

Complex Octahedral Tilt Phases in the Ferroelectric Perovskite System $\text{Li}_x\text{Na}_{1-x}\text{NbO}_3$

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Supplementary information

In addition to the Figures and Tables herein and CIFs for refined models at selected compositions and temperatures (listed below), we deposit the following extra supplementary file:

Simultaneous MRT tilt systems.docx: output from the ISODISTORT program showing all 96 possible models arising from simultaneous presence of the R4+, M3+ and T4 (1/2,1/2,1/4) irreps, as referred to in the text.

CIF files for review and deposition:

| Refined data and model | Filename (.cif) |
|---|----------------------|
| 1. LNN-3 at 20 °C, space group $P2_1ma$ | LNN3_20C_phaseQ |
| 2. $P4/mbm$ idealized model with T_4 mode at $\gamma = 6/20$ and $7/20$ (Phase S''') | LNN3_P4mbm_6_20_7_20 |
| 3. LNN-3 at 500 °C, space group $Cmcm$ | LNN3_550C_T1 |
| 4. LNN-3 at 600 °C, space group $P4/mbm$ | LNN3_600C_T2 |
| 5. LNN-3 at 900 °C, space group $Pm\bar{3}m$ | LNN3_900C_U |
| 6. LNN-8 at 150 °C, space group $P2_1ma$ | LNN8_150C_Q |
| 7. $P4/mbm$ idealised model for phase S'' with T_4 mode at $\gamma = 4/15$ | P4mbm_30ap_S'' |
| 8. Idealised model pertaining to the complex tilt system shown in Fig. S7, for LNN-8. | P4mbm_4_15 |
| 9. LNN-8 at 600 °C, space group $Cmcm$ | LNN8_600C_T1 |
| 10. LNN-8 at 650 °C, space group $P4/mbm$ | LNN8_650C_T2 |
| 11. LNN-8 at 900 °C, space group $Pm\bar{3}m$ | LNN8_900C_U |
| 12. LNN-12 at 150 °C, space group $P2_1ma$ | LNN12_150C_Q |
| 13. LNN-12 at 400 °C, space group $Pnma$ | LNN12_400C_S' |
| 14. LNN-12 at 650 °C, space group $Cmcm$ | LNN12_650C_T1 |
| 15. LNN-12 at 700 °C, space group $P4/mbm$ | LNN12_700C_T2 |
| 16. LNN-12 at 900 °C, space group $Pm\bar{3}m$ | LNN12_900C_U |

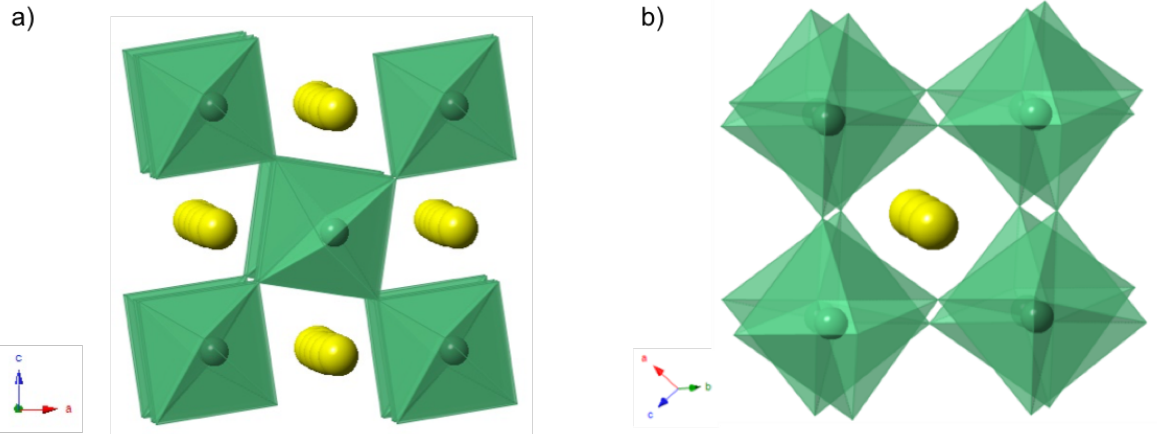


Figure S1: Crystal structure of phase Q (a) looking down the *b*-axis and highlighting the in-phase tilt mode, and phase N (b) highlighting the out of phase tilt along each of the crystallographic axes.

