

Supporting Information

Analysis of the Phase Stability of LiMO₂ Layered Oxides (M = Co, Mn, Ni)

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Supplementary note 1. Details about the structure and magnetic properties of transition metal oxides, Li₂O and metallic lithium.

CoO, NiO and MnO present a cubic structures belonging to Fm $\bar{3}$ m space group. ⁽²⁵⁾ All TMs ions are in 2+ oxidation state in the high-spin (HS) electronic configuration, that for:

- Co²⁺ is t_{2g}⁵ (↑↓↑↓↑) e_g² (↑↑);
- Ni²⁺ is t_{2g}⁶ (↑↓↑↓↑↓) e_g² (↑↑);
- Mn²⁺ is t_{2g}³ (↑↑↑) e_g² (↑↑).

All oxides present an antiferromagnetic structure; they are made of alternatively packed ferromagnetic (111) planes along the [111] direction of the cubic cell, as shown in Figure S4 (b), in Supporting Information. (26)

So, we have used a supercell 2x2x2 containing 64 atoms (32 M, 32 O where M=Co, Ni, Mn) in order to consider the magnetic properties, as shown in Figure S5 (a), in Supporting Information.

α-Mn₂O₃ crystallizes in an undistorted cubic bixbyite structure, with Ia $\bar{3}$ symmetry, and below 302 K it has the crystal structure of an orthorhombically distorted bixbyite, described by the space group Pcab. For our calculations we have considered Pcab structure. In this structure Mn³⁺ ions are octahedrally coordinated to O²⁻ ions that have four Mn neighbours. This material has a challenging magnetic structure. We considered the magnetic structure proposed by M. Reguluski et al.[1], and thus we modelled a 2x2x2 supercell containing 80 atoms (32 Mn, 48 O), as shown in Figure S6, in Supporting Information.

Li₂O has a cubic structure belonging to Fm $\bar{3}$ m space group, while metallic Li crystallizes in a cubic structure as well belonging to Im $\bar{3}$ m space group. In both case we have computed a single unit cell containing 12 atoms (8 Li, 4 O) and 2 atoms for Li respectively, as shown in Figure S7, in Supporting Information.

Supplementary note 2. Bulk modulus calculation

The bulk modulus estimate has been carried out by fitting the Birch-Murnaghan equation (non linear fitting) $E(V) = E_0 + \frac{9V_0B_0}{16} \left\{ \left[\left(\frac{V_0}{V} \right)^{\frac{2}{3}} - 1 \right]^3 B'_0 + \left[\left(\frac{V_0}{V} \right)^{\frac{2}{3}} - 1 \right]^2 \left[6 - 4 \left(\frac{V_0}{V} \right)^{\frac{2}{3}} \right] \right\}$ to the computational values. The equation constraints the possible fitting results to physically meaningful trends. Volumes have been scanned (5 datapoints) in the range ±3% in respect to the minimal energy structure and the corresponding cohesion energy values have been computed. For the ground state structures, (hR12, mC8 and oP8 for LCO, LNO and LMO, respectively) the analysis has been extended to the ±4.5% volume range (7 datapoints) in order to evaluate the computational accuracy and estimate errors.

