Supporting information

Prediction of possible $CaMnO_3$ modifications using an *ab initio* minimization data mining approach

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Table S1. A [5*s*4*p*1*d*] basis set (i.e., consisting of five *s*, four *p* and one *d* functions), was used in the case of Ca^{2+}. For Mn^{4+}, a [5*s*4*p*2*d*] basis set and for O^{2-} a [4*s*3*p*] all-electron basis set was used, respectively (Freyria-Fava et al, 1997).

	Ca all electron basis set			**Mn all electron basis set**			**O all electron basis set**		
Type	Exponent	Contraction coefficient	Contraction coefficient	Exponent	Contraction coefficient	Contraction coefficient	Exponent	Contraction coefficient	Contraction coefficient
s	191300.0 26970.0 5696.0 1489.4 448.3 154.62 60.37 25.09	0.0002204 0.001925 0.01109 0.04995 0.17014 0.3685 0.4034 0.1452		292601.0 42265.0 8947.29 2330.32 702.047 242.907 94.955 39.5777	0.000227 0.0019 0.0111 0.0501 0.1705 0.3691 0.4035 0.1437		8020.0 1338.0 255.4 69.22 23.90 9.264 3.851 1.212	0.00108 0.00804 0.05324 0.1681 0.3581 0.3855 0.1468 0.0728	
sp	448.6 105.7 34.69 13.50 5.820 1.819	-0.00575 -0.0767 -0.1122 0.2537 0.688 0.349	0.00847 0.06027 0.2124 0.3771 0.401 0.198	732.14 175.551 58.5093 23.129 9.7536 3.4545	-0.0053 -0.0673 -0.1293 0.2535 0.6345 0.2714	0.0086 0.0612 0.2135 0.4018 0.4012 0.2222	49.43 10.47 3.235 1.217	-0.00883 -0.0915 -0.0402 0.379	0.00958 0.069 0.2065 0.347
sp	20.75 8.40 3.597 1.408 0.726	-0.0020 -0.1255 -0.6960 1.029 0.944	-0.0365 -0.0685 0.1570 1.482 1.025	38.389 15.4367 6.1781 2.8235	0.0157 -0.2535 -0.8648 0.9337	-0.0311 -0.0969 0.2563 1.6552	0.4764	1.0	1.0
sp	0.453	1.0	1.0	1.2086	1.0	1.0	0.19	1.0	1.0
sp	0.246	1.0	1.0	0.4986	1.0	1.0			
d	3.191 0.8683 0.3191	0.16 0.313 0.406		22.5929 6.1674 2.0638 0.7401	0.0708 0.3044 0.5469 0.5102				
d				0.259	1.0				

Table S2. Comparison between structural models obtained using data mining (ICSD model) and Structure Prediction Diagnostic Software (SPuDS model). Later, these structural models were submitted to the *ab initio* local optimization. We note that majority of the experimental data (ICSD models) comes from various ABX_3 compounds; In order to simplify the table, the corresponding A and B cations have been replaced by proposed Ca^{2+} and Mn^{4+} cations, respectively.

