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Dopant effects on thermodynamic stability and oxygen vacancy formation in CaMnO_3 perovskites for chemical-looping combustion

Jonatan Gastaldi^{a,*}, Alfred Juhlin Onbeck^a, Joakim Brorsson^b, Anders Hellman^{b,c}, Tobias Mattisson^a

^a Department of Environmental and Energy Sciences, Division of Energy Technology, Chalmers University of Technology, Chalmersplatsen 4, Gothenburg SE-41296, Sweden

^b Department Physics, Division of Chemical Physics, Chalmers University of Technology, Chalmersplatsen 4, Gothenburg SE-41296, Sweden

^c Competence Centre for Catalysis, Chalmers University of Technology, Chalmersplatsen 4, Gothenburg SE-41296, Sweden

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ABSTRACT

The thermodynamic properties and phase stability of doped $\text{CaMnO}_{3-\delta}$ perovskites have been investigated over a range of oxygen non-stoichiometry (δ), from 1/16 to 6/16, to assess their suitability as oxygen carriers for chemical-looping combustion. The computational framework combines machine-learning interatomic potentials for structural relaxation, cluster expansions for configurational energetics, phonon calculations for vibrational contributions, and Monte Carlo simulations for configurational entropy. Doping was explored at the A-site (Ce, Sr, La, Bi) and B-site (Ti, Fe, Si, Cr, Cu, Mo, Mg) at substitution levels ranging from 1/16 to 6/16. Phase stability was evaluated using multi-component equilibrium calculations based on thermodynamic data derived from the calculated enthalpy, entropy, and heat capacity. Ce and Sr (A-site), Fe and Ti (B-site), were identified as promising dopants. Ce and Ti enhanced the overall thermodynamic stability of CaMnO_3 , whereas Fe and Sr promoted oxygen vacancy formation, reflecting a trade-off between reducibility and thermodynamic stability. Where experimental data is available, these trends show good agreement with previously reported studies. These results demonstrate that targeted doping enables systematic tuning of thermodynamic behavior in CaMnO_3 -based perovskites, providing guidance for balancing thermodynamic stability and oxygen release in chemical-looping applications.

1. Introduction

Chemical-looping combustion (CLC) has emerged as a promising technology for energy conversion with inherent CO_2 capture. In this process, a solid oxygen carrier transfers oxygen between fuel and air reactors, enabling combustion without direct contact between the fuel and air streams [1]. The performance and efficiency of chemical-looping systems, therefore, depend strongly on the thermodynamic stability, oxygen transport capacity, and redox behavior of the oxygen carrier material [2].

Perovskite oxides have attracted considerable attention as oxygen carriers because their structural and compositional flexibility enables reversible changes in oxygen content [3–6]. $\text{CaMnO}_{3-\delta}$ is particularly interesting because it combines relatively inexpensive constituent elements with substantial oxygen non-stoichiometry and favorable redox thermodynamics, experimental studies have quantified its oxygen non-

stoichiometry, oxidation enthalpy, and reductive decomposition behavior [7–10].

The applicability of CaMnO_3 -based materials to chemical looping has subsequently been demonstrated under several operating conditions. Low-cost $\text{CaMnO}_{3-\delta}$ materials have shown useful oxygen-carrier behavior [10], while Ti-substituted CaMnO_3 has been evaluated in both batch and continuously operated fluidized-bed reactors [11,12]. Spray-dried materials containing Ti, Fe, or Mg have also been investigated for CLC and CLOU [13], and Mg-containing compositions have been tested in a 10 kWth chemical-looping unit [14]. Other studies have examined sulfur tolerance [15,16], the microstructural stability of Fe- and Ti-containing compositions during redox operation [17], and the reactivity of Mg-containing materials for H_2 production in CLC conditions [18] and the reduction and oxidation kinetics in CLC [19]. The Mg studies cited here do not establish the extent of Mg incorporation on the Mn site. We therefore investigate B-site Mg substitution as an

* Corresponding author.

E-mail address: gastaldi@chalmers.se (J. Gastaldi).

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exploratory model, while recognizing that the experimental materials may contain secondary phases and differ from the modeled compositions. These experimental results, nonetheless, demonstrate the potential of CaMnO_3 -based oxygen carriers, while also showing that phase composition, reactivity, and cycling stability depend strongly on the selected dopant and operating conditions.

Cation substitution provides a means of modifying the behavior of CaMnO_3 -based oxygen carriers. Changes on the A- or B-site can affect oxygen-vacancy formation, lattice-oxygen transport, electronic properties, and redox thermodynamics [20–22]. Experimental screening has considered several B-site dopants, including Al, V, Fe, Co, and Ni [23], while more recent studies have investigated A- and B-site substitution for controlling the electrical, thermoelectric, and thermochemical properties of CaMnO_3 [24,25]. These studies show that dopant substitution can substantially alter material behavior, but no single dopant improves all properties relevant to chemical-looping operation.

At the atomistic level, first-principles studies have examined oxygen-vacancy formation in pristine CaMnO_3 , including the effects of strain and vacancy concentration [26,27]. DFT calculations have also been used to investigate selected dopants and their associated defect-compensation mechanisms [28,29]. These studies have generally considered a limited number of dopants, concentrations, or defect configurations. Systematic comparisons that combine extensive configurational sampling with vibrational and configurational contributions and competing phase stability under conditions which are relevant to CLC remain scarce.

Direct DFT calculations become computationally demanding when large supercells and numerous dopant and oxygen-vacancy arrangements must be relaxed and evaluated. The present framework addresses this limitation by using CHGNet to efficiently evaluate a broader configurational space, cluster expansions and Monte Carlo simulations to describe configurational effects, and thermodynamic modeling to assess temperature-dependent and competing-phase stability. This enables a consistent comparison of multiple A- and B-site dopants across a range of concentrations and oxygen-deficiency levels. Machine-learning interatomic potentials trained on first-principles data have emerged as a promising approach for bridging the gap between accuracy and computational efficiency [28–32]. CHGNet [33] is a graph-neural-network, which is trained on large datasets of DFT calculations and predicts energies, forces, and structural properties of solid materials [34]. By enabling simulations of larger supercells and more extensive configurational sampling than is typically feasible with DFT, these models provide new opportunities to study doped materials and defect chemistry. More recently, computational methods have also been used to identify promising oxygen carriers. For example, autonomous active-learning approaches have been applied to discover high-entropy perovskite compositions with potential for chemical-looping applications [35,36].

In this work, the effects of cation substitution in CaMnO_3 have been investigated using CHGNet with a particular focus on how different dopant chemistries affect material properties. Dopants were introduced on both the A-site (Ce, Sr, La, and Bi) and the B-site (Ti, Fe, Si, Cr, Cu, Mo, and Mg) in order to explore how different substitution chemistries influence the structural stability and defect energetics of the material. Several substitution concentrations were considered using supercell models to evaluate trends in dopant behavior while maintaining realistic substitution levels. The results provide insights into how cation substitution modifies the thermodynamic properties of CaMnO_3 and contribute to a better understanding of doped perovskite oxygen carriers for chemical-looping applications.

The results are organized to systematically examine the structural and thermodynamic effects of dopant substitution in CaMnO_3 . First, the structural stability of the doped systems is evaluated based on the calculated ground-state configurations. Next, thermodynamic properties, including formation enthalpy and heat capacity, are analyzed to assess the impact of cation substitution on the energetics of the

perovskite structure. Particular attention is given to oxygen vacancy formation, which plays a central role in determining the redox behavior of CaMnO_3 -based oxygen carriers. The phase stability of doped $\text{CaMnO}_{3-\delta}$ is subsequently evaluated as a function of temperature and oxygen partial pressure. Finally, the implications of these results for CLC applications are discussed.

