Supplemental Information

Structural transformations of the $La_{2-x}Pr_xNiO_{4+\delta}$ system probed by high-resolution synchrotron and neutron powder diffraction

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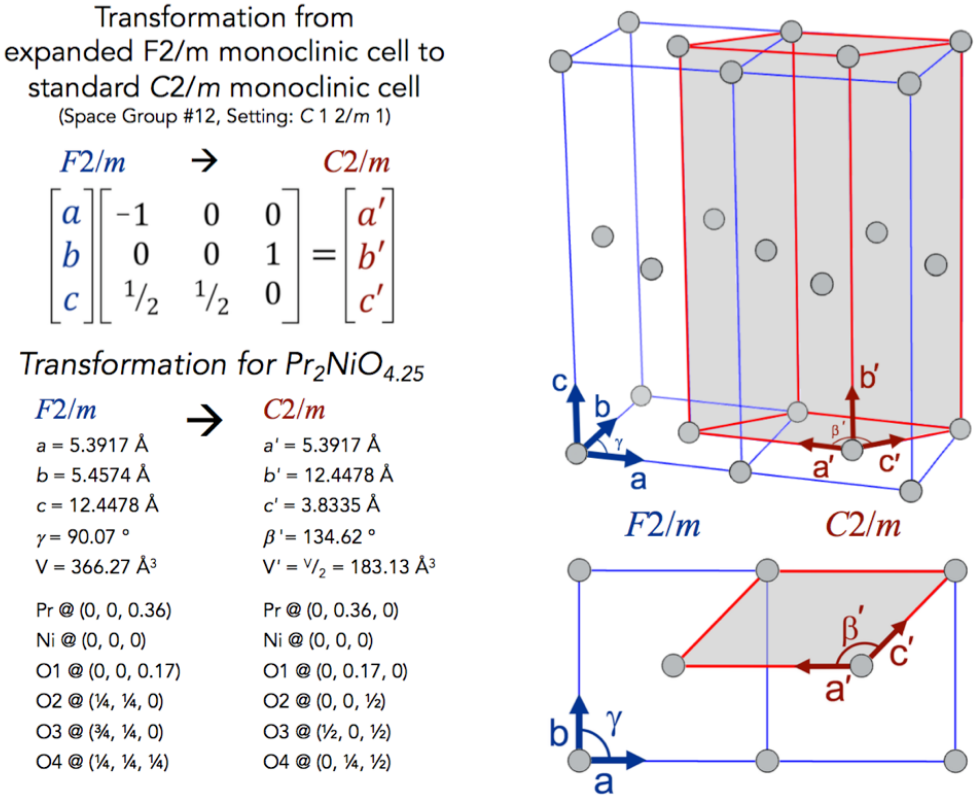
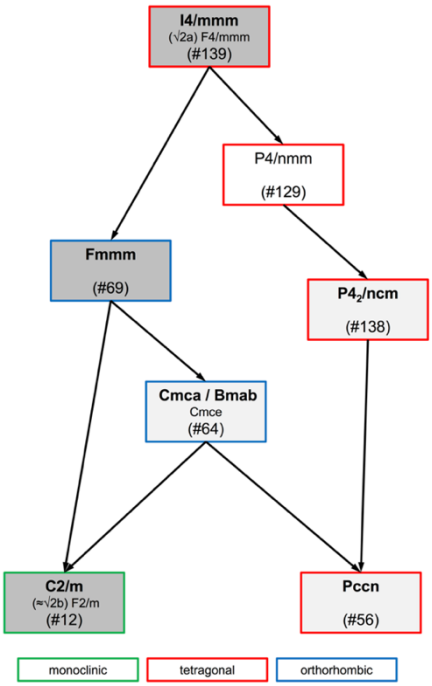
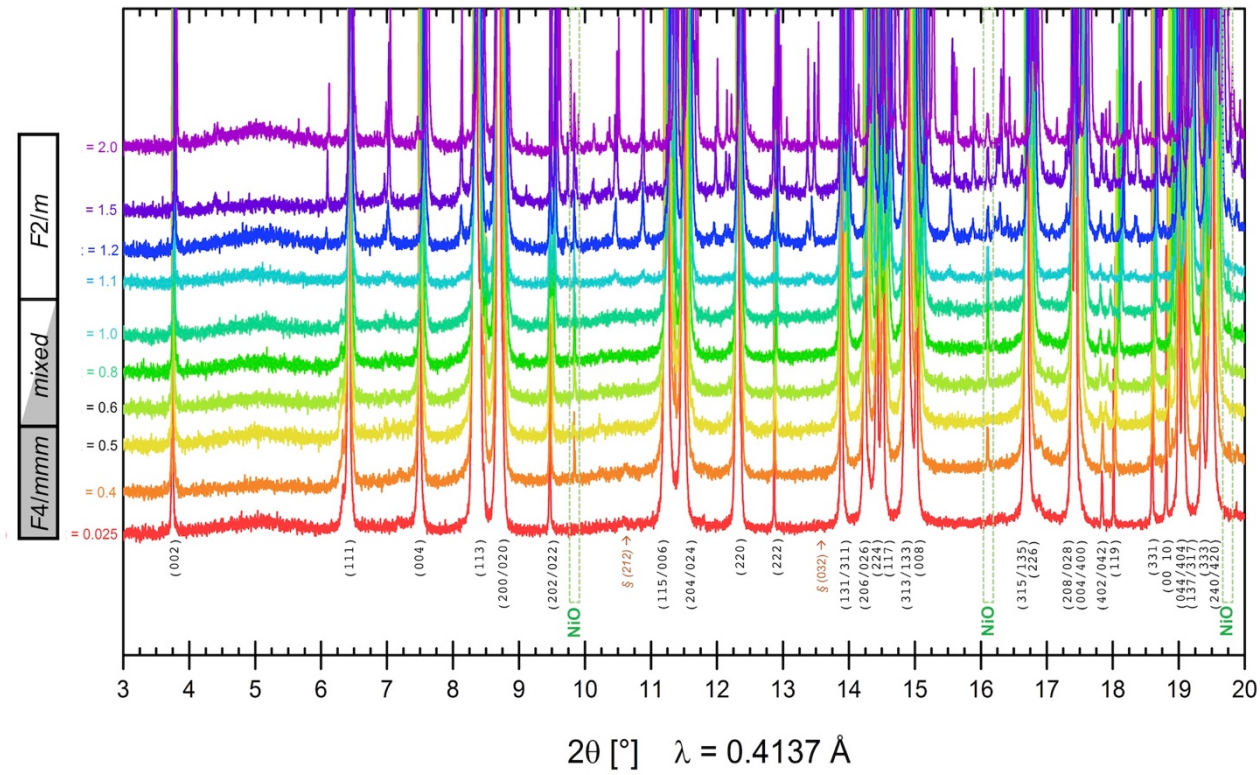