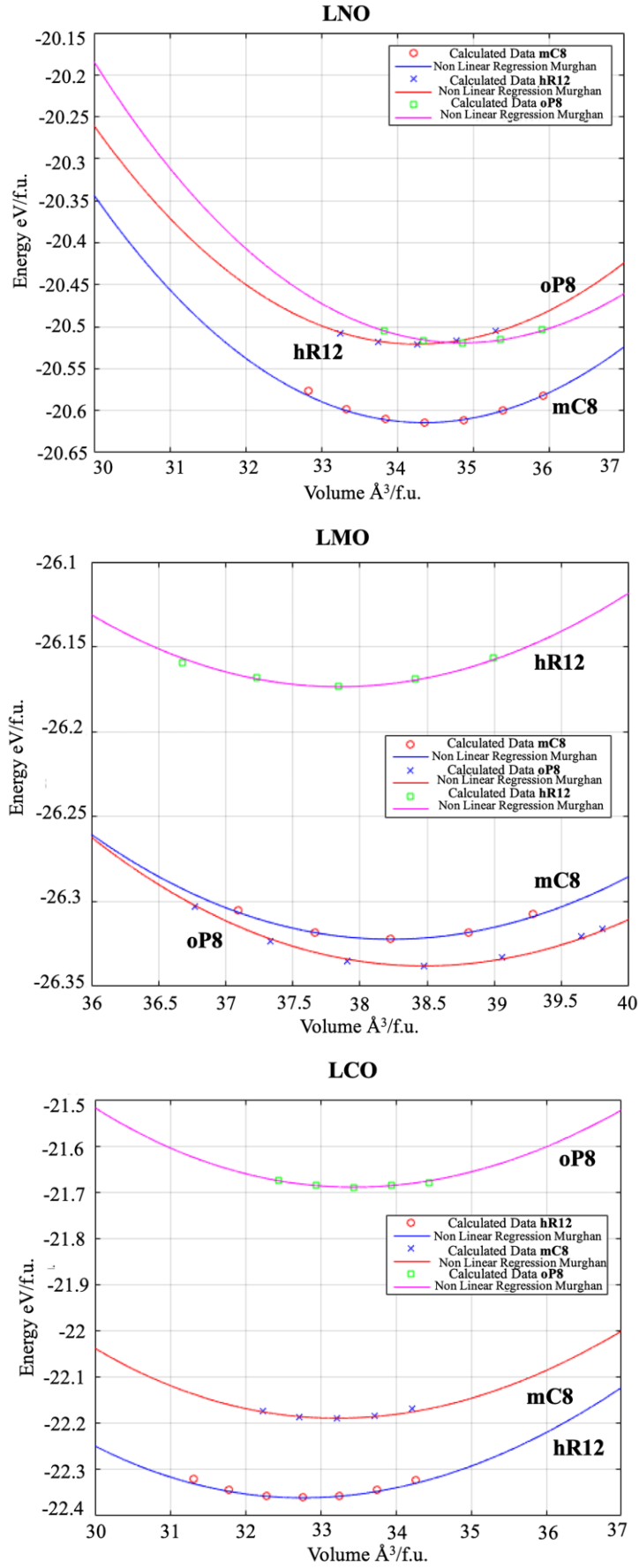


Figure S1. Bulk modulus of LMO, LNO and LCO estimated for all structures.

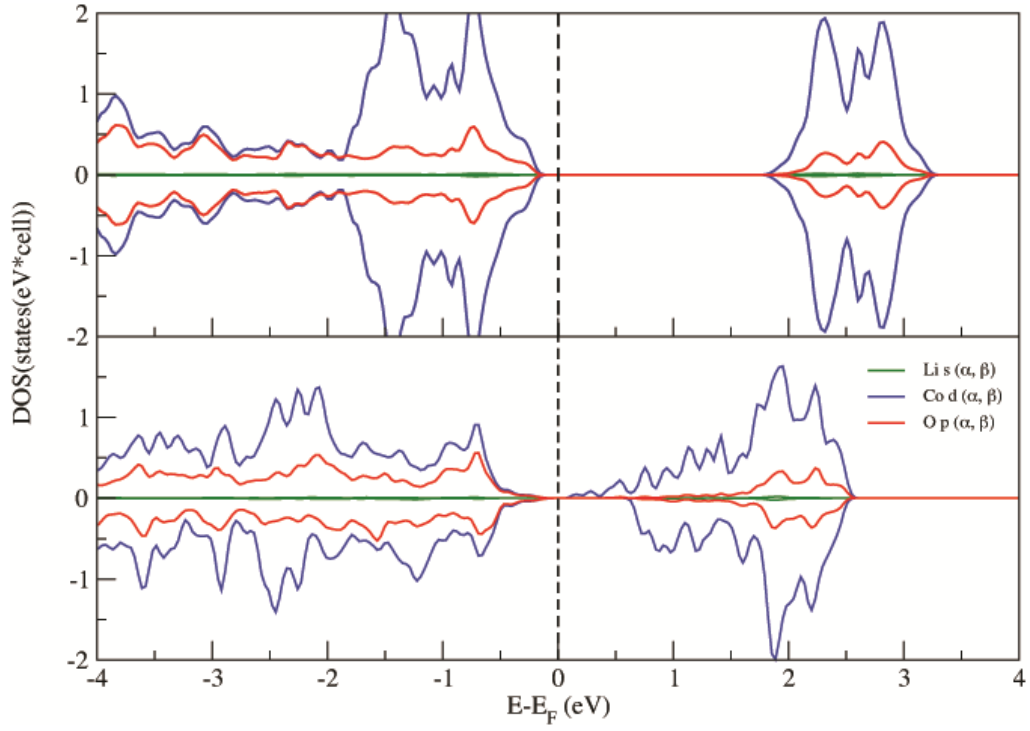


Figure S2. PDOS of LCO compound for mC8 and oP8 structures. Upper panel monoclinic electronic structure of LCO (mC8) and bottom panel orthorhombic electronic structure of LCO (oP8). Colour Code: Li green, Co blue, O red.

