Supporting information for: Dopants in lanthanum manganite: Insights from first principles chemical space exploration

Sridevi Krishnan,[*,†,‡] Vinit Sharma,[†,‡,¶] Prabhakar Singh,[†,§] and Rampi Ramprasad[*,†,‡]

†*Materials Science and Engineering, University of Connecticut, Storrs, CT, USA*

‡*Institute of Material Science, University of Connecticut, Storrs, CT, USA*

¶*Current address: Materials Science and Technology Division, Oak Ridge National Laboratory, Oak Ridge, TN 37831, USA.*

§*Center for Clean Energy Engineering, University of Connecticut, Storrs, CT, USA*

E-mail: sridevi.krishnan@uconn.edu; rampi.ramprasad@uconn.edu

Structure and energetics of dopant binary oxides

The binary oxides and their PBE optimized structure used in this study are listed in the table S1. The formation energy of the oxides E_f is calculated according to the following equation

$$E_f = E_{D_yO_x} - y\mu_D - x\mu_O \quad (1)$$

where $E_{D_yO_x}$ is the energy of the binary oxide and μ_D and μ_O are the dopant and the oxygen chemical potentials.

Table S1: Structural properties and energetics of the binary oxides of the dopants included in the study.

	Lattice parameters						Space group	E_f **(eV)**
D_yO_x	**a**	**b**	**c**	α	β	γ		
AgO	4.42	4.88	5.62	90.00	90.00	90.00	$Cccm(66)$	-0.2802
As_2O_3	8.31	4.69	9.90	90.00	100.60	90.00	$P2_1/c(14)$	-6.1063
Au_2O_3	4.04	10.60	12.97	90.00	90.00	90.00	$Fdd2(43)$	-0.4738
BaO	5.61	5.61	5.61	90.00	90.00	90.00	$Fm\bar{3}m(225)$	-4.9610
Bi_2O_3	5.94	8.32	7.56	90.00	112.70	90.00	$P2_1/c(14)$	-6.1569
CaO	4.84	4.84	4.84	90.00	90.00	90.00	$Fm\bar{3}m(225)$	-5.9473
CdO	4.78	4.78	4.78	90.00	90.00	90.00	$Fm\bar{3}m(225)$	-2.0505
Co_3O_4	8.15	8.15	8.15	90.00	90.00	90.00	$Fd\bar{3}m(227)$	-7.0273
Cr_2O_3	5.09	5.09	13.78	90.00	90.00	120.00	$R\bar{3}c(167)$	-9.6532
Cs_2O_2	4.39	6.58	7.64	90.00	90.00	90.00	$Immm(71)$	-4.0919
CuO	2.94	2.94	5.16	90.00	90.00	90.00	$P4_2/mmc(131)$	-1.1972
Fe_2O_3	13.47	9.47	9.49	90.00	134.80	90.00	$P2_1/c(14)$	-5.7616
Ga_2O_3	12.45	3.08	5.88	90.00	103.70	90.00	$C2/m(12)$	-9.2243
GeO_2	5.09	5.09	5.76	90.00	90.00	120.00	$P3_121(152)$	-4.8569

