†Electronic Supplementary Information (ESI) for

Oxygen migration and proton diffusivity in transition-metal (Mn, Fe, Co, Cu) doped Ruddlesden-Popper oxides

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Tables S1 Total energies of LNO214 and LNO 327 with different magnetic structures

Total Energy (eV)	FM	A-AFM	C-AFM	G-AFM
LNO_{214}	-410.026684	-410.026831	-410.362840	-410.362841
LNO_{327}	-681.890553	-681.894059	-681.176649	-681.609565

Table S2 Energy barriers of proton migration along the pathway PT1 for LNO (**n1**, and **n2**) without TM-doping

PT1	**R12**	**T23**	**R34**	**T45**
n1	0.0	2.19	0.0	3.53

n2	0.0	0.52	0.50	3.94

Table S3 The effective charge (*e*) of proton along the pathway PT2 for LNO (**n1**) with and without TM-doping

PT2(**n1**)	P1	P2	P3	P4	P5	P6
Mn	0.541	0.553	0.445	0.561	0.554	0.451
Fe	0.438	0.575	0.572	0.472	0.563	0.469
Co	0.551	0.598	0.528	0.528	0.589	0.427
Ni	0.478	0.446	0.449	0.449	0.486	0.448
Cu	0.625	0.554	0.552	0.547	0.601	0.445

Table S4 The effective charge (*e*) of proton along the pathway PT2 for LNO (**n2**) with and without TM-doping

PT2(**n2**)	P1	P2	P3	P4	P5	P6
Mn	0.576	0.525	0.521	0.523	0.568	0.570
Fe	0.565	0.572	0.574	0.572	0.586	0.559
Co	0.553	0.547	0.554	0.551	0.564	0.529
Ni	0.481	0.545	0.531	0.477	0.547	0.549
Cu	0.544	0.555	0.557	0.557	0.559	0.564

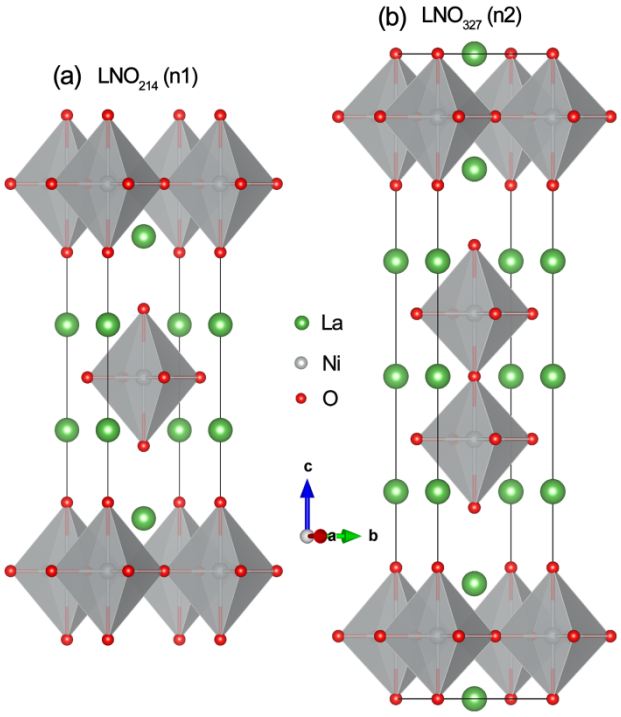

Figure S1 (a) Primitive La_2NiO_4 (LNO_{214}) with single-layered Ruddlesden-Popper (RP) phase. (b) $La_3Ni_2O_7$ (LNO_{327}) with double-layered PR phase.

The formation energy of the TM-doped LNO systems E_f is defined as:

$$E_f = E^{tot}_{doped} - E^{tot}_{LNO} - n(E_{TM} - E_{Ni})$$

where E^{tot}_{LNO} and E^{tot}_{doped} are total energy of LNO and TM-doped LNO, E_{TM} and E_{Ni} are the chemical potential of TM and Ni atoms, n is the number of substitutions of Ni with TM. The calculation results of each E_f are summarized in the Figure S2.

