Anion order in perovskite oxynitrides

Minghui Yang¹, Judith Oró-Solé², Jennifer A. Rodgers¹, Ana Belén Jorge², Amparo Fuertes²* and J. Paul Attfield¹*

Transition-metal oxynitrides with perovskite-type structures are an emerging class of materials with optical, photocatalytic, dielectric and magnetoresistive properties that may be sensitive to oxide–nitride order, but the anion-ordering principles were unclear. Here we report an investigation of the representative compounds SrMO₂N (M = Nb, Ta) using neutron and electron diffraction. This revealed a robust 10/2(O₀.5N₀.5) partial anion order (up to at least 750 °C in the apparently cubic high-temperature phases) that directs the rotations of MO₂N₂ octahedra in the room-temperature superstructure. The anion distribution is consistent with local cis-ordering of the two nitrides in each octahedron driven by covalency, which results in disordered zigzag M–N chains in planes within the perovskite lattice. Local structures for the full range of oxynitride perovskites are predicted and a future challenge is to tune properties by controlling the order and dimensionality of the anion chains and networks.

Transition-metal oxynitrides are an important class of emerging materials that, in optimal cases, may combine the advantages of oxides and nitrides. Generally, their stabilities in air and moisture are greater than those of the pure nitrides, but with smaller bandgaps than those of comparable oxides. This leads to useful electronic and/or optical properties, such as the N-doping of TiO₂ to tune the bandgap from the ultraviolet to the visible useful electronic and smaller bandgaps than those of comparable oxides. This leads to photophysical properties, such as the N-doping of TiO₂ to tune the bandgap from the ultraviolet to the visible range of AMO₃–Nₓ perovskites.

The properties of perovskites are sensitive to small, structural distortions that may arise from tilting or electronic deformations of the MX₆ octahedra. Oxide/nitride anion order is also expected to be important, for example in directing the M-cation displacements in dielectric materials, but consistent models are not reported, even for representative oxynitride perovskites such as SrMO₂N (M = Nb, Ta), in which the anion content is close to the ideal stoichiometry. Here, we report an investigation of anion order in these phases using variable-temperature neutron diffraction and electron diffraction. This revealed a robust, partial anion order that is consistent with local cis-ordering of the two nitrides in each octahedron. The order directs the tilting of the octahedra in the low-temperature pseudotetragonal superstructure. The local anion order may be described as the formation of disordered zigzag M–N chains in two dimensions at low temperatures, changing towards three dimensions at high temperatures. These principles are applied to predict local structures across the range of AMO₃–Nₓ oxynitride perovskites.

Results

Diffraction study. The cubic AMX₃ perovskite structure consists of a network of corner-linked MX₆ octahedra and ideally has cubic Pm₃m symmetry, but this may be lowered through internal perturbations (including anion order) or rotations and tilts of the octahedra. This often leads to structural phase transitions such as those observed for SrMO₂N (M = Nb, Ta). Additional superstructure diffraction peaks that arise from ordered rotations of the octahedra were seen at room temperature (Fig. 1), but only the peaks expected from a cubic perovskite were observed above 300 °C for SrNbO₂N and above 200 °C for SrTaO₂N.

Neutron diffraction is sensitive to small anion displacements because the scattering lengths of the light and heavy atoms are comparable, and it also offers high O/N scattering contrast (the neutron-scattering lengths b are bNb = 0.702 fm, Nb = 0.705 fm, bTa = 0.691 fm, bO = 0.581 fm and bN = 0.936 fm). However, the sensitivity of powder neutron data to anion order in a perovskite depends on the magnitude of the accompanying lattice distortion that broadens or splits the diffraction peaks. If the cell distortion is small, then O/N ordered and disordered models give very similar diffraction intensities, as confirmed by the simulated patterns shown in the Supplementary Information. Hence, although the high-temperature SrMO₂N neutron data are fitted satisfactorily by a statistically disordered cubic perovskite model in which all the anion sites are equivalent, we also tested a tetragonal P4/mbm symmetry model to investigate possible long-range anion order.