2. Methodology

The thermodynamic properties of doped $\text{CaMnO}_{3-\delta}$ were evaluated using a computational framework combining machine-learning interatomic potentials, configurational sampling techniques, and thermodynamic modeling. Structural relaxations and energy evaluations were performed using the CHGNet machine-learning potential [33], enabling efficient exploration of the large configurational spaces associated with dopant substitution and oxygen vacancy formation. Cluster expansion (CE) models were employed to describe the configurational energetics of doped systems and to identify ground-state structures across a range of compositions. Vibrational and configurational contributions to thermodynamic quantities were subsequently evaluated using lattice dynamics calculations and Monte Carlo simulations. Finally, the calculated reaction energetics were combined with experimentally tabulated thermochemical data to estimate temperature-dependent thermodynamic properties and phase stability of doped $\text{CaMnO}_{3-\delta}$ under varying oxygen partial pressures. The overall workflow is shown in Fig. 1.

2.1. Computational framework

An approach determining the thermodynamic properties of stoichiometric systems, originally presented by Brorsson et al. [37], was recently generalized by Gastaldi et al. [38] in order to account for the presence of oxygen vacancies. This work further extends this computational framework by considering doped perovskites. Chemical reactions were formulated, using binary metal oxides as reference compounds. These reference compounds provide the thermodynamic basis for calculating the properties of the mixed-metal oxides and enable comparison with experimental thermodynamic data. The corresponding reactions are presented in Table 1. These were selected based on the availability of reliable thermochemical data and their chemical similarity to the target compounds. In cases where sufficient thermodynamic reference data were not available to balance the reaction, molecular oxygen was included to maintain stoichiometric consistency. This adjustment was required for dopants La, Bi, and Mg.

Ground-state crystal structures were obtained primarily from the Materials Project database [39]. For systems not directly available in the database, including doped structures and configurations containing oxygen vacancies, candidate configurations were generated from the pristine CaMnO_3 ground state using atomic cluster expansions, as implemented in the ICET package [40]. Specifically, this method allows the dependence of the energy on the specific arrangement of dopants and oxygen vacancies within the crystal to be determined, thereby enabling efficient screening of large numbers of configurations that would be computationally infeasible to evaluate individually. The pristine CaMnO_3 structure was considered in its orthorhombic perovskite form, which is the most stable phase from room temperature up to at least 900 °C [41,42].

The generated configurations were relaxed using CHGNet with the BFGS optimizer. Both atomic positions and cell parameters were optimized until the maximum residual force was below 0.001 eV Å⁻¹. All calculations were performed using charge neutral periodic cells. Atomic charges and formal oxidation states were not specified as input. CHGNet implicitly accounts for charge-state-dependent effects on the local environments and calculated energetics. However, formal oxidation states and the associated charge-compensation pathways were not explicitly determined or analyzed in the present work. The present study therefore evaluates dopant compatibility through structural and thermodynamic

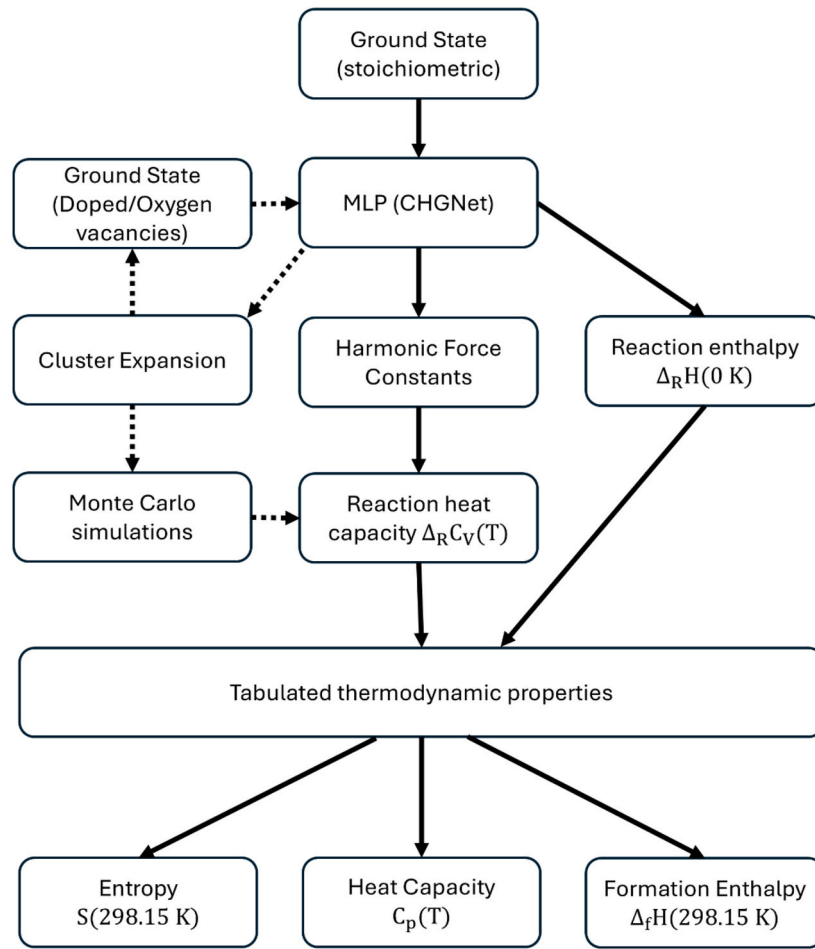


Fig. 1. Methodology framework describing the steps used to determine the ground state of a stoichiometric material, optimize the structure and calculate the thermodynamic properties.

Table 1
Chemical reactions used in thermodynamic estimations

Dopant (Site)	Chemical reaction
Ce (A)	$Ca_{1-x}Ce_xMnO_{3-\delta} + xCeO_2 + (2-3\delta)MnO = (1-x)CaO + (1-\delta)Mn_3O_4 + xCe_2O_3$
Sr (A)	$Ca_{1-x}Sr_xMnO_{3-\delta} + (2-3\delta)MnO = (1-x)CaO + (1-\delta)Mn_3O_4 + xSrO$
La (A)	$Ca_{1-x}La_xMnO_{3-\delta} + \frac{x}{4}O_2 + (2-3\delta)MnO = (1-x)CaO + (1-\delta)Mn_3O_4 + \frac{x}{2}La_2O_3$
Bi (A)	$Bi_xCa_{1-x}MnO_{3-\delta} + \frac{x}{4}O_2 + (2-3\delta)MnO = (1-x)CaO + (1-\delta)Mn_3O_4 + \frac{x}{2}Bi_2O_3$
Ti (B)	$CaMn_{1-x}Ti_xO_{3-\delta} + (2-2x-3\delta)MnO = CaO + (1-x-\delta)Mn_3O_4 + xTiO_2$
Fe (B)	$CaFe_xMn_{1-x}O_{3-\delta} + xFeO + (2-2x-3\delta)MnO = CaO + (1-x-\delta)Mn_3O_4 + xFe_2O_3$
Si (B)	$CaMn_{1-x}Si_xO_{3-\delta} + (2-2x-3\delta)MnO = CaO + (1-x-\delta)Mn_3O_4 + xSiO_2$
Cr (B)	$CaCr_xMn_{1-x}O_{3-\delta} + (2-2x-3\delta)MnO = CaO + (1-x-\delta)Mn_3O_4 + xCrO_2$
Cu (B)	$CaCu_xMn_{1-x}O_{3-\delta} + xCu_2O + (2-2x-3\delta)MnO = CaO + (1-x-\delta)Mn_3O_4 + 3xCuO$
Mo (B)	$CaMn_{1-x}Mo_xO_{3-\delta} + (2-2x-3\delta)MnO = CaO + (1-x-\delta)Mn_3O_4 + xMoO_2$
Mg (B)	$CaMg_xMn_{1-x}O_{3-\delta} + (2-2x-3\delta)MnO = CaO + (1-x-\delta)Mn_3O_4 + xMgO$

properties rather than through explicit electronic-structure or charge-

compensation analysis.

