

Directed Lifting of Inversion Symmetry in Ruddlesden-Popper Oxide-Fluorides – Towards Ferroelectric and Multiferroic Behavior.

Ronghuan Zhang, Mark S. Senn and Michael A. Hayward*.

Supporting Information

Figure S1. Thermogravimetric data collected from $\text{La}_3\text{Ni}_2\text{O}_{5.5}\text{F}_{3.5}$ under a 10:90 $\text{H}_2:\text{N}_2$ atmosphere.

Figure S2. Observed calculated and difference plots from the structural refinement of $\text{La}_3\text{Ni}_2\text{O}_{5.5}\text{F}_{3.5}$ against neutron powder diffraction data collected at 300 K.

Figure S3. Comparison of octahedral rotations and A-cation displacements of *Amam*, *A2₁am* and *Pnam* distorted $\text{A}_3\text{B}_2\text{O}_7\text{F}_2$ phases.

Symmetry Analysis of the *Pnam* Phase.

Figure S4: Representation of NiO_6 octahedra in *A2₁am* and *Pnam* distorted phases superimposed on top of each other.

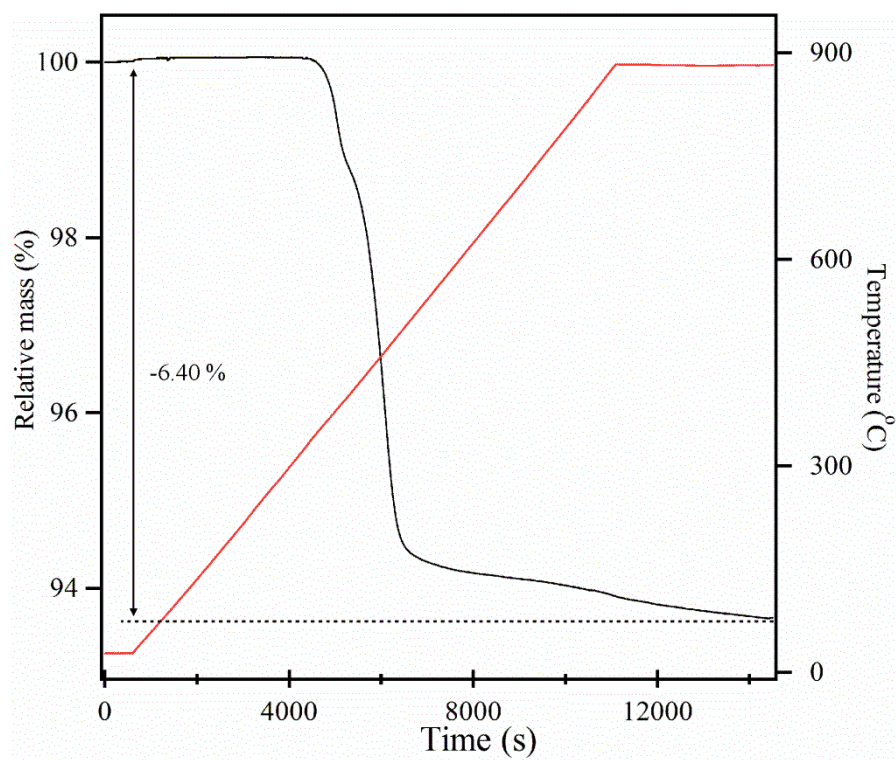


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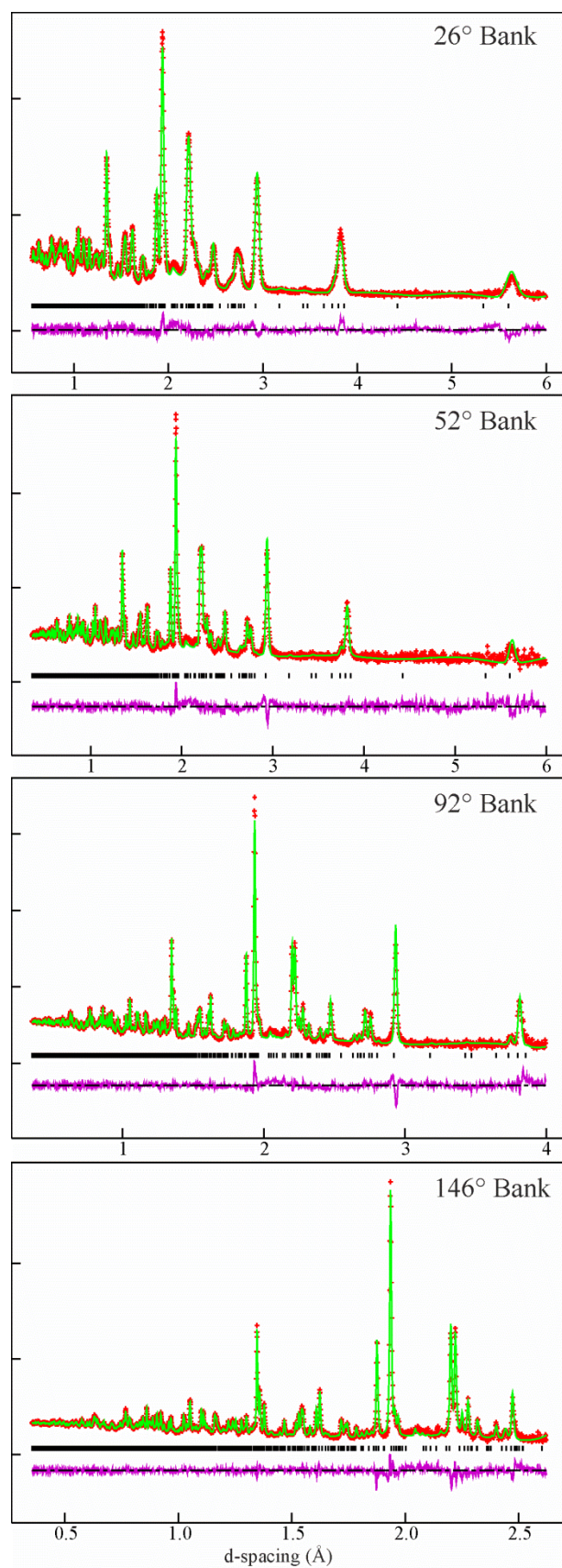


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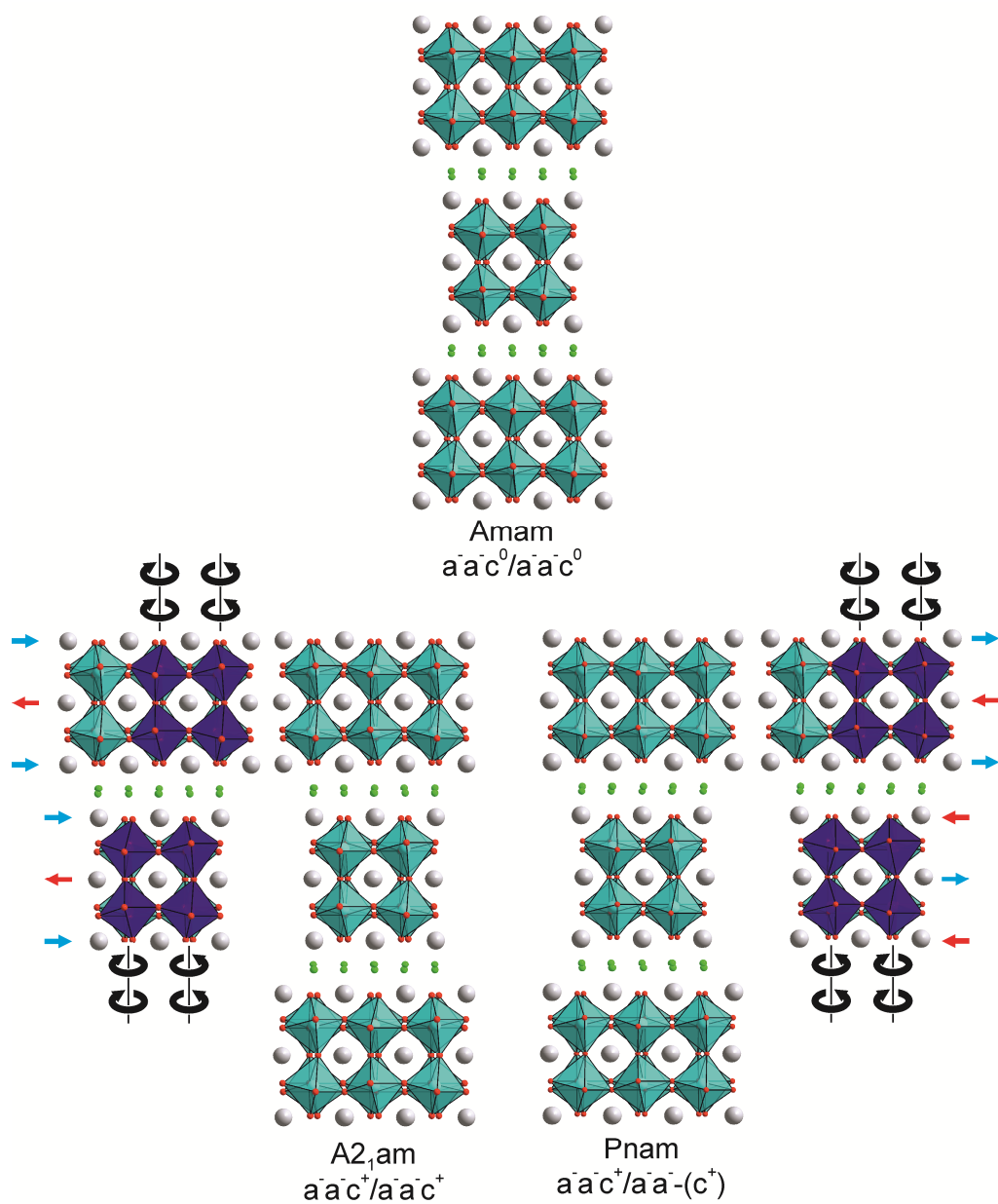


