Engineering of Ferroic Orders in Thin Films by Anionic Substitution

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Multiferroics are a unique class of materials where magnetic and ferroelectric orders coexist. The research on multiferroics contributes significantly to the fundamental understanding of the strong correlations between different material degrees of freedom and provides an energy-efficient route toward the electrical control of magnetism. While multiple ABO₃ oxide perovskites are identified as being multiferroic, their magnetoelectric coupling strength is often weak, necessitating the material search in different compounds. Here, the observation of room-temperature multiferroic orders in multi-anion SrNbO₃₋ₓNₓ thin films is reported. In these samples, the multi-anion state enables the room-temperature ferromagnetic ordering of the Nb d-electrons. Simultaneously, ferroelectric responses that originate from the structural symmetry breaking associated are found with both the off-center displacements of Nb and the geometric displacements of Sr, depending on the relative O-N arrangements within the Nb-centered octahedra. The findings not only diversify the available multiferroic material pool but also demonstrate a new multiferroism design strategy via multi-anion engineering.

1. Introduction

Ferromagnetism and ferroelectricity are essential phenomena for modern electronic technologies, ranging from advanced computing to sensing. The quest for materials where these two properties are intimately connected (i.e., multiferroic and magnetoelectric materials) has become an important effort to advance technological efficiency and fundamental understanding. [1] It is widely known that magnetic ordering often arises from the d-electrons of transition metal elements, but d-orbital occupancy has the tendency to suppress ferroelectric distortions. This dilemma reflects the competing factors in generating multiferroism in bulk materials. To try to address this dilemma, several efforts have been focused on layered perovskite-like materials such as SrTb₂Fe₂O₇, [3] Ca₃Mn₂O₇, [4] BaCuF₄, [5] and (Ca₅Sr₁₋ₓ)₁₋ₓTbₓFe₂O₇, [6] where atomic sites holding magnetically active d-levels and octahedral rotations, the latter associated to polar displacements, are combined in such a way that can give rise to multiferroic and magnetoelectric behavior.

In perovskite materials, the most widely exploited strategy to tune several ferroic orders in single-phase compounds is to combine separate functionalities from the A- and B-site cations. For example, d-electrons from transition metals that occupy the B-site can drive ferromagnetism while the A-site cations can provide the necessary driving force for structural distortions due to either an anisotropic distribution of unbound valence electrons or size-dependent space-filling effects. This approach has successfully led to the discovery of most of the single-phase multiferroic materials identified to date, such as BiFeO₃, [10] YMnO₃, [11] LuFe₂O₄, [12] and ABF₃ fluoride compounds. [13–15]

Instead of focusing on the cations, ferroelectricity and magnetism can also be stabilized by introducing a multi-anion state in perovskite oxides. To illustrate, replacing oxide ligands in the coordination octahedra by nitrogen creates an ABO₃₋ₓNₓ oxynitride. The nitrogen substitutions in this example result in two possible anion configurations: the two nitrogen ions can occupy either adjacent (cis-type) or opposite (trans-type) sites in the BO₃Nₓ octahedron as shown in Figure 1. Both arrangements break local symmetry which can drive polar distortions. For instance, the trans-type ordering may drive the off-center displacement of Ta ions that cause ferroelectricity in BaTaO₂N. [16] Furthermore, density functional theory (DFT) calculations have shown that ferroelectricity can exist in both trans- and cis-type LaTiO₂N thin films stabilized by compressive and tensile strain, respectively, having different saturation polarization and coercive fields. [17] In addition, the multiple anions introduce a mixed oxidation state which can also promote magnetic ordering. Colossal magnetoresistance has been revealed in EuWO₃₋ₓNₓ₋ₓ structures, [18] demonstrating this principle as well as the possibility for magnetoelectric coupling.
Although the cis-type coordination maximizes the overlap between the nitrogen 2p and transition metal d orbitals and it is energetically preferred over the trans-type configuration,[19–21] most bulk oxynitrides do not show long-range anion order. The coexistence of both cis- and trans-type structures provides a new dimensionality that can be used to engineer multiferroism. In this work, we have synthesized SrNbO$_3$–$x$N$_x$ thin films epitaxially, characterizing them both experimentally and theoretically. The magnetic and ferroelectric properties of the thin films studied are found to be sensitively dependent on the nitrogen content. Additionally, the epitaxial strain also plays an important role in stabilizing and enhancing the ferroelectric ordering. As such, our results demonstrate multi-anion enabled room-temperature multiferroism for the first time.