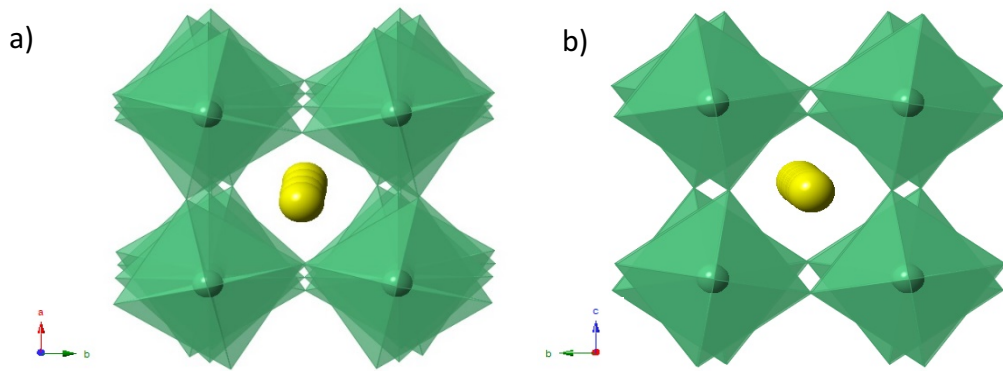


Figure S2: Representations of the two configurations of the T_4 ($\mathbf{k} = (\frac{1}{2}, \frac{1}{2}, \frac{1}{4})$) octahedral tilting mode as a) A0C0 and b) AACC.

Table S1: Crystallographic data for Phase S' in LNN-12 at 400 °C. $a = 7.82835(15)$ Å, $b = 7.8196(2)$ c = 15.6409(4) Å.

| Atom | Wyckoff position | x | y | z | 100 * U_{iso} (Å ²) |
|------|------------------|-------------|-------------|------------|-----------------------------------|
| Na1* | 4c | 0.236(5) | 0.25 | 0.873(3) | 2.30(12) |
| Na2 | 4c | 0.242(16) | 0.25 | 0.122(2) | 2.30(12) |
| Na3 | 4c | 0.249(7) | 0.25 | 0.376(3) | 2.30(12) |
| Na4 | 4c | 0.250(6) | 0.25 | 0.376(3) | 2.30(12) |
| Nb1 | 4a | 0 | 0 | 0 | 0.70(3) |
| Nb2 | 8d | 0.00010(8) | 0.0005(7) | 0.2506(8) | 0.70(3) |
| O1 | 8d | 0.0252(11) | 0.0334(14) | 0.8752(9) | 1.57(3) |
| O2 | 8d | 0.0235(12) | 0.0182(11) | 0.3749(9) | 1.57(3) |
| O3 | 8d | 0.2500(17) | -0.0359(10) | -0.0161(6) | 1.57(3) |
| O4 | 8d | 0.2483(12) | 0.0151(9) | 0.2690(7) | 1.57(3) |
| O5 | 4c | 0.039(2) | 0.25 | 0.0144(10) | 1.57(3) |
| O6 | 4c | -0.0076(16) | 0.25 | 0.2345(12) | 1.57(3) |
| O7 | 4c | -0.033(2) | 0.25 | 0.5214(9) | 1.57(3) |
| O8 | 4c | 0.0290(19) | 0.25 | 0.7260(8) | 1.57(3) |

*positions Na1-Na4 have fixed occupancy Na_{0.88}Li_{0.12}.

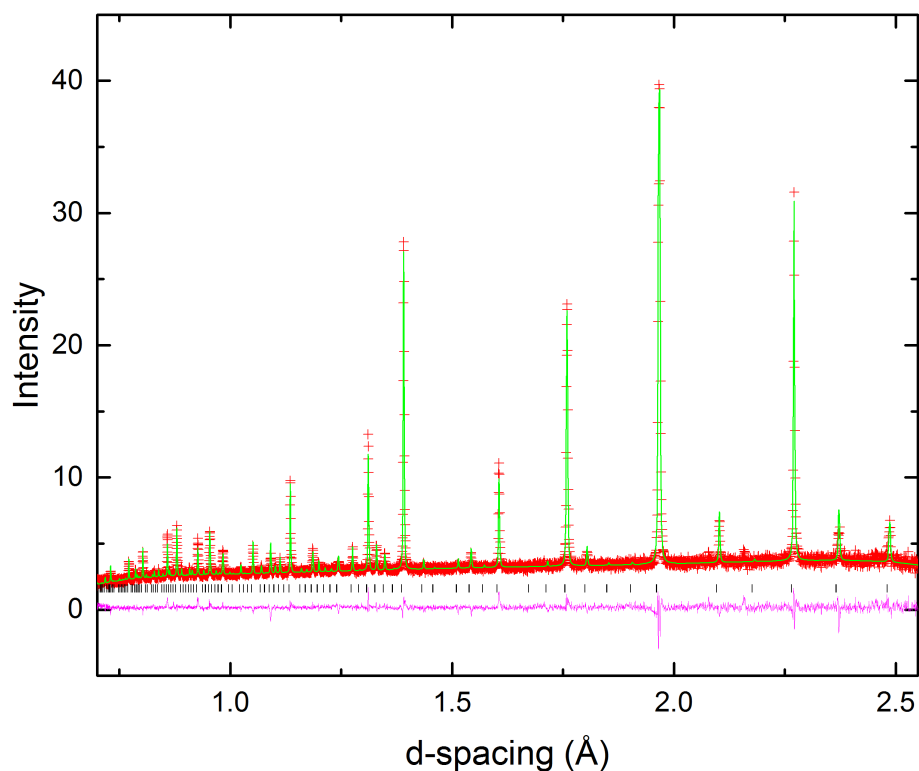


Figure S3: Rietveld refinement of T1, *Cmcm* phase of LNN-12 at 650 °C; $\chi^2 = 1.68$, $R_{wp} = 0.0454$.

