

Electronic Supplementary Information

for

Bulk and surface properties of the Ruddlesden-Popper oxynitride $\text{Sr}_2\text{TaO}_3\text{N}$

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S1.Bulk

In the case of the 14-atom unit cell, all possible nitrogen sites (apical and/or equatorial) were considered respecting the $\text{Sr}_2\text{TaO}_3\text{N}$ stoichiometry. Relaxing all configurations showed that - in agreement with experiment - the energetically favoured configuration is the one having nitrogen atoms in equatorial sites as presented in the main text. The relative energies of the different configurations are shown in Table S1.

Table S1 Relative energies of the 14-atom unit cell with different arrangements of the two N ions.

N sites in octahedra	Relative energy (eV)
equatorial	0.00
apical (+z)	0.36
apical (-z)	0.36
apical and equatorial	0.23

In Fig. S1 we present the projected density of states (PDOS) for the supercell (56 atoms) with a *cis* nitrogen arrangement with and without octahedral rotations. Compared to the PDOS without octahedral rotations (Fig. S1a), the one with rotations (Fig. S1b) reveals a narrower valence band (6 eV vs. 7 eV). This is the result of the decreased overlap between Ta 5d and O/N 2p states with increasing octahedral rotation angles. The decreased overlap manifests in a reduction of both the valence and conduction band widths, which, under the assumption of rigid band centres, results in an increased band gap as observed in Fig. S1b).

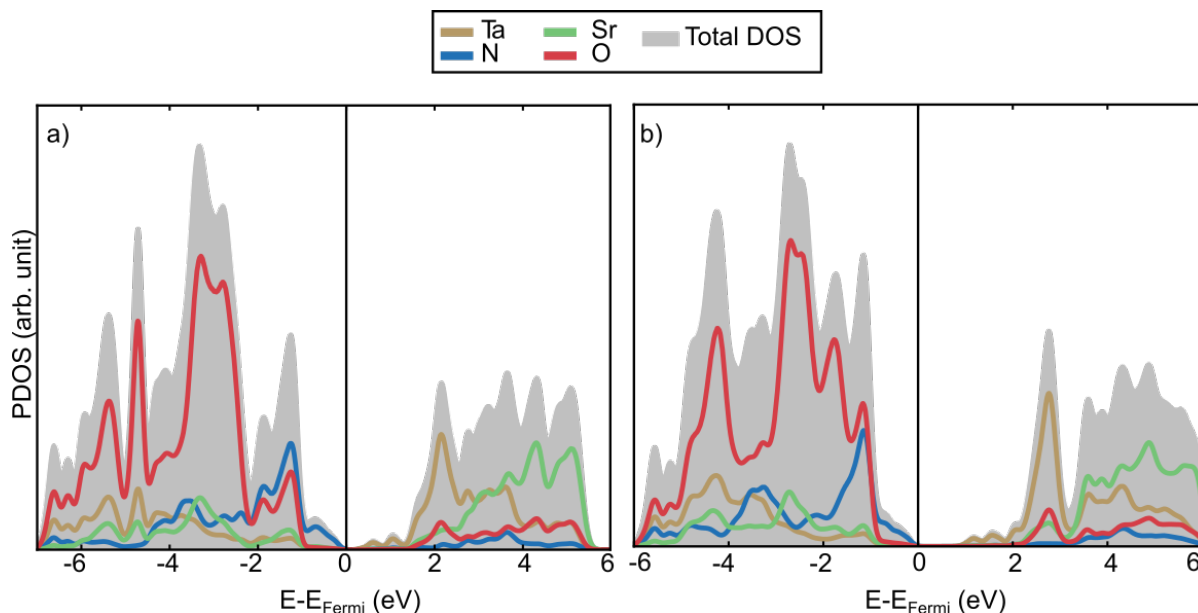


Figure S1 Projected electronic density of the 56-atom supercell $\text{Sr}_2\text{TaO}_3\text{N}$ structure a) without and b) with octahedra rotations.

S2.Surfaces

In Figs. S2-S4 we present the layer-resolved PDOS of all the surfaces before and after relaxation. We observe that in all cases the bulk tantalum states retain the dispersive character they had in the bulk structure. Due to this dispersive character they form the bottom of the conduction band in all cases.

The SrO-terminated (001) surface is formed by cleaving in the rock-salt layer. This results in the formation of surface Sr states with lower energies than in the bulk (Fig. S2). After relaxation, the SrO-terminated surface does not show major changes in its electronic structure, reflecting the absence of major ionic relaxations.

