Supplementary Materials for

The hidden story in $BaNiO_3$ to $BaNiO_2$ reduction: adaptive structural series and NiO exsolution.

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XPS experiments were carried out in a Kratos AXIS Ultra DLD spectrometer, using a monochromatic Al Kα radiation (1486.6 eV). High-resolution spectra were collected using an analysis area of ≈ 300µm×700 µm and a 40 eV pass energy. Instrument base pressure was 4×10^{-10} Torr. The bending energy scale was calibrated taking C 1s peak at 284.8 eV as reference. High-resolution spectra were collected at the center of the crater using an analysis area of 110 µm in diameter.

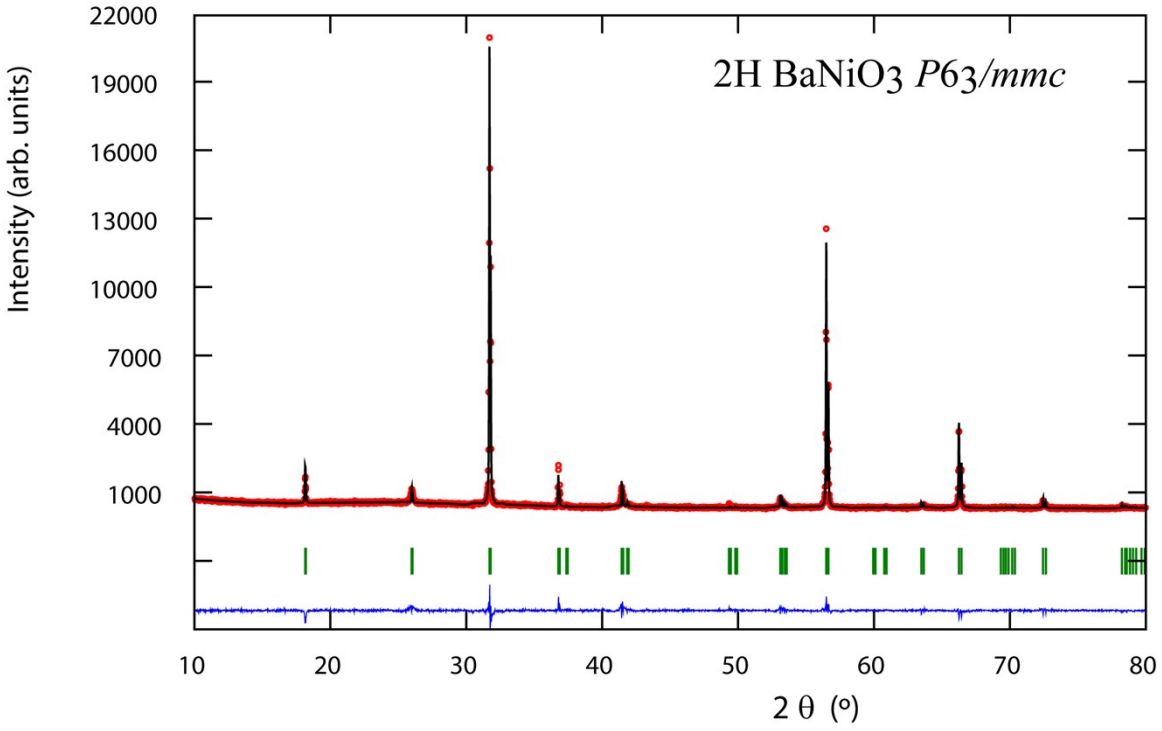

Figure S1: Rietveld refinement of $BaNiO_3$ from crushed single crystals, used for High Temperature XRD.