Table S2: Crystallographic data for LNN-12 at 650 °C modelled in the *Cmcm* (T1) space group; $a = 7.86345(17)$ Å, $b = 7.85644(17)$ Å, $c = 7.786992(17)$ Å. U_{iso} values for all A-site cations (Na,Li) are constrained together.

| Atom | Wyckoff position | x | y | z | $100 * U_{iso}$ (Å ²) |
|------|------------------|-----------|------------|-----------|-----------------------------------|
| Na1* | 4c | 0 | 0.005(3) | 0.25 | 4.6(6) |
| Na2 | 4c | 0 | 0.493(3) | 0.25 | 3.7(5) |
| Nb | 8d | 0.25 | 0.25 | 0 | 1.16(3) |
| O1 | 8e | 0.2832(6) | 0 | 0 | 3.50(14) |
| O2 | 8f | 0 | 0.2312(6) | 0.0129(8) | 2.25(15) |
| O3 | 8g | 0.2653(8) | 0.2635(10) | 0.25 | 3.38(13) |

*positions Na1 and Na2 have fixed occupancy $\text{Na}_{0.88}\text{Li}_{0.12}$.

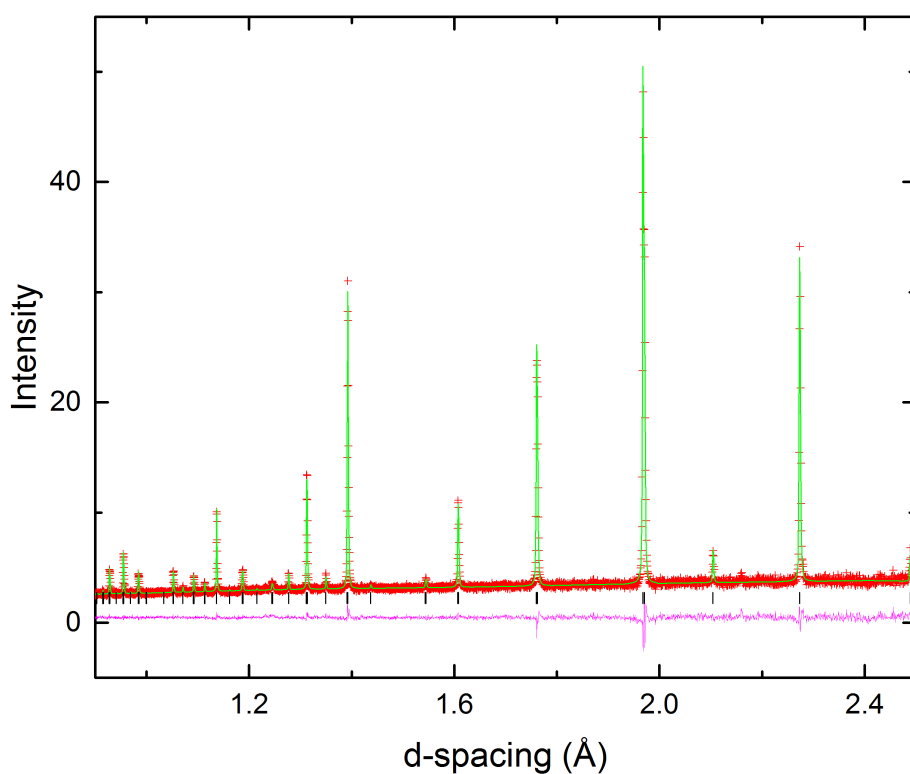


Figure S4: Fit to PND data at 700 °C on LNN-12 for the tetragonal phase, T2, with $P4/mbm$ symmetry.

$\chi^2 = 1.44$, $R_{wp} = 0.0316$.

Table S3: Crystallographic data for LNN-12 at 700 °C modelled in the $P4/mbm$ space group. $a = 5.56482(8)$ Å, $c = 3.94063(6)$ Å. U_{iso} values for all A-site cations (Na,Li) are constrained together.

| Atom | Wyckoff position | x | y | z | $100 * U_{11/22}$ (Å ²) | $100 * U_{12}$ (Å ²) | $100 * U_{33}$ (Å ²) |
|------|------------------|-------------|-------------|-----|--|-------------------------------------|-------------------------------------|
| Na* | 2a | 0 | 0.5 | 0.5 | 4.71(17) | -0.72(2) | 3.1(3) |
| Nb | 2c | 0 | 0 | 0 | 1.23(6) | 0 | 1.25(12) |
| O1 | 2b | 0 | 0 | 0.5 | 7.0(2) | 0 | 0.86(14) |
| O2 | 4g | 0.27136(18) | 0.22865(18) | 0 | 2.34(8) | -0.158(9) | 6.36(14) |

*position Na has fixed occupancy $Na_{0.88}Li_{0.12}$.