HfO_2	5.14	5.19	5.32	90.00	99.70	90.00	$P2_1/c(14)$	-10.7280
HgO	3.74	5.80	6.73	90.00	90.00	90.00	$Pnma(62)$	-0.5773
In_2O_3	10.30	10.30	10.30	90.00	90.00	90.00	$Ia\bar{3}(206)$	-7.9189
IrO_2	4.54	4.54	3.19	90.00	90.00	90.00	$P4_2/mnm(136)$	-2.4024
K_2O_2	6.83	7.06	6.57	90.00	90.00	90.00	$Cmca(64)$	-4.2960
La_2O_3	11.40	11.40	11.40	90.00	90.00	90.00	$Ia\bar{3}(206)$	-17.3766
Mn_2O_3	9.50	9.50	9.50	90.00	90.00	90.00	$Ia\bar{3}(206)$	-8.4510
MoO_2	4.75	4.75	3.24	90.00	90.00	90.00	$P4_2/mnm(136)$	-5.3615
Nb_2O_5	19.79	3.87	20.81	90.00	115.70	90.00	$P2(3)$	-19.0775
NiO	4.20	4.20	4.20	90.00	90.00	90.00	$Fm\bar{3}m(225)$	-0.9813
OsO_2	4.52	4.52	3.21	90.00	90.00	90.00	$P4_2/mnm(136)$	-2.6571
PbO	4.06	4.06	5.30	90.00	90.00	90.00	$P4/nmm(129)$	-2.0658
PdO	3.10	3.10	5.44	90.00	90.00	90.00	$P4_2/mmc(131)$	-0.9664
PtO_2	3.18	4.54	4.60	90.00	90.00	90.00	$Pnnm(58)$	-1.5157
Rb_2O_3	9.38	9.38	9.38	90.00	90.00	90.00	$I\bar{4}3d(220)$	-4.6977
ReO_3	5.37	5.37	3.79	90.00	90.00	90.00	$P4/mbm(127)$	-6.4073
RhO_2	4.56	4.56	3.13	90.00	90.00	90.00	$P4_2/mnm(136)$	-2.5197
RuO_2	4.54	4.54	3.14	90.00	90.00	90.00	$P4_2/mnm(136)$	-3.1827
Sb_2O_5	12.74	4.83	5.46	90.00	103.70	90.00	$C2/c(15)$	-8.7846
Sc_2O_3	9.91	9.91	9.91	90.00	90.00	90.00	$Ia\bar{3}(206)$	-17.8331
SnO_2	4.83	4.83	3.24	90.00	90.00	90.00	$P4_2/mnm(136)$	-4.9440
SrO	5.21	5.21	5.21	90.00	90.00	90.00	$Fm\bar{3}m(225)$	-5.4849
Ta_2O_5	12.94	4.93	5.60	90.00	103.20	90.00	$C2/c(15)$	-19.9874
$Tc2O7$	5.89	7.82	14.27	90.00	90.00	90.00	$Pbca(61)$	-12.8299
TiO_2	12.31	3.77	6.62	90.00	106.90	90.00	$C2/m(12)$	-9.2415

Tl_2O_3	10.77	10.77	10.77	90.00	90.00	90.00	$Ia\bar{3}(206)$	-3.4448
V_2O_3	9.57	9.57	9.57	90.00	90.00	90.00	$Ia\bar{3}(206)$	-10.9194
WO_3	7.54	7.71	7.86	90.00	90.00	90.00	$Pbcn(60)$	-8.6993
Y_2O_3	0.70	10.70	10.70	90.00	90.00	90.00	$Ia\bar{3}(206)$	-18.1084
ZnO	3.29	3.29	5.31	90.00	90.00	120.00	$P6_3mc(186)$	-2.8885
ZrO_2	5.23	5.27	5.42	90.00	100.10	90.00	$P2_1/c(14)$	-10.3957

Formation energies of the doped LMO compounds

The formation energy of a compound can be defined in many ways based on the reference chosen for elemental chemical potentials. One way to define the formation energy is based on the binary oxides (bo) of La, Mn and the dopants ($E^D_{f_{bo}}$), since most of the synthesis processes start from these binary oxides. Accordingly, the reaction for the formation of the La-site doped perovskite from the binary oxides of the cations without ($La_{1-a}D_aMnO_3$, $\delta = 0$) and with ($La_{1-a}D_aMnO_{3-\delta}$) an oxygen vacancy is

$$\frac{(1-a)}{2}La_2O_3 + \frac{1}{2}Mn_2O_3 + \frac{a}{y}D_yO_x + \Big(\frac{3a}{4} - \frac{ax}{2y} - \frac{\delta}{2}\Big)O_2 \rightarrow La_{1-a}D_aMnO_{3-\delta} \qquad (2)$$

Here, $\delta = 0$ & $\delta \neq 0$ corresponds to the compounds without and with an oxygen vacancy respectively.