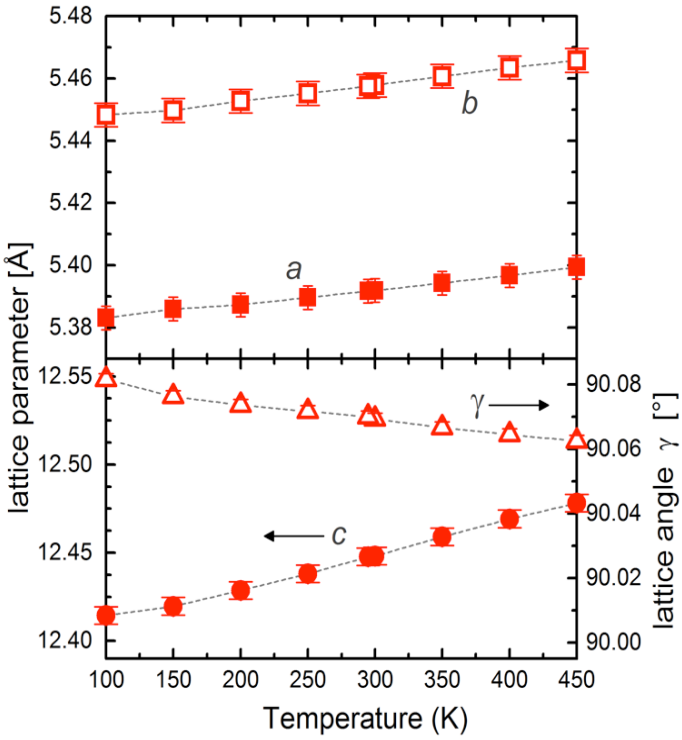
Supplemental Figure S1: Relationship between expanded *F*2/*m* monoclinic unit cell (full name *F*112/*m* with unique axis c) used in this work and its equivalent reduced conventional *C*2/*m* cell in its standard crystallographic setting (full name *C*12/*m*1 with unique axis *b*). On the left, the transformation matrix is given, and corresponding lattice values and atomic positions are given for the $Pr_2NiO_{4.25}$ composition. On the right, a schematic diagram of the relationship between the *F*2/*m* cell (in blue) and *C*2/*m* cell (in red) is shown. For clarity, only the Ni atom is plotted in the unit cell.