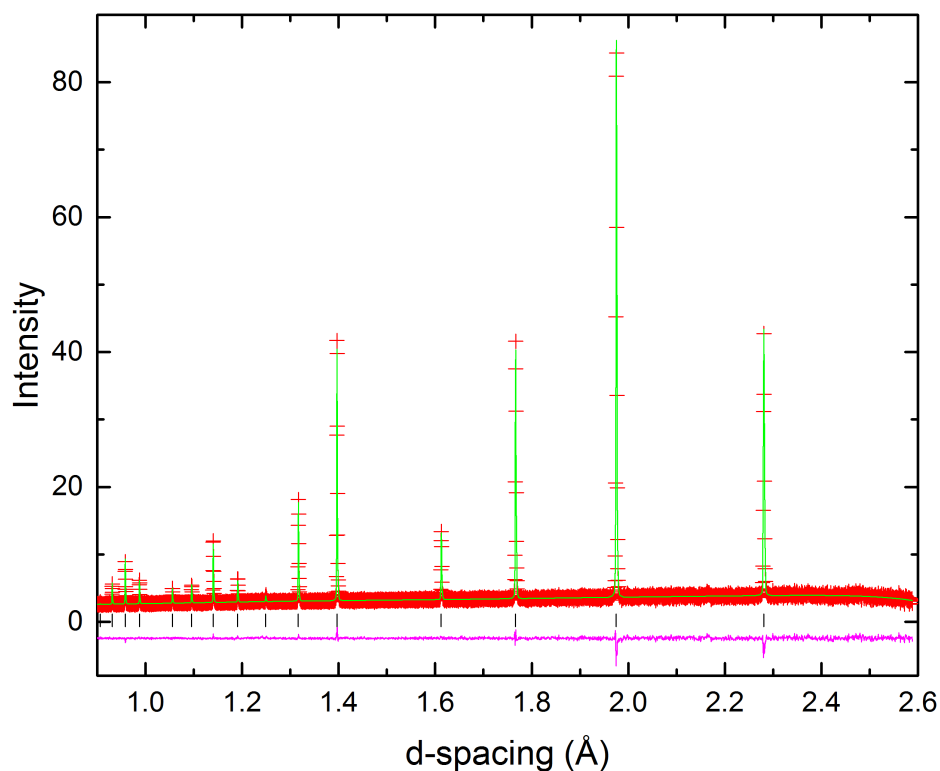


Figure S5: Fit to PND data at 900 °C on LNN-12 for the cubic phase, U , $Pm\bar{3}m$ symmetry. $\chi^2 = 1.30$, $R_{wp} = 0.0301$.

Table S4: Crystallographic data for LNN-12 at 900 °C modelled in the $Pm\bar{3}m$ (U) space group. $a = 3.95246(3)$ Å. U_{aniso} values for all A-site cations (Na,Li) are constrained together.

| Atom | Wyckoff position | x | y | z | 100 * U_{11} (Å ²) | 100* $U_{22/33}$ (Å ²) |
|------|------------------|-----|-----|-----|----------------------------------|------------------------------------|
| Na* | 2a | 0 | 0 | 0 | 6.07(5) | 6.07(5) |
| Nb | 2c | 0.5 | 0.5 | 0.5 | 1.299(18) | 1.299(18) |
| O | 2b | 0 | 0.5 | 0.5 | 0.95(3) | 6.49(3) |

*position Na has fixed occupancy $\text{Na}_{0.88}\text{Li}_{0.12}$.

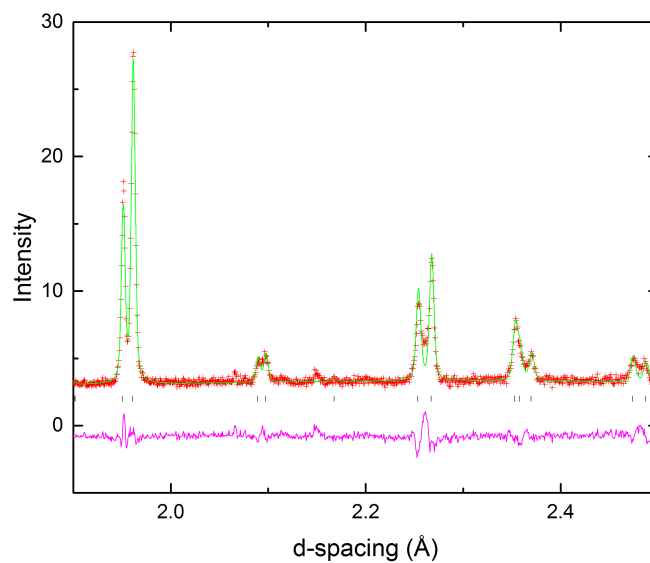


Figure S6: Rietveld refinement of LNN-8 at 300 °C showing that phase Q is the sole phase present at this temperature; $\chi^2 = 1.79$, $R_{wp} = 0.0402$.

