Electronic Supplementary Material (ESI) for Dalton Transactions.

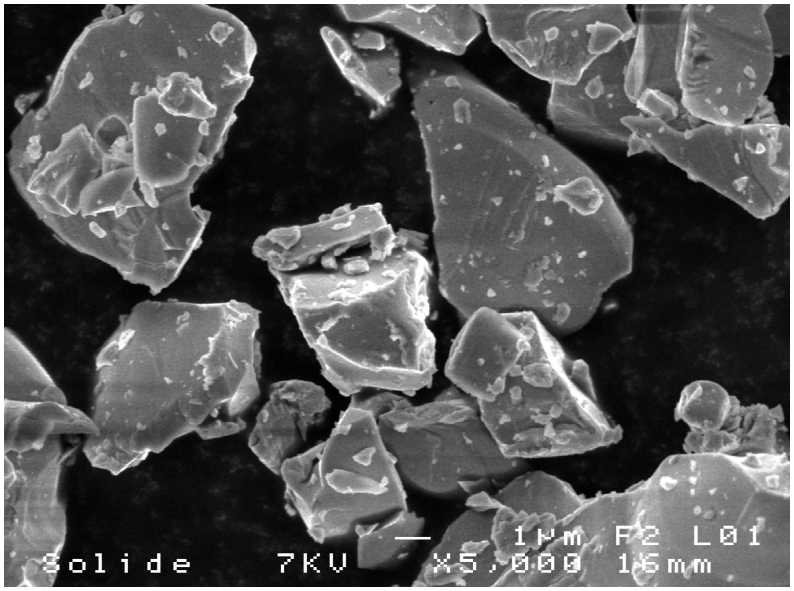

Figure S1. SEM picture of as prepared $Pr_2NiO_{4.22}$.

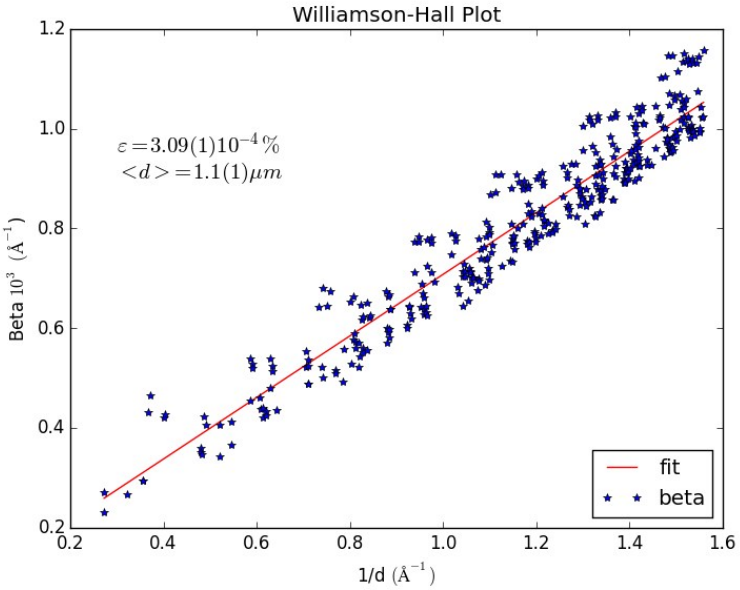

Figure S2. Williamson-Hall plot and estimation of size (<*d*>) and microstrains (ε) at RT.

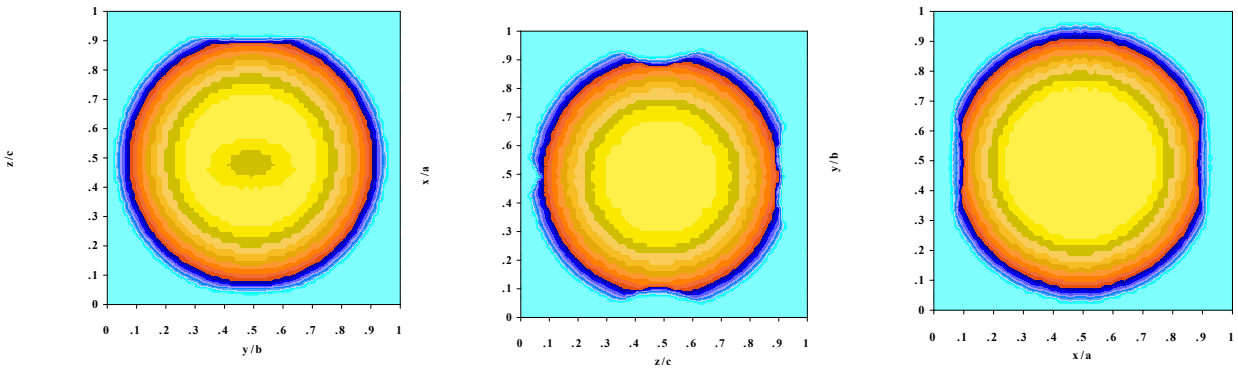

Figure S3. Projection along the three crystal axes of average particle size at RT using profile terms Y00, Y40, Y44+, Y44-. Average apparent particle size and standard deviation estimated by FullProf: 1.7 (1.0) μm. Average maximum strain and standard deviation estimated by FullProf: 3.5(0.4)×10^{-4} %.