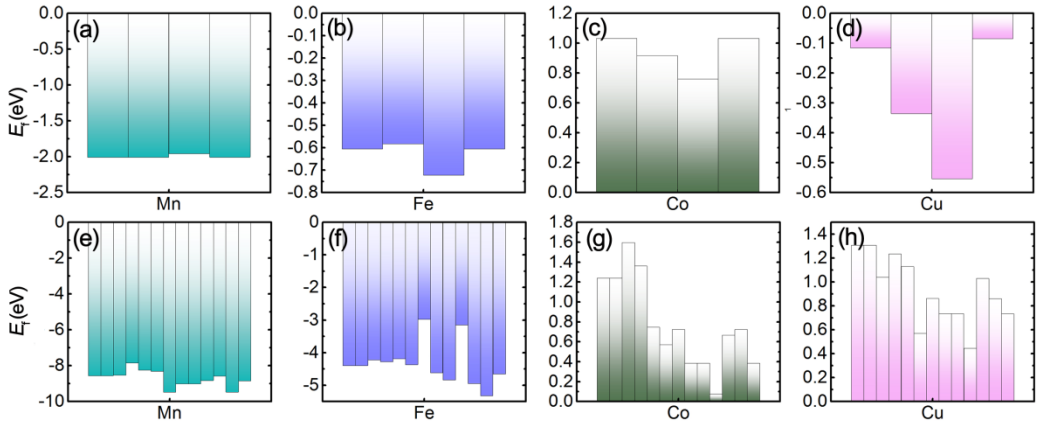

Figure S2 (a)-(d) Formation energies (E_f) for single-layer (**n1**) RP structure LNO ($La_2Ni_{1-x}(TM)_xO_4$, x = 0.25, TM = Mn, Fe, Co and Cu) with four different TM-doped constructions. (e)-(h) Formation energies (E_f) for double-layer (**n2**) RP structure LNO ($La_3Ni_{2(1-x)}(TM)_{2x}O_7$, x = 0.25, TM = Mn, Fe, Co and Cu) with thirteen different TM-doped constructions.