2. Results and Discussion

2.1. Epitaxial Growth of SrNbO$_3$–$x$N$_x$ Thin Films

First, 30 nm SrNbO$_3$ (SNO) films were grown on SrTiO$_3$ (STO) (001) single crystal substrates by pulsed laser deposition (PLD). The synthesis process was monitored in situ by Reflection High Energy Electron Diffraction (RHEED) with the grazing incidence of the high energy electron beam along the STO [100] direction. The temporal changes in the 01 peak intensity during the deposition are shown in Figure 2a. Clear RHEED oscillations are observed, indicating a layer-by-layer growth mode. At the early stage of growth, the oscillation signal exhibits signatures of frequency doubling. Similar phenomena have also been observed in the growth of Ge,[22] LaFeO$_3$,[23] and SrTiO$_3$,[23,24] films, which can be attributed to the inelastic scattering by periodic surface roughing. Similar to what is described by the step density model, the diffraction intensity first decreases when island formation roughens the surface and then increases when the islands coalesce.[24–27] Therefore, the presence of the frequency doubling in the first few oscillation cycles indicates that the interface between SNO and STO substrate may not be atomically sharp.

The crystalline quality of the SNO films was further studied by X-ray diffraction (XRD) (Figure 2b,c). As shown by the reciprocal space mapping (RSM) (Figure 2b), the SNO film grown is not completely commensurate to the substrate and experiences a small compressive strain. The in-plane and out-of-plane...
lattice constants of the SNO film are found to be $a = 4.00 \text{ Å}$ and $c = 4.02 \text{ Å}$. In comparison, bulk SNO has a reported pseudo-cubic lattice constant of 4.023 Å.\(^{28}\)

Nitrogen was introduced into this oxide structure by annealing the grown SNO films in NH$_3$ gas (see Experimental Section). Using this method, the nitrogen concentration in the resultant Sr$_{3-x}$Nb$_x$O$_{3}$ (SNON) films can be tuned by controlling the sample temperature, NH$_3$ flux, and annealing time. Figure 2c,d shows the 0–2θ XRD scans and the rocking curves acquired from three samples annealed with different NH$_3$ fluxes (SNON #1, SNON #2, and SNON #3). Among them, SNON #1 corresponds to the most flux, and SNON #3 corresponds to the least. Each of the annealed SNON samples exhibits comparable crystallinity to the unannealed SNO film.

The nitrogen concentration in the annealed films was quantified by X-ray photoemission spectroscopy (XPS) measurements. As shown in Figure 3a, annealing the samples in NH$_3$ gas significantly affects the XPS characteristics associated with the anions. After annealing, a nitrogen 1s peak emerges near 395 eV, and the oxygen 1s peak near 530 eV splits into two. While the first feature is directly linked to the incorporation of nitrogen, the second feature is linked to it implicitly. Due to the different valences between O$^{2-}$ and N$^{3-}$, the introduction of N inevitably changes the effective valence of oxygen in the lattice, leading to the splitting of the O (1s) peak. XPS curves of the three annealed samples near the O (1s) and N (1s) peaks are compared in Figure 3b,c. As the NH$_3$ flux used during the annealing process increases (from SNON#3 to SNON#1), the N concentration increases, and the O concentration reduces.

2.2. Magnetic Properties

In Sr$_{3-x}$Nb$_x$O$_3$, Nb$^{4+}$ has the electronic configuration 4d$^3$, resulting in the intrinsic conductivity discussed previously in the literature.\(^{24}\) After introducing nitrogen into the structure, the Nb cation could oxidize from Nb$^{4+}$ to Nb$^{5+}$ due to the difference in the oxidation state between O$^{2-}$ and the N$^{3-}$ substitution. The introduction of an anion with a different oxidation state has a profound effect on the magnetic properties, as revealed by the vibration sampling magnetometry (VSM) measurements performed along the in-plane orientation. While pure SNO is not magnetic at room temperature, the annealed SNON samples all show clear magnetic hysteresis (see Figure 4a). Although the magnetization is enabled by the introduction of N, it weakens as the N concentration further increases. As shown in Figure 4a,b, the measured saturation magnetization decreases by around 50% as the N concentration increases from $x = 0.3$ to $x = 0.6$. Meanwhile, the coercive field becomes larger at higher N concentrations.