Refinements of the P4/mbm model, which allows for possible 1:2 anion order over inequivalent sites X₁ and X₂, gave a striking result. For both SrNbO₂N and SrTaO₂N, the fits converged to an ordered model with the X₁ site fully occupied by O, and the X₂ sites occupied by a near 50/50 O/N mixture, as shown in Table 1. For SrNbO₂N the refined anion composition of SrNbO₂.07N₀.93 revealed a small oxygen excess, consistent with the chemical analysis and previous studies of this phase and this composition was used in the fits to other diffraction profiles. SrTaO₂N was found to be stoichiometric by analysis and neutron refinement. The slight decrease of the tetragonal c-dimension relative to the a-dimension is consistent with the anion order, as oxide is slightly smaller than nitride, but the lattice distortion is too small to result in visible peak broadenings and the anion segregation in the refinement is driven by the slight difference in intensities of the composite powder diffraction peaks, as illustrated by an improvement in the structure factor-squared residual (RFₚ) from 5.22 to 4.96% for the odd h + k + l reflections, which are sensitive to the anion distribution. The oxygen occupancies of the X₁ site...
Figure 1 | Powder neutron diffraction patterns for SrNbO$_2$N. Fits are shown with the observed points as crosses, calculated profiles as full lines and the difference and reflection markers offset below. The 300 °C fit is of the pseudocubic (tetragonal $P4/mmm$) model in Table 1, with barely resolvable broadenings that arise from the anion order. Superstructure peaks caused by the rotational order of octahedra are evident at 25 °C, and the fit is of the constrained monoclinic $I12/m$ model in Table 2.

Table 1 | Refined structures for the pseudocubic phases of SrMO$_2$N.

<table>
<thead>
<tr>
<th>Atom</th>
<th>$x$</th>
<th>$y$</th>
<th>$z$</th>
<th>$U_{eq}$ (Å$^2$)</th>
<th>O/N occupancy</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sr</td>
<td>0.5</td>
<td>0.5</td>
<td>0.5</td>
<td>0.0170(5)</td>
<td></td>
</tr>
<tr>
<td>Nb</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0.0130(5)</td>
<td></td>
</tr>
<tr>
<td>Ta</td>
<td>0</td>
<td>0</td>
<td>0.5</td>
<td>0.0525(4)</td>
<td></td>
</tr>
<tr>
<td>X1</td>
<td>0</td>
<td>0</td>
<td>0.5</td>
<td>0.0225(4)</td>
<td>0.0187(3)</td>
</tr>
<tr>
<td>X2</td>
<td>0.5</td>
<td>0</td>
<td>0</td>
<td>0.0187</td>
<td>0.51(3)/0.49</td>
</tr>
</tbody>
</table>

Results for SrNbO$_2$N at 300 °C and for SrTaO$_2$N (given in italics where different) at 200 °C; those for other temperatures are given in the Supplementary Information. Atomic coordinates ($x$, $y$ and $z$) in tetragonal space group $P4/mmm$, isotropic thermal factors ($U_{eq}$) and refined O/N occupancies at the two anion sites are listed. Estimated standard deviations in the independently refined parameters are in parentheses. Lattice parameters and agreement factors, SrNbO$_2$N: $a = 4.054(2)$ Å, $c = 4.051(4)$ Å, $\chi^2 = 4.12$, $R_w = 5.61\%$ (wp = weighted profile); SrTaO$_2$N: $a = 4.044(3)$ Å, $c = 4.042(3)$ Å, $\chi^2 = 2.81$, $R_w = 5.25\%$, $R = 3.62\%$.