Modification, Space group and Wyckoff position	**Cell parameters (Å) and fractional coordinates**	
	ICSD model	SPuDS model
$CaMnO_3$-(1) *Pnma* (62) Ca 4*c* Mn 4*b* O1 4*c* O2 8*d*	(Bozin *et al.*, 2008) *a* = 5.2790(2), *b* = 7.4438(3), *c* = 5.2583(2) 0.0344(1) 1/4 0.9931(1) 1/2 0 0 0.4877(1) 1/4 0.0671(1) 0.2873(1) 0.0346(1) 0.7109(1)	*a* = 5.36, *b* = 7.54, *c* = 5.31 0.0123 1/4 0.0030 1/2 0 0 0.4955 1/4 -0.0479 0.2735 0.0240 0.7260
$CaMnO_3$-(2) $R\bar{3}c$ (167) Ca 6*a* Mn 6*b* O 18*e*	(Yanchevskii *et al.*, 2008) *a* = 5.474(3), *c* = 13.376(7) 0 0 1/4 0 0 0 0.450(7) 0 1/4	*a* = 5.31, *c* = 13.18 0 0 1/4 0 0 0 0.4529 0 1/4
$CaMnO_3$-(3) *Imma* (74) Ca 4*e* Mn 4*b* O1 4*e* O2 8*g*	(Damay *et al.*, 1998) *a* = 5.4312(2), *b* = 7.6250(3), *c* = 5.4729(2) 0 1/4 0.0011(3) 0 0 1/2 0 1/4 0.5525(3) 1/4 -0.0267 3/4	*a* = 5.38, *b* = 7.51, *c* = 5.31 0 1/4 0.0030 0 0 1/2 0 1/4 0.5581 1/4 -0.0291 3/4
$CaMnO_3$-(4) $P4_2/nmc$ (137) Ca1 2*a* Ca2 2*b* Ca3 4*d* Mn1 8*e* O1 8*f* O2 8*g* O3 8*g*	(Caracas & Wentzcovitch, 2006)* *a* = 6.81, *c* = 6.96 3/4 1/4 3/4 3/4 1/4 1/4 1/4 1/4 0.2510 0 0 0 0.0016 -0.0016 1/4 1/4 0.0325 0.0015 3/4 0.0325 0.5016	*a* = 7.53, *c* = 7.58 3/4 1/4 3/4 3/4 1/4 1/4 1/4 1/4 0.2413 0 0 0 0.0165 -0.0165 1/4 1/4 0.0367 -0.0140 3/4 -0.0332 0.5171
$CaMnO_3$-(5) *Cmcm* Ca1 4*c* Ca2 4*c* Mn 8*d* O 8*e* O 8*f* O 8*g*	(Darlington *et al.*, 1983) *a* = 7.86, *b* = 7.87, *c* = 7.88 0 0.5026(14) 1/4 0 0.0022(14) 1/4 1/4 1/4 0 0.2230(4) 0 0 0 0.2741(4) 0.0203(3) 0.2710(3) 0.2489(7) 1/4	*a* = 7.51, *b* = 7.56, *c* = 7.56 0 0.4910 1/4 0 -0.0071 1/4 1/4 1/4 0 -0.2209 1/2 0 0 0.2207 0.0293 0.2795 0.2517 1/4
$CaMnO_3$-(6) *P4/mbm* (127) Ca 2*c* Mn 2*a* O1 2*b* O2 4*g*	(Caracas & Wentzcovitch, 2006)* *a* = 4.83, *c* = 3.68 0 1/2 1/2 0 0 0 0 0 1/2 0.2065 0.7065 0	*a* = 5.31, *c* = 3.81 0 1/2 1/2 0 0 0 0 0 1/2 0.2080 0.7080 0
$CaMnO_3$-(7)	(Kennedy *et al.*, 2009)	