To unveil the source of the magnetic behavior, we built a model from first-principles simulations, starting from the ground state crystal phase of Sr$_{3}$Nb$_{1}$O$_{3}$ ($x = 0$ in Sr$_{3-x}$Nb$_x$O$_3$) that belongs to the orthorhombic $Pnma$ symmetry space group\(^{29}\) with an octahedral rotation pattern denoted by $a' a'' c^*$ in Glazer’s notation.\(^{30}\) When Sr$_{3}$NbO$_3$ is exposed to in-plane strain (i.e., beyond ~2.1%), our theoretical calculations indicate that its symmetry group and octahedral rotation goes to $I4/mcm$ and $a'' a' c^*$, respectively (see Figure S1 in the Supporting Information). We also find that in Sr$_{3-x}$Nb$_x$O$_3$ ($x = 1$ in Sr$_{3-x}$Nb$_x$O$_3$), the incorporation of N suppresses the $a^*$ and $a^*$ rotations and results in a structure with the same $I4/mcm$ symmetry group and $a'' a' c^*$-rotation pattern in the absence of strain (see Figure 1a). This structural phase has been reported in the literature for temperatures $T > 300 \text{ K}$ for Sr$_{3}$Nb$_2$O$_5$.\(^{31}\) However, it is worth noticing that this space group is assigned considering indistinguishable N/O occupations in the corner octahedral sites. Given these results in our electronic structure computations, we took the Sr$_{3}$NbO$_3$ structure in the $I4/mcm$ symmetry group to be the parent structure for the N substitutions. From the parent material we replaced the corresponding number of oxygen atoms by nitrogen to realize the different N-concentrations, i.e., $x = 0, 0.25, 0.5, 0.75,$ and $1.0$ for Sr$_{3-x}$Nb$_x$O$_3$. Then for each of the structures we fully optimized the geometry to arrive at the ground state configurations for each N concentration.

To theoretically investigate the ground state magnetic properties for each value of $x$, we calculated the total energy of the A-, C-, and G-type antiferromagnetic (AFM) ordering as well as the ferromagnetic state. When $x = 0$ (corresponding to the parent material Sr$_{3}$NbO$_3$), the magnetic moment per Nb atom is about $m = 0.815 \mu_B$, and the magnetic ground state is A-type.

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**Figure 3.** Composition characterizations of Sr$_{3-x}$Nb$_x$O$_3$ films. a) XPS spectra measured on the same sample (SNON #3) before and after the NH$_3$ annealing. b,c) Oxygen 1s and nitrogen 1s XPS peaks measured on the three Sr$_{3-x}$Nb$_x$O$_3$ films.
Figure 4. Magnetic properties of SrNbO$_3$$_x$N$_x$ films. a) The magnetic hysteresis curves experimentally measured on four films with different N contents. b) In films annealed in NH$_3$, as the content of N increases, the saturation magnetization decreases and the coercive field increases. c) Theoretically obtained magnetic moment per unit cell as a function of the nitrogen x-content for the cis- and trans-type configurations.

antiferromagnetic. Experimentally, no saturation magnetization was measured in the SrNbO$_3$ thin films, which agrees with our theoretical results. As the N concentration increases in our model, the magnetic moment per formula unit, $\mu_B$ per f.u. (each formula unit hosts 5 atoms while our unit cell contains 20 atoms for the considered SrNbO$_3$$_x$N$_x$ structure) first increases, reaching a maximum when the nitrogen concentration is between $x = 0.2$ and $x = 0.4$, as shown in Figure 4c. For higher concentrations, the magnetic moment per formula unit decreases and finally vanishes at $x = 1.0$. More careful analysis of our calculations reveals that the nonmonotonic behavior of the magnetic moment corresponds to a nontrivial magnetic phase transition as a function of the nitrogen concentration. As the nitrogen content increases, the computed magnetic ground state undergoes a transition from A-type AFM state at $x = 0$ to a ferromagnetic state at $x = 0.25$. The ferromagnetic state remains for $x = 0.5$ and 0.75 and before arriving at a nonmagnetic state for $x = 1.0$, where the Nb ions have the valence state of $+4$ with 4$d^0$ configuration. The effect of the strain imposed by the substrate was also considered in our analysis. In Figure 4c, we compare the results from calculations with and without strain for the lowest energy cis-type and trans-type configurations for each concentration. The epitaxial strain clearly shifts the nitrogen concentration corresponding to the maximum magnetic moment to greater value, but the overall behavior is not altered. Consequently, both models fairly reproduce and explain the experimentally found magnetic behavior condensed in Figure 4a,b.