The pretrained CHGNet model has reported mean absolute errors of 30 meV atom⁻¹ for energy, 77 meV Å⁻¹ for forces, and 0.348 GPa for stress on its test dataset [33]. To estimate the applicability of CHGNet to the investigated systems, representative calculations were compared with DFT for undoped, Ti-doped, and Sr-doped CaMnO₃ with $\delta = 0, 0.125, 0.375$. The same Materials Project-compatible energy convention was used for both methods. Across the nine structures, the CHGNet energies gave an MAE of 17.5 meV atom⁻¹ and an RMSE of 21.4 meV atom⁻¹ relative to DFT. The positional RMSDs between the CHGNet- and DFT-relaxed structures ranged from 0.013 to 0.078 Å. Differences in cell volume and individual lattice parameters remained below 0.68% and 0.53%, respectively. The largest energy deviations, approximately 32–34 meV atom⁻¹, occurred for the strongly reduced doped structures. Taken together, the good agreement in energies, atomic positions, and cell parameters indicates that CHGNet provides sufficient accuracy for the comparative screening of dopant and oxygen-vacancy trends performed in this study. The complete data of this validation is provided in [Tables S1–3 in the SI](#).

The resulting energies from the relaxations were used to train CE models describing the configurational energetics of doped CaMnO₃ systems. Ground-state configurations were subsequently identified from the optimized CE models.

Reaction enthalpies at 0 K were obtained from the calculated ground-state energies. Vibrational contributions at finite temperatures were included by computing harmonic force constants using the HiPhive package [43], from which phonon properties and harmonic heat capacities were obtained with Phonopy [44].

The phonon density of states (DOS) describes the distribution of vibrational modes as a function of frequency and is used to compute vibrational contributions to thermodynamic properties. The reaction heat capacity, $\Delta_R C_V$, was computed from the vibrational properties of the compound and the reference oxides.

Configurational thermodynamic properties were evaluated using the MCHAMMER module of the ICET package [40]. Simulations were carried out in the canonical ensemble (NVT) using supercells containing 480 atoms (including vacancies), with 8,000 Monte Carlo cycles, with each cycle consisting of a number of trial steps equal to the number of sites in the supercell. The first 2,000 cycles were discarded for equilibration, and thermodynamic averages were evaluated over the remaining 6,000 cycles. Monte Carlo simulations were performed between 0 and 2000 K at intervals of 100 K. Statistical uncertainties were estimated using the MCHAMMER data analysis procedure, which accounts for autocorrelation between successive Monte Carlo samples through estimation of the correlation length.

To ensure consistency with experimentally reported thermochemical data, calculated thermodynamic quantities were adjusted using experimental reference data for binary oxides obtained from the NIST-JANAF thermochemical tables [45]. For oxides not available in the JANAF database, thermochemical data were taken either from the FactSage databases (FToxid, FactPS) [46], which were required for Bi_2O_3 , Ce_2O_3 , CeO_2 , and La_2O_3 , or from other literature sources, as in the case of MnO [47] and Mn_3O_4 [48]. To ensure consistency between calculated formation energies and experimental thermodynamic data in the FactSage database, a common correction of -45 kJ mol^{-1} per CaMnO_3 formula unit was applied to align the calculated CaMnO_3 reference with the experimental formation enthalpy. The effects of dopant concentration and oxygen non-stoichiometry were included through the balanced reference reactions, for which the amounts of the corresponding oxides and oxygen vary with composition. Separate empirical corrections were not fitted for each dopant or value of δ because suitable experimental reference data are unavailable. This correction ensures consistency between the calculated and experimental reference states. Because it is applied consistently, it does not affect relative trends between dopants or the relative energy ordering of vacancy arrangements with the same composition.

2.2. Doping strategy

Because of the orthorhombic crystal symmetry of CaMnO_3 , the smallest computational unit cell is $\text{Ca}_4\text{Mn}_4\text{O}_{12}$. To investigate a range of dopant concentrations while avoiding unrealistically high substitution levels, a $2 \times 2 \times 1$ supercell was constructed, yielding the composition $\text{Ca}_{16}\text{Mn}_{16}\text{O}_{48}$. Substitution of one cation in this supercell corresponds to a dopant concentration of 6.25%, enabling several concentrations to be investigated without requiring prohibitively large configurational searches. In particular, the supercell represents the commonly investigated concentrations of 12.5% and 25% exactly, allowing direct comparison with previous experimental and computational studies.

The selection of dopant elements was guided by a combination of experimental knowledge and theoretical screening based on the Bartel tolerance factor, τ , and charge considerations, see Fig. S1 in the Supplementary information (SI). Oxygen carrier materials based on a wide range of metals, such as Mg, Al, Ca, Mn, Fe, Cu, Ni, and Ti, have been extensively studied experimentally, investigated both as single oxides (e.g., CuO [49,50], Fe_2O_3 [51]) and in multicomponent systems such as CaMnO_3 [52,53] and more complex compositions (e.g., Mn–Cu–Mg–Fe–Ti–O systems [54]).

Experimental studies under CLC/CLOU conditions exist for Sr-substituted CaMnO_3 on the A-site [55] and for Ti-, Fe-substituted CaMnO_3 on the B-site, and Mg-containing materials [3,11–13,18,19,23,56]. La-, Ce-, Bi-, Cr-, Cu-, Mo-, and Si-substituted CaMnO_3 materials have also been studied experimentally, primarily for structural, magnetic, electronic, or thermoelectric applications

[57–64]. While this shows that they can be prepared, it does not establish their stability under repeated CLC redox cycling.

Based on this experimental background, the suitability of potential dopants for substitution at the A- and B-sites of CaMnO_3 was evaluated using τ , as shown in the Supplementary Information. The value of τ provides a measure of the geometric compatibility of ions within the perovskite structure, with values of τ below 4.18 generally indicating compatibility with perovskite formation [65]. While this threshold was originally developed for ABX_3 compounds, where it achieves an accuracy of approximately 92%, it has also been shown to perform well for related systems such as double perovskites (A_2BBX_6), with an accuracy of around 91%. This suggests that the model remains applicable for the present study, even if some limitations may exist for doped structures.

In addition to geometric considerations, charge differences between the dopants and the host Ca and Mn ions were evaluated as an additional measure of the chemical plausibility of substitution. The value of τ was calculated according to

$$\tau = \frac{r_O}{r_B} - n_A \left(n_A - \frac{r_A/r_B}{\ln(r_A/r_B)} \right)$$

where r_A and r_B are the ionic radii of the A- and B-site cations, respectively, and $r_O = 1.40 \text{ \AA}$ is the ionic radius of oxygen. Ionic radii were obtained from the Shannon database [66].