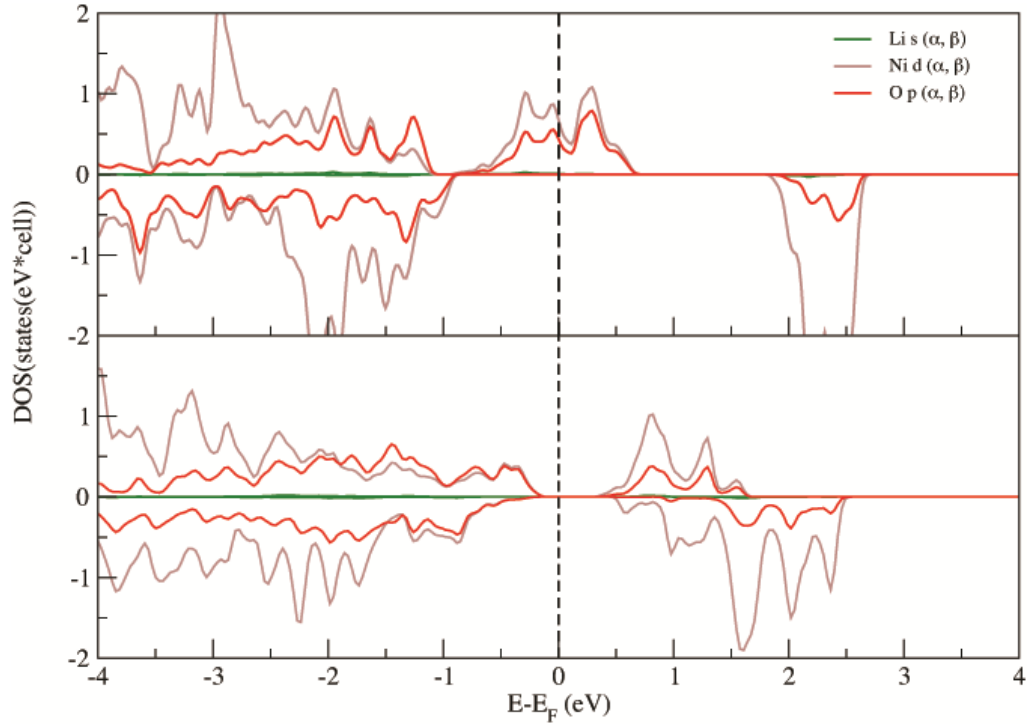


Figure S3. PDOS of LNO compound for hR12 and oP8 structures. Upper panel rhombohedral electronic structure of LNO (hR12) and bottom panel orthorhombic electronic structure of LNO (oP8). Colour Code: Li green, Ni brown, O red.