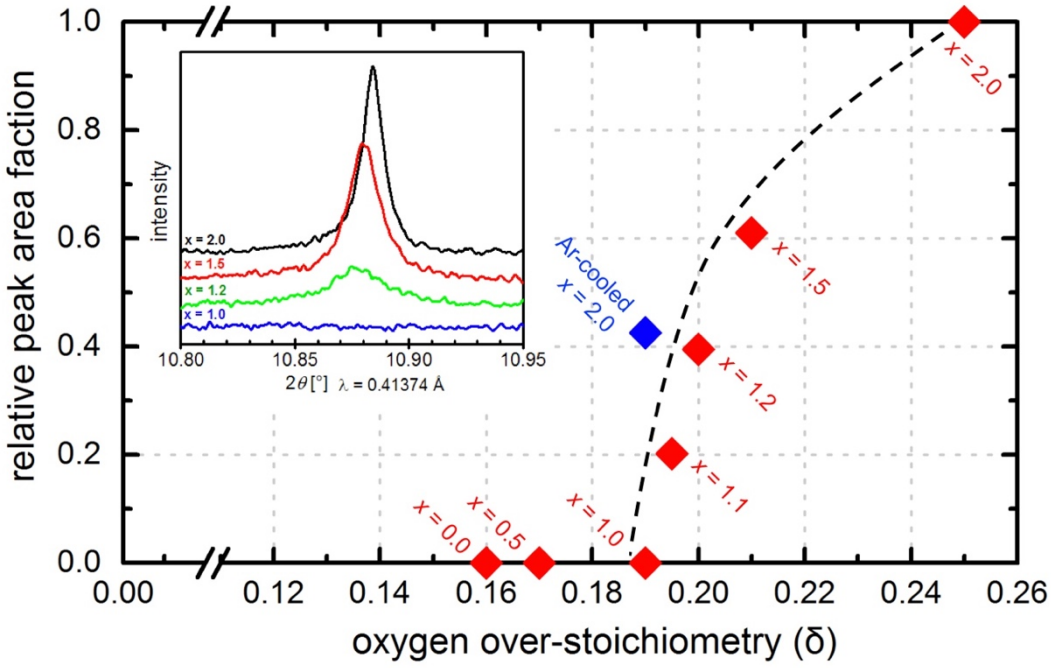
Supplemental Figure S2: Selected group/subgroup relationship paths between different space groups commonly referenced in the $La_2NiO_{4+\delta}$ and $Pr_2NiO_{4+\delta}$ literature; from the Bilbao Crystallographic Server [52]. Shaded space groups are reported for the LPNO system in the current study.