In the case of the TaON-terminated (001) surface (Fig. S3), the bandgap is much smaller than in the bulk due to the nitrogen surface states that contribute at higher energy in the valence band after cleavage. Moreover, due to cutting of Ta-O bonds, the surface Ta states are less dispersive and located at higher energies than in the bulk. Changes in the electronic structure of the TaON-terminated (001) slab are observed after relaxation: surface nitrogen states relax to lower energies and surface tantalum states in the conduction band regain some dispersive character, while subsurface strontium states move to higher energies in the conduction band.

Cleaving perpendicular to the [100] direction results in surface and subsurface anion states with higher contributions at the top of the valence band compared to the corresponding bulk states (Fig. S4). After relaxation, the surface anion states shift to lower energies than the ones of bulk anion states. Simultaneously, surface Ta and Sr states move to higher energies than the respective states in the bulk.

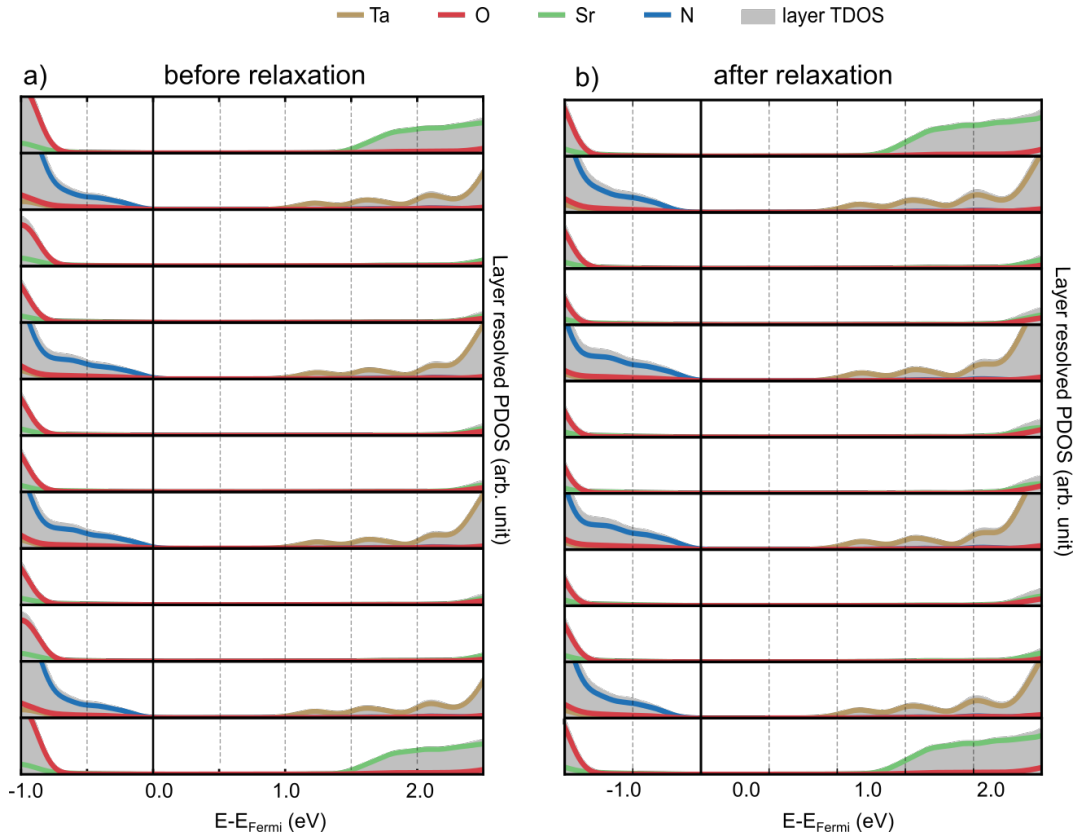


Figure S2 Projected electronic density of the SrO-terminated (001) surface a) before and b) after relaxation.