*I*4/*mcm* (140) Ca 4*b* Mn 4*c* O1 4*a* O2 8*h*	*a* = 5.3442(1), *c* = 7.6373(4) 0 1/2 1/4 0 0 0 0 0 1/4 0.2280(4) 0.7280(4) 0	*a* = 5.31, *c* = 7.61 0 1/2 1/4 0 0 0 0 0 1/4 0.2920 0.7920 0
$CaMnO_3$-(8) $Im\bar{3}$ (204) Ca1 2*a* Ca2 6*b* Mn 8*c* O 24*g*	(Caracas & Wentzcovitch, 2006)* *a* = 7.09 0 0 0 0 1/2 1/2 1/4 1/4 1/4 0 0.2627 0.2367	 *a* = 7.55 0 0 0 0 1/2 1/2 1/4 1/4 1/4 0 0.2263 0.2717
$CaMnO_3$-(9) *I*4/*mmm* (139) Ca1 2*a* Ca2 2*b* Ca3 4*c* Mn 8*f* O1 8*h* O2 16*n*	(Caracas & Wentzcovitch, 2006)* *a* = 7.11, *c* = 7.07 0 0 0 0 0 1/2 0 1/2 0 1/4 1/4 1/4 0.2338 0.2338 0 0 0.2504 0.2666	 *a* = 7.56, *c* = 7.52 0 0 0 0 0 1/2 1/2 0 0 1/4 1/4 1/4 0.2219 0.2219 0 0 0.2516 0.2783
$CaMnO_3$–(10) *C*2/*c* (15) Ca 8*f* Mn1 4*e* Mn2 4*d* O1 8*f* O2 8*f* O3 8*f*	(Boukhalov & Solovyev, 2010) *a* = 9.69, *b* = 5.57, *c* = 9.80, *β* = 110.38 0.1358 0.2241 0.1236 0 0.2270 3/4 1/4 1/4 1/2 0.0924 0.1893 0.5805 0.1508 0.5471 0.3768 0.3518 0.5377 0.1618	*a* = 9.27, *b* = 5.35, *c* = 9.27, *β* = 109.47 0.0750 0.3000 0.1250 0 1/4 3/4 1/4 1/4 1/2 0.1236 0.1980 0.6236 0.1236 0.5246 0.4010 0.3764 0.5274 0.1510
$CaMnO_3$-(11) $Pm\bar{3}m$ (221) Ca 1*a* Mn 1*b* O 3*c*	(Trang *et al.*, 2011)* *a* = 3.78 0 0 0 1/2 1/2 1/2 1/2 1/2 0	 *a* = 3.81 0 0 0 1/2 1/2 1/2 1/2 1/2 0
$CaMnO_3$-(12) *Immm* (71) Ca 4*j* Mn1 2*a* Mn2 2*c* O1 8*n* O2 4*i*	(Panunzio Miner *et al.*, 2007) *a* = 5.56733(1), *b* = 5.56796(1), *c* = 7.90224(2) 1/2 0 0.2476(2) 0 0 0 1/2 1/2 0 0.2295(1) 0.2809(2) 0 0 0 0.2509(3)	—
$CaMnO_3$-(13) *C*2/*m* (12) Ca 4*i* Mn 4*e* O1 4*h* O2 4*g* O3 4*i*	(Moussa *et al.*, 2001) *a* = 8.5548(1), *b* = 8.4808(1), *c* = 6.0118(1), *β* = 134.806(1) 0.2532(5) 0 0.5022(12) 1/4 1/4 0 0 0.2850(5) 1/2 0 0.7235(5) 0 0.19269(3) 0 -0.0624(8)	—
$CaMnO_3$-(14) *R*3*c* (161) Ca 6*a* Mn 6*a* O 18*b*	(Weitin *et al.*, 2009) *a* = 5.58, *c* = 13.87 0 0 0 0 0 0.2208 0.4371 0.0182 0.9495	—
$CaMnO_3$-(15)	(Shirako *et al.*, 2009)	—

Cmcm (63) Ca 4*c* Mn 4*a* O1 4*c* O2 8*f*	*a* = 3.1013(1), *b* = 9.8555(2), *c* = 7.2643(1) 0 0.2521(3) 1/4 0 0 0 1/2 0.4279(3) 1/4 1/2 0.1226(5) 0.0548(6)	
$CaMnO_3$ -(16) $R\bar{3}$ (148) Ca 6*c* Mn 6*c* O 18*f*	(Yamanaka, 2005) *a* = 5.08810(4), *c* = 14.0910(1) 0 0 0.355430(9) 0 0 0.146429(9) 0.31717(9) 0.02351(9) 0.24498(3)	—

* denotes only theoretically proposed ABX_3 model

— SPuDS does not provide perovskite model in the $CaMnO_3$ compound

Table S3. Structural data of the energetically non-favorable $CaMnO_3$ perovskite modifications found after local optimization on LDA, B3LYP and HF level.