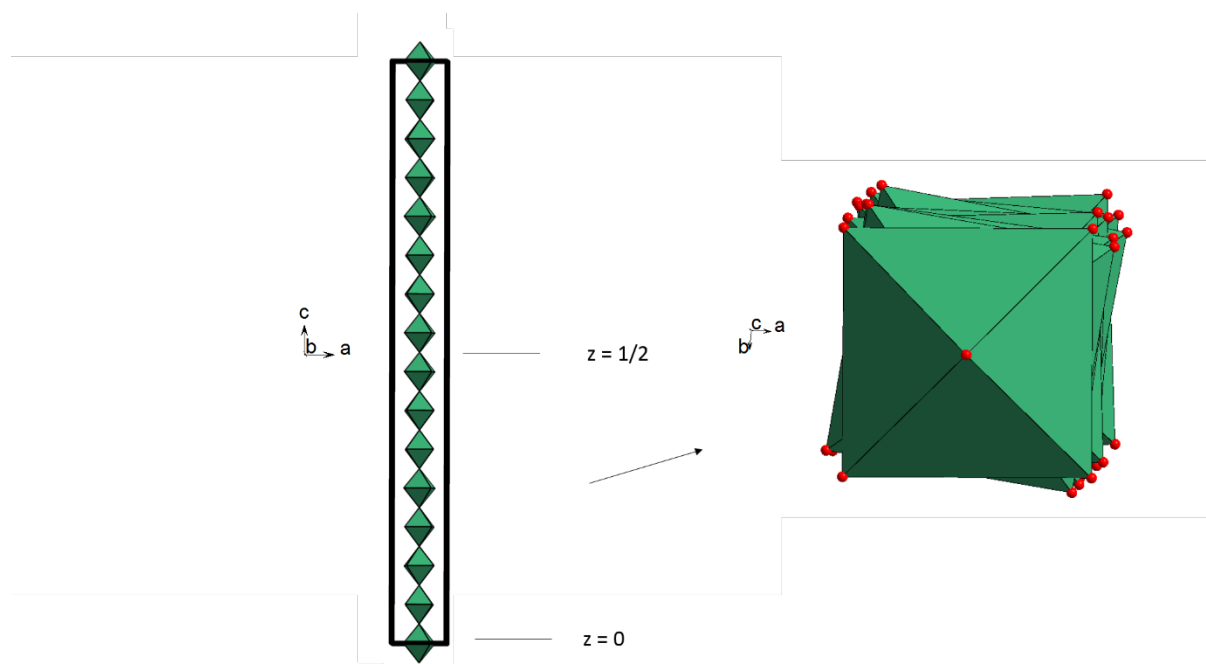


Figure S7: Complex octahedral tilt (T4 mode $(1/2, 1/2, 4/15)$) for Phase S'' of LNN-8, space group $P4/mbm$. The left-hand plot shows the 15-fold superlattice along c . The right-hand plot shows a plan view of the tilt system. Only octahedra between $z = 0$ and $z = 1/2$ are shown; the mirror plane at $z = 1/2$ completes the unit cell.