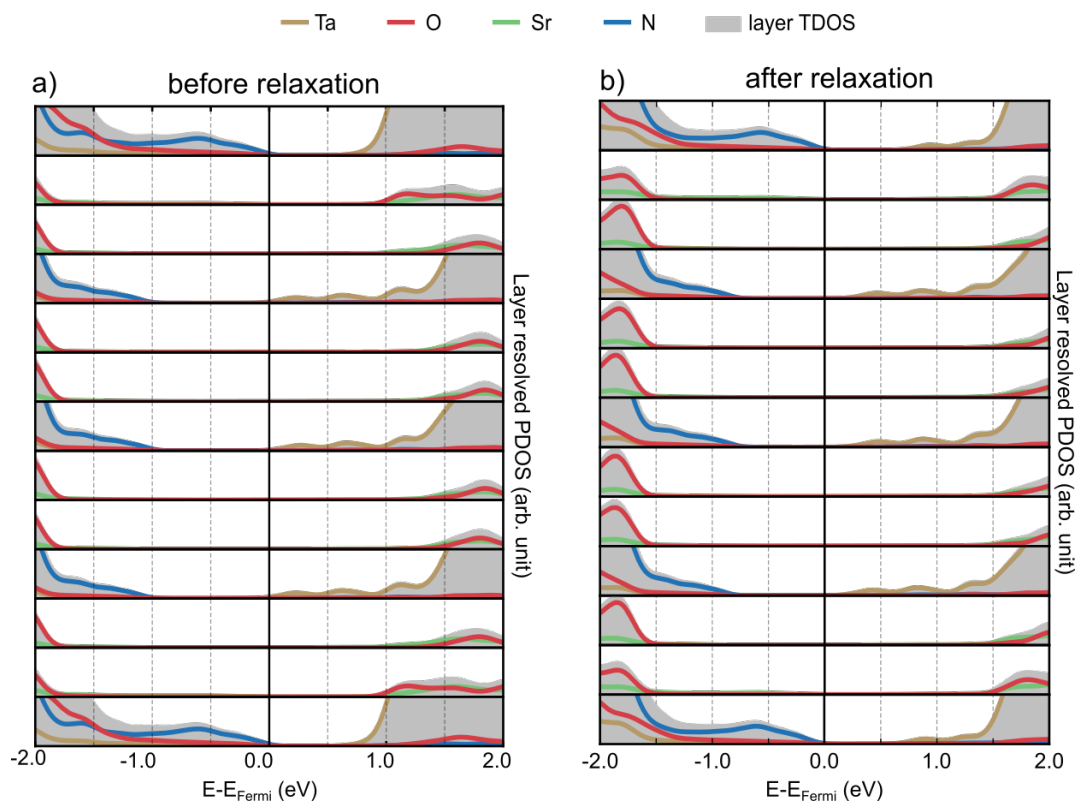


Figure S3 Projected electronic density of the TaON-terminated (001) surface a) before and b) after relaxation.

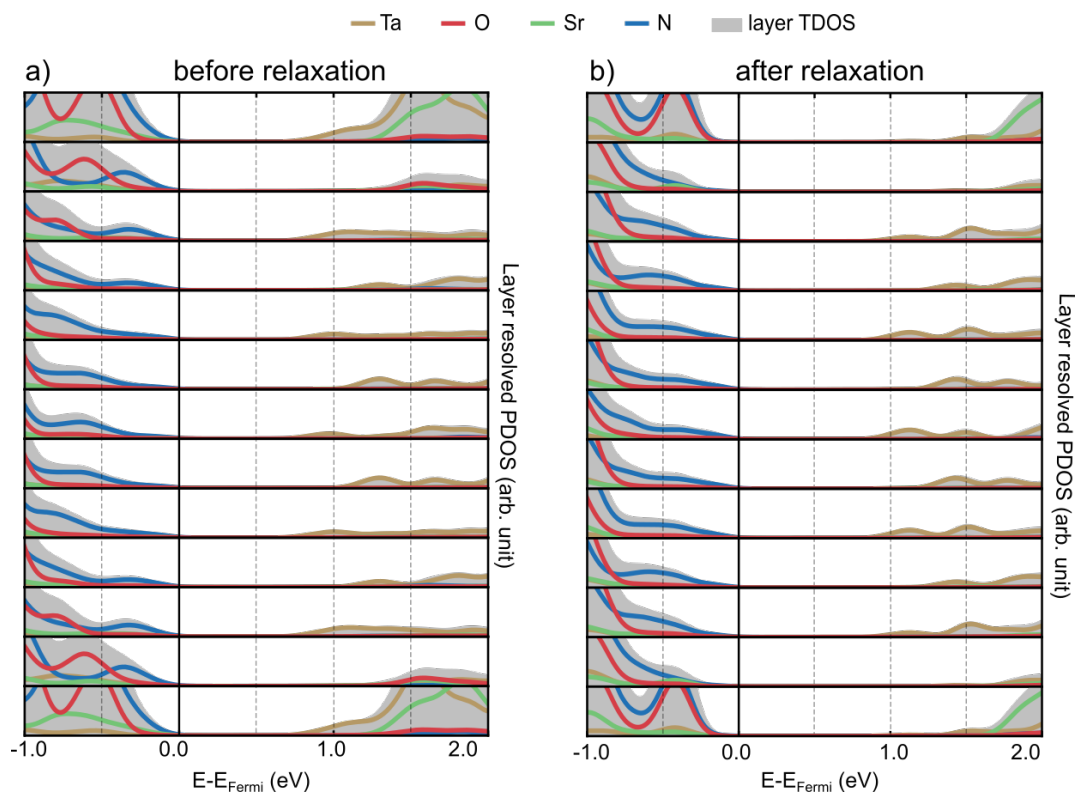


Figure S4 Projected electronic density of the (100) surface a) before and b) after relaxation.