f) RC_3c, g-h) RC_3a_3b and i-l) RC_3a_b_ac unit cell.

| **Table S7:** Rietveld refined parameters for supercells. | | | | | |
|---|---|---|---|---|---|
| | R_C_3a | R_C_3b | R_C_3c | R_C_3a_3b | R_C_3a_b_ac |
| **Lithium ion layer** | **(2d) ( 0 ½ ½ ) OF(Li)=1** | **(2d) ( 0 ½ ½ ) OF(Li)=1** | **(2d) ( 0 ½ ½ ) OF(Li)=1** | **(2d) ( 0 ½ ½ ) OF(Li)=1** | **(2c) ( 0 0 ½ ) OF(Li)=1** |
| | **(4i) ( 0.833 0 0.5) OF(Li)=1** | **(4h) ( 0 0.825 0.5 ) OF(Li)=1** | **(4i) ( 0.5 0 0.845 ) OF(Li)=1** | **(4h) ( 0 0.823 ½ ) OF(Li)=1** | **(4i) ( 0.667 0 0.5 ) OF(Li)=1** |
| | | | | **(4i) ( 0.166 0 0.479 ) OF(Li)=1** | |
| | | | | **(8j) ( 0.833 0.328 0.49 ) OF(Li)=1** | |
| **Metal ions blend layer** | **(2a) ( 0 0 0 ) OF(Li)=0.28 OF(TM)=0.72** | **(2a) ( 0 0 0 ) OF(Li)=0.28 OF(TM)=0.72** | **(2a) ( 0 0 0 ) OF(Li)=0.28 OF(TM)=0.72** | **(2a) ( 0 0 0 ) OF(Li)=0.28 OF(TM)=0.72** | **(2a) ( 0 0 0 ) OF(Li)=0.28 OF(TM)=0.72** |
| | **(4i) ( 0.666 0 -0.006 ) OF(Li)=0.28 OF(TM)=0.72** | **(4g) ( 0 0.669 0 ) OF(Li)=0.28 OF(TM)=0.72** | **(4i) ( 0.004 0 0.668 ) OF(Li)=0.28 OF(TM)=0.72** | **(4g) ( 0 0.66 0 ) OF(Li)=0.28 OF(TM)=0.72** | **(4i) ( 0.67 0 -0.003 ) OF(Li)=0.28 OF(TM)=0.72** |
| | | | | **(4i) ( 0.331 0 -0.014 ) OF(Li)=0.28 OF(TM)=0.72** | |
| | | | | **(4i) ( 0.665 0.337 0.007 ) OF(Li)=0.28 OF(TM)=0.72** | |
| **Oxygen ions layers** | **(4i) ( 0.914 0 0.266 ) OF(O)=1** | **(4i) ( 0.708 0 0.217 ) OF(O)=1** | **(4i) ( 0.752 0 0.747 ) OF(O)=1** | **(4i) ( 0.085 0 0.739 ) OF(O)=1** | **(4i) ( 0.826 0 0.266 ) OF(O)=1** |
| | **(4i) ( 0.585 0 0.256 ) OF(O)=1 (4i) ( 0.248 0 0.266 ) OF(O)=1** | **(8j) ( 0.244 0.319 0.726 ) OF(O)=1** | **(4i) ( 0.746 0 0.43 ) OF(O)=1** | **(8j) ( 0.919 0.37 0.294 ) OF(O)=1** | **(4i) ( 0.504 0 0.232 ) OF(O)=1** |
| | | | **(4i) ( 0.734 0 0.08 ) OF(O)=1** | **(4i) ( 0.419 0 0.773 ) OF(O)=1** | **(4i) ( 0.156 0 0.277 ) OF(O)=1** |
| | | | | (8j) ( 0.583 0.339 0.307 ) OF(O)=1 | |
| | | | | (4i) ( 0.754 0 0.768 ) OF(O)=1 | |
| | | | | (8j) ( 0.251 0.345 0.282 ) OF(O)=1 | |