Modification, Space group and Wyckoff position	**Cell parameters (Å), unit cell volume (Å^3) and fractional coordinates**		
	LDA	B3LYP	HF
$CaMnO_3$-(2) $R\bar{3}c$ (167) Ca 6*a* Mn 6*b* O 18*e*	*a* = 5.21, *c* = 12.48 *V* = 293.61 0 0 3/4 0 0 1/2 1/3 0.1026 0.4167	*a* = 5.32, *c* = 12.90 *V* = 316.48 0 0 3/4 0 0 1/2 1/3 0.0987 0.4167	*a* = 5.39, *c* = 13.53 *V* = 340.90 0 0 3/4 0 0 1/2 1/3 0.1176 0.4167
$CaMnO_3$-(6) *P*4/*mbm* (127) Ca 2*d* Mn 2*b* O1 2*a* O2 4*h*	*a* = 5.03, *c* = 3.84 *V* = 97.02 0 1/2 0 0 0 1/2 0 0 0 0.8175 0.3175 1/2	*a* = 5.02, *c* = 4.14 *V* = 104.35 0 1/2 0 0 0 1/2 0 0 0 0.8152 0.3152 1/2	*a* = 5.30, *c* = 4.01 *V* = 112.65 0 1/2 0 0 0 1/2 0 0 0 0.7875 0.2875 1/2
$CaMnO_3$-(7) *I*4/*mcm* (140) Ca 4*b* Mn 4*c* O1 4*a* O2 8*h*	*a* = 5.13, *c* = 7.41 *V* = 195.20 0 1/2 1/4 0 0 0 0 0 1/4 0.2498 0.7502 0	*a* = 5.11, *c* = 8.07 *V* = 210.92 0 1/2 1/4 0 0 0 0 0 1/4 0.2495 0.7505 0	*a* = 5.44, *c* = 6.91 *V* = 204.16 0 1/2 1/4 0 0 0 0 0 1/4 0.2761 0.7761 0
$CaMnO_3$-(8) $Im\bar{3}$ (204) Ca1 2*a* Ca2 6*b* Mn 8*c* O 24*g*	*a* = 7.31 *V* = 389.85 0 0 0 0 1/2 1/2 1/4 1/4 1/4 0 0.2804 0.2221	*a* = 7.50 *V* = 421.84 0 0 0 0 1/2 1/2 1/4 1/4 1/4 0 0.2846 0.2215	*a* = 7.69 *V* = 454.90 0 0 0 0 1/2 1/2 1/4 1/4 1/4 0 0.2243 0.2260
$CaMnO_3$-(11) $Pm\bar{3}m$ (221) Ca 1*a* Mn 1*b* O 3*c*	*a* = 3.67 *V* = 49.49 0 0 0 1/2 1/2 1/2 1/2 1/2 0	*a* = 3.75 *V* = 52.53 0 0 0 1/2 1/2 1/2 1/2 1/2 0	*a* = 3.71 *V* = 50.90 0 0 0 1/2 1/2 1/2 1/2 1/2 0
$CaMnO_3$-(14) *R*3*c* (161) Ca 6*a* Mn 6*a* O 18*b*	*a* = 5.16, *c* = 12.45 *V* = 286.70 0 0 0 0 0 0.2495 -0.1208 0.2127 0.6661	*a* = 5.32, *c* = 13.02 *V* = 318.75 0 0 0 0 0 0.2487 -0.2272 -0.3327 0.6610	*a* = 5.39, *c* = 13.53 *V* = 340.90 0 0 0 0 0 0.2497 -0.2135 -0.3333 0.6664

Table S4. Calculated interatomic distances (Å) and angles (°) for the energetically most relevant perovskite modifications of $CaMnO_3$ using B3LYP functional. V12/V6 is the relation of the coordination Ca (V12) and Mn (V6) polyhedra volumes.