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Symmetry Analysis of the *Pnam* Phase

Formally we may decompose the octahedral tilts and rotations present in a distorted structure as transforming according to irreducible representations of a hypothetical undistorted “parent” structure. In this case, the parent structure has *I4/mmm* symmetry and presents the highest possible symmetry that this class of materials can crystallise in. Unfortunately, in some circumstances, the precise irreducible representations that characterise a particular symmetry lowering distortion can depend on the setting of the parent structure used. In the present analysis we specify the following setting of the structure:

		x	y	z
La 1	2b	0	0	½
La 2	4e	0	0	z
Ni 1	4e	0	0	z
O 1	2a	0	0	0
O 2	4e	0	0	z
O 3	8g	0	½	z
F 1	8g	½	0	z

With respect to this parent setting, the distortions that characterise the octahedral rotation perpendicular to the crystallographic *c*-axis transform as the irreducible representation X_2^+ , and the combined tilts around the *a* and *b*- axes transform as X_3^- . Here the X denotes the symmetry point (in this case $X = [\frac{1}{2}, \frac{1}{2}, 0]$) of the Brillion Zone of the parent structure in which the structural instability arises, and also represents the propagation vector which describes the main additional superstructure peaks observed in our neutron diffraction studies. The number refers to the tabulation order used by the web-based program ISODISTORT¹ and has no further significance. The minus and plus sign indicate whether the distortion breaks the inversion centre at the origin of the structure (-), or the inversion centre which occurs at the midpoint between two unit cell origins related by a lattice translation (+). In this case, the relevant Wyckoff positions of the inversion centres of the parent structure are 2a (0,0,0) and 2b (0,0, ½). Hence, combining distortions transforming as both X_2^+ and X_3^- as in the hybrid improper ferroelectric $\text{Ca}_3\text{Mn}_2\text{O}_7$, has the effect of lowering the parent *I4/mmm* symmetry to a polar space group by breaking both these inversion centres simultaneously, and giving the structure:

$A2_1am$, basis={ (1,-1,0), (-1,-1,0), (0,0,-1) }, origin=($\frac{1}{4}, \frac{1}{4}, -\frac{1}{2}$), k-active= [$\frac{1}{2}, \frac{1}{2}, 1$]; [$\frac{1}{2}, \frac{1}{2}, 1$]

There is at least one “active” propagation vector (k-active) associated with each distortion which transform as one of the unique irreducible representations, and in the above case both propagation vectors are the same, namely $k = [\frac{1}{2}, \frac{1}{2}, 1]$. There is another choice of propagation vector possible: $k = [\frac{1}{2}, \frac{1}{2}, 0]$. These two propagation vectors are equivalent in *I4/mmm* due to the body centring of the cell, and so the above structural distortion could have equally been achieved through k-active= [$\frac{1}{2}, \frac{1}{2}, 0$]; [$\frac{1}{2}, \frac{1}{2}, 0$]. However, there exists a further possibility to combine the distortions transforming as X_2^+ and X_3^- , by setting one with propagation vector [$\frac{1}{2}, \frac{1}{2}, 1$] and the other with propagation vector [$\frac{1}{2}, \frac{1}{2}, 0$]. This leads to a structural distortion which is distinct from that of the $A2_1am$ phase:

Pnam, basis={ (1,1,0), (-1,1,0), (0,0,1) }, origin=($\frac{1}{4}, \frac{1}{4}, \frac{1}{4}$), k-active= [$\frac{1}{2}, \frac{1}{2}, 1$]; [$\frac{1}{2}, \frac{1}{2}, 0$]

Superimposing the *Pnam* and $A2_1am$ structures (generated with equivalent distortion amplitudes) demonstrates that it is the phase with which the X_2^+ rotations and X_3^- tilts are combined which differentiates these two structures in real space. While it is possible to superimpose either the tilts or the rotations, it is never possible to achieve the superposition of both across all of the perovskite blocks (see Figure S4).