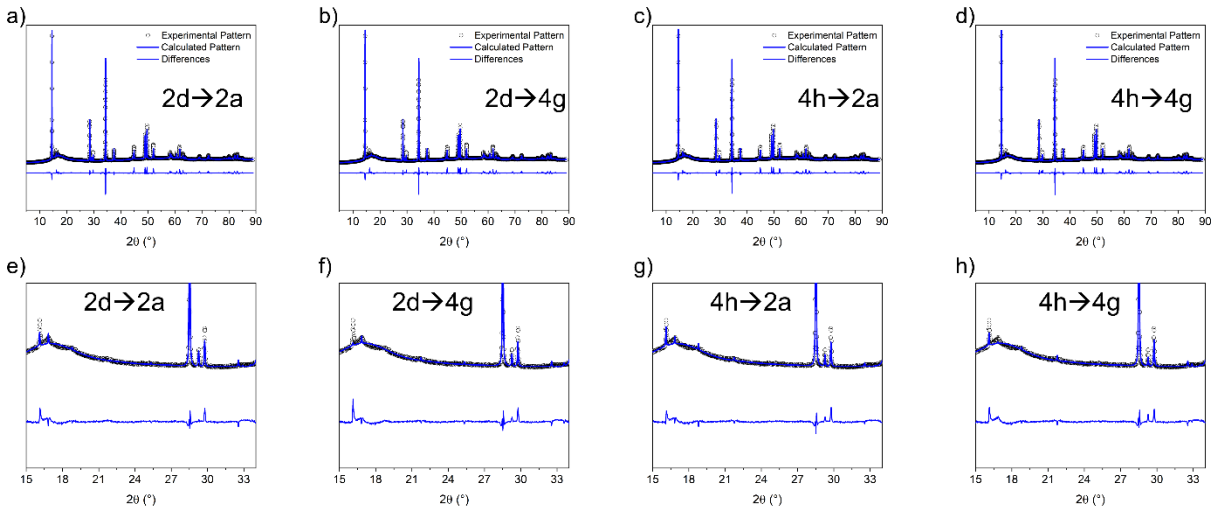


**Figure S10:** Calculated patterns vs experimental pattern using RC_3b with anti-site defects.

| **Table S8:** Rietveld refined parameters for RC_3b with antisite defects. | | | | |
|---|---|---|---|---|
| | **2d2a (Z=79)** | **4h4g (Z=79)** | **2d4g (Z=79)** | **4h2a (Z=79)** |
| **Lithium ion layer** | (2d) ( 0 ½ ½ )<br>OF(Li)=0.9195<br>OF(TM)=0.0805 | (2d) ( 0 ½ ½ )<br>OF(Li)=1 | (2d) ( 0 ½ ½ )<br>OF(Li)=0.927<br>OF(TM)=0.073 | (2d) ( 0 ½ ½ )<br>OF(Li)=1 |
| | (4h) ( 0 0.814 0.5 )<br>OF(Li)=1 | (4h) ( 0 0.823 0.5 )<br>OF(Li)=0.959<br>OF(Ni)=0.0410 | (4h) ( 0 0.825 0.5 )<br>OF(Li)=1 | (4h) ( 0 0.815 0.5 )<br>OF(Li)=0.967<br>OF(Ni)=0.033 |
| **Metal ions blend layer** | (2a) ( 0 0 0 )<br>OF(Li)=0.3605<br>OF(TM)=0.6395 | (2a) ( 0 0 0 )<br>OF(Li)=0.28<br>OF(TM)=0.72 | (2a) ( 0 0 0 )<br>OF(Li)=0.28<br>OF(TM)=0.72 | (2a) ( 0 0 0 )<br>OF(Li)=0.346<br>OF(TM)=0.654 |
| | (4g) ( 0 0.667 0 )<br>OF(Li)=0.28<br>OF(TM)=0.72 | (4g) ( 0 0.668 0 )<br>OF(Li)=0.321<br>OF(TM)=0.679 | (4g) ( 0 0.668 0 )<br>OF(Li)=0.3165<br>OF(TM)=0.6835 | (4g) ( 0 0.667 0 )<br>OF(Li)=0.28<br>OF(TM)=0.72 |
| **Oxygen ions layers** | (4i) ( 0.746 0 0.273 )<br>OF(O)=1 | (4i) ( 0.728 0 0.237 )<br>OF(O)=1 | (4i) ( 0.732 0 0.252 )<br>OF(O)=1 | (4i) ( 0.732 0 0.251 )<br>OF(O)=1 |
| | (8j) ( 0.246 0.314 0.741 )<br>OF(O)=1 | (8j) ( 0.236 0.316 0.721 )<br>OF(O)=1 | (8j) ( 0.237 0.319 0.728 )<br>OF(O)=1 | (8j) ( 0.239 0.319 0.730 )<br>OF(O)=1 |