Figure 2 | Anion order in the SrMO$_2$N perovskites. a, Structural model that shows the relationship between the unique axes for anion order ($c_{an}$) and octahedral rotation ($c_{rot}$) in the room-temperature phase. Shown is the correspondence between the X1 (oxide, unshaded atoms) and X2 (50% occupancy, half-shaded) sites produced by anion order, and the inequivalent Y1 and Y2 sites created by rotational order. b, The oxygen occupancies of the X1 site in the pseudocubic $M = Nb$ and Ta phases at high temperatures.
Neutron refinement of the room-temperature O/N occupancies in the I4/mcm model gave a near 50/50 population at the Y1 site, which showed that this corresponds to one of the X2 sites in the high-temperature structure. This implies that the two Y2 sites in the room-temperature structure are not equivalent, as one should correspond to the X1 site (100% O) and the other should be the remaining X2 (50/50 O/N) site, as shown in Fig. 2a. This inequivalence lowers the space-group symmetry from tetragonal I4/mcm to monoclinic I112/m (non-standard setting of C2/m) and we attempted to fit an I112/m model to the room-temperature neutron data (Table 2). No stable monoclinic refinement was possible for SrTaO2N, and the model shown is equivalent to an I4/mcm description with O/N ratios of 50/50 at the Y1 site and an average 75/25 at the two Y2 positions. The same distributions were reported in previous studies of SrTaO2N (ref. 9) and CaTaO2N (ref. 8), in which further octahedral tilting lowered the apparent symmetry to orthorhombic Pbnm and anion order is predicted to result in a monoclinic P1121/m structure by analogy with the I112/m distortion.

For SrNbO2N, it was possible to refine the occupation factors of the three anion sites independently, subject to the fixed overall composition, with lattice parameters and atomic positions constrained by tetragonal I4/mcm symmetry. The results given in Table 2 support the above expectation as the Y2(X1) site has a high (87%) O occupancy, but the Y2(X2) site has an occupancy of 51% O. This anion order leads to the loss of the c-glide plane symmetry observed in the electron diffraction patterns (Fig. 3).

From these refinements, we conclude that a robust 1O/2(0.53N0.47) anion order is present over the three available sites for SrMO2N (M = Nb, Ta) perovskites, up to at least ~1,000 K for M = Ta. The anion order controls the ordering of octahedral rotations below ~500 K, but the unique axis for anion order does not correspond to the unique axis for octahedral rotation (Fig. 2a). Although the anion order is well-defined, it results in very small metric distortions of the apparent high-temperature Pnma and room temperature I4/mcm structures. High-resolution powder neutron diffraction data enabled the high-temperature

### Table 2 | Refined models for the rotational superstructures of SrMO2N.

<table>
<thead>
<tr>
<th>Atom</th>
<th>x</th>
<th>y</th>
<th>z</th>
<th>U_iso (Å²)</th>
<th>O/N occupancy</th>
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</thead>
<tbody>
<tr>
<td>Sr</td>
<td>0</td>
<td>0.5</td>
<td>0.25</td>
<td>0.0094(4)</td>
<td>100% O</td>
</tr>
<tr>
<td>Nb1</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0.0069(3)</td>
<td>100% O</td>
</tr>
<tr>
<td>Ta1</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0.0069(4)</td>
<td>100% O</td>
</tr>
<tr>
<td>Nb2</td>
<td>0</td>
<td>0</td>
<td>0.5</td>
<td>0.0069</td>
<td>100% O</td>
</tr>
<tr>
<td>Ta2</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0.0069</td>
<td>100% O</td>
</tr>
<tr>
<td>Y1(X2)</td>
<td>0</td>
<td>0</td>
<td>0.25</td>
<td>0.0145(3)</td>
<td>66.6/0.32</td>
</tr>
<tr>
<td>Y2(X1)</td>
<td>0.7249(2)</td>
<td>0.7751</td>
<td>0</td>
<td>0.0145</td>
<td>84.6/0.16</td>
</tr>
<tr>
<td>Y2(X2)</td>
<td>0.7751</td>
<td>0.2751</td>
<td>0</td>
<td>0.0145</td>
<td>57.6/0.43</td>
</tr>
</tbody>
</table>