For each dopant, site preference was assessed based on three criteria:

- Oxidation state, selecting the state with the smallest charge mismatch relative to the host cation;
- Coordination number, using 12-fold coordination for the A-site and 6-fold for the B-site;
- Spin state, where applicable, which meant selecting the configuration that yielded the lower tolerance factor. For example, Cr^{2+} yields $\tau = 4.196$ in the high-spin state but $\tau = 4.178$ in the low-spin state, bringing it below the stability threshold.

The theoretical screening generally aligns with systems reported in experimental literature but also identifies additional candidate dopants that may be of interest. The final selection therefore includes both experimentally established elements and those predicted to be promising based on tolerance factor. Thus, our ambition was to perform a comprehensive computational screening with the objective of identifying promising dopants.

The selected dopants have different levels of experimental precedent. Sr-substituted CaMnO_3 and Ti-, Fe-, and Mg-containing calcium manganite materials have previously been investigated as CLC or CLOU oxygen carriers. For Mg, the studies cited here do not establish the extent of incorporation on the Mn site, and some report a separate MgO phase. These studies motivate investigating Mg-containing compositions, while B-site Mg substitution is treated here as an exploratory model. The preliminary Bartel tolerance-factor assessment supported its inclusion in the screening but does not establish site occupancy or synthesis feasibility. Moreover, Mg^{2+} substitution on nominal Mn^{4+} sites introduces a valence mismatch, motivating investigation of the associated oxygen-deficient compositions where the Mg^{2+} might be accommodated more easily than in the fully oxidized structure. Several other substitutions have primarily been synthesized for thermoelectric, magnetic, or structural studies. Their incorporation in CaMnO_3 under those conditions does not necessarily establish stability under repeated CLC redox cycling. The present screening therefore examines their thermodynamic potential without assuming that all investigated compositions are equally synthesizable or resistant to dividing into multiple new phases during operating conditions.

It should be noted that τ was evaluated using the ideal cubic perovskite structure of CaMnO_3 , whereas the thermodynamic calculations were performed for the orthorhombic structure. This choice was motivated by the observation that applying the tolerance factor directly

to the orthorhombic structure yielded unrealistic predictions. The primary difference between these structures lies in the coordination environment of the Ca ion: in the cubic phase, Ca is 12-fold coordinated, while in the orthorhombic phase, it is 8-fold coordinated. This leads to a significant change in the effective ionic radius of Ca^{2+} (from 1.12 Å for CN = 8 to 1.34 Å for CN = 12), which strongly influences the calculated tolerance factor.

Dopant elements were introduced either on the A-site (Ce, Sr, La, Bi) or on the B-site (Ti, Fe, Si, Cr, Cu, Mo, Mg). For each dopant and concentration, symmetrically distinct substitution configurations were generated and subsequently evaluated within the computational framework described above. A summary of the simulated systems and dopants is given in Table 1.

2.3. Cluster expansion (CE)

CE models were constructed to describe the configurational energetics associated with dopant substitution and oxygen vacancy formation in CaMnO_3 .

Training structures for doped systems were generated using the structure annealing method implemented in the ICET package [40], yielding a set of 400 configurations. The sampling procedure was biased toward higher-entropy configurations, resulting in a larger representation of structures at higher dopant concentrations, reflecting their greater configurational space. All generated configurations were relaxed using CHGNet, and the resulting energies were used to train CE models within the ICET framework. Pair interaction cutoffs of approximately 7.0 Å and triplet cutoffs of approximately 5.4 Å were typically employed. For certain dopants, these values were slightly reduced to improve the numerical stability of the regression procedure used for training the CE model.

For systems containing oxygen vacancies, the ground-state structures obtained for the doped compositions were used as primitive cells from which vacancy configurations were generated. A set of 300 vacancy-containing structures was sampled for each system. The introduction of oxygen vacancies significantly reduced the symmetry of the structures, often lowering the crystal class from orthorhombic to triclinic. Consequently, shorter cutoff distances were required in the CE models, with typical values ranging from 4.5 to 3.5 Å for pair interactions and 2.5–1.5 Å for triplets.

CE models were trained using automatic relevance determination regression (ARDR), with the regularization parameter optimized through a line-scan procedure. Ground-state configurations were subsequently identified using the GroundStateFinder module in ICET, which employs mixed-integer programming to determine the lowest-energy configurations [40]. The identified ground-state structures were subsequently relaxed and evaluated using CHGNet. The final energies used in the thermodynamic analysis were therefore obtained using the same energy model for all systems, rather than being compared directly between different CE models.

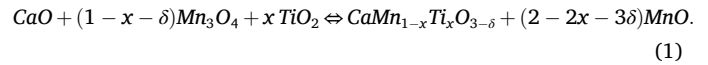
In a small number of cases, loss of symmetry or incompatible sublattice definitions led to poorly conditioned fitting problems, resulting in unstable CE models. This indicates that reliable model parameters could not be obtained. These systems (specifically, Si doping with vacancies and Fe doping at 2/16 concentration) were therefore excluded from further analysis.

2.4. Thermodynamic analysis

The thermodynamic properties of doped CaMnO_3 were estimated using a reaction-based thermodynamic framework developed by Brorsen et al. [37], in which the compound is expressed as a combination of binary oxides with known experimental thermodynamic data to estimate the entropy, $S(298.15\text{ K})$, the formation enthalpy, $\Delta_f H(298.15\text{ K})$, and the heat capacity $C_p(T)$.

Chemical reactions representing the formation of the doped CaMnO_3

phases from binary oxides were defined. An example reaction for CaMnO_3 doped with Ti is shown in Eq. (1). The full set of reactions used in this work is listed in Table 1.



where x represents the doping concentration and δ represents the oxygen non-stoichiometry.

The reaction heat capacity at constant volume was calculated as

$$\Delta_R C_V = C_{V,\text{CaMn}_{1-x}\text{Ti}_x\text{O}_{3-\delta}} - (C_{V,\text{CaO}} + (1 - x - \delta)C_{V,\text{Mn}_3\text{O}_4} + xC_{V,\text{TiO}_2} - (2 - 2x - 3\delta)C_{V,\text{MnO}}). \quad (2)$$

The reaction enthalpy at 0 K was approximated from the change in internal energy obtained from CHGNet-relaxed structures, assuming that the volume contribution is negligible at 0 K:

$$\begin{aligned} \Delta_R H^{0\text{ K}} &= \Delta_R U^{0\text{ K}} + P\Delta_R V^{0\text{ K}} \approx \Delta_R U^{0\text{ K}} \\ &= U_{\text{CaMn}_{1-x}\text{Ti}_x\text{O}_{3-\delta}}^{0\text{ K}} \\ &- \left(U_{\text{CaO}}^{0\text{ K}} + (1 - x - \delta)U_{\text{Mn}_3\text{O}_4}^{0\text{ K}} + xU_{\text{TiO}_2}^{0\text{ K}} - (2 - 2x - 3\delta)U_{\text{MnO}}^{0\text{ K}} \right). \end{aligned} \quad (3)$$