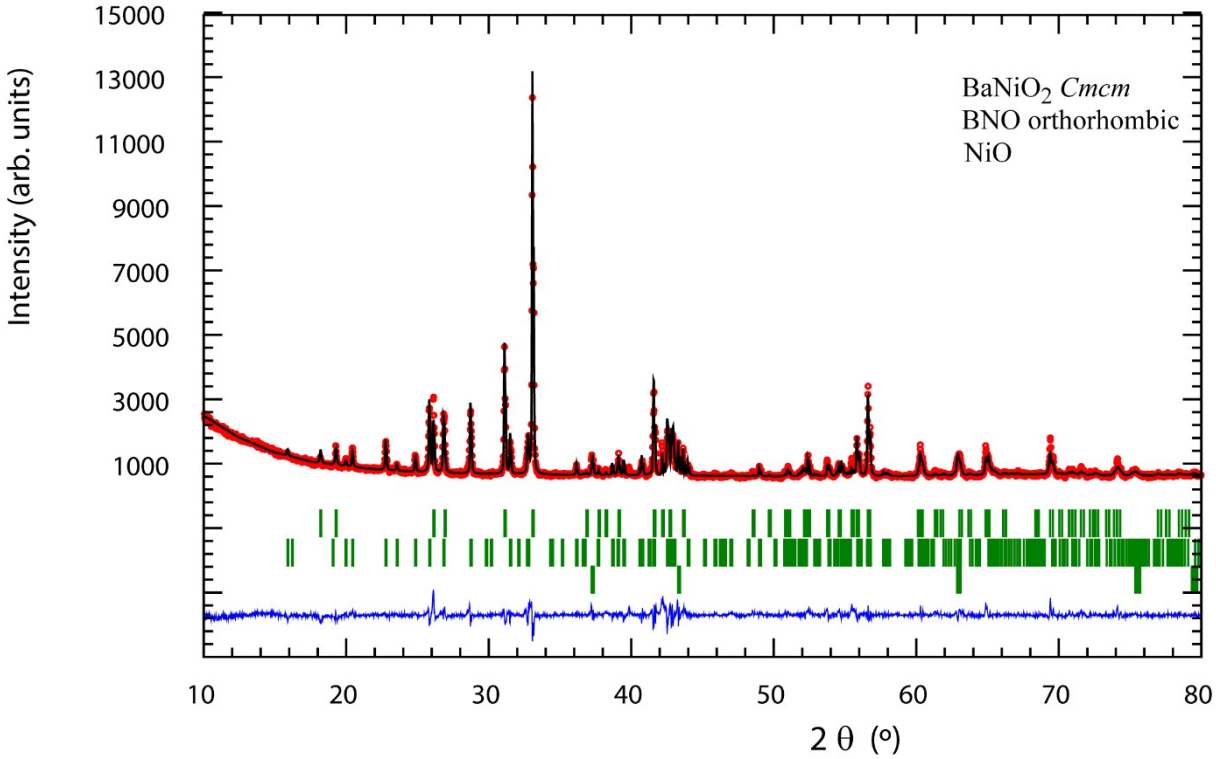

Figure S2: Rietveld refinement of $BaNiO_2$ cooled from 900 °C but kept under inert N_2 atmosphere. BNO was treated in a Lebail-mode. NiO is refined to *ca.* 20% compared to the main phase.