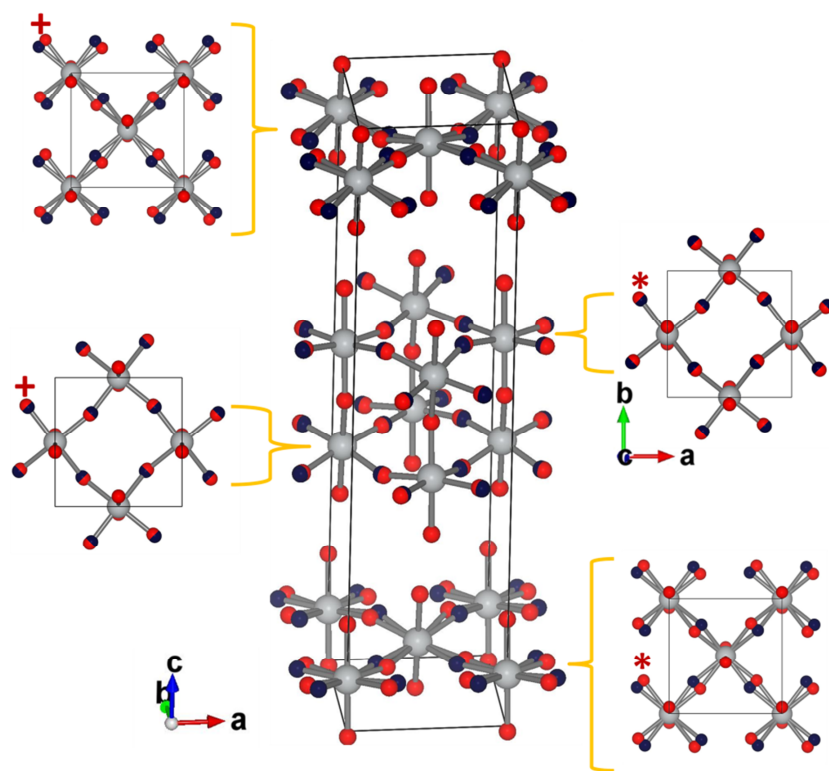


Figure S4: Representation of the NiO_6 octahedra in the $A2_1am$ (red oxygens) and $Pnam$ (blue oxygens) structures superimposed on top of each other. For ease of comparison, both structures are generated in $P1$, basis= $\{(-1,1,0),(-1,-1,0),(0,0,1)\}$, origin= $(0,0,0)$ with appropriate symmetry constraints applied. It is possible to superimpose either the octahedral rotations or the tilts (as shown here) but never both. In $A2_1am$ the lattice centring is preserved by the combined rotation and tilt pattern of the oxygens, with * and + denoting two pairs of equivalent points where red oxygen atoms may be superimposed by applying the A-centring lattice operation (+ $(0, \frac{1}{2}, \frac{1}{2})$, this is derived from the I-centring condition of $I4/mmm$ after transformation to the $P1$ setting used to compare the two structures). No such equivalent points exist for the $Pnam$ structure (blue oxygens), and hence the combination of oxygen tilts and rotations have violated the I-centring of the parent $I4/mmm$ structure.

This subtlety has profound consequences for the way in which these rotations and tilts couple to other further distortions in the structure, and hence the resulting physical properties of phases with these distortions. Most notably, in $A2_1am$ distorted phases secondary polar distortions occur, whereas in $Pnam$ distorted phases the secondary distortions are anti-polar in nature. The origin of the secondary anti-polar distortions in the $Pnam$ structure is the violation of lattice centring discussed above (see Figure S4). This may be formally understood by considering a linear combination of the two active propagation vectors $[\frac{1}{2}, \frac{1}{2}, 1] + [\frac{1}{2}, \frac{1}{2}, 0]$ that lead to the $Pnam$ structure. This linear combination gives a secondary propagation vector of $[1 \ 1 \ 1]$ which is the propagation vector associated with violating the I-centring extinction conditions of the parent cell. Indeed, weak superstructure reflections indexing as $hkl + [1 \ 1 \ 1]$ are visible in the 2.4 -2.5 Å d-spacing region of the neutron powder diffraction data (see Figure 4 of main paper). The distortions associated with these weak superstructure peaks transform as the irreducible representation M_5^- .

[1] Campbell, H. T. Stokes, D. E. Tanner, and D. M. Hatch, "ISODISPLACE: An Internet Tool for Exploring Structural Distortions." J. Appl. Cryst. 39, 607-614 (2006).