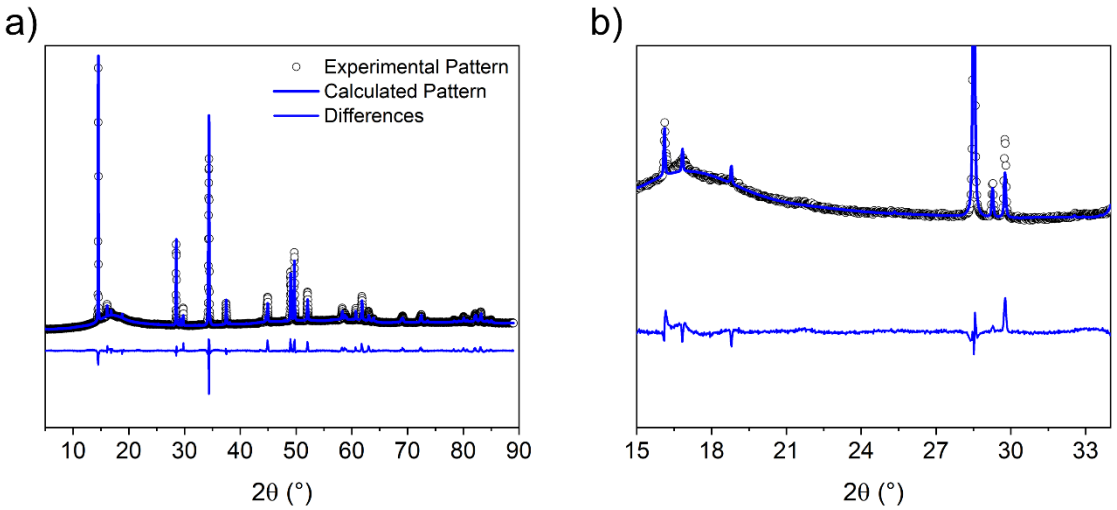


**Figure S11:** Calculated patterns vs experimental pattern using RC_3b with anti-site defects and Li-TM mixing (4g-2a).

| **Table S9:** Rietveld refined parameters for RC_3b with Li-TM mixing and 4h2a anti site defects. | |
|---|---|
| | **2d2a ((Z=76)** |
| **Lithium ion layer** | (2d) ( 0 ½ ½ )<br>OF(Li)=0.9195<br>OF(TM)=0.0805 |
| | (4h) ( 0 0.814 0.5 )<br>OF(Li)=1 |
| **Metal ions blend layer** | (2a) ( 0 0 0 )<br>OF(Li)=0.3645 OF(TM)=0.5714 |
| | (4g) ( 0 0.667 0 )<br>OF(Li)=0.2377 OF(TM)=0.7623 |
| **Oxygen ions layers** | (4i) ( 0.746 0 0.273 )<br>OF(O)=1 |
| | (8j) ( 0.246 0.314 0.741 )<br>OF(O)=1 |