Results for SrNbO2N and SrTaO2N (given in italics where different) follow 2 × 2 × 2 rotational superstructures at room temperature are in monoclinic space group P12/m; but the refined cell parameters and atom positions were constrained by tetragonal I4/mcm symmetry. The anion labels show how the I4/mcm anion sites (Y) are related to those in the model (X sites; see Fig. 2a). For SrNbO2N occupancies at the three anion sites were refined independently, subject to the overall composition SrNbO2N. This was not possible for the SrTaO2N refinement and the two Y2 site occupancies were constrained as equal and subject to the stoichiometry SrTaO1.95N0.05. This refinement is equivalent to an I4/mcm fit. Lattice parameters and agreement factors, SrNbO2N: a = b = 5.7077(2) Å, c = 8.1026(3) Å, γ = 90°, χ² = 3.78, R_m = 5.22%, R_w = 3.78%; SrTaO2N: a = b = 5.7063(2) Å, c = 8.0877(4) Å, γ = 90°, χ² = 2.64, R_m = 5.00%, R_w = 4.16%.

Figure 3 | Electron diffraction images of SrMO2N crystallites. a,b. The (100) and (010) zones are shown for M = Nb (a) and M = Ta (b). The presence of weak (0k1) and (0h1) (k or h = odd) reflections (diagonal arrows) shows that the c-glide symmetry expected for the I4/mcm model of rotational order is broken by anion order.
P4/mmm (pseudocubic Pn3m) structures to be refined freely, but this was not possible for the expected room-temperature I112/m models, which have I4/mcm pseudosymmetry. Further improvements may be possible using higher resolution powder diffraction data, but the O/N disorder over the two X2 sites resulted in an intrinsic strain broadening of diffraction peaks, which might limit the achievable resolution.

**Structural principles**

The neutron diffraction results show that a robust, partial anion order is present in the SrMO3N (M = Nb, Ta) perovskites over a wide temperature range, with oxide anions ordered on one axis of the pseudocubic cell with a 50/50 O/N mixture present on the other two. This distribution is difficult to rationalize from electrostatic repulsions between O²⁻ and N³⁻, but is consistent with a well-defined, short-range order driven by covalent effects, as described below.

Two strongly bonded ligands in octahedral complexes of high valence {\(d^8\)} transition-metal ions invariably adopt a cis-(90°) configuration to maximize \(M(d_{\text{p}})X(p_{\text{a}})\) covalency, such as in \(\text{Mo}(NR)_2\) (R = alkyl or aryl group) or \(\text{MoO}_2\) complexes\(^{11,12}\). Hence, covalency favours the formation of cis-\(\text{MN}_2\)O₄ octahedra over the trans-(180°) arrangement in SrMO₃N perovskites, as the nitride is bonded more strongly to the M cations than is the oxide. This is supported by electronic structure calculations for ATaO₂N perovskites, which showed that cis-ordered structures have lower energies\(^{13,14}\), and by a pair-distribution function analysis of the total neutron scattering from BaTaO₂N, which found cis-coordination to be more likely than trans-coordination\(^5\).