The reaction enthalpy and entropy at 298.15 K were estimated using

$$\Delta_R H^{298.15\text{ K}} \approx \Delta_R H^{0\text{ K}} + \int_0^{298.15} \Delta_R C_V dT, \quad (4)$$

$$\Delta_R S^{298.15\text{ K}} = \Delta_R S^{0\text{ K}} + \int_0^{298.15} \frac{\Delta_R C_V}{T} dT. \quad (5)$$

In Eq. (5) the entropy at 0 K is estimated to be equal to 0, $\Delta_R S^{0\text{ K}} = 0$. As explained in Section 2.1, experimental thermodynamic data, $\Delta_f H_x^{298.15\text{ K}}$ and $S_x^{298.15\text{ K}}$, for the binary oxides were taken from the NIST-JANAF tables, FactSage databases, or other literary sources and used to estimate the formation enthalpy and entropy of the doped and non-stoichiometric material.

$$\begin{aligned} \Delta_f H^{298.15\text{ K}} &= \Delta_R H^{298.15\text{ K}} + \Delta_f H_{\text{CaO}}^{298.15\text{ K}} \\ &+ (1 - x - \delta)\Delta_f H_{\text{Mn}_3\text{O}_4}^{298.15\text{ K}} + x\Delta_f H_{\text{TiO}_2}^{298.15\text{ K}} \\ &- (2 - 2x - 3\delta)\Delta_f H_{\text{MnO}}^{298.15\text{ K}} \end{aligned} \quad (6)$$

$$\begin{aligned} S^{298.15\text{ K}} &= \Delta_R S^{298.15\text{ K}} + S_{\text{CaO}}^{298.15\text{ K}} \\ &+ (1 - x)S_{\text{Mn}_3\text{O}_4}^{298.15\text{ K}} + xS_{\text{TiO}_2}^{298.15\text{ K}} \\ &- 2(1 - x)S_{\text{MnO}}^{298.15\text{ K}} \end{aligned} \quad (7)$$

The heat capacity of the compound (C_p) was extended to higher temperatures by equating two expressions for the enthalpy of formation,

$$\Delta_f H^T = \Delta_f H^{0\text{ K}} + \int_0^T C_p dT' \quad (8)$$

$$\begin{aligned} \Delta_f H^T &\approx \Delta_R H^{0\text{ K}} + \int_0^T \Delta_R C_V dT' + \Delta_f H_{\text{CaO}}^T + x\Delta_f H_{\text{TiO}_2}^T \\ &+ (1 - x - \delta)\Delta_f H_{\text{Mn}_3\text{O}_4}^T - (2 - 2x - 3\delta)\Delta_f H_{\text{MnO}}^T. \end{aligned} \quad (9)$$

Equating these expressions yields an approximate relation for the integrated heat capacity:

$$\begin{aligned} \int_0^T C_p dT' &\approx -\Delta_f H^{0\text{ K}} + \Delta_R H^{0\text{ K}} + \int_0^T \Delta_R C_V dT' \\ &+ \Delta_f H_{\text{CaO}}^T + x\Delta_f H_{\text{TiO}_2}^T + (1 - x - \delta)\Delta_f H_{\text{Mn}_3\text{O}_4}^T \\ &- (2 - 2x - 3\delta)\Delta_f H_{\text{MnO}}^T. \end{aligned} \quad (10)$$

Following Gastaldi et al. [38], tabulated thermochemical data for the binary oxides were used to improve the accuracy of the calculated thermodynamic properties. The thermochemical data for CaO and TiO_2 are taken from the NIST-JANAF tables, while values for Mn_3O_4 and MnO are obtained from other studies [47,48]. Each formation enthalpy term is defined by

$$\Delta_f H_X^T = \Delta_f H_X^0 + \int_0^T C_{p,X} dT, \quad (11)$$

where $X \in (\text{CaO}, \text{Mn}_3\text{O}_4, \text{MnO}, \text{TiO}_2)$. Substituting these expressions into the previous equation allows the compound's heat capacity to be simplified to

$$C_p(T) \approx \Delta_R C_V(T) + C_{p,\text{CaO}}(T) + (1-x-\delta)C_{p,\text{Mn}_3\text{O}_4}(T) + xC_{p,\text{TiO}_2}(T) - (2-2x-3\delta)C_{p,\text{MnO}}(T). \quad (12)$$

The heat capacity, $C_p(T)$, is then fitted to a sum of power functions to enable comparisons with data from FactSage:

$$C_p(T) = k_0 + k_1 T^{-0.5} + k_2 T^{-3} + k_3 T^{-2}. \quad (13)$$

3. Results and discussion

3.1. Thermodynamic properties and structural stability

Experimental thermodynamic data for both doped and oxygen-deficient CaMnO_3 systems are scarce, which limits direct validation of the calculated properties. However, experimental data are available for pristine CaMnO_3 and are therefore used as a benchmark for evaluating the present methodology. As shown in Fig. 2, the calculated heat capacity shows only minor deviations from values reported in FactSage and by Bakken et al. [7,8,46]. The calculated formation enthalpy also shows good agreement with experimental measurements, with deviations within the typical $\pm 10\%$ uncertainty reported in previous thermodynamic assessments.

A discrepancy is observed in the entropy obtained from the present calculations, $S = 84.73 \text{ J mol}^{-1} \text{ K}^{-1}$, compared to the value, $S = 96.32 \text{ J mol}^{-1} \text{ K}^{-1}$, reported by Gastaldi et al. [38]. Although notable given the similarity of the underlying methodology, this difference is relatively small and likely originate from the use of CHGNet instead of DFT. The calculated formation enthalpy shows closer agreement with the values reported in the same work [38], yielding $\Delta H_f = -1.192 \times 10^3 \text{ kJ mol}^{-1}$ compared to $\Delta H_f = -1.189 \times 10^3 \text{ kJ mol}^{-1}$, which shows that the

methodology employed here fares well compared with DFT calculations.

For doped systems, experimental thermodynamic data are largely unavailable. Values from the FactSage aiMP database were used for comparison [67]. As shown in Fig. 3, the formation enthalpies obtained in the present work are in good agreement with those reported in the database, supporting the internal consistency of the computational approach. Although the entropy comparison does not show the same level of agreement, the calculated entropy increases with the number of oxygen vacancies while the FactSage data shows the opposite trend.

This difference likely reflects the distinct methods used to estimate entropy. In aiMP, entropy at 298.15 K is predicted using a machine-learning model trained on thermodynamic data for a broad range of compounds [67]. By contrast, the present approach explicitly includes structure-specific vibrational and configurational contributions for each oxygen-deficient composition. The aiMP values therefore provide a useful reference, but the entropy comparison should be interpreted with caution because the two approaches do not represent vacancy-dependent entropy in the same way.

The influence of doping is illustrated in Fig. 4 using Ti substitution as a representative example, see figures S2-S12 in the SI for the other dopants investigated in this work. Doping has a clear effect on the formation enthalpy of the perovskite phase. The temperature dependence of the formation enthalpy is relatively weak, indicating that evaluating it at a single reference temperature (e.g., 298.15 K) is sufficient for identifying thermodynamic trends. Furthermore, entropy changes are small compared to enthalpy changes, meaning that enthalpy largely determines the thermodynamic trends. Consequently, formation enthalpy serves as a reliable metric for assessing the thermodynamic stability of doped CaMnO_3 .

The structural stability of doped CaMnO_3 was evaluated based on the formation enthalpy ΔH_f at 298.15 K for different dopants and substitution sites relative to pristine CaMnO_3 . As shown in Fig. 5, the effect of doping on the formation enthalpy varies significantly with the dopant element.