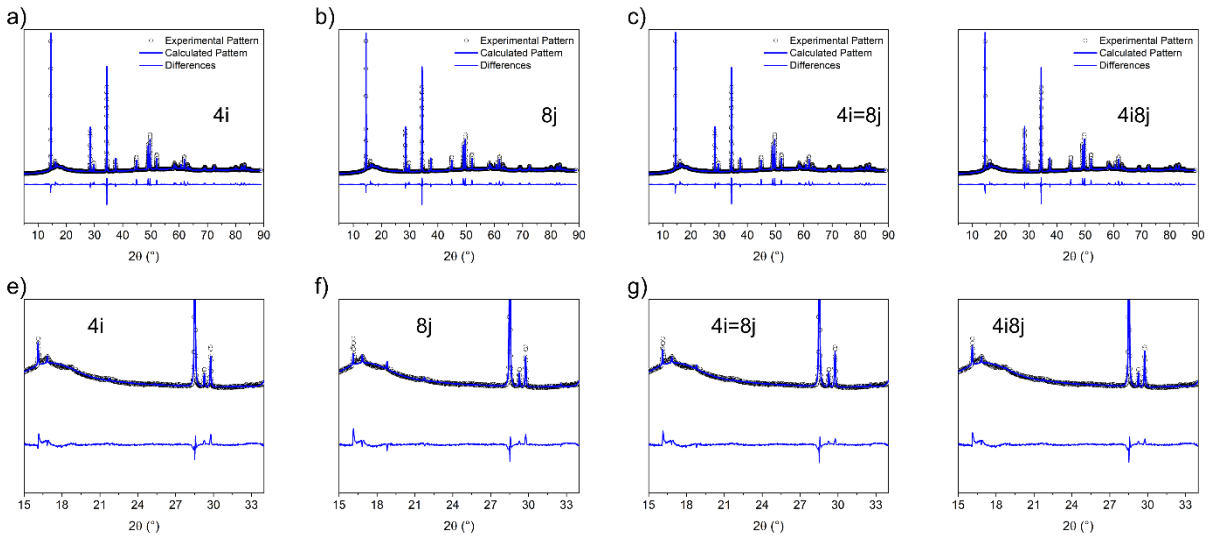


**Figure S12:** Calculated patterns vs experimental pattern using RC_3b with oxygen vacancies.

| **Table S10:** Rietveld refined parameters for RC_3b with oxygen vacancies. | | | | |
|---|---|---|---|---|
| | **4i (Z=73)** | **8j (Z=72)** | **4i=8j (Z=70)** | **4i8j (Z=70)** |
| **Lithium ion layer** | (2d) ( 0 ½ ½ )<br>OF(Li)=0.9195<br>OF(TM)=0.0805 | (2d) ( 0 ½ ½ )<br>OF(Li)=0.9195<br>OF(TM)=0.0805 | (2d) ( 0 ½ ½ )<br>OF(Li)=0.9195<br>OF(TM)=0.0805 | (2d) ( 0 ½ ½ )<br>OF(Li)=0.9195<br>OF(TM)=0.0805 |
| | (4h) ( 0 0.814 0.5 )<br>OF(Li)=1 | (4h) ( 0 0.814 0.5 )<br>OF(Li)=1 | (4h) ( 0 0.814 0.5 )<br>OF(Li)=1 | (4h) ( 0 0.814 0.5 )<br>OF(Li)=1 |
| **Metal ions blend layer** | (2a) ( 0 0 0 )<br>OF(Li)=0.3645<br>OF(TM)=0.5714 | (2a) ( 0 0 0 )<br>OF(Li)=0.3645<br>OF(TM)=0.5714 | (2a) ( 0 0 0 )<br>OF(Li)=0.3645<br>OF(TM)=0.5714 | (2a) ( 0 0 0 )<br>OF(Li)=0.3645<br>OF(TM)=0.5714 |
| | (4g) ( 0 0.667 0 )<br>OF(Li)=0.2377<br>OF(TM)=0.7623 | (4g) ( 0 0.667 0 )<br>OF(Li)=0.2377<br>OF(TM)=0.7623 | (4g) ( 0 0.667 0 )<br>OF(Li)=0.2377<br>OF(TM)=0.7623 | (4g) ( 0 0.667 0 )<br>OF(Li)=0.2377<br>OF(TM)=0.7623 |
| **Oxygen ions layers** | (4i) ( 0.732 0 0.245 )<br>OF(O)=0.8661 | (4i) ( 0.732 0 0.247 )<br>OF(O)=1 | (4i) ( 0.732 0 0.243 )<br>OF(O)=0.9259 | (4i) ( 0.733 0 0.242 )<br>OF(O)=0.8661 |
| | (8j) ( 0.241 0.322 0.730 )<br>OF(O)=1 | (8j) ( 0.239 0.321 0.730 )<br>OF(O)=0.9341 | (8j) ( 0.240 0.321 0.723 )<br>OF(O)=0.9259 | (8j) ( 0.242 0.322 0.730 )<br>OF(O)=0.9513 |

