

Cationic surface segregation in doped LaMnO_3 : A first principles thermodynamics study

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Background

- $(\text{La},\text{M})\text{MnO}_3$ and $(\text{La},\text{M})\text{CoO}_3$ are commonly found in several catalytic and electrochemical devices, for example, as cathodes in solid oxide fuel cells (SOFCs).¹
- Under the prevailing oxygen-rich and moisture-rich conditions that such oxides encounter in typical SOFCs, preferential segregation of the M atoms to the surfaces is commonly observed.
- This surface segregation is detrimental to the overall performance as it leads to reduced oxygen reduction activity and cathode stability.
- The surface cation chemistry in $(\text{La},\text{A})\text{MnO}_3$ ($A = \text{Ca}, \text{Sr}$ and Ba) has been studied using first-principles thermodynamics.²
- Over a range of temperature-pressure conditions, the effect of different chemical environments (presence of O_2 and water vapor reservoirs) is explored.^{2,3}

Model Details

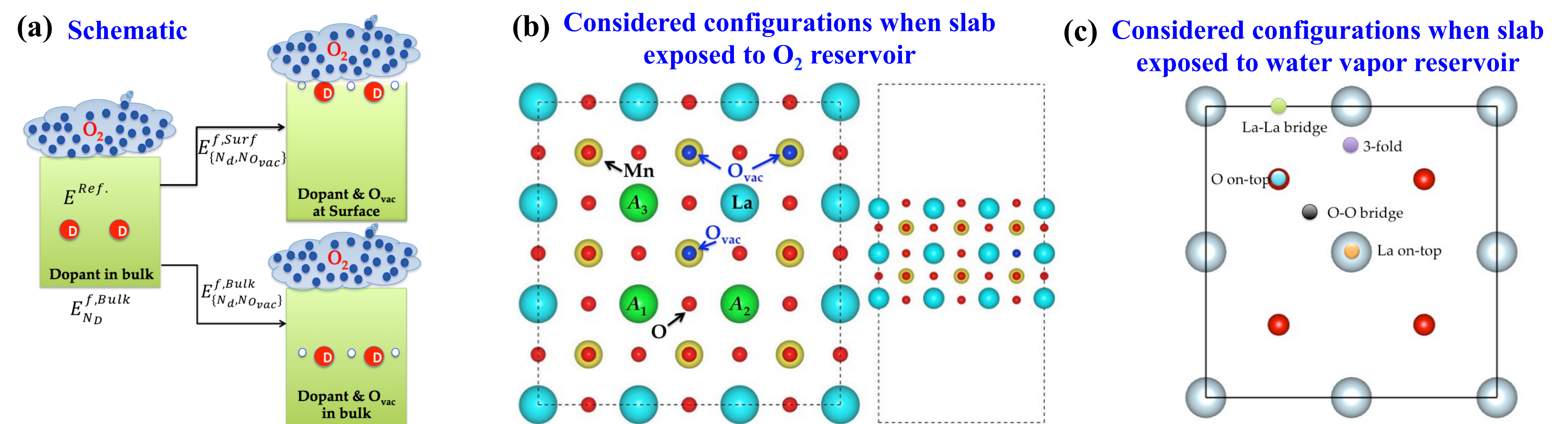


Fig 1: (a) Schematic representation of the surface segregation of dopants in $(\text{La},\text{A})\text{O}$ terminated ($A = \text{Ca}, \text{Sr}$ and Ba) slab exposed to pure O_2 reservoir. (b) Top-view and side-view of the $(\text{La},\text{A})\text{O}$ terminated (001) surface model. Several possible bulk and surface configurations with two dopants at a time along with a range of O vacancies starting from 0 to 3 are considered. (c) Top-view of the LaO-terminated surface model used in the present study. Host atoms La and O are shown as silver and red spheres, respectively. The various initial positions of water molecule relative to the LaO-terminated surface are also marked.