Several dopants, including Ce, La, Mo, Si, and Ti, reduce the formation enthalpy relative to pristine CaMnO_3 , indicating a stabilizing

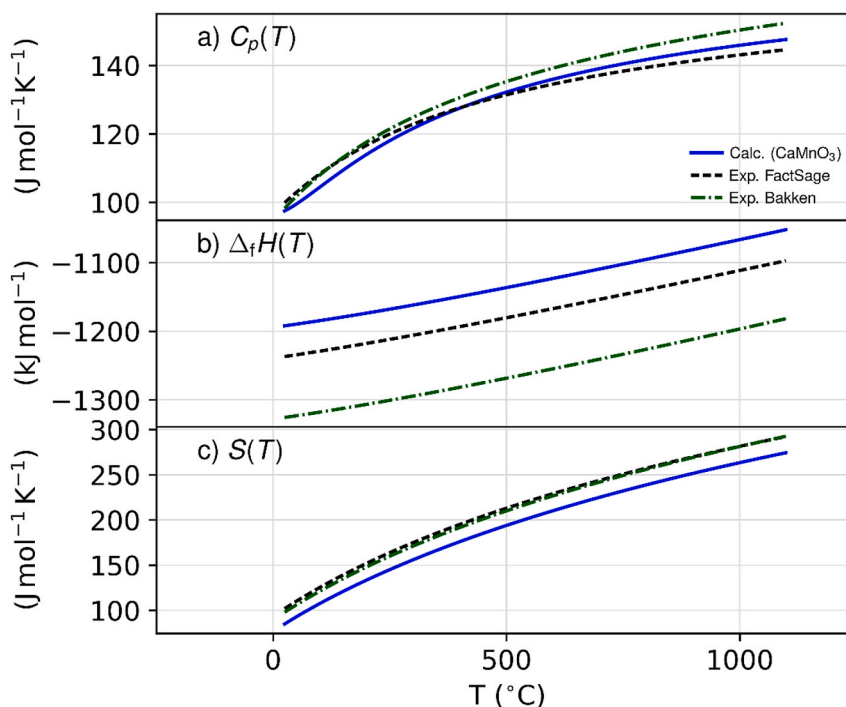


Fig. 2. Comparison of calculated thermodynamic properties of pristine CaMnO_3 with literature data. (a) Heat capacity, (b) formation enthalpy, and (c) entropy as functions of temperature. Calculated values are compared with thermodynamic data reported in the FactSage database and by Bakken et al. [8,46].

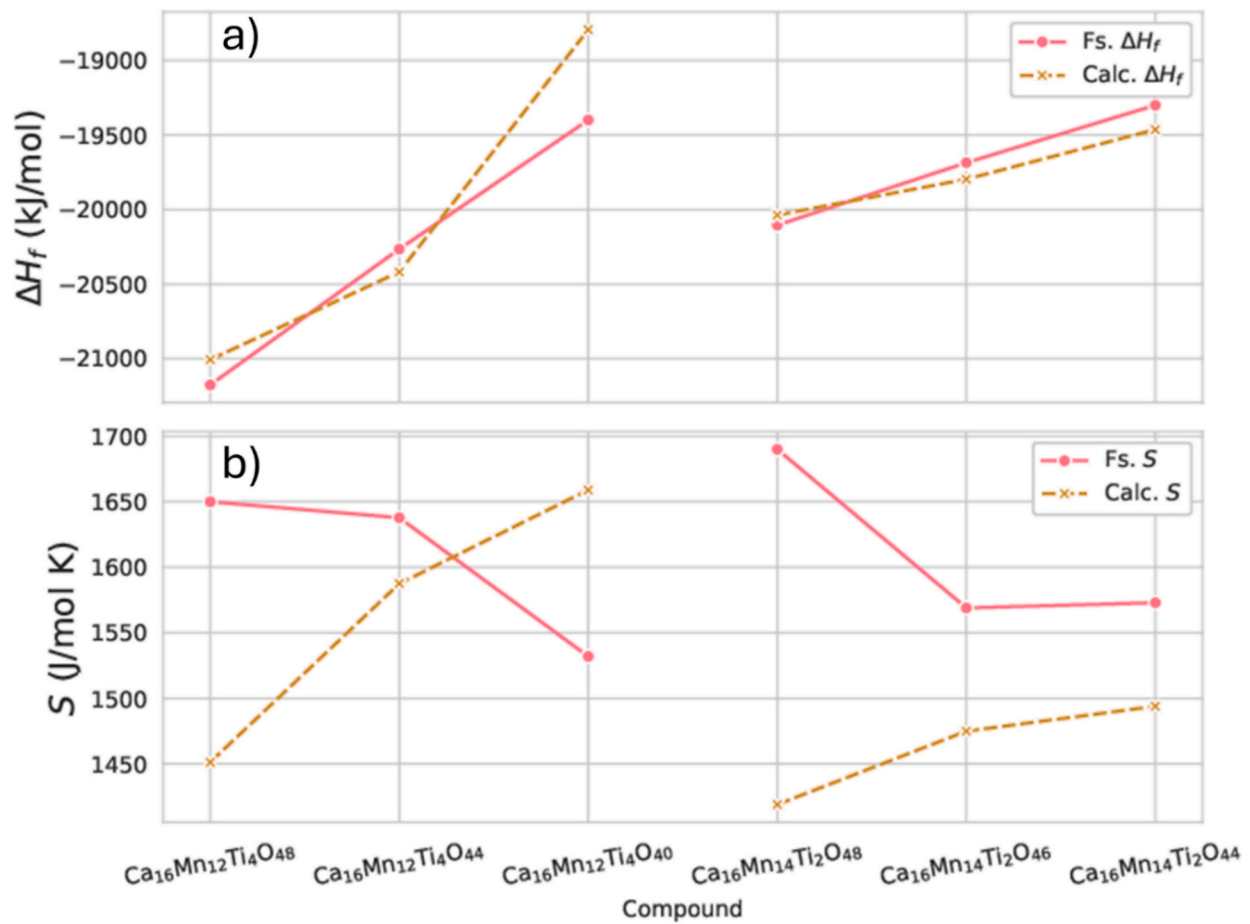


Fig. 3. Comparison of (a) formation enthalpy (ΔH_f) and (b) entropy (S) between data from FactSage (Fs.) and calculations (Calc.) performed in this work on $\text{Ca}_{16}\text{Mn}_{12}\text{Ti}_4\text{O}_{48-\delta}$ and $\text{Ca}_{16}\text{Mn}_{14}\text{Ti}_2\text{O}_{48-\delta}$.