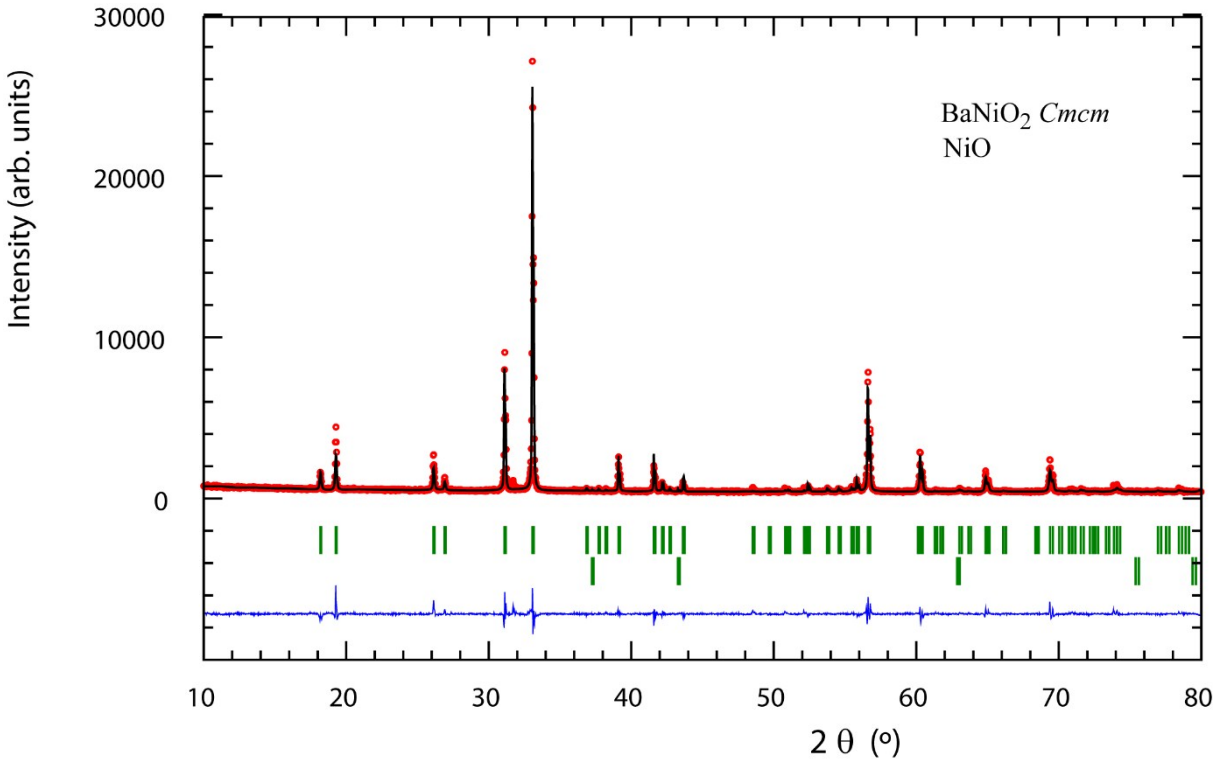

Figure S3: Rietveld refinement of $BaNiO_2$ recovered from 900 °C and exposed to air. BNO vanished, with NiO now represents only few w% of the sample.