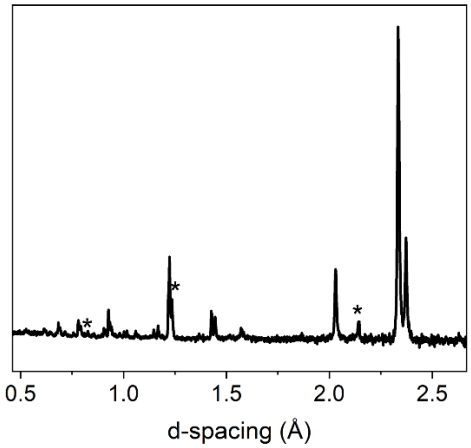


**Figure S13:** Neutron Diffraction data of $Li_{1.28}Mn_{0.54}Ni_{0.13}Co_{0.02}Al_{0.03}O_2$ from bank 5 detector.

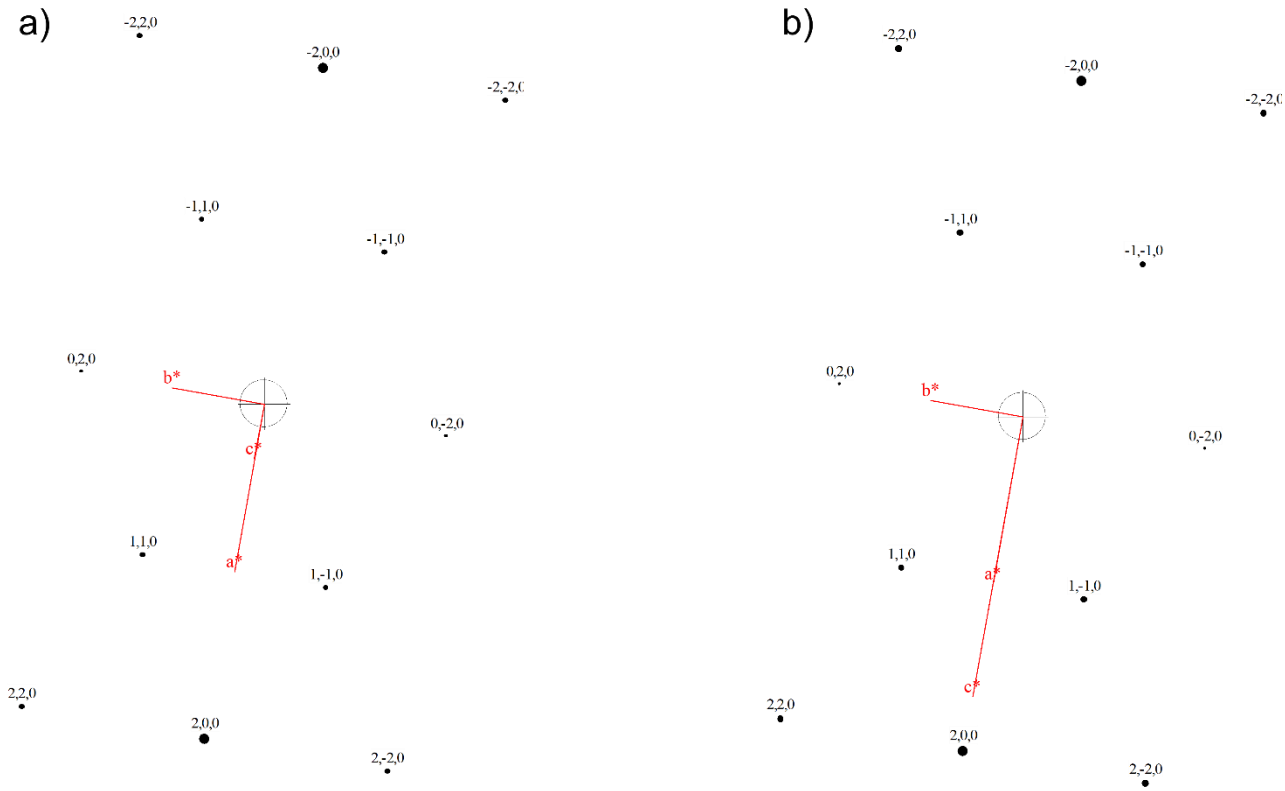


**Figure S14:** Single-crystal ED pattern along the [001] axis zone for a) $M_{def}$ and b) $SC_{def}$.

| **Table S11:** Rietveld refined lattice parameters obtained from Neutron Diffraction pattern. | | | | |
|---|---|---|---|---|
| | **a (Å)** | **b (Å)** | **c (Å)** | **β (°)** |
| **$M_{def}$** | 4.938 | 8.555 | 5.022 | 109.24 |
| **$SC_{def}$** | 9.625 | 8.553 | 5.022 | 151.01 |