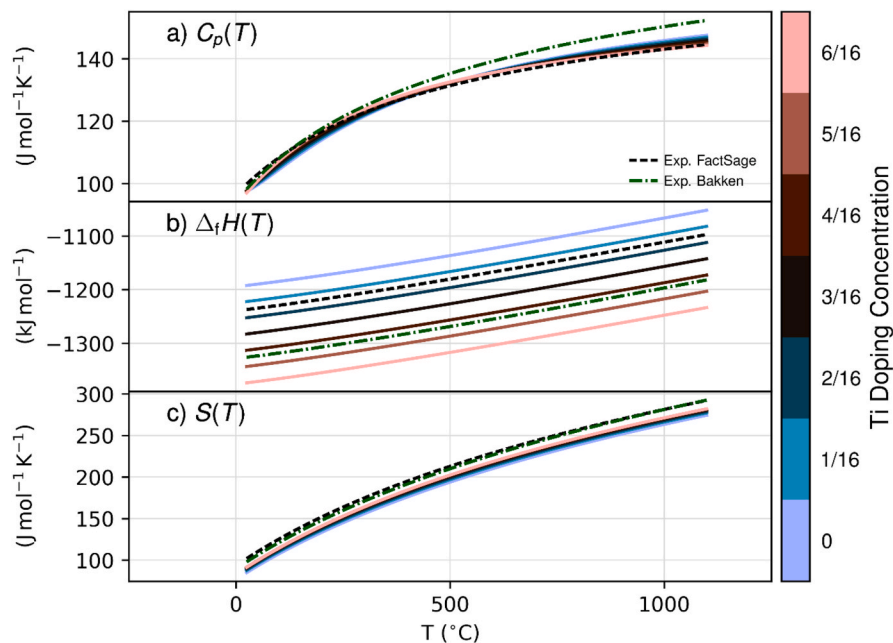


Fig. 4. Comparison of calculated thermodynamic properties of CaMnO_3 doped with Ti with literature data of pristine CaMnO_3 . (a) Heat capacity, (b) formation enthalpy, and (c) entropy as functions of temperature. Calculated values are compared with thermodynamic data reported in the FactSage database and in the work Bakken et al. [8,46].

effect. In contrast, Bi, Cr, and Cu increase the formation enthalpy. Other dopants, including Sr, Fe, and Mg, produce comparatively small changes

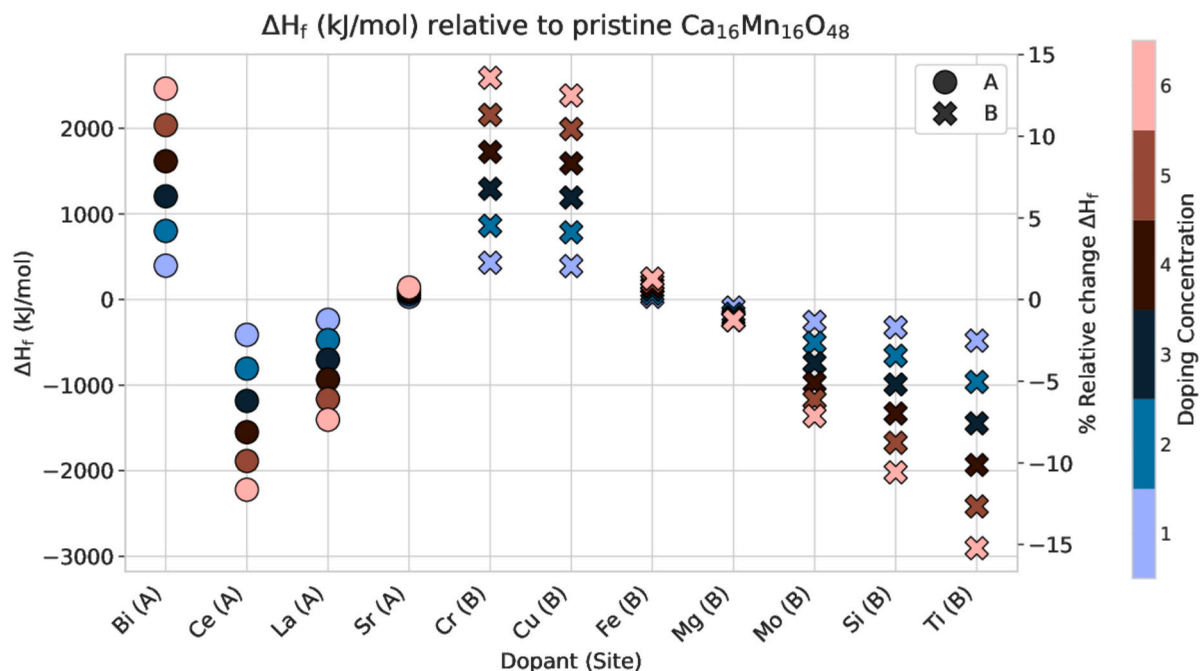


Fig. 5. Changes in relative formation enthalpies (ΔH_f) of doped CaMnO_3 .

in the formation enthalpy, indicating a limited effect on the overall stability of the perovskite lattice. These observations provide a basis for understanding oxygen vacancy formation and phase stability, which are examined in the following sections.

3.2. Configurational and vibrational insights

To further assess the thermodynamic behavior of the doped systems, both configurational and vibrational contributions to the heat capacity were examined using Ti-doped CaMnO_3 as a representative example, see figures S13–S23 in the SI for the other dopants investigated in this work.

The configurational contribution for fully oxidized compositions ($\delta = 0$) is shown in Fig. 6. The configurational heat capacity, C_V^{conf} , exhibits pronounced peaks as a function of temperature, which are characteristic of order-disorder transitions associated with cation rearrangement. The position and width of these peaks vary with Ti concentration, reflecting changes in configurational entropy and the degree of disorder in the system. In general, increasing Ti content shifts the peaks to higher temperatures and broadens of them, indicating modified interaction strengths and increased configurational complexity.

The effect of oxygen vacancies is illustrated in Fig. 7, where the corresponding quantities are shown for Ti-doped $\text{CaMnO}_{3-\delta}$, see figures S24–S49 in the SI for the other dopants and oxygen non-stoichiometry investigated in this work. In the presence of vacancies, the configurational heat capacity peaks become broader and less well-defined, consistent with increased disorder and reduced symmetry. These results indicate that oxygen vacancies enhance configurational disorder and increase the entropy contribution at elevated temperatures.

The vibrational contribution was analyzed through the phonon density of states (DOS), as shown in Fig. 8 for Ti-doped CaMnO_3 , see figures S50–S60 in the SI for the other dopants investigated in this work. No imaginary phonon frequencies are observed for the relaxed stoichiometric structures, indicating dynamical stability of the Ti-doped system. The corresponding vibrational heat capacity exhibits the expected temperature dependence, increasing smoothly with temperature and approaching the classical limit at high temperatures. Only minor variations are observed across different doping levels, reflecting the similar vibrational characteristics of the doped systems. This indicates that Ti substitution has a limited impact on the overall phonon spectrum

of CaMnO_3 .

As oxygen vacancies are introduced in the doped CaMnO_3 -system, the heat capacity is lowered, as expected since the number of atoms drop as the level of oxygen vacancies increase. Fig. 9 show the results for Ti-doped CaMnO_3 , see figures S61–S92 in the SI for the other dopants and non-stoichiometry investigated in this work. At the higher level of oxygen vacancies, imaginary modes appear, as shown in Fig. 9 as negative frequencies in the Phonon DOS. These imaginary modes could indicate an unstable structure or be artifacts of the calculations. However, note that the number of such frequencies is small and should only have a minor impact on the calculated heat capacity.

The results from calculations of the other dopants show similar results as that of the example with Ti. No imaginary phonon modes were found for the stoichiometric doped structures. Small imaginary contributions appeared in some oxygen-deficient structures, the highest fraction was 2.38% of the integrated Phonon DOS across the investigated systems. Their limited fraction of the total Phonon DOS suggests that their influence on the calculated vibrational thermodynamic properties is small, although the affected structures should be interpreted with caution. The figures of the calculated Phonon DOS and heat capacities for each doping concentration and for oxygen vacancies can be found in the SI. Together, the configurational and vibrational contributions provide a consistent description of the thermodynamic response of the system. While configurational effects contribute to entropy at elevated temperatures, particularly in the presence of oxygen vacancies, the formation enthalpy remains the dominant factor governing the stability trends discussed in the following sections.