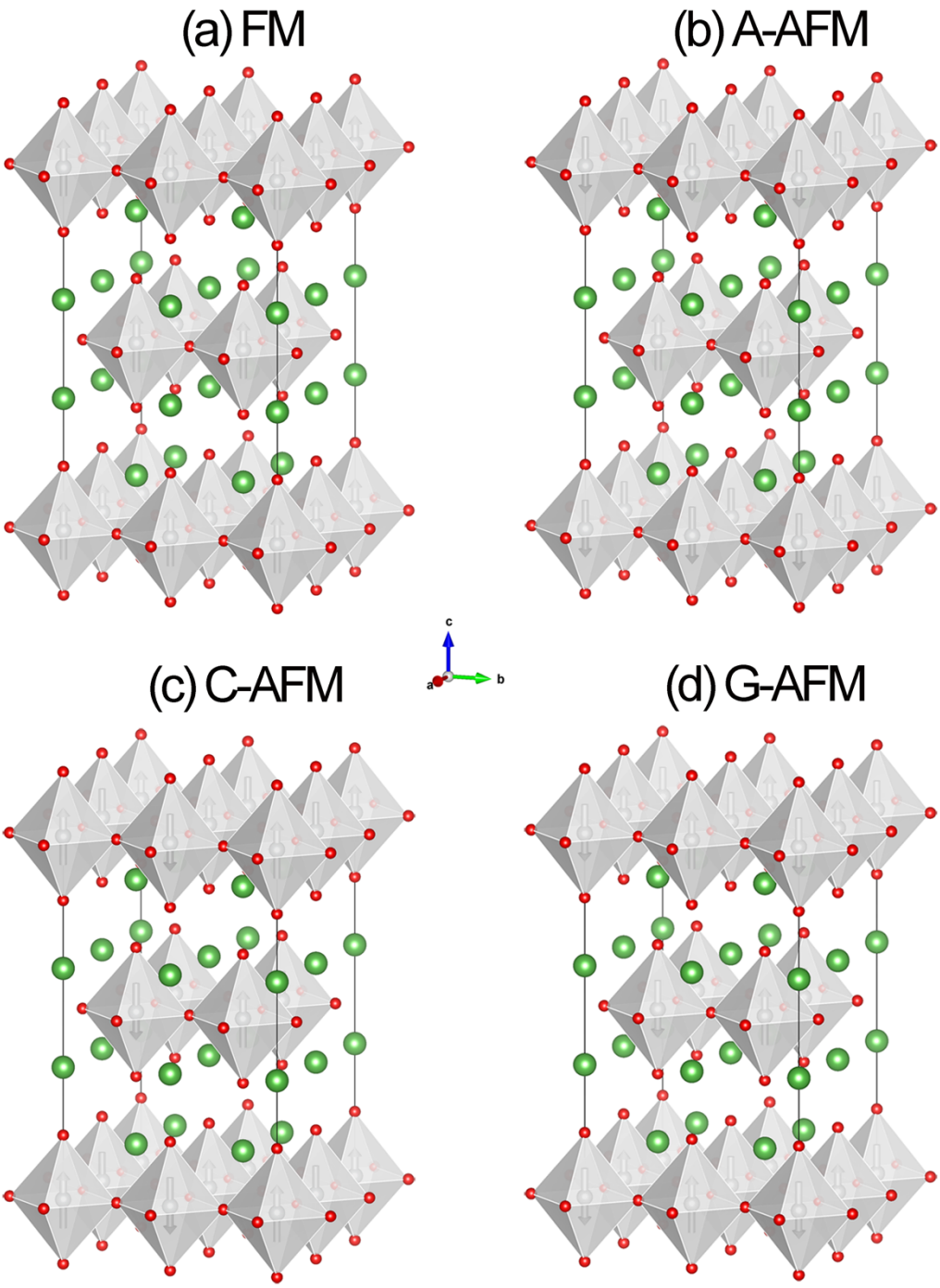

Figure S3 LNO_{214} supercells with difference magnetic structures. (a) FM, (b)A-AFM, (c) C-AFM and (d) G-AFM.