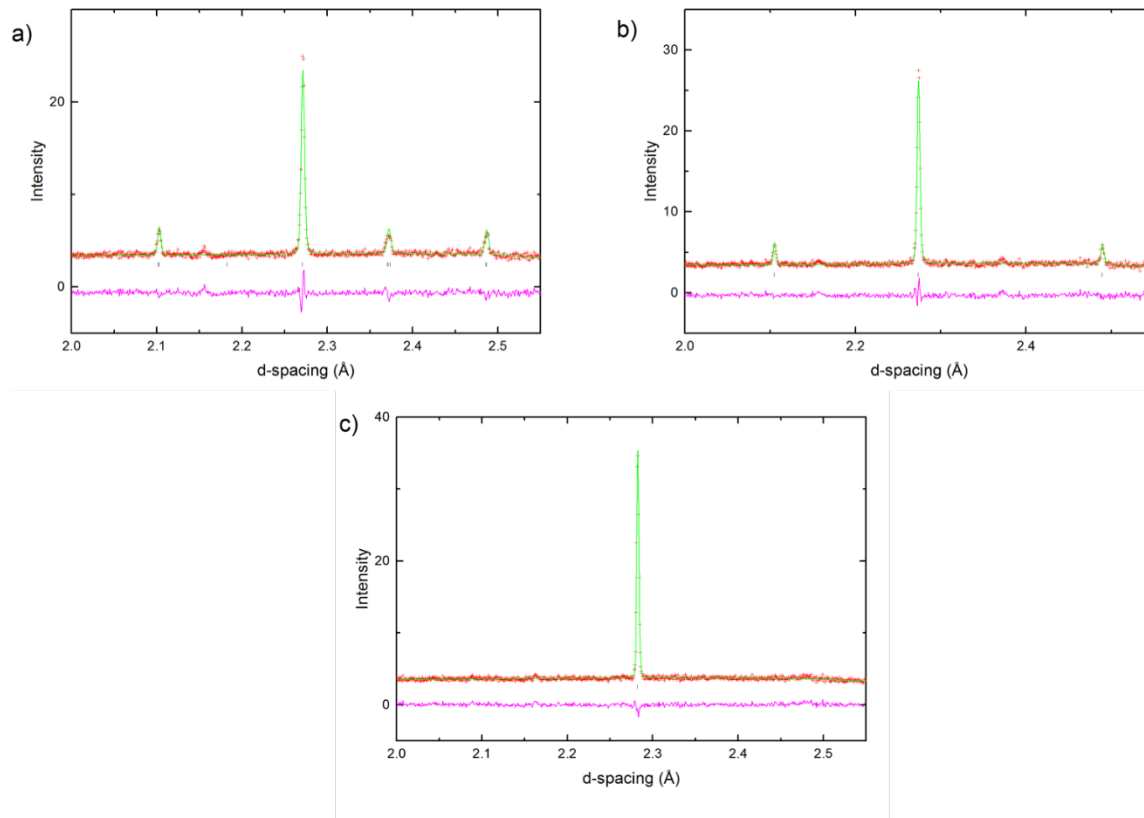


Figure S8: Rietveld plots of for LNN-8: phases T1 at 600 °C (a), T2 at 650 °C (b), and U at 900 °C (c).

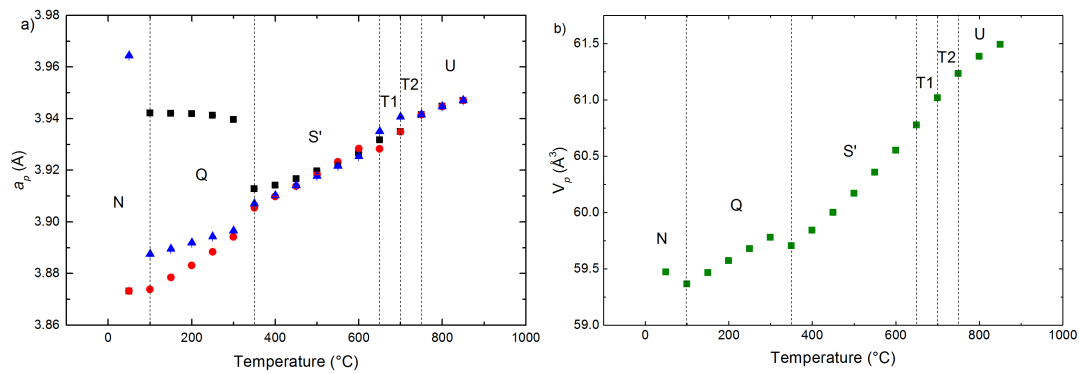


Figure S9 (a): Thermal evolution of normalised lattice parameters (a) and normalised unit cell volume (b) for a sample of LNN-12. The a lattice parameter is represented by black squares, b by red circles and c by blue triangles. For regions in which a phase co-existence is present only the majority phase is depicted.