Supplemental Figure S3: Near background intensity zoomed view of HR-SPD data (295 K) for $La_{2-x}Pr_xNiO_{4+\delta}$ series. Assigned space groups in this study are marked on the left near the composition (*x*). Numerous weak intensity non-indexed peaks are clear for compositions with *x* > 1.0. Main peaks are labeled with *hkl* indexing for a generic *F*-centered orthorhombic cell (*hkl* condition; all *even* or all *odd*). Characteristic positions of (212) and (032) superlattice reflections allowed in *Bmab* and $P4_2/ncm$ space groups that arise from ordered in-plane tilting of NiO_6 octahedra are marked by §. NiO impurity peaks (cubic *Fm*3*m* cell with *a* = 4.176 Å) are marked.



Supplemental Figure S4: Evolution of refined lattice parameters (*a, b, c*, γ) as a function of temperature for $Pr_2NiO_{4.25}$. Lattice values were obtained from refinements of *in-situ* variable temperature HR-SPD data using the *F*2/m monoclinic unit cell.



Supplemental Figure S5: Evolution of the relative integrated peak area fraction observed in HR-SPD data at room temperature as a function of oxygen over-stoichiometry (δ) for Pr-rich $La_{2-x}Pr_xNiO_{4+\delta}$ compositions. The small inset upper figure inset plots the evolution of the reference non-indexed weak intensity peak (at 2θ ≈ 10.88°) for select air-cooled compositions. The integrated peak area was defined as 1.0 for δ = 0.25, and normalized for each scan as a fraction of the integrated area for a *F*2/*m* indexed (004) peak at 2θ ≈ 7.60°. Red plotted diamonds show air-cooled samples; the blue diamond represents the Ar-cooled *x* = 2.0 sample with reduced δ. The dashed black curve is a guide for the eye. See main text Section 4.4 for details and discussion.

Supplemental Table S1: Summary of Rietveld refined structural parameters and fit statistics for compositions (*x*) in the $La_{2-x}Pr_xNiO_{4+\delta}$ system. Refined values are followed by the uncertainty in brackets. The lack of an uncertainty value indicates a fixed non-refined parameter. Other symbols described in footnotes below.