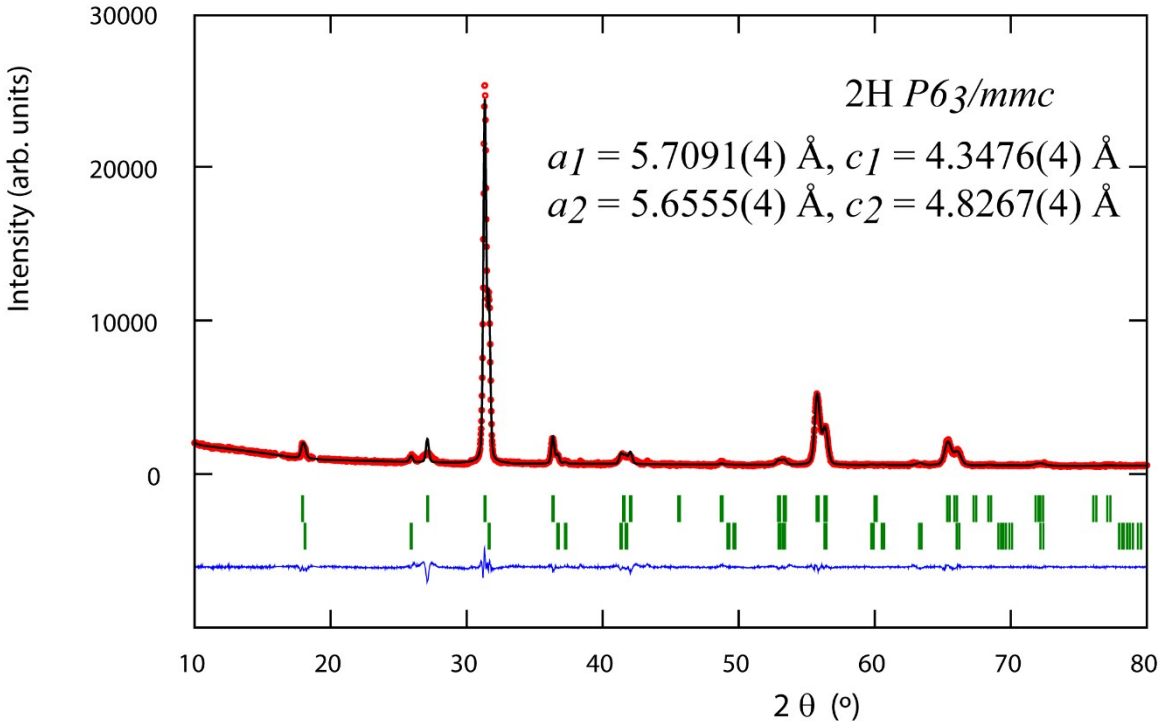

Figure S4: LeBail fit after re-oxydation of $BaNiO_2$ single crystals during TG under flowing air (900°C). Grinding the crystals shows a mixture of two 2H-$BaNiO_{3-x}$ phases with distinct mixed valent $Ni^{3/4+}$ states. The analogy of the refined lattice parameters for those listed in ref[1] after systematic nickel titration in the $BaNiO_{3-x}$ series gives : for the main phase (a1, c1) $BaNiO_{\sim 2.4}$ and for the second one (a2, c2) $BaNiO_{\sim 2.5}$.

S5: $Ba_{1.16}NiO_3$ Crystal structure refinement

Starting from an hexagonal 2H-ABO3 compound, the reduction of $[BO_3]_\infty$ 1D-chains of face sharing octahedra (B_O) of the 2H-perovskite, induce the removal of MO_3 units which locally creates a trigonal prism (B_P) in the octahedral chains with stoichiometry $A_{1+x}BO_3$. In the studied system, evidence of the reduction product $Ba_7Ni^{4+}{}_5Ni^{2+}$ predicted to occur above 600°C was given by single crystal XRD in the sample heated at 700°C and cooled down. The new isolated $Ba_{1.16}NiO_3$ structure presents a sequence of 5 octahedra per 1 trigonal prism with an average nickel oxidation state of +3.666. The structure was refined in Jana2006 [2] as a composite, following the methodology proposed in a number of prior works. [3-7]

The crystal structure was treated according to the composite description, for which the strategy and key parameter and relations are well described.[3-7] In few words the trigonal lattice parameters $[NiO]_{1-x}$ and [Ba] composite lattices are refined as a= 9.842(1), c_1=2.5600(6) , c2=4.4082(8). The system is treated with a (3+1)D symmetry considering $\gamma=c_1/c_2=0.58074$ (i.e. 7/12 in a commensurate approximation) and the modulation wave vector of the two composite parts $q_1^*=c_2^*=\gamma c_1^*$ and $q_2^*=c_1^*=\gamma^{-1}c_2^*$. According to the specificities of each lattice, the super space group pair is R-3m(00γ) : P-3c1(00γ^{-1}). Finally it is of primordial importance that in this system c_1 and c_2 reflecting the average NiO_6 polyhedron height (averaging P and O) and the mean Ba-Ba interlayer distances, the final composition $Ba_{1+x}(NiO_3)$ is γ dependent such that $\gamma = (1+x)/2$. In our case we find $Ba_{1.162}NiO_3$ (i.e.1/6 in a commensurate approximation). Automatically, one can deduce the ideal (i.e. commensurate) 2x [1P/5O] sequence along c using a 12 fold supercell approximation γ=7/12 and x =1/6. Using the composite setting, both reflexions of the two sublattices are main reflections and the collected "true" satellites of 1st and 2nd orders are due to the interaction between the two lattices. The final R% are 4.97%(all), 3.84% (main), 12.83%(1st order) and 12.71% (2nd order) using positional waves of 4th, 1st, 4th orders and thermal parameters waves of 2nd, 1st and 0th orders for the three Ni, O and Ba atoms. The oxygen occupancy is responsible for the octahedral *vs.* prismatic cavities and was modelled by a Crenel function (width

along x4 : Δ = 0.5, center $x4_0$ = 0.25) smoothed by one harmonic.[6] Finally the refinement of the crystal structure in a commensurate approximation whatever the origin of t is, seriously damaged the R% values, especially on the satellites (R_{satt} 1st ~16 to 20 %), which the reality of an incommensurate sequence where the 5O/1P sequence is sometimes broken.