The formation energy of the compound with dopant in the La site ($La_{1-a}D_aMnO_{3-\delta}$) without ($E^{D,\delta=0}_{f_{bo}}$) and with ($E^{D,\delta\neq0}_{f_{bo}}$) an oxygen vacancy is calculated from the energy of its binary oxides as

$$E^{D,\delta}_{f_{bo}} = E^{D,\delta}_{(L,D)MO} - \frac{(1-a)}{2}E_{La_2O_3} - \frac{1}{2}E_{Mn_2O_3} - \frac{a}{y}E_{D_yO_x} - \Big(\frac{3a}{4} - \frac{ax}{2y} - \frac{\delta}{2}\Big)E_{O_2} \qquad (3)$$

where $E_{La_2O_3}$, $E_{Mn_2O_3}$ and $E_{D_yO_x}$ are the total energies of binary oxides of La, Mn and the dopant respectively. $E^{D,\delta}_{(L,D)MO}$ is the total energy of the La-site doped $La_{1-a}D_aMnO_{3-\delta}$ without and with an adjacent O vacancy (depending on the value of δ). E_{O_2} is the total energy of an isolated oxygen molecule. When there is no oxygen vacancy ($\delta = 0$), $E^{D,\delta}_{f_{bo}}$ becomes $E^{D,\delta=0}_{f_{bo}}$ which is the dopant formation energy and $E^{D,\delta=0}_{(L,D)MO}$ is the total energy of the doped LMO without an oxygen vacancy. Similarly, in the presence of an oxygen vacancy ($\delta \neq 0$), $E^{D,\delta}_{f_{bo}}$ becomes $E^{D,\delta\neq0}_{f_{bo}}$ which is the combined formation energy of the dopant with an oxygen vacancy and $E^{D,\delta\neq0}_{(L,D)MO}$ is the total energy of the doped LMO with an oxygen vacancy. Finally the oxygen vacancy formation energy ($E^{D,Ovac}_{f_{bo}}$) in the La-site doped system is found from the difference between the formation energy of the doped compound without and with the oxygen vacancy as

$$E^{Ovac}_{f_{bo}} = E^{D,\delta\neq0}_{f_{bo}} - E^{D,\delta=0}_{f_{bo}} \tag{4}$$

Another way to calculate formation energy is to introduce the chemical potentials (cp) of only the dopant atom and that of the host atom it replaces.[S1] The formation energy ($E^{D,\delta}_{f_{cp}}$) in this case becomes

$$E^{D,\delta=0}_{f_{cp}} = E^{D,\delta=0}_{LMO} - E^{H,\delta=0}_{LMO} - \mu_D + \mu_H \tag{5}$$

where $E^{D,\delta=0}_{(L,D)MO}$ and $E^{H,\delta=0}_{LMO}$ are the total energies of the doped LMO and pure host LMO systems in the absence of an O vacancy. μ_D & μ_H are the chemical potentials of the dopant and the host that is replaced respectively. The chemical potential of the dopant or the host is defined from its binary oxides (DyOx) as

$$\mu_D = \frac{1}{y}\Big(E_{D_yO_x} - \frac{x}{2}E_{O_2}\Big) \tag{6}$$

where $E_{D_yO_x}$ is the total energy of the most stable binary oxide of the host or the dopant.

The dopant formation energy ($E^{D,\delta\neq0}_{f_{cp}}$) with an oxygen vacancy is defined as

$$E^{D,\delta\neq0}_{f_{cp}} = E^{D,\delta\neq0}_{LMO} - E^{H,\delta=0}_{LMO} - \mu_D + \mu_H + \frac{1}{2}\mu_{O_2} \tag{7}$$

where $E^{D,\delta\neq0}_{(L,D)MO}$ is the total energy of the system with an oxygen vacancy and μ_{O_2} is the oxygen chemical potential. The oxygen vacancy formation energy is obtained by the difference in equations 5 and 7, which will becomes exactly equal to the equation 4.