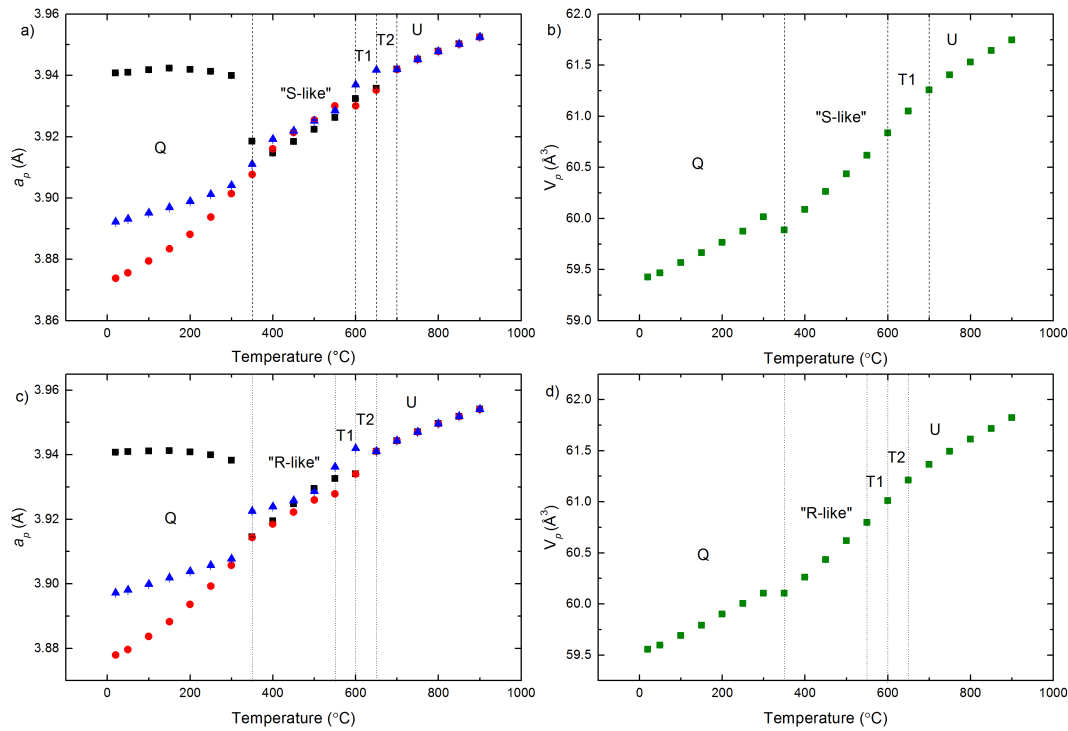


Figure S10: Thermal evolution of normalised lattice parameters and normalised unit cell volume obtained from PND data on a sample of LNN-8, (a and b) and LNN-3, (c and d). The a lattice parameter is represented by black squares, red circles denote b and blue triangles denote c . Lattice parameters from the majority phase only in regions of phase co-existence are shown.

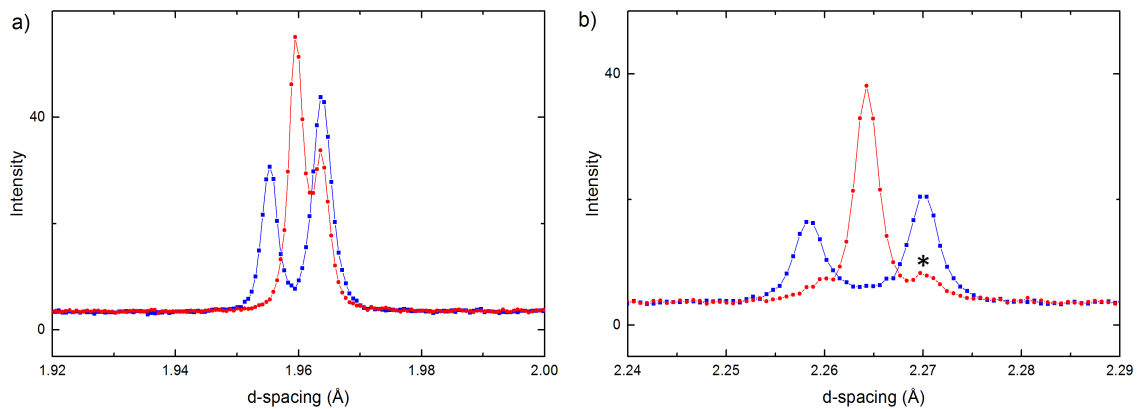


Figure S11: Raw PND data taken from bank 1 on LNN-3 at 300 °C (blue) and 350 °C (red) highlighting the 1st order nature of the phase transition, as evidenced by the change in the peak profile in (a), and the small residual amount of phase Q* (b).