Modification and Space group	Mn–O	<Mn–O>	<Ca–O>	short Ca-Mn	V12/V6	Mn–O1–Mn	Mn–O2(O3)–Mn
$CaMnO_3$-(1) *Pnma*	2 x 1.8528 (O1) 2 x 1.8989 (O2) 2 x 1.9660 (O2)	1.9059	2.6646 (XII) 2.5715 (X)	3.11	4.83	160.24	157.45
$CaMnO_3$-(2) $R\bar{3}c$	6 x 1.9098	1.9098	2.6642(XII)	3.22	4.68	158.16	-
$CaMnO_3$-(3) *Imma*	2 x 1.8923 (O1) 4 x 1.9250 (O2)	1.9141	2.6675 (XII)	3.20	4.66	154.49	158.70
$CaMnO_3$-(4) $P4_2/nmc$	2 x 1.8483 (O1) 2 x 1.9322 (O2) 2 x 1.9306 (O3)	1.9037	2.6721(XII) Ca1 2.6608(XII)Ca2 2.5709(X)Ca3	3.18	4.93	161.10	157.89 158.40
$CaMnO_3$-(5) *Cmcm*	2 x 1.9131 (O1) 2 x 1.9365 (O2) 2 x 1.8618 (O3)	1.9038	2.5686(X) Ca1 2.6643(XII)Ca2	3.19	4.88	162.67	155.1872 163.3492
$CaMnO_3$-(6) *P4/mbm*	2 x 2.0724 4 x 1.8333	1.9130	2.6701(XII)	3.25	4.86	180	150.76
$CaMnO_3$-(7) *I4/mcm*	2 x 2.0170 4 x 1.8077	1.8775	2.6579(XII)	3.26	4.99	180	179.77
$CaMnO_3$-(8) $Im\bar{3}$	6 x 1.9049	1.9049	2.6410(XII)Ca1 2.6693(XII)Ca2	3.25	4.99Ca1 4.89Ca2	159.67	-
$CaMnO_3$-(9) *I4/mmm*	2 x 1.9138 (O1) 4 x 1.8964 (O2)	1.9022	2.6709(XII) Ca1 2.4796(VIII)Ca2 2.6567(XII)Ca3	3.25	4.94 5.02	157.23	163.12
$CaMnO_3$-(10) *C2/c*	2 x 1.9439 (O1) 2 x 1.9237 (O2) 2 x 1.9332 (O3) 2 x 1.7831 (O1) 2 x 1.9245 (O2) 2 x 1.9091 (O3)	1.9336(Mn1) 1.8722 (Mn2)	2.6644(XII)	3.19	4.55 5.02	158.06	164.08 161.12
$CaMnO_3$-(11) $Pm\bar{3}m$	6 x 1.8726	1.8726	2.6482(XII)	3.24	5.00	180	-
$CaMnO_3$-(12) *Immm*	2 x 1.9206 (O1) 4 x 1.8827 (O2) 2 x 1.8288 (O1) 4 x 1.8889 (O2)	1.9079(Mn1) 1.8488(Mn2)	2.6567(XII)	3.24	4.7699 5.2456	179.70	180
$CaMnO_3$-(13) *C2/m*	2 x 1.9192 (O1) 2 x 1.9186 (O2) 2 x 1.8699 (O3)	1.9026	2.6607(XII)	3.21	4.73	162.13	162.09 156.33
$CaMnO_3$-(14) *R3c*	3 x 1.8779 3 x 1.9378	1.9079	2.6687(XII)	3.24	4.75	160.25	-