Computational Methods

- Density Functional Theory (DFT) as implemented in VASP was used.
- The fully relaxed bulk structure of LaMnO_3 is used to construct the $(\text{La})\text{O}$ -terminated surfaces (001).
- The slab model was $\sim 16 \text{ \AA}$ thick and contains 5 atomic symmetric layers, in which the bottom three atomic layers were always fixed at their respective bulk positions in the cubic perovskite phase.
- Using a $4 \times 4 \times 1$ Monkhorst-Pack k-point mesh, all other substrate atoms were allowed to fully relax until the absolute value of all corresponding forces dropped below 0.05 eV/\AA .
- Only doped LaO-terminated (001) surfaces are considered as they are more stable as compare to MnO_2 -terminated (001) surface.

Choice of Dopants

- Dopant selection was made by exploring the underlying physicochemical trends pertaining to dopants across the Periodic Table.⁴
- We considered the $3d$, $4d$, and $5d$ transition metals along with the neighboring IA through VA Group elements in our study.
- It is found that Group I A and II A dopants prefer to be substituted at the La site.
- Preliminary analysis suggests, that the stability and the location of a dopant is mainly governed by the mismatch of the ionic size and oxidation state of the dopant with respect to the host atom.

First Principles Thermodynamics

Formation energy is defined as

$$E_{\{n_D, n_{O_{vac}}\}}^{f, Surf/Bulk} = (E_{\{n_D, n_{O_{vac}}\}}^{Surf/Bulk} - E_{\{n_D, n_{O_{vac}}=0\}}^{Bulk}) + \frac{n_{O_{vac}}}{2} \mu_{\text{O}_2}$$

The chemical potential of O_2 is defined as

$$\mu_{\text{O}_2}(T, P_{\text{O}_2}) = E_{\text{O}_2}^{DFT} + \Delta \mu_{\text{O}_2}(T, P_{\text{O}_2})$$

$$\Delta \mu_{\text{O}_2}(T, P_{\text{O}_2}) = E_{\text{O}_2}^{DFT} + E_{\text{O}_2}^{ZPE} + \Delta \mu'_{\text{O}_2}(T, P_{\text{O}_2}) + kT \ln(P_{\text{O}_2}/P_0)$$

$$\Delta \mu'_{\text{O}_2}(T, P_{\text{O}_2}) = kT \ln \left(\frac{P_0}{\left(\frac{2\pi m k T}{h^2} \right)^{1.5}} - kT \ln \frac{T}{2\theta_t} + kT \ln(1 - e^{-\theta_v/T}) - kT \ln 3 \right)$$