As it is widely known, ferromagnetism in complex oxides can arise from the double exchange interaction as a consequence of the incorporation of multiple oxidation states. Since each compound in the SrNbO$_3$$_x$N$_x$ series host a ratio of the Nb oxidation states of the two stochiometric endpoints, double exchange is a plausible mechanism for the emergent magnetism. However, the anisotropy and screening seen in the exchange parameters (see Figures S2–S6, Supporting Information) suggest an alternative or cooperative mechanism. Specifically, the exchange parameters are an order of magnitude larger along the c-axis than the parameters within the a-b plane for each structure. Likewise, the exchange parameters are sensitive to the local chemical environment as seen in the distinction between the interactions across the Nb–O–Nb and N–Nb–N bond chains, as well as in the reduced magnetization that accompanies the $a^4a^4c^0$ rotations in the $x = 0.75$ cis-type structure in contrast with the $a^4a^4c^-$ trans-type structure with the same stoichiometry (see Figures S5 and S6, Supporting Information). Qualitatively, these factors suggest that the magnetism may be influenced by the orbital overlap in addition to the partial orbital filling.

Performing an analysis with the LOBSTER$^{[12–34]}$ code, we obtained some insights into the nature of the orbital overlap between Nb–O and Nb–N pairs (see Figure S10, Supporting Information). The Crystal Orbital Hamilton Population (COHP)$^{[33]}$ analysis allows the visualization of the accumulation (positive values) or depletion (negative values) of the charge density between the pairs of atoms compared with nonbonding atomic orbitals. The COHP reveals that the incorporation of N is accompanied by a significant reduction in the charge density between the Nb 4d orbitals and the O 2p orbitals in each of the magnetic cases. The depletion indicates that the Fermi level states are antibonding. Fermi level antibonding is an instability that is generally alleviated through structural distortions or through charge redistribution that results in an itinerant magnetic moment.$^{[35]}$ In each of the ferromagnetic SrNbO$_3$$_x$N$_x$ structures, the antibonding is reduced by an energy penalty placed on one of the spin channels, driving exchange splitting. Itinerant magnetism is further supported by correlating the size of the exchange splitting with the spontaneous magnetization. As the nitrogen content increases, the fermi level lowers in energy. Consequently, the antibonding at the fermi level reduces as the fermi level moves toward the tail of the Nb 4d energy levels. Since there is less antibonding intrinsically, the exchange splitting required reduces with increasing nitrogen content, tracing the evolution of the magnetization. Additionally, the $a^4a^4c^0$ rotations in the $x = 0.75$, cis-type structure appear to mitigate the antibonding in competition with the itinerant mechanism, reducing the magnetization compared with the trans-type structure with the same nitrogen content. Moving forward, X-ray magnetic dichroism can be employed in investigations aiming to explore the magnetic behavior of these oxynitrides in detail and to define the possible existence of a magnetic structure in SrNbO$_3$ thin films unambiguously.

2.3. Ferroelectric Properties

Pure SNO is centrosymmetric. Substituting oxygen with nitrogen breaks the local symmetry and can lead to the onset of spontaneous electric polarization. Figure 5a shows the piezoresponse force microscopy (PFM) images measured from the three SNON samples. Before imaging, a standard box-in-box
biased contact scan procedure was carried out. Here, a 2 μm square is first scanned with a probe bias of 10 V. Then the smaller 1 μm square region at the center is scanned for a second time with a probe bias of −10 V. Persistent ferroelectric switching features are observed in SNON #3, where the regions scanned with opposite biases exhibit maximized PFM magnitudes and a relative phase shift of π, consistent with the formation of opposite residual polarizations. In comparison, such effects are much weaker in SNON #2 and completely vanish in SNON #1. Similar to the magnetic ordering, the ferroelectricity in these samples requires the introduction of nitrogen, but is strongest when the N concentration is small.

According to our simulations, the polar behavior exists in both cis- and trans-type configurations. Moreover, it is worth noticing that it is advantageous to work with the SrNbO$_3$-$x$N$_x$ crystals compared to other oxynitrides, because the energy difference between the cis- and trans-type configurations is found to be approximately $\Delta E = 65 – 170$ meV per f.u., depending on the nitrogen content. This energy difference is remarkably smaller than the values found in other oxynitrides such as BaTaO$_2$N ($\Delta E \approx 300$ meV per f.u.)\cite{16,19} and SrTaO$_2$N ($\Delta E \approx 200$ meV per f.u.).\cite{37} Hence, the smaller energy difference would allow the experimental realization of coexisting cis and trans domains SrNbO$_3$-$x$N$_x$ in thin films, where the strain from the substrate may help stabilize the energetically unfavored trans-type structures.