				region of 2-phase coexistence												
Composition (*x*)	0.0	0.25	0.4	0.5		0.6		0.8		1.0		1.1	1.2	1.5	2.0	2.0 (Ar cooled)
Space Group †	*Fmmm*	*F*4/*mmm*	*F*4/*mmm*	*F*2/*m*	*F*4/*mmm*	*F*2/*m*	*F*4/*mmm*	*F*2/*m*	*F*4/*mmm*	*F*2/*m*	*F*4/*mmm*	*F*2/*m*	*F*2/*m*	*F*2/*m*	*F*2/*m*	*F*2/*m*
weight fraction ▲	--	--	--	0.66	0.34	0.76	0.24	0.84	0.16	0.92	0.08	--	--	--	--	--
a (Å)	5.45985(1)	5.45992(1)	5.45700(1)	5.44209(2)	5.45492(2)	5.43737(2)	5.45279(3)	5.42874(1)	5.44904(2)	5.42111(1)	5.44482(2)	5.41771(1)	5.41440(1)	5.40572(1)	5.39172(1)	5.39757(1)
b (Å)	5.46471(1)	= *a*	= *a*	5.46796(2)	= *a*	5.46892(2)	= *a*	5.46962(1)	= *a*	5.46904(1)	= *a*	5.46865(1)	5.46809(1)	5.46422(1)	5.45749(1)	5.45416(1)
c (Å)	12.6862(2)	12.6582(1)	12.6414(1)	12.6396(3)	12.6315(2)	12.6195(2)	12.6207(1)	12.5939(1)	12.5952(1)	12.5706(2)	12.5702(1)	12.5572(2)	12.5443(1)	12.5091(1)	12.4478(1)	12.4386(2)
g (°)	90	90	90	90.003(1)	90	90.003(2)	90	90.005(2)	90	90.010(2)	90	90.011(2)	90.026(2)	90.047(2)	90.070(2)	90.062(2)
Vol. (Å^3), Z = 4	378.510(1)	377.351(1)	376.447(1)	375.888(1)	375.867(2)	375.259(1)	375.251(4)	373.994(1)	373.976(3)	372.695(1)	372.656(1)	372.036(1)	371.391(1)	369.495(1)	366.278(1)	366.181(1)
Pr/La (0, 0, *z*)	0.36064	0.36046(1)	0.36040(1)	0.36042(4)	0.36020(5)	0.36025(3)	0.36036(9)	0.36024(3)	0.35946(9)	0.36017(2)	0.3584(2)	0.35993(2)	0.35994(2)	0.35960(2)	0.35910(2)	0.35958(2)
fixed occupancy	$La_{1.0}$	$Pr_{0.125}La_{0.87}$	$Pr_{0.20}La_{0.80}$	$Pr_{0.25}La_{0.75}$		$Pr_{0.30}La_{0.70}$		$Pr_{0.40}La_{0.60}$		$Pr_{0.50}La_{0.50}$		$Pr_{0.55}La_{0.45}$	$Pr_{0.60}La_{0.40}$	$Pr_{0.75}La_{0.25}$	$Pr_{1.0}$	$Pr_{1.0}$
U_{iso} ×100 (Å^2)	0.75(1)	0.88(1)	0.91(1)	0.88(1)		0.82(1)		0.84(1)		0.85(1)		0.82*	0.91*	0.96*	0.95*	1.02(1)
Ni (0, 0, 0)																
U_{iso} ×100 (Å^2)	0.32(1)	0.46(1)	0.48(1)	0.47(2)		0.52(2)		0.41(2)		0.41(1)		0.52*	0.59*	0.54*	0.55*	0.46(1)
O(1) (0, 0, *z*)	0.1722(2)	0.1729(1)	0.1727(2)	0.1732(2)		0.1734(1)		0.1741(2)		0.1741(2)		0.1740(3)	0.1733(1)	0.1730(1)	0.1731(1)	0.1743(2)
U_{iso} ×100 (Å^2)	2.94(2)	2.9*	3.18*	4.1(2)	2.2(2)	4.78*	2.29*	3.8(1)	1.5(1)	4.65*	2.2(3)	5.00*	5.02*	5.29*	6.16*	3.96(6)
O(2) (¼, ¼, 0)																
U_{iso} ×100 (Å^2)	1.06(2)	0.86(4)	0.96(4)	1.17(5)		1.15(2)		0.93(5)		0.95(5)		0.96(6)	1.51*	1.45*	1.73*	1.51(6)
O(3) (¾, ¼, 0)																
U_{iso} ×100 (Å^2)	--	--	--	1.17(5)	--	1.15(2)	--	0.93(5)	--	0.95(5)	--	0.96(6)	1.66*	1.75*	1.76*	1.43(8)
O(4) (¼, ¼, ¼)																
U_{iso} ×100 (Å^2)	1.06(2)	0.86(4)	0.96(4)	1.17(5)		1.15(2)		0.93(5)		0.95(5)		1.5(3)	2.9(3)	2.9(3)	2.59(3)	2.6(1)
occupancy	0.08	0.08	0.08	0.06(3)		0.08(2)		0.09(2)		0.09(2)		0.10(1)	0.11(1)	0.11(1)	0.12(1)	0.08(1)
oxygen δ estimate §	0.16	0.16	0.16	0.17		0.17		0.18		0.19		0.20	0.20	0.21	0.25	0.19
δ (diffraction)	0.16	0.16	0.16	0.13(5)		0.16(3)		0.18(3)		0.18(3)		0.20(2)	0.20(2)	0.22(2)	0.24(2)	0.17(2)
δ (TGA)	0.16	--	--	0.17		--		--		0.19		--	--	0.21	0.25	0.19
refined data sets ❖	SPD	SPD	SPD	SPD		SPD+NPD		SPD		SPD		SPD	SPD+NPD	SPD+NPD	SPD+NPD	SPD
SPD R_{wp}	9.68%	11.44%	10.73%	12.91%		13.62%		13.21%		13.87%		15.61%	13.46%	12.1%	12.8%	10.6%
SPD+NPD R_{wp}	--	--	--	--		11.85%		--		--		--	10.97%	10.6%	10.4%	--
Total Reduced χ^2	4.32	6.40	7.18	11.69		16.88		11.97		13.72		8.95	13.97	12.79	10.01	6.49