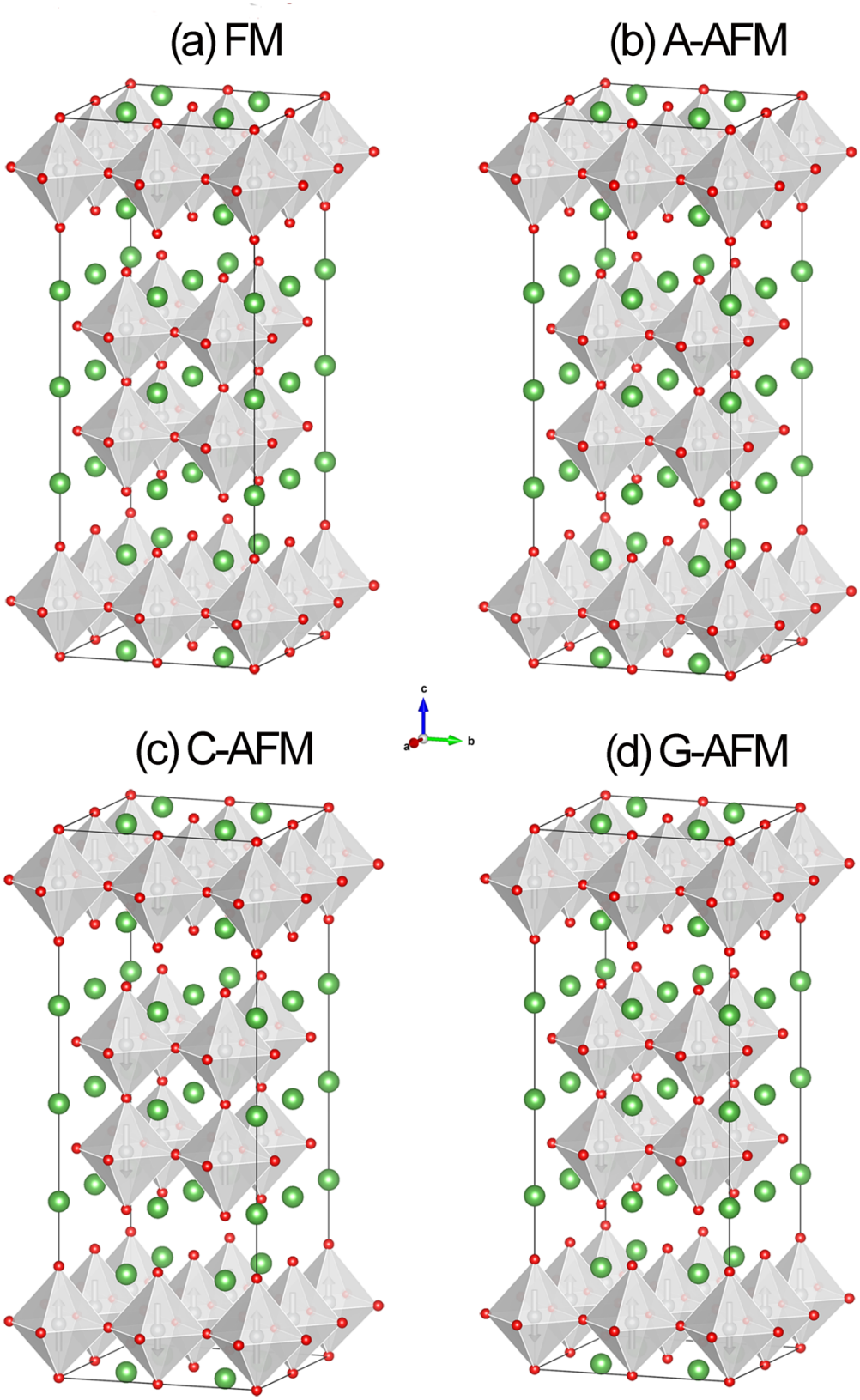

Figure S4 LNO_{327} supercells with difference magnetic structures. (a) FM, (b)A-AFM, (c) C-AFM and (d) G-AFM.

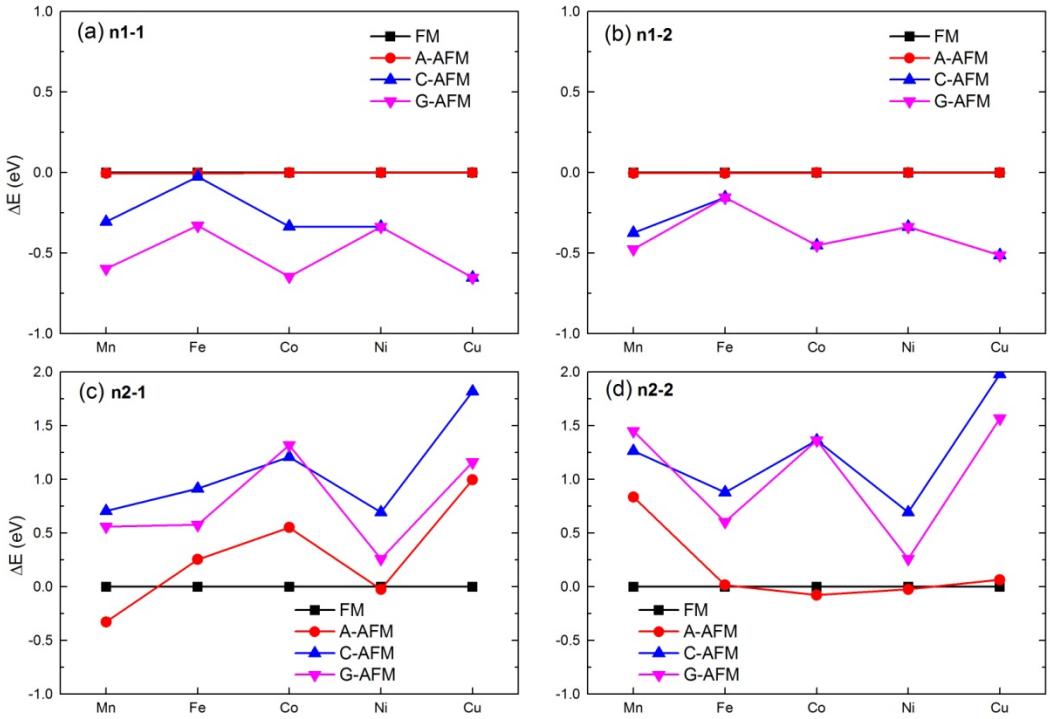

Figure S5 Relative energies TM-doping LNO with different magnetic configurations.

(a) for **n1-1**, (b) for **n1-2**, (c) for **n2-1** and (d) for **n2-2**, respectively.