Based on the analysis of the phonon-dispersion curves, the existence of the polar Pmc2$_1$ symmetry group (No. 26) was identified in the cis-type anionic configuration and explained in terms of the unstable $\Gamma_3^-$ phonon mode at its Pnma high-symmetry phase.\cite{38} In the ferroelectric phase, the octahedral rotations couple to the Sr displacements driving the ferroelectric distortion in this particular anionic ordering, as expected from the associated displacement of the $\Gamma_3^-$ polar mode, see Figure 5b,c. We find that strain applied both out-of-plane (i.e., the N-Nb-N zig-zag chains are aligned in the plane) as well as in-plane (i.e., the zig-zag chains are aligned out of plane) enhances the polar distortion considerably, denoted by the energy profiles shown in Figure 5b. In the out of plane case, the symmetry group remains Pmc2$_1$ whereas for the in-plane strain case, the symmetry is lowered to the Pm (No. 6) group. When comparing the unstrained and strained SrNbO$_2$N, we observed a gain in energy of 238 and 83 meV per f.u for the out-of plane and in-plane strain, respectively, as observed from Figure 5b.

Regarding the trans-type configuration of SrNbO$_2$N, the vibrational landscape also reveals the mechanism for the origin of the polar ground state. As shown in Figure 5d, a $\Gamma_3^-$

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**Figure 5.** Ferroelectric response in SrNbO$_3$-$x$N$_x$. a) Piezo response force microscopy, PFM, images measured on the three annealed samples. Before the PFM imaging, an identical box-in-box biased AFM writing sequence is applied to all three samples, which is shown in the topography images using red and blue lines. Persistent polarization switching effects are only observed in the sample with the lowest N concentration (SNON #3). Switchable polar distortion and the computed double-well energy curves obtained by freezing or condensing (i.e., introduction the atomic displacements associated with a particular phonon vibration) the $\Gamma_3^-$ mode for the b,c) cis-type, and d,e) at the trans-type structures. For the cis-type structure, the transition goes from the Pnma (No. 51) to the Pmc2$_1$ (No. 26) polar space group. For the trans-type anionic ordering, the distortion leads the structure from the I4/mcm (No. 140) to the I4m (No. 108). In (b) and (d) the total energy per formula unit is computed as a function of the gradual introduction of the atomic displacements, associated to the $\Gamma_3^-$ mode, and it is related to the high-symmetry total energy. Here, the relaxed, out-of-plane, and in-plane strained data is denoted by filled squares, empty squares and triangles, respectively.
phonon, which is also unstable in its high-symmetry structure, condenses into the $I4/mcm$ space group (No. 140), leading the structure to the polar $I4cm$ (No. 108) space group. In the trans-type anionic ordering, this $I_1$ mode involves the off-centering of the Nb sites inside the NbO$_4$N$_2$ octahedra. Here, the octahedral rotations and the polarization coexist, as shown in Figure 5e. Interestingly, the energy-well curves computed in each case (see Figure 5d,e) demonstrate an energy increase of 37 and 68 meV per f.u. as a result of the condensed mode for the unstrained and out-of-plane strained films, respectively. These energies indicate a tangible spontaneous polarization in the oxynitride compound, where the strain enhances the polar distortion. When the strain from STO is applied in-plane, the symmetry reduces from $I4cm$ (No. 108) to $Fmmm$ (No. 69) where the polar Nb distortions are not allowed as suggested by the single-energy well presented in Figure 5d.