The formation energy of the dopant without and with an oxygen vacancy calculated from binary oxides and chemical potentials are listed in table S2. It should be noted that the difference between the two formation energies (Eqn. 3 & 5) is simply the formation energy of the pure host (LMO) from its binary oxides.

Table S2: Formation Energies of the doped LMO compounds defined from binary oxides and chemical potentials

Dopant	**From binary oxide** (Eqn. 2 with $\delta = 0$ & $\delta \neq 0$)				**From chemical potentials** (Eqn. 4 & 6)			
	$E^{D}_{f_{bo}}$		$E^{D+Ovac}_{f_{bo}}$		$E^{D}_{f_{cp}}$		$E^{D+Ovac}_{f_{cp}}$	
	A-site	**B-site**	**A-site**	**B-site**	**A-site**	**B-site**	**A-site**	**B-site**
K	-0.765	0.056	-0.343	0.330	-0.481	0.340	-0.059	0.614
Ca	-0.479	-0.148	-0.076	0.465	-0.195	0.136	0.208	0.749
Sc	0.194	-0.064	0.340	0.606	0.478	0.220	0.624	0.890
Ti	0.573	0.090	0.824	0.736	0.856	0.374	1.108	1.020
V	0.224	-0.223	0.272	0.434	0.507	0.061	0.556	0.718
Cr	0.135	-0.175	0.432	0.473	0.419	0.108	0.716	0.757
Mn	-0.008	-0.284	0.317	0.399	0.275	0.000	0.601	0.682
Fe	-0.005	-0.245	0.274	0.361	0.279	0.039	0.557	0.645
Co	-0.012	-0.291	0.244	0.301	0.272	-0.007	0.528	0.585
Ni	-0.249	-0.442	-0.019	0.100	0.035	-0.158	0.265	0.384
Cu	-0.352	-0.389	-0.062	0.141	-0.068	-0.105	0.222	0.425

Zn	-0.195	-0.273	0.074	0.262	0.088	0.011	0.358	0.546
Ga	-0.098	-0.127	0.280	0.490	0.186	0.157	0.564	0.774
Ge	0.145	0.076	0.459	0.688	0.429	0.360	0.743	0.972
As	0.158	0.066	0.203	0.585	0.442	0.350	0.487	0.869
Rb	-0.643	0.539	-0.225	0.520	-0.359	0.823	0.059	0.803
Sr	-0.587	0.191	-0.151	0.637	-0.303	0.475	0.133	0.921
Y	-0.041	0.180	0.251	0.820	0.243	0.464	0.535	1.104
Zr	0.609	0.299	0.624	0.981	0.893	0.582	0.908	1.265
Nb	0.930	0.442	0.947	1.117	1.214	0.726	1.231	1.401
Mo	0.555	0.105	0.503	0.820	0.839	0.389	0.787	1.104
Tc	0.773	0.526	0.839	1.099	1.057	0.810	1.123	1.383
Ru	0.299	0.064	0.553	0.592	0.583	0.348	0.837	0.876
Rh	0.146	-0.020	0.329	0.468	0.430	0.264	0.613	0.752
Pd	-0.334	-0.158	-0.095	0.134	-0.051	0.126	0.189	0.418
Ag	-0.584	-0.166	-0.216	0.074	-0.300	0.117	0.068	0.358
Cd	-0.362	-0.104	-0.065	0.264	-0.078	0.180	0.219	0.548
In	-0.165	0.081	-0.053	0.546	0.118	0.365	0.231	0.829
Sn	0.017	0.281	0.391	0.770	0.301	0.565	0.675	1.054
Sb	0.261	0.417	0.469	0.879	0.545	0.700	0.752	1.163
Cs	-0.615	1.144	-0.217	1.554	-0.331	1.428	0.067	1.838
Ba	-0.615	0.866	-0.164	0.750	-0.331	1.150	0.119	1.034
La	-0.284	0.564	0.399	1.037	0.000	0.848	0.682	1.321
Hf	0.713	0.272	0.647	0.958	0.997	0.556	0.931	1.242
Ta	1.129	0.464	1.021	1.143	1.413	0.748	1.305	1.427
W	1.300	0.666	1.075	1.310	1.584	0.950	1.359	1.594