Translational Rotational Vibrational Electronic

Cationic surface segregation under oxygen environment

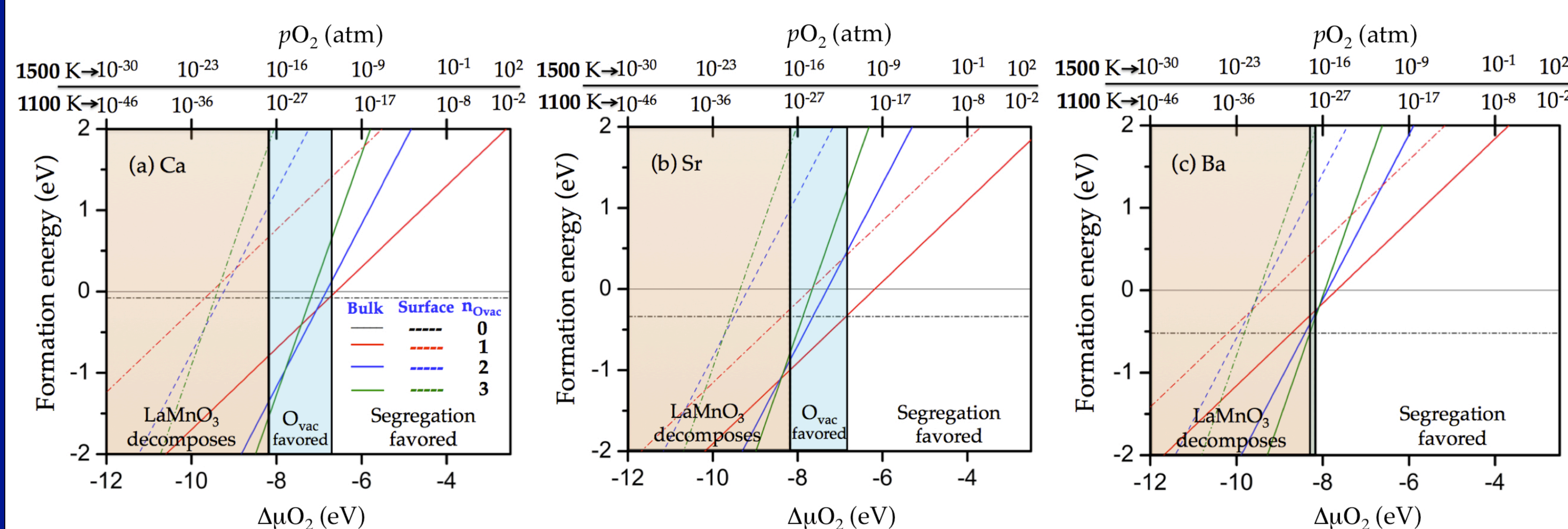


Fig 2: The formation energies of $(\text{La},\text{A})\text{MnO}_3$, where A is (a) Ca, (b) Sr, and (c) Ba, and $n_{\text{O}_{vac}}$ O vacancies at the surface or the bulk as a function of the O_2 chemical potential. The lines at zero represent the energies of the system with two dopants in bulk, Bulk and considered as a reference line. To capture the SOFCs operating conditions, the dependence of chemical potential of O_2 in the gas phase is translated into the pressure scales at 1100 K and 1500 K. The shaded part represents the regions, where host material decomposes (orange), favored the formation of $n_{\text{O}_{vac}}$ (blue) and segregates towards the surface (white).²

Key findings

- The dependence of our surface segregation energy results and trends on the type of dopant, is studied using first principles thermodynamics.
- At prevailing oxygen pressures that SOFC systems encounter, such as $1-10^{-6}$ atm (for both choices of T), surface segregation (devoid of O vacancies) is indeed favored.²
- It is only at rather low O_2 pressures and/or high T that the segregation behavior is suppressed, but this regime comes close to conditions that favor decomposition of LaMnO_3 .²
- These findings are consistent with recent experimental observations indicating that the extent of dopant segregation was largest at ~ 1 atm which decreases with decreasing oxygen pressure ($\sim 10^{-12}$ atm) at 1100 K.⁵
- Based on this thermodynamic analysis, it can be concluded that surface segregation of dopants in $(\text{La},\text{A})\text{MnO}_3$ (when exposed to O_2) is an inevitable consequence of thermodynamics.²

Acknowledgments

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Conclusions

(a) Dopant selection

- The stability and the site preference are mainly dominated by the mismatch of the ionic size and oxidation state of the dopant with respect to the host atom.

(b) Surface in contact with O_2 reservoir

- Surface remains significantly enriched with dopants under all realistic conditions.
- Over a wide range of T - p_{O_2} conditions the cation surface segregation is favored.
- Under low O_2 pressures and/or high T that the segregation behavior is suppressed.
- With increasing dopant size the tendency for cation surface segregation increases.

(c) Future directions

- Preliminary results indicate that in the presence of moisture, the surface is predicted to be covered with dissociated water species.
- Effect of water on cation segregation and role of oxygen vacancies is under investigation.
- Understanding of the other factors/chemical environments that lead to segregation and consequent degradation (e.g., in the presence of CO_2).

References

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