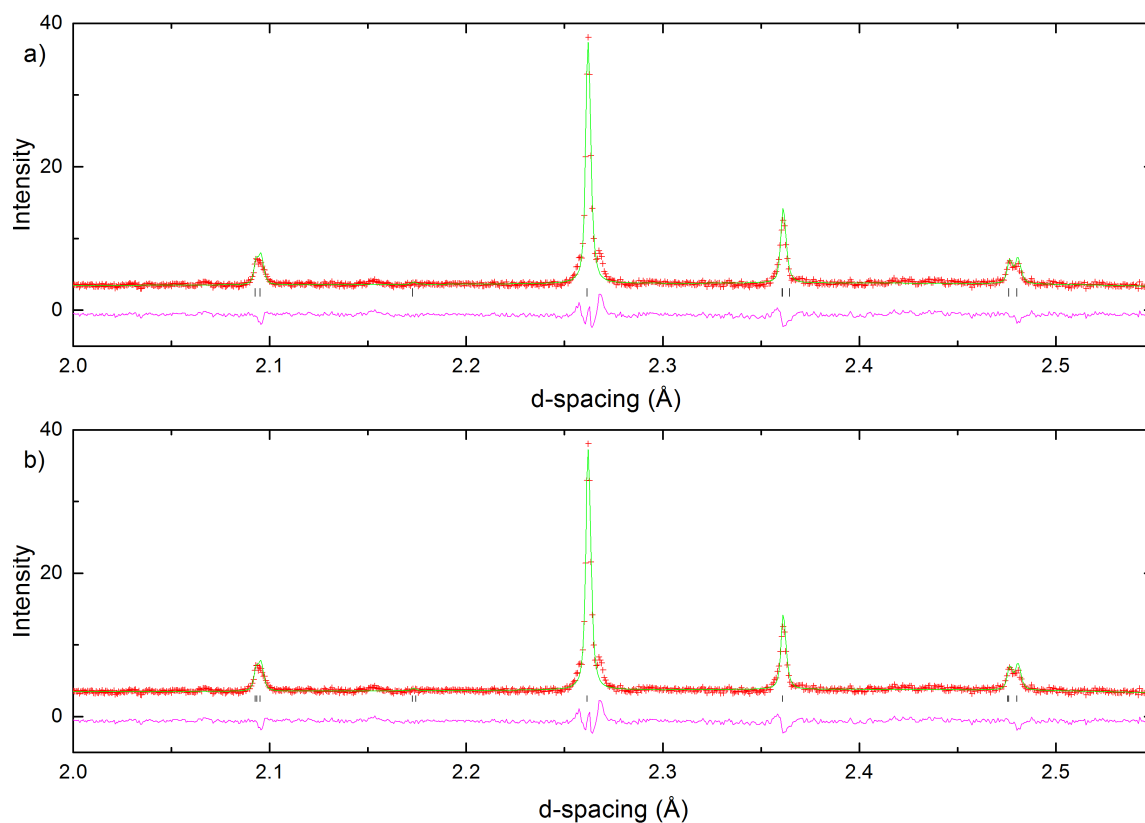


Figure S12: Results of Rietveld refinement on LNN-3 sample at 350 °C modelled using bank 1 data in (a) the $Cmcm$ space group and (b) the $P4_2/nmc$ space group.

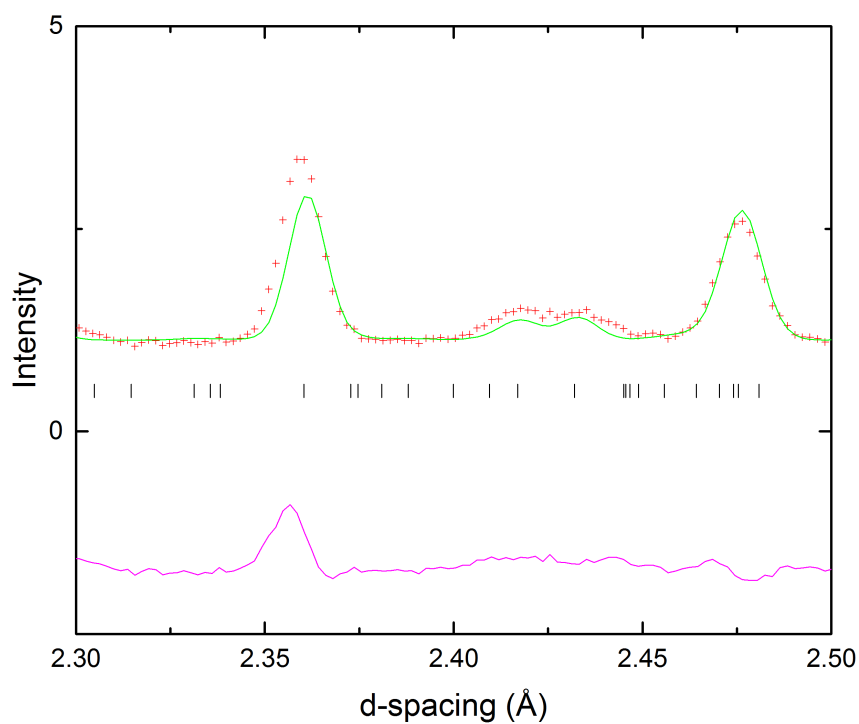


Figure S13: Modelling of the T_4 peaks ($d \sim 2.40\text{-}2.45 \text{ \AA}$) in LNN-3 at 400 °C in the $P4/mbm$ spacegroup with a $\sqrt{2} a_p \times \sqrt{2} a_p \times 20 a_p$ with T_4 modes with $\gamma = 6/20$ and $7/20$. In this simple model the R_4^+ , M_3^+ and T_4 modes all act along the c -axis.

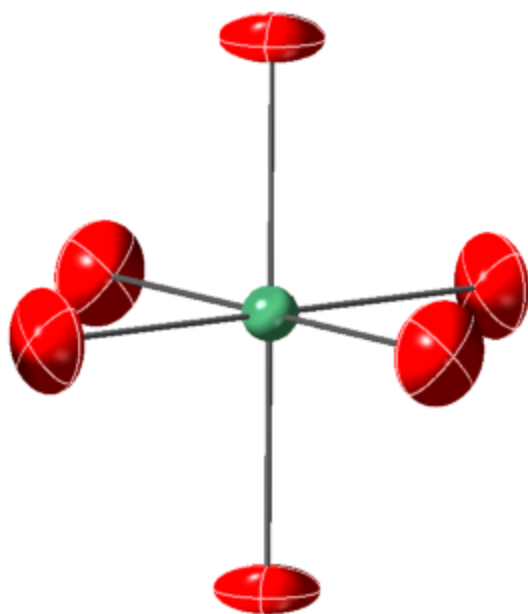


Figure S14: Thermal ellipsoids for cubic phase taken from Rietveld refinement of LNN-3 at 900 °C, highlighting anisotropic nature of the O atom ellipsoids.