Re	1.059	0.583	0.887	1.152	1.342	0.866	1.171	1.436
Os	0.561	0.168	0.650	0.654	0.845	0.452	0.934	0.937
Ir	0.430	0.099	0.446	0.552	0.714	0.383	0.730	0.836
Pt	0.061	0.119	0.101	0.481	0.345	0.403	0.385	0.765
Au	-0.357	0.101	-0.174	0.081	-0.073	0.385	0.110	0.365
Hg	-0.474	0.098	-0.220	0.143	-0.190	0.382	0.063	0.427
Tl	-0.492	0.249	-0.113	0.402	-0.208	0.533	0.170	0.686
Pb	-0.467	0.300	-0.076	0.526	-0.183	0.584	0.208	0.810
Bi	-0.105	0.434	0.181	0.813	0.179	0.718	0.465	1.096

Correlation between the decomposition and formation energies

We seek to find the correlations between the decomposition energies and the formation energies. We observe an interesting correlation between the formation energy ($E^D_{f_{bo}}$) calculated from the binary oxides and decomposition energy (E^D_d in main article) calculated from the LP approach is (figure S1). The obvious difference between these two energies arises because, in $E^D_{f_{bo}}$ the reference for the elements (La, Mn & Dopant) are always from their binary oxides, whereas the decomposition product in E^D_d always has a fraction of $LaMnO_3$, binary oxide and metallic elements. The balancing coefficients in E^D_d are obtained based on the most thermodynamically favorable products. Therefore, depending on these minimized c_i coefficients, some of the energies are uniformly shifted from the diagonal line for the La and Mn site dopants. This shift is the formation energy of undoped LMO from its binary oxides. However, in the presence of oxygen vacancies there are larger deviations in the formation energy compared to the decomposition energy since the minimized products in E^D_d are very different (refer bubble chart in main article) from that in $E^D_{f_{bo}}$. Since the decomposition energy, E^D_d solves for the most thermodynamically favorable product without any a priori bias on the choice of reaction products, we will employ this for all further analysis.

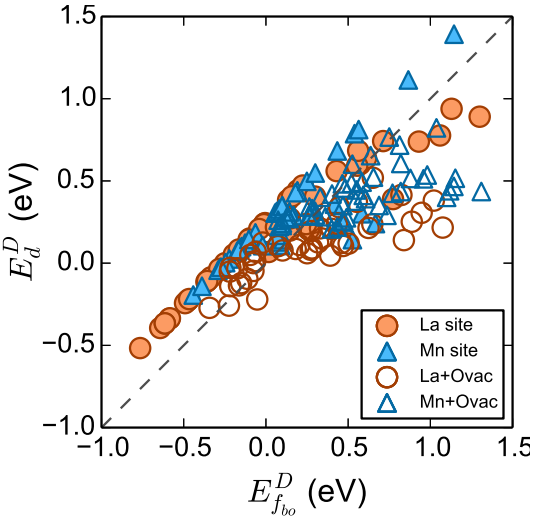

Figure S1: Correlation between the formation energy calculated from binary oxide ($E_{f_{bo}}^D$:Equation 3) and the decomposition energy (E_d^D in main article). The formation energies for the dopant in the La and Mn site without and with the oxygen vacancies are also compared. The dashed gray line represents the line where the x and y values are equal.