Footnotes

† *F*2/*m* (full name *F*112/*m*) is a non-standard setting of *C*2/*m* (no 12); *F*4/*mmm* is a non-standard *I*4/*mmm* setting (no 139)

▲ refined phase weight fractions for 2-phase compositions

§ estimated oxygen δ values reported in Table 1; determined (primarily) from TGA data or from (secondarily) diffraction data structural refinements

* U_{iso} equivalent for refined U_{aniso} values (see supplemental information)

❖ Synchrotron Powder Diffraction (SPD), Neutron Powder Diffraction (NPD)

Supplemental Table S2: Summary of Rietveld refined anisotropic displacement parameter (ADP) values (U_{aniso}) for selected Pr-rich compositions (x) in the $La_{2-x}Pr_xNiO_{4+\delta}$ system.

Composition (x)	1.1	1.2	1.5	2.0
Space Group	*F*2/*m*	*F*2/*m*	*F*2/*m*	*F*2/*m*
refined data sets	SPD	SPD+NPD	SPD+NPD	SPD+NPD
Pr/La: U_{aniso} ×100 (Å^2)				
U11	0.69(1)	0.77(1)	0.85(1)	0.84(1)
U22	0.99(1)	1.19(1)	1.26(1)	1.34(1)
U33	0.74(1)	0.76(1)	0.75(1)	0.67(1)
U12	-0.18(4)	-0.14(1)	-0.22(1)	-0.24(1)
Ni: U_{aniso} ×100 (Å^2)				
U11	0.23(4)	0.37(2)	0.26(2)	0.22(2)
U22	0.16(4)	0.32(3)	0.30(2)	0.25(2)
U33	0.92(4)	1.07(2)	1.05(2)	1.17(3)
U12	-0.2(1)	-0.25(3)	0.18(3)	-1.10(3)
O(1): U_{aniso} ×100 (Å^2)				
U11	4.9(3)	5.30(8)	5.23(8)	5.91(8)
U22	9.9(4)	9.15(12)	10.06(12)	11.90(12)
U33	0.1(2)	0.61(5)	0.59(5)	0.69(5)
U12	6.4(4)	6.02(11)	5.30(12)	5.41(13)
O(2): U_{aniso} ×100 (Å^2)				
U11	--	0.90(11)	0.71(14)	0.82(11)
U22	--	0.31(13)	0.27(14)	0.33(11)
U33	--	3.63(30)	3.36(31)	4.14(29)
U12	--	-0.40(8)	-0.27(8)	-0.25(7)
O(3): U_{aniso} ×100 (Å^2)				
U11	--	0.39(10)	0.34(13)	0.26(10)
U22	--	0.95(12)	0.57(15)	0.53(11)
U33	--	3.64(33)	4.34(35)	4.38(30)
U12	--	0.18(7)	0.21(8)	0.21(6)

Supplemental Table S3: Summary of selected bond distances determined from Rietveld refined structural models for compositions (x) in the $La_{2-x}Pr_xNiO_{4+\delta}$ system.