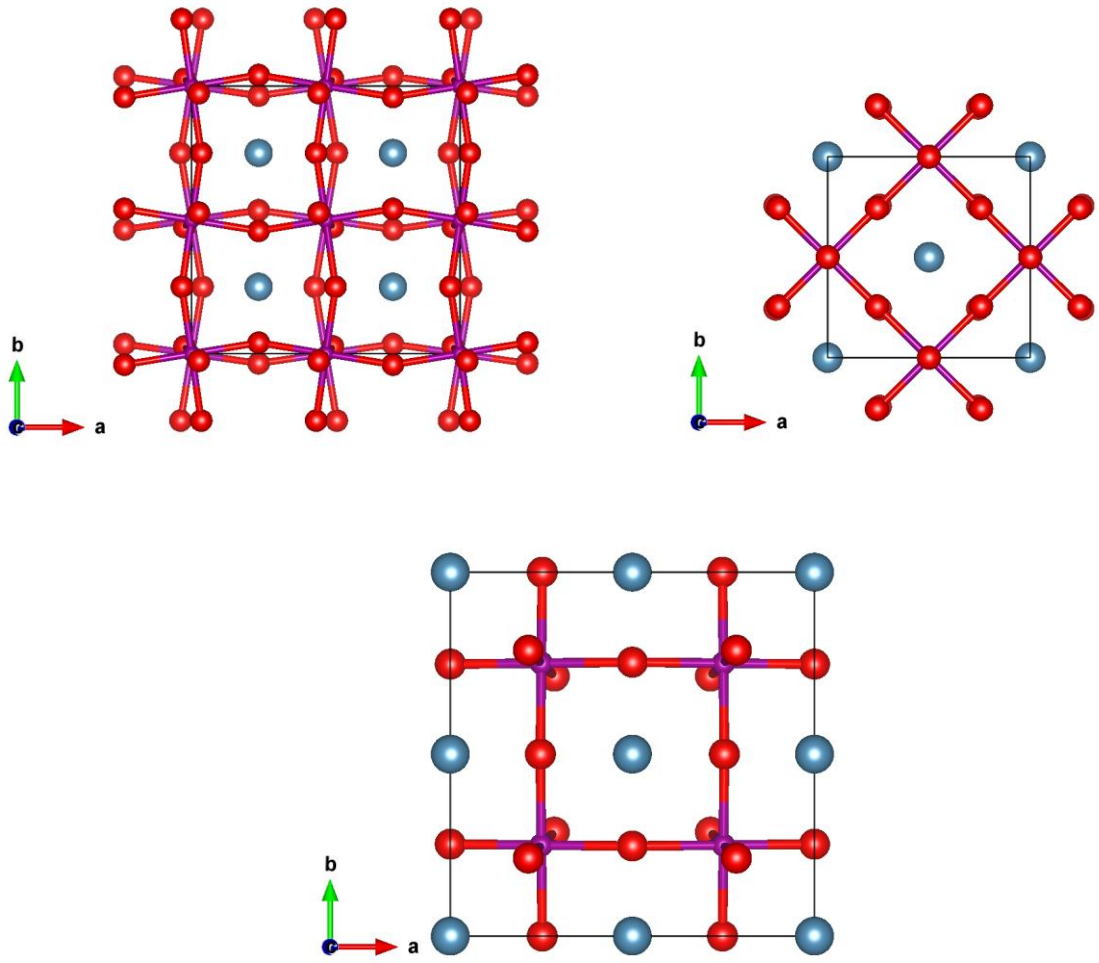
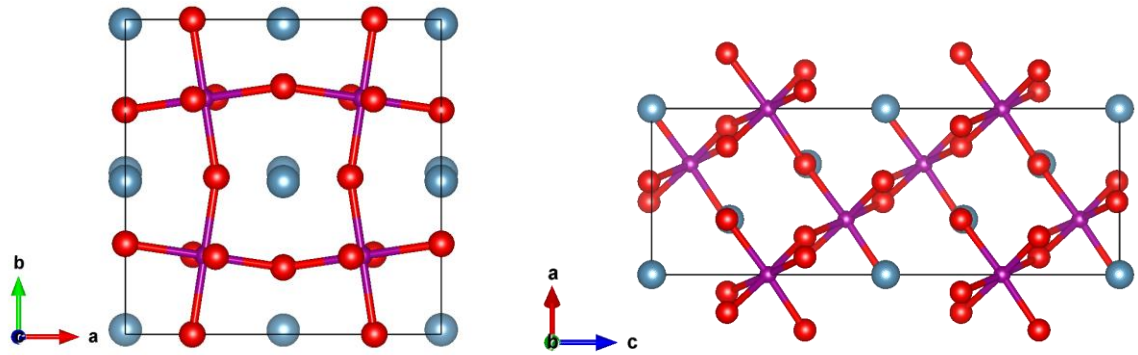
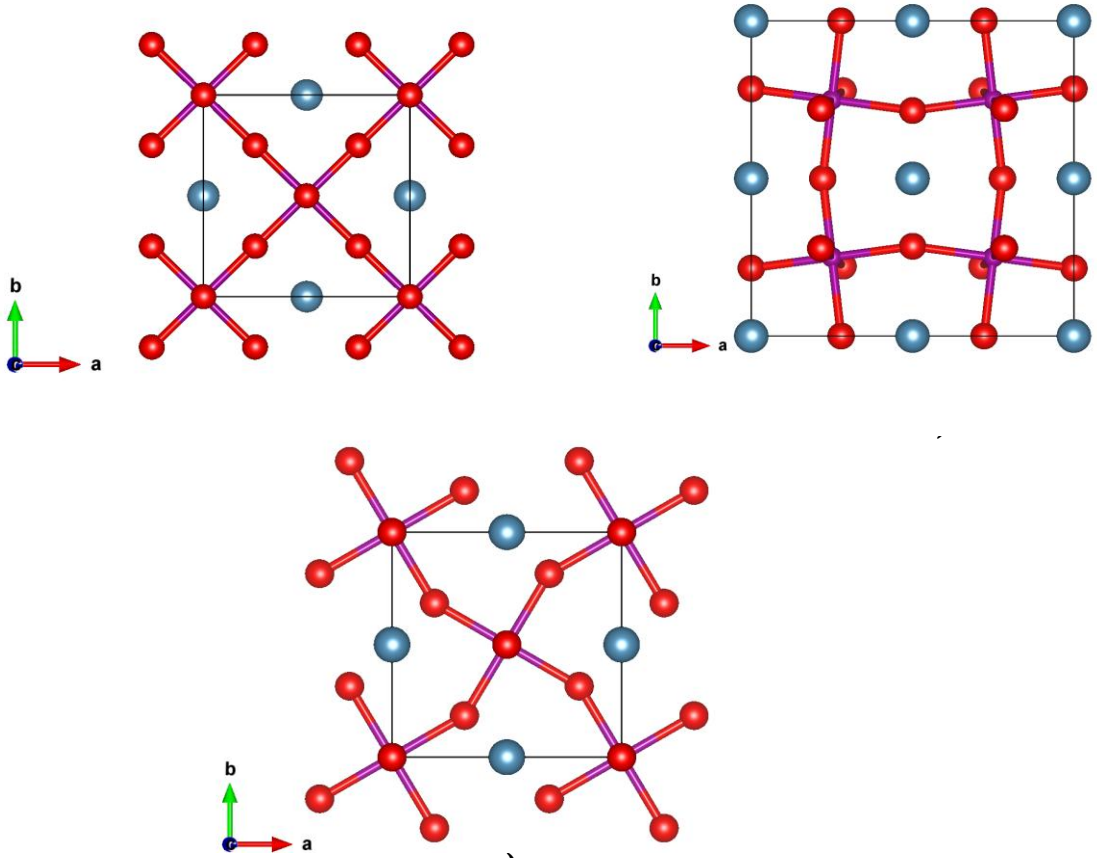


Figure. S1. Calculated $CaMnO_3$ modifications using B3LYP approximation: a) $CaMnO_3$-(4) in space group $P4_2/nmc$; b) $CaMnO_3$-(12) in space group *Immm* and c) $CaMnO_3$-(9) in space group $I4/mmm$. Mn (violet) and O (red) atoms are bonded, while Ca atoms are colored blue. Unit cell is marked with quadrangle.



b)

Figure. S2. Calculated $CaMnO_3$ modifications using B3LYP approximation: a) $CaMnO_3$-(5) in space group *Cmcm* and b) $CaMnO_3$-(14) in space group *R*3*c*. Mn (violet) and O ed blue. Unit cell is marked with



c)

Figure. S3. Calculated $CaMnO_3$ modifications using B3LYP approximation: a) $CaMnO_3$-(7) in space group *I*4/*mcm*; b) $CaMnO_3$-(8) in space group $Im\bar{3}$ and c) $CaMnO_3$-(6) in space group *P*4/*mbm*. Mn (violet) and O (red) atoms are bonded, and Ca atoms are colored blue. Unit cell is marked with quadrangle.

Supplementary References

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