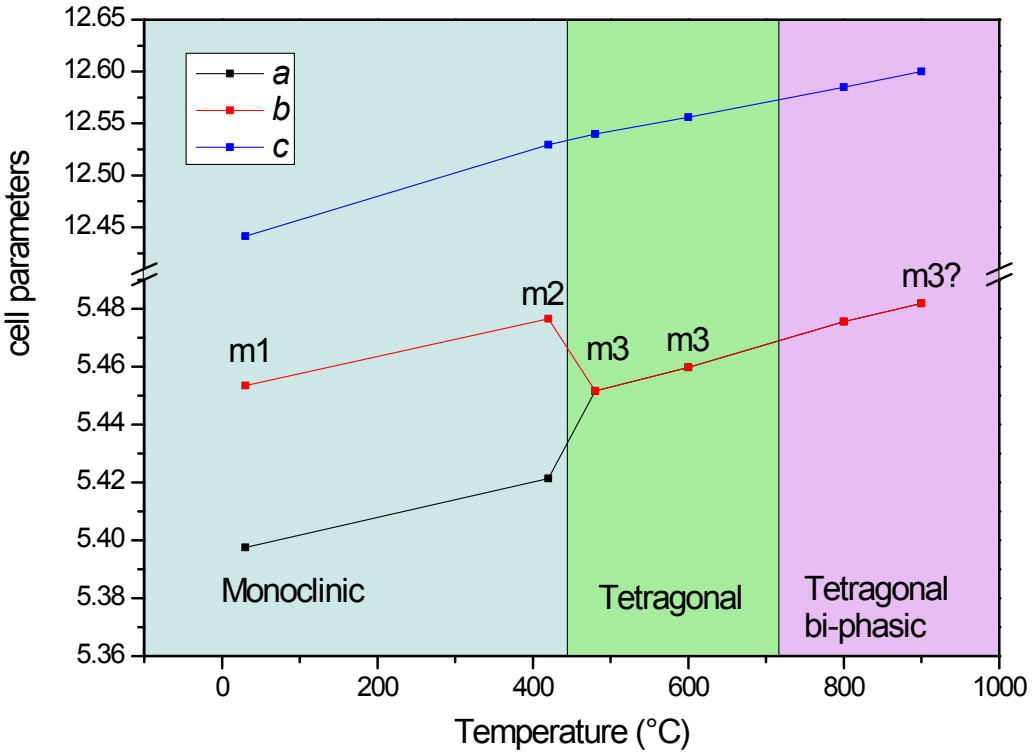

Figure S4. Tentative thermal phase diagram for $Pr_2NiO_{4.22}$ under O_2. Modulation type is indicated as m1, m2, m3. For high temperature it is impossible to define the resemblance with lower temperature satellite schemes because of the coexistence of phases and the small intensity of satellite peaks.

T (°C)	2θ-range (°)
25	0.002-46.998
420	0.002-46.998
480	0.002-46.998
600	0.002-46.998
800	0.002-46.998
900	0.002-46.998
950	0.002-46.998
700	0.002-46.998
480	0.002-46.998
420	0.002-46.998
50	0.002-46.998

T (°C)	2θ-range (°)
370-530 (each 10°C)	6.000-16.998
420	12.000-13.998
460	14.070-13.998
510	12.000-13.998
600	6.000-16.998
650-660 (each 10°C)	6.000-17.998
700	6.000-17.998
720	6.000-17.998
740	6.000-17.998
870	6.000-17.998

Table S1: Temperature of data collection on CRISTAL beam line under O_2 (1 bar, 100 ml/min: pO_2 = 1 bar) and 2θ-range (λ = 0.5113 Å).

T (°C)	2θ-range (°)
24	0.002-46.998
50	0.002-46.998
300	0.002-46.998
480	0.002-46.998
600	0.002-46.998
800	0.002-46.998
900	0.002-46.998
700	0.002-46.998
480	0.002-46.998
300	0.002-46.998

50	0.002-46.998

Table S2: Temperature of data collection on CRISTAL beam line under Ar (1 bar, 100 ml/min: $pO_2 = 10^{-3}$ bar) and 2θ-range ($\lambda = 0.5113$ Å).