The combination of the cis-coordination of each M cation by two nitrides and the linear coordination of each nitride by two M cations results in the formation of zigzag –M–N– chains within the SrMO₃N perovskites, as represented in Fig. 4. In an ideal, fully ordered structure, such as in Fig. 4a, the chains have a regular arrangement that gives rise to an anion-ordered superstructure in the a–b plane. However, zigzag –M–N– chains, like those of organic polymers, are very susceptible to disorder as there are two choices for the 90° turn at each M atom. This produces disordered chains and rings within the planes (Fig. 4b) and results in the average anion distribution observed in the neutron experiments, with an exact average 50/50 O/N composition at the a–b plane (X2 anion sites because of the two cis-nitrides at each M site. On heating (for example,SrTaO₂N to 750 °C), the ~10% occupancy of the c-axis X1 site by the nitride corresponds to the propagation of chains or rings between adjacent planes, as shown in Fig. 4c, which could lead to complete randomization of the chains in all three dimensions at higher temperatures (Fig. 4d). Hence, even a true cubic AMO₃N perovskite with an average 67/33 O/N distribution at each site is expected to have well-defined local order with cis-\(\text{MN}_2\)O₄ octahedra at each site. Cubic superstructures of three-dimensionally ordered –M–N– chains are also possible, although these may be difficult to realize.

The two-dimensional (Fig. 4b) and three-dimensional (Fig. 4d) disordered –M–N– chains in AMO₃N perovskites provide well-constrained physical realizations of the self-avoiding walk (SAW) model in statistical mechanics\(^5\). The chain structures in AMO₃N correspond to a random journey on a square or cubic lattice with the constraints of visiting each point once and making a 90° turn at each point. SAW models were used extensively to describe the physical chemistry of linear polymers\(^{17}\), and they should be applicable directly to the statistics of the –M–N– chains in AMO₃N perovskites. The anion orders can also be described by applying Pauling’s ice rules for the local arrangements of protons in ice or magnetic moments in spin ices\(^{18}\) to square or cubic lattices, in which M–N or M–O bonds, respectively, represent short or long O–H bonds or inward- or outward-pointing moments, but with the additional constraint that only cis-N–M–N connections are allowed. Pauling’s famous estimate for the residual entropy (S) of ice is \(S = \ln(n/4)\), where \(n = 6\) is the number of possible configurations per \(H_2O\) molecule and \(R\) is the molar gas constant. The same analysis on a square lattice with only cis-bonds has \(n = 4\) so \(S = 0\), which implies that a single long-range ordered state should form. Although this is intuitively incorrect, as the disordered configurations in Fig. 4b show, it demonstrates that the local chain structures are highly constrained despite the lack of long-range crystallographic order.

The above principle of local anion order driven by different M–N bond strengths predicts the local structure across the range of AMO₃−ₙNₙ perovskites. The preference for the more strongly bonded nitride ligands to be mutually cis results in a symmetry between nitride order in AMO₃−ₙNₙ and oxide order in the corresponding AMO_{N_{1-x}} composition. For example, greater M–N covalency favours the cis-\(\text{MN}_2\)O₄ arrangement in AMO₃N, described above, and also the cis-\(\text{MN}_2\)O₄ octahedral configuration for AMO₃N. This is verified by coordination complexes such as \(\text{MoO}_2\)F₂(thf)₂ (thf = tetrahydrofuran; ref. 19) and \(\text{Mo(NBu}_2\)Cl₄(py)₂ (py = pyridine; ref. 20) in which the two most strongly bonded anions (oxide or t-butylimido) are cis, as are the

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**Figure 4 | Illustrations of cis-(MX)ₙ (X = N,O) chain formations that arise from anion order in oxynitride perovskites.**