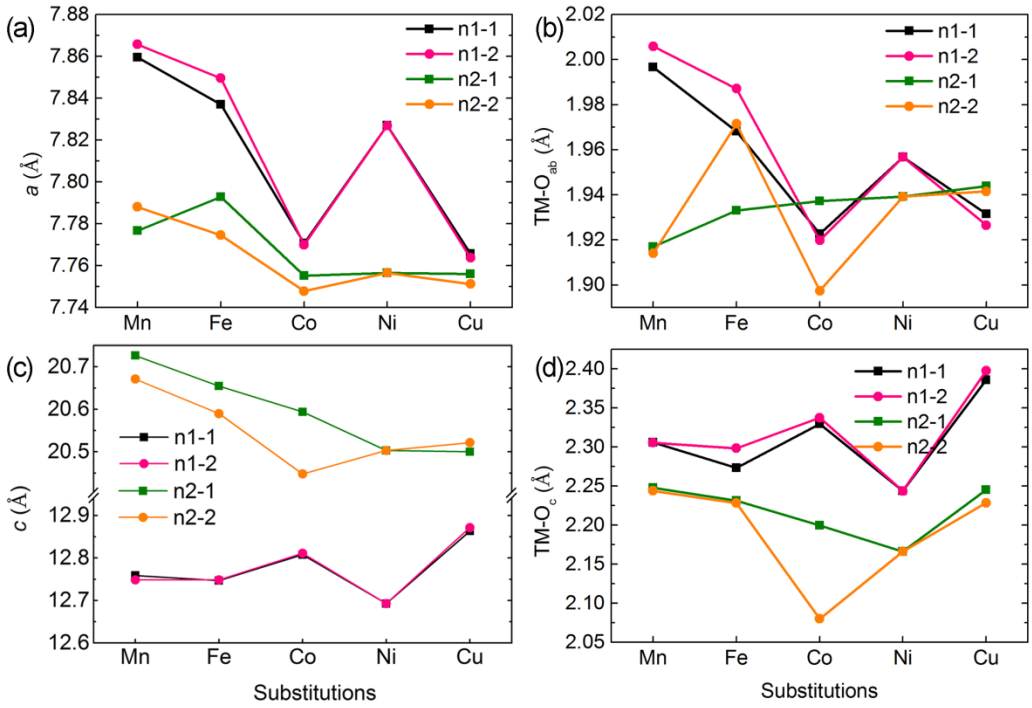

Figure S6 The structural information of the TM-doped LNO_{214}/LNO_{327}. (a) and (c) The lattice parameters *a* and *c* of each structure, (b) and (d) the variation of the TM-O_{ab} bond length along *a*-*b* plane and TM-O_c bond length along *c*-axis as function of TM-substitutions.

As we know that the tolerance factor, *t*, is a commonly used empirical measure that relates the chemical composition of a particular perovskite to its tendency to undergo a structural distortion and is defined as:

$$t = \frac{R_{\mathrm{A-O}}}{\sqrt{2}R_{\mathrm{B-O}}}$$

where $R_{\mathrm{A\text{-}O}}$ and $R_{\mathrm{B\text{-}O}}$ are the bond lengths of A-O and B-O. The calculation results are displayed as below in Fig. S7.

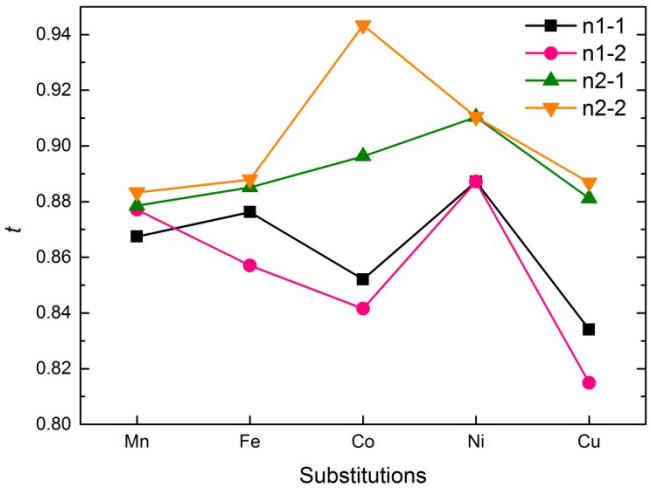

Figure S7 The tolerance factor *t* as function of TM-substitutions from Mn to Cu.