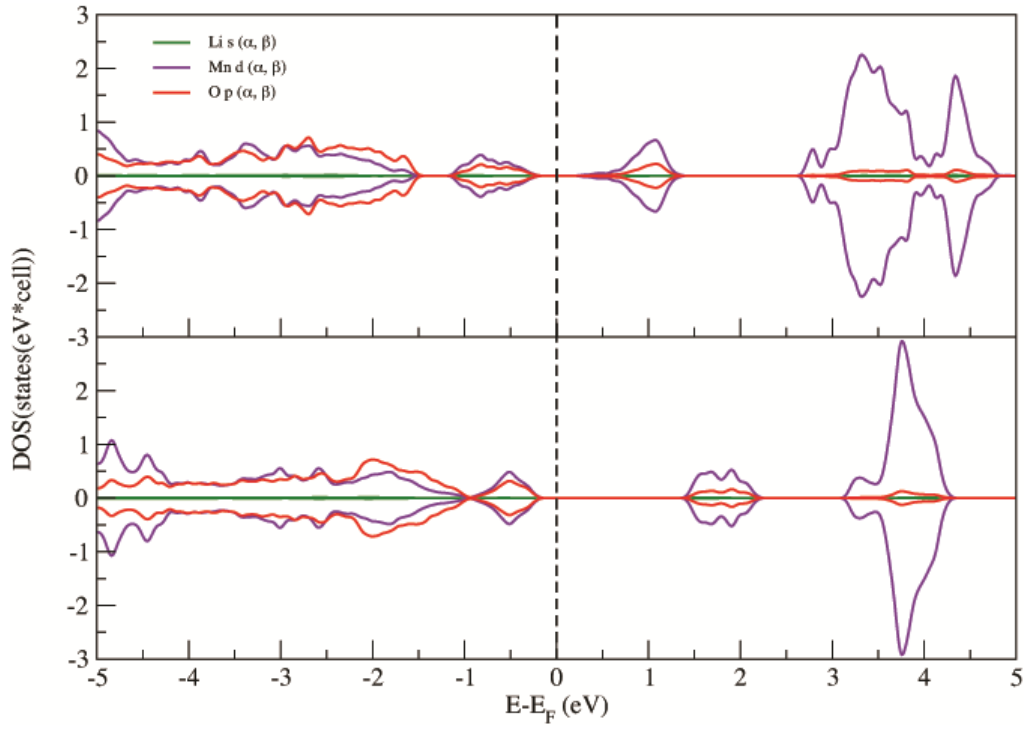


Figure S4. PDOS of LMO compound for hR12 and mC8 structures. Upper panel rhombohedral electronic structure of LMO (hR12) and bottom panel monoclinic electronic structure of LMO (mC8). Colour Code: Li green, Ni brown, O red.

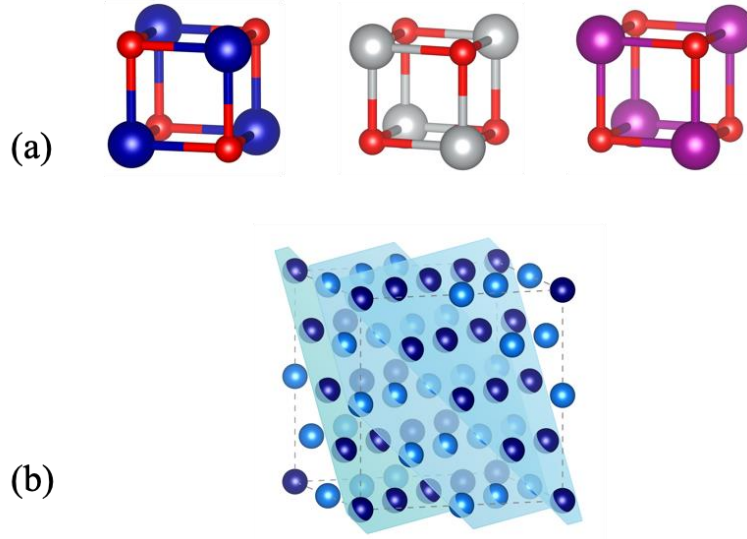


Figure S5. (a) Single *unit cell* of TMs oxide, CoO, NiO and MnO that present a cubic structures belonging to $Fm\bar{3}m$ space group[2]. (b) AFM structure of TMs oxide, that are made of alternatively packed ferromagnetic (111) planes along the $[1\ 1\ 1]$ direction of the cubic cell. Colour Code: (a) blue Co, grey Ni, purple Mn, red O; (b) spin up blue, spin down light blue.

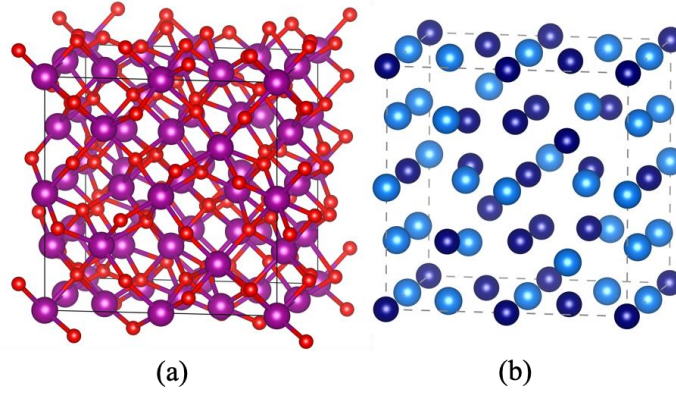


Figure S6. (a) α - Mn_2O_3 2x2x2 supercell[2]. (b) AFM structure of TM oxide. Colour Code: (a) purple Mn, red O; (b) spin up blue, spin down light blue.