**a,b** An ideal two-dimensional order of chains (a), but disorder leads to the statistical anion distribution observed in the pseudocubic phase of SrNbO₄N at 300 °C (b). **c,d** At higher temperatures the partial occupation of the X1 site by the minority anion (for example, 10% nitride in SrTaO₂N at 750 °C) corresponds to the chains jumping between successive planes (c), and complete randomization results in average cubic symmetry with chains in all directions (d). **e** The local coordinations around M cations and the degree of polymerization of M–X–M units for the range of AMO₃Nₙ perovskites. In **a–d** heavy lines correspond to M–N–M units in AMO₃Nₙ types or to M–O–M units in AMO_{N_{1-x}} types.
two most weakly bonded ligands thf or py. Hence, the representations of –M–N– chains in AMO₃Nₓ in Fig. 4 are equally applicable to –M–O– chains in AMONₓ. This is corroborated by our observation of weak electron diffraction peaks that violate the Ih/mcm c-glide symmetry for the rotationally ordered phase of EuWON₂ (see Supplementary Information), as for SrMO₃Nₓ in Fig. 3. In addition, a recent low-temperature powder neutron diffraction study of LnBO₃Nₓ, which has orthorhombic Pbnnn symmetry, gave O/N occupancies at the Y₁ and Y₂-type sites of 0.44(3)/0.56 and 0.28(2)/0.72, respectively (see the SrMO₃Nₓ results in Table 2)²¹, in excellent agreement with the predictions of our model. The observation that the disordered 50/50 O/N site occupies the Y₁ position, which has the least displaceable order, in the superstructures of both SrMO₃Nₓ and LnBO₃Nₓ shows that the coupling between anion and rotational or tilt orders is entropy-driven.

The AMO₃₃-Nₓ structures are described by the formation of M–N–M monomers within a perovskite oxide matrix as x increases from 0 to 0.5. These are connected into cis-oligomers and then infinite chains or rings at x = 1 and with cis-crosslinking for 1 < x < 1.5 (Fig. 4e). This is mirrored by the creation of M–O–M monomers within a perovskite nitride matrix and their polymerization as x decreases from 3 to 1.5. At x = 1.5, facial (fac) MNO₃ octahedra in which the three nitrides or oxides are mutually cis are formed, by analogy with the fac-configuration observed in isolated [MoO₃F₃]₃⁻ complexes²². The fac-MNO₃ octahedra produce interpenetrating –M–N– and –M–O– networks of cis-crosslinked cis-chains in AMO₃₃Nₓ perovskites.

Discussion

Although cation order–disorder phenomena in perovskites and other extended inorganic structures have been studied extensively, anion-order studies are much fewer, in particular for isoelectronic species such as oxide and nitride. Our results reveal a spontaneous, partial long-range order in SrMO₃Nₓ (M = Nb, Ta) consistent with a robust, local anion order within MNO₃ octahedra. The key factor is the difference in M–N and M–O covalent bond strengths that results in a strong tendency for the cis-coordination of nitrides. The resulting –M–N– chains are intrinsically prone to disorder through the availability of several choices for the 90° turn at each M atom. Anion mobility in oxynitrides requires high temperatures, so carefull annealing will be needed to attempt to prepare fully ordered structures such as those in Fig. 4a.

SrNbO₃Nₓ and SrTaO₃Nₓ are representative transition-metal oxynitride perovskites and so the same structural principles are expected to apply to other AMO₃₃-Nₓ phases, as shown in Fig. 4e, and to other extended oxynitride or oxyfluoride structures. For example, the perovskite-like layers of the K₅NiF₃-type oxynitrides SrNbO₃Nₓ (ref. 23), SrTaO₃Nₓ (ref. 24) and Ba₂TaO₃Nₓ (ref. 9) show 50/50 O/N anion occupancies that are likely to arise from disordered cis-chains, like those in the SrNbO₃Nₓ and SrTaO₃Nₓ analogues. A combination of average and local structural probes is needed to explore the wealth of expected structures, which are also amenable to modelling using statistical models such as SAW or Pauling ice rules. The M–O and M–N distances appear to be very similar because nitride has a slightly larger ionic radius than oxide, but this is compensated by a greater shortening associated with the more strongly covalent bonds to the transition metal. Hence, the metric distortions that arise from anion order are very small and highly resolved neutron diffraction data are needed to exploit the good O/N scattering contrast.