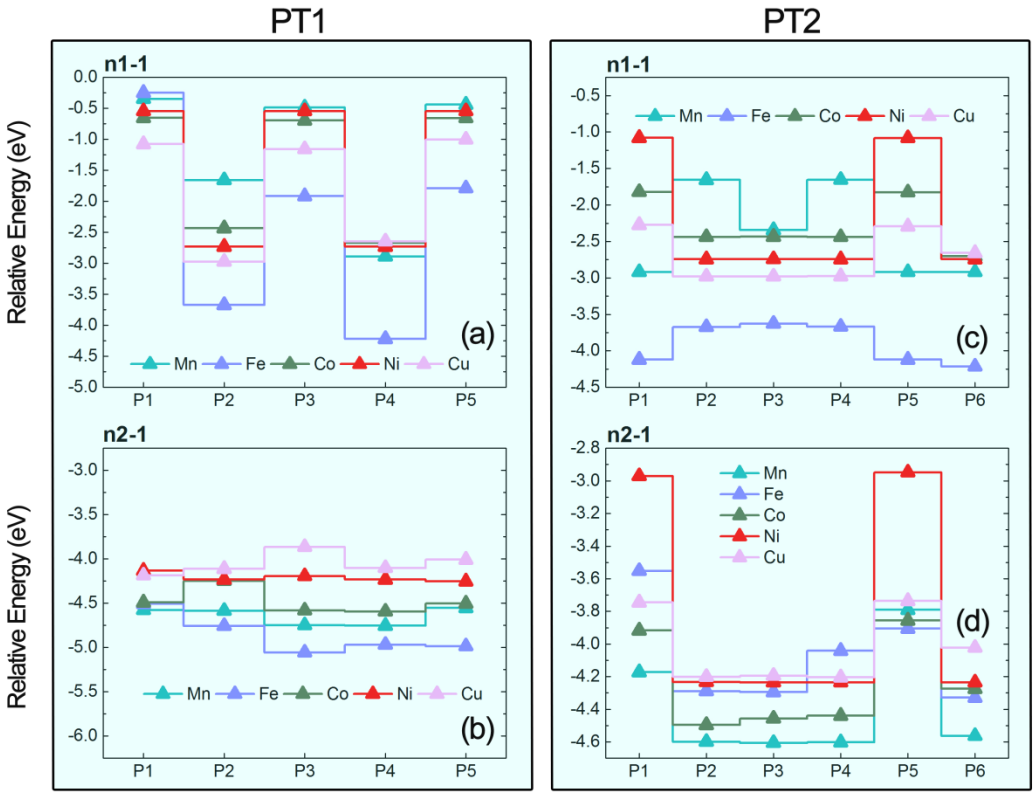

Figure S8 Relative energies of TM-doping LNO with one proton: (a) **n1-1** along PT1, (b) **n2-1** along PT1, (c) **n1-1** along PT2 and (d) **n2-1** along PT2.

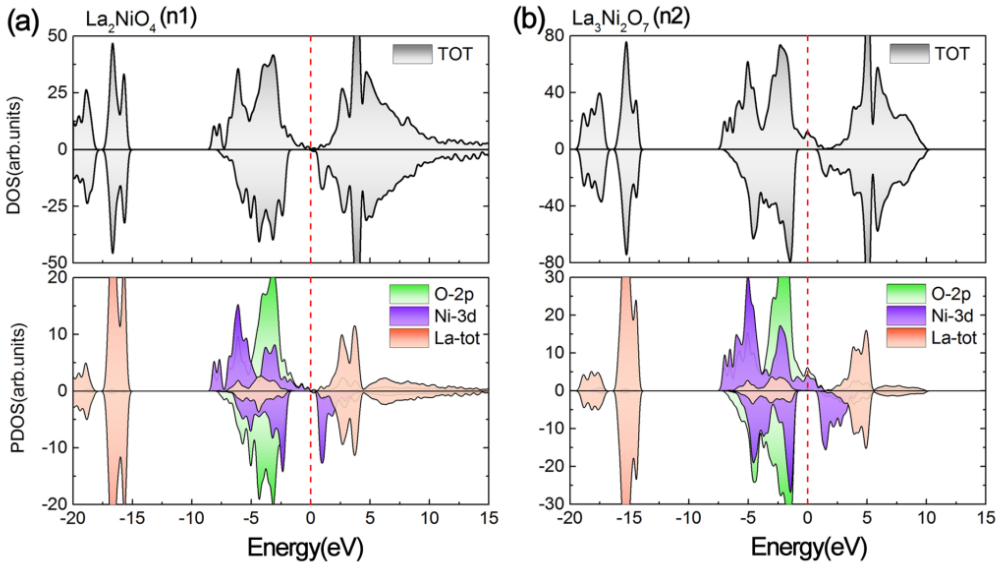

Figure S9 (a)-(d) Total density of states TDOS and atomic projected density of states PDOS for LNO: (a) for pristine La_2NiO_4 supercell and (b) for $La_3Ni_2O_7$ supercell.