				region of 2-phase coexistence												
Composition (x)	0.0	0.25	0.4	0.5		0.6		0.8		1.0		1.1	1.2	1.5	2.0	2.0 (Ar cooled)
Space Group	*Fmmm*	*F*4/*mmm*	*F*4/*mmm*	*F*2/*m*	*F*4/*mmm*	*F*2/*m*	*F*4/*mmm*	*F*2/*m*	*F*4/*mmm*	*F*2/*m*	*F*4/*mmm*	*F*2/*m*	*F*2/*m*	*F*2/*m*	*F*2/*m*	*F*2/*m*
refined data sets	SPD	SPD	SPD	SPD		SPD+NPD		SPD		SPD		SPD	SPD+NPD	SPD+NPD	SPD+NPD	SPD
Ni-O(1) (x2)	2.198(2)	2.188(2)	2.183(2)	2.188(3)	2.188(3)	2.188(2)	2.1878(2)	2.193(3)	2.193(3)	2.1886(2)	2.189(2)	2.185(3)	2.173(1)	2.164(1)	2.155(1)	2.168(3)
Ni-O(2) (x2, x4) †	1.9312(2)	1.9304(2)	1.9293(2)	1.9286(1)	1.9286(1)	1.9278(1)	1.9282(1)	1.9265(1)	1.9265(1)	1.9249(1)	1.9250(2)	1.9243(3)	1.9233(1)	1.9208(1)	1.9167(1)	1.9173(1)
Ni-O(3) (x2)	--	--	--	--	1.9287(1)	--	1.9278(1)	--	1.9268(1)	--	1.9253(2)	1.9246(3)	1.9242(1)	1.9224(1)	1.9191(1)	1.9194(1)
Pr/La-O(1) (x1)	2.378(2)	2.374(2)	2.373(2)	2.362(3)	2.365(3)	2.359(2)	2.359(2)	2.334(3)	2.344(3)	2.316(2)	2.3388(3)	2.335(3)	2.3417(2)	2.3338(2)	2.315(2)	2.305(3)
Pr/La-O(1) (x2, x4) †	2.7635(3)	2.7624(3)	2.7604(3)	2.7599(4)	2.7668(4)	2.7592(3)	2.7672(2)	2.7572(4)	2.7689(4)	2.7527(3)	2.7683(2)	2.7673(5)	2.7656(2)	2.7624(2)	2.7581(2)	2.7594(4)
Pr/La-O(1) (x2)	--	--	--	--	2.7540(4)	--	2.7516(2)	--	2.7487(4)	--	2.7445(1)	2.7422(5)	2.7390(2)	2.7335(2)	2.7255(2)	2.7315(4)
Pr/La-O(2) (x2, x4) †	2.6182(2)	2.6166(2)	2.6147(1)	2.6149(4)	2.6131(3)	2.6129(8)	2.6126(3)	2.6163(8)	2.6097(2)	2.6220(14)	2.6070(2)	2.6070(2)	2.6050(2)	2.6039(2)	2.5998(2)	2.5936(1)
Pr/La-O(3) (x2)	--	--	--	--	2.6132(3)	--	2.6128(3)	--	2.6096(2)	--	2.6068(2)	2.6073(2)	2.6057(2)	2.6027(2)	2.5981(2)	2.5951(1)
Pr/La-O(4) (x2)	2.3874(2)	2.3835(1)	2.3812(2)	2.3785(4)	2.3801(3)	2.3776(7)	2.3776(2)	2.3690(7)	2.3748(2)	2.3582(12)	2.3714(2)	2.3682(2)	2.3667(2)	2.3599(2)	2.3491(2)	2.3525(1)
Pr/La-O(4) (x2)	2.3874(2)	2.3835(1)	2.3812(2)	2.3785(4)	2.3802(3)	2.3776(7)	2.3779(2)	2.3690(7)	2.3749(2)	2.3582(12)	2.3716(2)	2.3685(2)	2.3674(2)	2.3612(2)	2.3510(2)	2.3542(1)

† Bond multiplicity is x2 for *F*2/*m*, but x4 for *F*4/*mmm* and *Fmmm* models, where O(2) and O(3) sites are equivalent