Table S6: crystal data and refinement parameters for $Ba_{1.16}NiO_3$

	$Ba_{1+x}NiO_3$
Refined X value/ideal	0.162 / 1/6
Composite approach	Sublattice 1 : [NiO_3]
Lattice 1	Rhombohedral
a1 (Å)	9.842(1,)
c1 (Å)	2.5600(6)
	Sublattice 2 : $[Ba]_{1+x}$
Lattice 2	Trigonal
a2 = a1	
c2 (Å)	4.4082(8).
γ =c1/c2	0.58074
Superspace group	R-3m(00γ)0s : P-3c1(00γ^{-1})
	Data Collection
Wavelength (Å)	0.71073 (Å)
$\theta_{min-max}$ (°)	2.71-31.42
scan	ω- φ
h,k,l $_{min,max}$	-14<h,k<-14 ; -5<l<-5
	Refinement
Ref. Program	JANA 2006
Convergence/weight	Refinement on F, w=1/(σ^2(F)+0.0001F^2)
N Ref. (all/I>3σ(I)) - R_{obs}/wR_{obs} (%)	4.96/5.26
N Main – R_{obs}/wR_{obs} (%)	417/152 – 3.83/4.16
N 1st order – R_{obs}/wR_{obs} (%)	499/72 – 12.83/16.78
N 2nd order – R_{obs}/wR_{obs} (%)	326/10 – 12.81/15.16
R_{int} (%) (-3m Laue class)	14.4
$\Delta\rho$ $_{min/max}$ (e/Å^3)	4.87/-5.35
Twin (obv/Rev)	0.488(4)/0.512(4)

Table S7: atomic parameters and displacement for $Ba_{1.16}NiO_3$

	x	y	z	U iso/eq (Å^2)
Ni1 3(a)	**0**	**0**	**0**	**0.0324(9)**
$Sin^1_{x,y,z}$	0	0	0	
$Cos^1_{x,y,z}$	0	0	0	
$Sin^2_{x,y,z}$	0	0	-0.063(2)	
$Cos^2_{x,y,z}$	0	0	0	
$Sin^3_{x,y,z}$	0	0	0	
$Cos^3_{x,y,z}$	0	0	0	
$Sin^4_{x,y,z}$	0	0	0.024(3)	
$Cos^4_{x,y,z}$	0	0	0	
O1 18(g), **Cresnel x_{40} = ¼ , Δ = ½**	**0.1427(7)**	**0.1427(7)**	**0.5**	**0.041(4)**
$Sin^1_{x,y,z}$	-0.0011(10)	-0.0011(10)	-0.171(6)	
$Cos^1_{x,y,z}$	0.002(2)	0.002(2)	0	
Ba1 36(i), Occ. 1/6 **Cresnel x_{40} = 0 , Δ = 1**	**1/3**	**1/4**	**0.0139(15)**	
$Sin^1_{x,y,z}$	0.025(5)	0.013(2)	-0.013(10)	
$Cos^1_{x,y,z}$	0	0.000(6)	0	
$Sin^2_{x,y,z}$	0.002(7)	0.001(4)	-0.0.029(7)	
$Cos^2_{x,y,z}$	0	0.004(5)	0	
$Sin^3_{x,y,z}$	0.000(10)	0.000(5)	0.050(15)	
$Cos^3_{x,y,z}$	0	0.012(11)	0	
$Sin^4_{x,y,z}$	-0.014(6)-	0.007(3)	-0.059(12)	
$Cos^4_{x,y,z}$	0	0.038(15)	0	

Table S8: ADP parameters and displacement for $Ba_{1.16}NiO_3$

	U11	U22	U33	U12	U13	U23
Ni1	0.0326(9)	0.0326(9)	0.0321(19)	0.0163(4)	0	0
Sin^1_U	0	0	0	0	0	0
Cos^1_U	0	0	0	0	0	0
Sin^2_U	0	0	0	0	0	0
Cos^2_U	-0.019(2)	-0.019(2)	-0.021(3)	-0.0097(11)	0	0
O1	0.038(4)	0.038(4)	0.051(7)	0.021(4)	-0.008(3)	0.008(3
Sin^1_U	0.028(8)	-0.028(8)	0	0	-0.026(7)	-0.026(7)
Cos^{21}_U	- 0.024(12)	-0.024(12)	0.09(2)	-0.047(13)	-0.032(11)	0.032(11)

Table S9: Main distances for $Ba_{1.16}NiO_3$

	Average	**min**	**max**
Ni-O (6x) :	1.911(13)	1.744(16)	2.333(16)
Ba-O (6x) :	2.850(3)	2.60(2)	3.02(3)
Ba-O (6x) :	2.983(3)	2.90(3)	3.41(4)

References

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