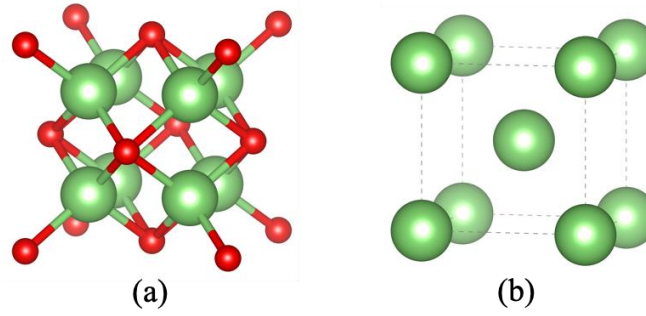


Figure S7. Cubic structures [3,4] of (a) Li_2O and (b) Li Colour Code: green Li, red O.

Table S1. Calculated bond lengths for LCO [5,6], LNO [7]and LMO [8] for all lattices; inter parentheses are reported the corresponding values from experimental structures, where available.

	$d_{\text{M-O}} (\text{\AA})$		
	R	M	O
LCO	1.930 (1.921)	1.990 / 1.918	2.210 / 1.902 / 1.856
LNO	1.974 (1.97)	2.186 / 1.887 (1.96/1.94)	2.244 / 1.891 / 1.868
LMO	2.123 / 1.940	2.328 / 1.958 (2.31/1.92)	2.321 / 1.974 / 1.935 (2.30/1.92/1.94)

Table S2. Computed cohesion energies (eV/at) for all ground state lattices/phase.

Phase	Lattice/Phase	E (eV at ⁻¹)
CoO	$\text{Fm}\bar{3}\text{m}$	-5.526
NiO	$\text{Fm}\bar{3}\text{m}$	-5.25
MnO	$\text{Fm}\bar{3}\text{m}$	-7.7625
α - Mn_2O_3	Pcab	-7.4524
Li_2O	$\text{Fm}\bar{3}\text{m}$	-4.771
Li	$\text{Im}\bar{3}\text{m}$	-1.912

Table S3. Energies of formation from the elements at T=298 K, TMs oxide and Li₂O [9].

	$\Delta_f E_{0K}$ kJ mol ⁻¹	
	(kJ mol ⁻¹)	(eV)
CoO	-238.1	-2.47
NiO	-238.1	-2.47
MnO	-384.7	-3.99
α -Mn ₂ O ₃	-959.0	-9.94
Li ₂ O	-592.4	-6.14

Table S4. Calculated Energy of formation at 0K from elements for all the polymorphs (hR12, mC8 and oP8) of the LCO, LMO and LNO compounds.

		$\Delta_f E_{0K}$ kJ mol ⁻¹		
	Reaction		hR12	mC8
LiCoO ₂	Co(s) + Li(s) + O ₂ (g) → LiCoO ₂ (s)		-725±7	-709±7
LiNiO ₂	Ni(s) + Li(s) + O ₂ (g) → LiNiO ₂ (s)		-601±7	-610±7
LiMnO ₂	Mn(s) + Li(s) + O ₂ (g) → LiMnO ₂ (s)		-811±6	-825±6

Table S5. Experimental and estimated absolute entropies at 298K and thermal effects at 298 K for the LCO, LMO and LNO compounds.

			S_{298K}^0 J K ⁻¹ mol ⁻¹			$H_{298K}^0 - H_{0K}^0$ kJ mol ⁻¹
	KK model [10]	NKR model [7]	DFT phonon calculations [9]	Exp. [10]	Adopted values	KK model [7]
LiCoO ₂	54.5	67.5	50	52.5	56.1 ± 3.9	9.9 ± 1.0
LiNiO ₂	64.2	52.3	67		61.2 ± 4.5	9.8 ± 1.0
LiMnO ₂	55.5	101	80		79.0 ± 13.3	9.3 ± 1.0

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