Atom	*x*/*a*	*y*/*b*	*z*/*c*	$U_{aniso\ or\ iso}$ (Å²)	Occupancy
Pr	0	0	0.35943(2)	$U_{11} = 0.02033(10)$, $U_{22} = 0.0235(2)$ $U_{33} = 0.01526(10)$, $U_{12} = -0.00082(4)$	1
Ni	0	0	0	$U_{11} = 0.0104(3)$, $U_{22} = 0.01078(17)$ $U_{33} = 0.0267(4)$, $U_{12} = 0.0012(3)$	1
O_{ap}	0	0	0.1747(2)	$U_{11} = 0.064(3)$, $U_{22} = 0.133(3)$ $U_{33} = 0.014(1)$, $U_{12} = 0.043(4)$	1
O_{eq1}	0.25	0.75	0	0.025(2)	1
O_{eq2}	0.25	0.25	0	0.029(2)	1
O_{int}	0.25	0.75	0.25	0.025(2)	0.10

Table S3. Structural parameters of $Pr_2NiO_{4.20}$ at 420°C (LTM phase) under O_2. Space group: *F*112/*m*. Unit cell parameters: 5.42129(11), $b = 5.47653(6)$, $c = 12.52950(4)$ Å; $\gamma = 90.037(1)°$. $R_{wp} = 6.91$, $R_p = 4.98$, $R_{Bragg} = 2.52$, $R_F = 2.05$ % and $S = 1.38$. Interstitial oxygen occupancy fixed at the value obtained by TGA and $U_{iso}(O_{int})$ constrained to the value of $U_{iso}(O_{eq1})$.

Atom	*x*/*a*	*y*/*b*	*z*/*c*	$U_{aniso\ or\ iso}$ (Å²)	Occupancy
Pr	0	0	0.35979(2)	$U_{11} = 0.02314(7)$, $U_{22} = 0.02314(7)$ $U_{33} = 0.01471(8)$	1
Ni	0	0	0	$U_{11} = 0.0121(2)$, $U_{22} = 0.0121(2)$ $U_{33} = 0.0256(3)$	1
O_{ap}	0	0	0.1762(2)	$U_{11} = 0.097(2)$, $U_{22} = 0.097(2)$ $U_{33} = 0.008(1)$	1
O_{eq}	0.25	0.75	0	$U_{11} = 0.0126(8)$, $U_{22} = 0.0126(8)$	1

				U_{33} = 0.052(2)	
O_{int}	0.25	0.75	0.25	0.003(4)	0.09

Table S4. Structural parameters of $Pr_2NiO_{4.18}$ at 480°C (HTT phase) under O_2. Space group: *F*4/*mmm*. Unit cell parameters: *a* = 5.45162(1), *c* = 12.53970(2) Å. R_{wp} = 7.19, R_p = 5.34, R_{Bragg} = 2.99, R_F = 2.11 % and *S* = 1.30. Interstitial oxygen occupancy fixed at the value obtained by TGA.

Atom	*x*/*a*	*y*/*b*	*z*/*c*	$U_{aniso\ or\ iso}$ (Å²)	Occupancy
Pr	0	0	0.36000(2)	U_{11} = 0.02514(8), U_{22} = 0.02514(8) U_{33} = 0.0164(1)	1
Ni	0	0	0	U_{11} = 0.0129(2), U_{22} = 0.0129(2) U_{33} = 0.0302(4)	1
O_{ap}	0	0	0.1761(2)	U_{11} = 0.088(2), U_{22} = 0.088(2) U_{33} = 0.012(1)	1
O_{eq}	0.25	0.75	0	U_{11} = 0.0135(9), U_{22} = 0.0135(9) U_{33} = 0.061(2)	1
O_{int}	0.25	0.75	0.25	0.010(6)	0.08

Table S5. Structural parameters of $Pr_2NiO_{4.16}$ at 600°C (HTT phase) under O_2. Space group: *F*4/*mmm*. Unit cell parameters: *a* = 5.45976(1), *c* = 12.55600(3) Å. R_{wp} = 7.47, R_p = 5.70, R_{Bragg} = 3.07, R_F = 3.00 % and *S* = 1.17. Interstitial oxygen occupancy fixed at the value obtained by TGA.

		a(Å)	b(Å)	c(Å)
800°C	Phase 1	5.460(3)	5.460(3)	12.554(7)
	Phase 2	5.465(3)	5.465(3)	12.559(7)
900°C	Phase 1	5.479(3)	5.479(3)	12.595(8)
	Phase 2	5.484(3)	5.484(3)	12.604(8)
950°C	Phase 1	5.4819(6)	5.4819(6)	12.6000(6)
	Phase 2	5.4873(6)	5.4873(6)	12.6094(9)

Table S6. Structural parameters of $Pr_2NiO_{4.16}$ in the biphasic region (2 HTT phase) from 800 °C to 950 °C under O_2. Space group: *F*4/*mmm*.