Anion order in oxynitrides is expected to have a strong influence on physical properties²⁸, especially when these are sensitive to local distortions. All the intermediate cation coordinations in AMO₃₃-Nₓ perovskites for 0 < x < 3 (Fig. 4e) lack inversion symmetry, so off-centre M cation displacements and local dipoles result at each octahedron. Hence, the bulk materials are expected to have high dielectric constants, as reported for BaTaO₃Nₓ (ref. 4). Simple ferroelectric orders, such as that in BaTiO₃, are less probable in the cubic oxynitride perovskites, as the spontaneous alteration of strong and weak bonds to equivalent anions in the former material (schematically O–O–O–O–Ti–O) is likely to be suppressed by the formation of strong bonds to nitride and weak bonds to oxide in the latter (O–O–N–O–M–O–O), which tends to oppose local dipoles. However, the coupling of anion order to rotational or tilt order of octahedra, as we observed for SrNbO₃Nₓ and SrTaO₃Nₓ, may result in structural arrangements that possess a net dipole. The absence of local inversion symmetry around the M cations (and A cations given the disorder of surrounding anion chains) may also increase significantly the intensities of optical transitions in pigments and luminescent oxynitride materials.

In conclusion, the structures of SrNbO₃Nₓ and SrTaO₃Nₓ evidence a well-defined local anion order with disordered cis –M–N– chains confined to planes within the three-dimensional perovskite framework. The anion order controls the axis around which the octahedra rotate to form a superstructure at room temperature. The anion order is robust, but the resultant lattice distortions are very small so that high-resolution neutron diffraction is needed to determine such structures. A wealth of similar local structures is expected across the range of AMO₃₃-Nₓ perovskites and further work is needed to establish their influence on structural and physical properties.

Methods

Polycrystalline samples (2 g) of SrMO₃Nₓ (M = Nb, Ta) were prepared by reaction of stoichiometric amounts of SrCO₃ (99.9%, Baker) and Nb₂O₅ (99.9%, Aldrich) or Ta₂O₅ (99.99%, Aldrich) at 1,000 °C in NH₃ (99.9%, Carburos Metálicos) for several cycles of 40–50 hours, with pelletizing and intermediate regrounding. The flow rate of ammonia was 180 cm³ min⁻¹. Syntheses of EuNbO₃Nₓ, EuTaO₃Nₓ and EuWON₂ are described elsewhere²³. Nitrogen contents were determined by combustion analysis using a Carlo Erba instrument. The resulting stoichiometries for the samples investigated by neutron and electron diffraction were SrTaO₃Nₓ: SrTaO₃N₀.44(3)–0.56(4), EuNbO₃Nₓ: EuNbO₃N₀.56(2)–0.72(2) and EuWO₃Nₓ: EuWO₃N₀.28(1)–0.56(2).

Powder neutron diffraction data were collected using the Super-D2B diffractometer at the Institut Laue Langevin (ILL, Grenoble, France). Neutrons of wavelength 1.5943 Å were incident on an 8 mm vanadium can contained in a furnace. Patterns were collected at temperatures of 25–750 °C in the angular range 5 < 2θ < 160° with steps of 0.05° and collection times of 3 hours.

Electron diffraction patterns from individual microcrystallites of the above oxynitride perovskites were obtained using a JEOL 1210 transmission electron microscope operating at 120 kV equipped with a side entry 60/30° double-tilt Gatan 645 specimen holder. The samples were prepared by depositing the powders in ethanol and depositing a droplet of this suspension on a carbon-coated holey film supported on a copper grid. To observe the diffraction intensities in the (100) and (010) planes, the sample stage was rotated about the c-axis of the pseudotetragonal (H/mcm) superstructure.

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Author contributions

J.P.A. and A.F. conceived and designed the study. Samples were prepared by A.B.J., J.O. and
M.Y. J.O. recorded the electron diffraction images and J.O. and M.Y. performed the neutron
diffraction experiment. Neutron diffraction data were analysed by M.Y. with guidance from
J.P.A. and J.A.R. J.P.A. and A.F. co-wrote the manuscript with comments and contributions
from the other authors.

Additional information

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