Data mining

Principal component analysis (PCA)

The PCA is a powerful dimensionality reduction method which creates principal components from linear combination of the features. The PCA analysis for each site doping reveals correlation between the features. We observe that in both La and Mn site doping cases, the first two principal components accounts for close to 80 % of the variance in the data. The PCA loadings plot is plotted using these two principal components and the correlation of the features is shown figure S2. For the La-site, the OSM and the decomposition energy are highly correlated and the IRM is negatively correlated, whereas in Mn-site cluster, the decomposition energy appears to be weakly correlated to the IRM and the OSM is negatively correlated. In summary, the IRM and OSM are the two mostly correlated features to the the decomposition energy E_d^D.

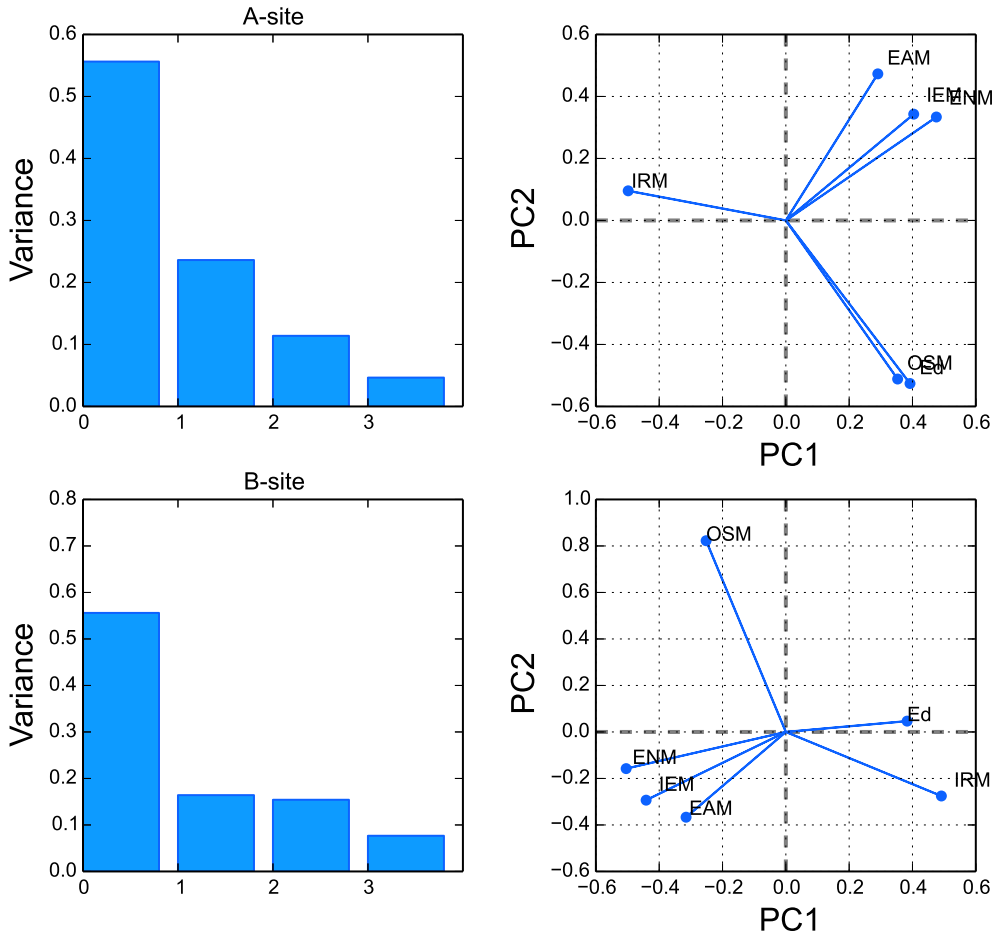

Figure S2: PCA loadings plot for La site and Mn Site dopants in LMO.

References

(S1) Sharma, V.; Pilania, G.; Rossetti, G. A.; Slenes, K.; Ramprasad, R. Comprehensive examination of dopants and defects in $BaTiO_3$ from first principles. *Phys. Rev. B* **2013**, *87*, 134109.