Finally, we studied the effect of electron doping on the polar distortions of the cis- and trans-type anionic orders in the presence of out-of-plane epitaxial strain in order to explore regions with equivalent low nitrogen concentrations. Since the O:N ratio changes the Nb oxidation state from +4 to +5, the electronic reconstruction results in partial charge occupation of the Nb-4d level. As such, for nitrogen contents close to $x = 1$, the Nb exhibits a 4$d^0$ configuration, whereas, for $x = 0$ a 4$d^1$ is agreed in agreement with our results. Thus, electron doping of 0.00, 0.25, 0.50, 0.75, and 1.00 e per f.u. corresponds to nitrogen contents of $x = 1.00$, 0.75, 0.50, 0.25, and 0.00, respectively. This analysis helps us to understand and explain the existence of the polar distortion and magnetic response close to $x = 0.30$. In Figure 6, we show that the cis-type ordering is enhanced, despite expecting the polar distortion to vanish due to the electron doping in SrNbO$_3$-$N_x$. In contrast, the polar distortion is destroyed in the trans-type ordering in agreement with the mechanism that drives the Nb ions off-center in this anionic configuration. The survival of the polar distortion has also been observed in BaTiO$_3$ and Bi$_2$WO$_6$. Moreover, the experimental feasibility of the ferroelectric switching has also been demonstrated for polar metals. These results suggest that polar distortions and magnetism can coexist in this oxynitride. Therefore, based on our calculations and analysis, we attribute the measured PFM response to the coexistence of both, cis- and trans-type configurations with ferroelectricity.

3. Conclusions

In conclusion, our theoretical and experimental analyses show the multiferroic nature of the multi-anion SrNbO$_3$-$N_x$ thin films. Since the energy difference between cis- and trans-type structures is small, both configurations can coexist in our samples. The measured ferromagnetism is ascribed to both the cis- and trans-type configurations, and the ferroelectric responses come from the displacement of the Nb cations from the centers of the octahedra in the trans-type and the coupling between the octahedral rotations and Sr-displacements in the cis-type configuration. These results highlight that through multi-anion configurations and epitaxial strain, a delicate balance, between the partial transition-metal d state occupation, responsible for the magnetic response, and the cation site distortions, responsible for ferroelectric polarization, can be tuned to design multiferroism.

4. Experimental Section

Sample Preparation: Prior to the growth experiments, as-received SrTiO$_3$ (001) substrates were first exposed to UV ozone illumination for 20 min then cleaned with acetone and methanol and rinsed with DI water. After cleaning, the substrates were etched by buffered-HF (BHF) for 60 s to make the surface TiO$_2$-terminated. After chemical treatment, STO substrates were annealed in a tube furnace at 1050°C for 5 h with the oxygen flow rate of 500 sccm. The regular terraces with the width of ~200 nm (the corresponding miscut angle is about 0.11°) were found by atomic force microscopy after thermal annealing. The deposition of SrNbO$_3$ (SNO) thin films were carried out by PLD at 730°C with the oxygen background pressure of 1E-5 Torr. The SrNbO$_3$-$N_x$ structures were created in a dedicated NH$_3$ annealing station, where the annealing temperature, the NH$_3$ flow rate and time can all be programmed. In the work, the annealing temperature and time was kept at 950°C and 3 h, respectively. By varying the NH$_3$ flow rate from 29 to 100 sccm, the nitrogen content was tuned in SrNbO$_3$-$N_x$ from $x = 0.6$ to $x = 0.6$.

Magnetism and Piezoelectricity Measurements: The ferromagnetic response was measured by Physical Properties Measurement System (PPMS) using the VSM insert. The piezo force microscopy was performed by Asylum MFP-3D system at ambient conditions.

DFT Calculations: First-principles calculations were performed within the density-functional theory, DFT, as implemented in the VASP code (version vasp5.3.3). The projected augmented wave (PAW) method was used to represent the valence and core electrons. The electronic configurations considered as valence electrons were: Sr (4s$^2$4p$^6$5s$^2$, version 07Sep2000), Nb (4s$^2$4p$^6$5s$^1$, version 08Apr2002), N (2s$^2$2p$^3$, version 08Apr2002), and O (2s$^2$2p$^4$, version 08Apr2002). The exchange-correlation was represented within the generalized gradient approximation (GGA) with the PBEsol approximation. The magnetic character was considered, and the d-electrons were corrected by means of the DFT+U within the Liechtenstein formalism with a U value of 4.0 eV. The periodic solution of these crystalline structures was
represented by using Bloch states with a Γ-centered k-point mesh of \(8 \times 8 \times 6\) and 600 eV of energy cut-off, which has been tested already to give forces convergence to less than 0.001 eV Å\(^{-1}\). With the aim to treat different O and N concentrations the site occupation disorder were computed based on the DFPT approach as implemented in the Abinit\(^{57,58}\) using the output files generated by TB2J. Finally, the electron was calculated from spin dynamics simulations as implemented in undoped case.\(^{59}\)

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Conflict of Interest

The authors declare no conflict of interest.

Data Availability Statement

The data that support the findings of this study are available from the corresponding author upon reasonable request.

Keywords

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