3.3. Oxygen vacancy formation

Oxygen vacancies play a central role in the redox behavior of CaMnO_3 -based oxygen carriers, as they govern oxygen release and uptake during operation. The effects of oxygen vacancy formation were therefore evaluated in doped CaMnO_3 systems with varying dopant concentrations and vacancy levels. As is evident from Fig. 10, the calculated changes in formation enthalpy are consistent with the structural-stability results, in which dopants such as Ti and Ce stabilize the oxidized perovskite structure.

The formation enthalpy generally increases with increasing vacancy

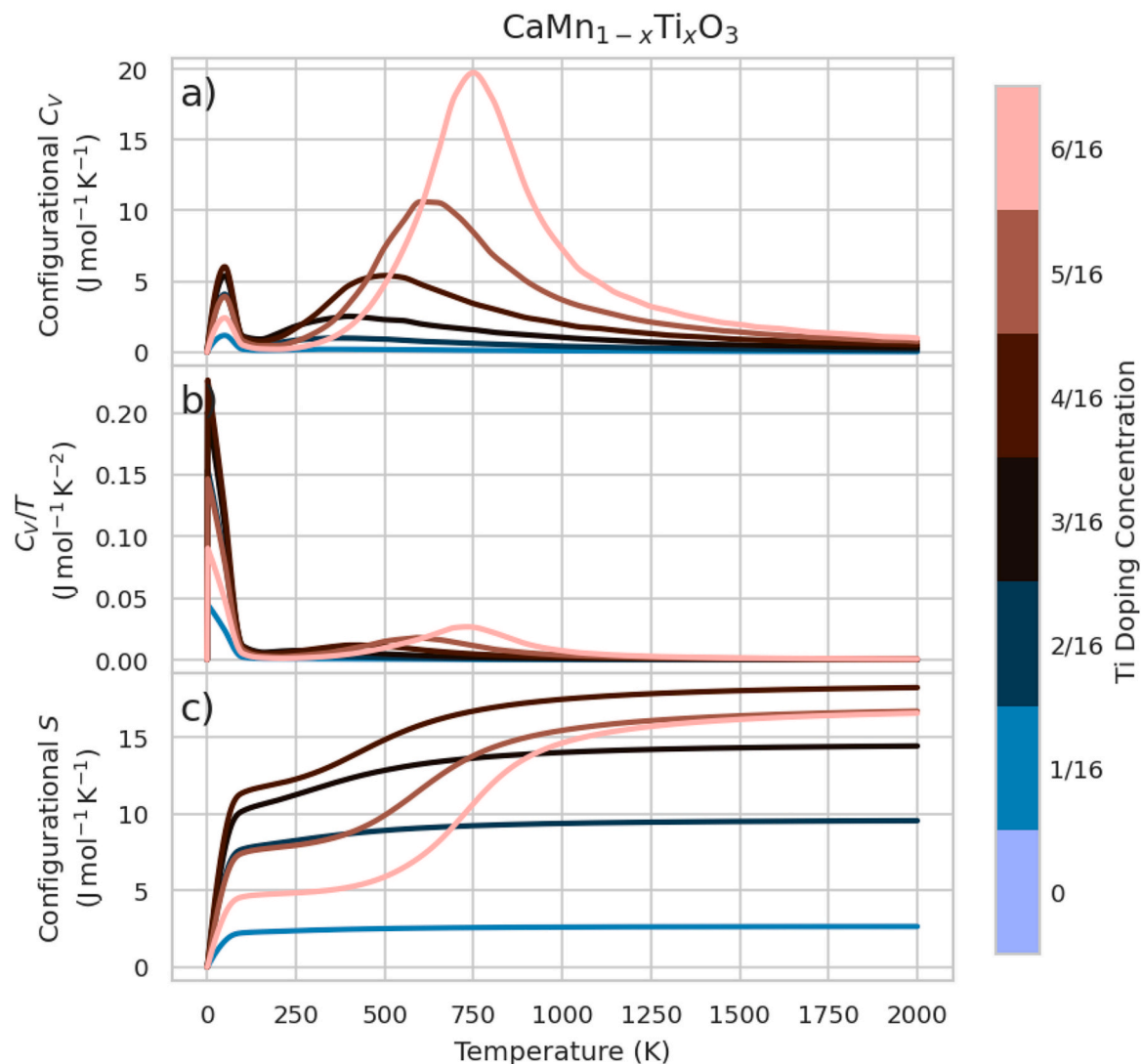


Fig. 6. Configurational thermodynamic properties for fully oxidized Ti-doped CaMnO_3 at different Ti substitution levels. a) Configurational heat capacity C_V^{conf} as a function of temperature, showing peaks associated with order–disorder transitions. b) C_V^{conf}/T . c) Configurational entropy, S_{conf} , calculated by integrating C_V^{conf}/T .

concentration, reflecting the energetic penalty associated with oxygen removal and the magnitude of this increase depends on both the dopant and its concentration.

Among the A-site dopants, the enthalpy increase per added vacancy is smallest for Sr, while Cu, Fe, and Mg show comparatively small increases among the B-site dopants. In contrast, larger increases are observed for Ce on the A-site and for Mo and Ti on the B-site.

The effect of doping on oxygen-vacancy formation may also involve changes in the oxidation states of Mn and the dopant. CHGNet provides energies for the modeled atomic configurations, but formal oxidation states and specific charge-compensation mechanisms were not determined explicitly. Therefore, no specific charge-compensation mechanism is assigned.

Overall, the results demonstrate a trade-off between the stability of the oxidized structure and its ability to accommodate oxygen vacancies. Several dopants associated with a smaller vacancy-related enthalpy increase also destabilize the perovskite structure, whereas Ti and Ce stabilize the oxidized structure but result in a larger enthalpy penalty upon oxygen removal. Sr and Fe provide a comparatively favorable balance between these properties. No single linear trend was observed across all compositions, indicating that the effect of successive vacancies also depends on the local dopant and vacancy arrangement.

3.4. Phase stability of doped $\text{CaMnO}_{3-\delta}$

The calculated formation enthalpies, entropies, and heat capacities were combined to generate temperature-dependent Gibbs energy descriptions for the doped phases, which were subsequently implemented in FactSage for equilibrium calculations. This included constructing equilibrium phase diagrams for doped $\text{CaMnO}_{3-\delta}$ to evaluate the thermodynamic stability of oxygen-deficient perovskite phases as a function of temperature and oxygen partial pressure ($p\text{O}_2$). These calculations were performed using the FactPS and FToxid databases [46]. The phase diagrams also provide a thermodynamic indication of redox reversibility. Oxygen-deficient perovskite phases that return to the fully oxidized phase with increasing oxygen partial pressure are thermodynamically capable of reoxidation under the investigated conditions. The equilibrium calculations do not establish whether the modeled substitutions can be achieved during synthesis, nor do they describe oxygen-exchange kinetics or structural degradation during repeated cycling. These aspects require experimental investigation.

Dopants such as La, Cr, Cu, Bi, and Mg were predicted to be thermodynamically unstable or stable only within narrow temperature and oxygen partial pressure ranges. Consequently, the corresponding phase diagrams are not shown here, the phase diagrams of Ce, Fe, La, Mo, Sr, Ti

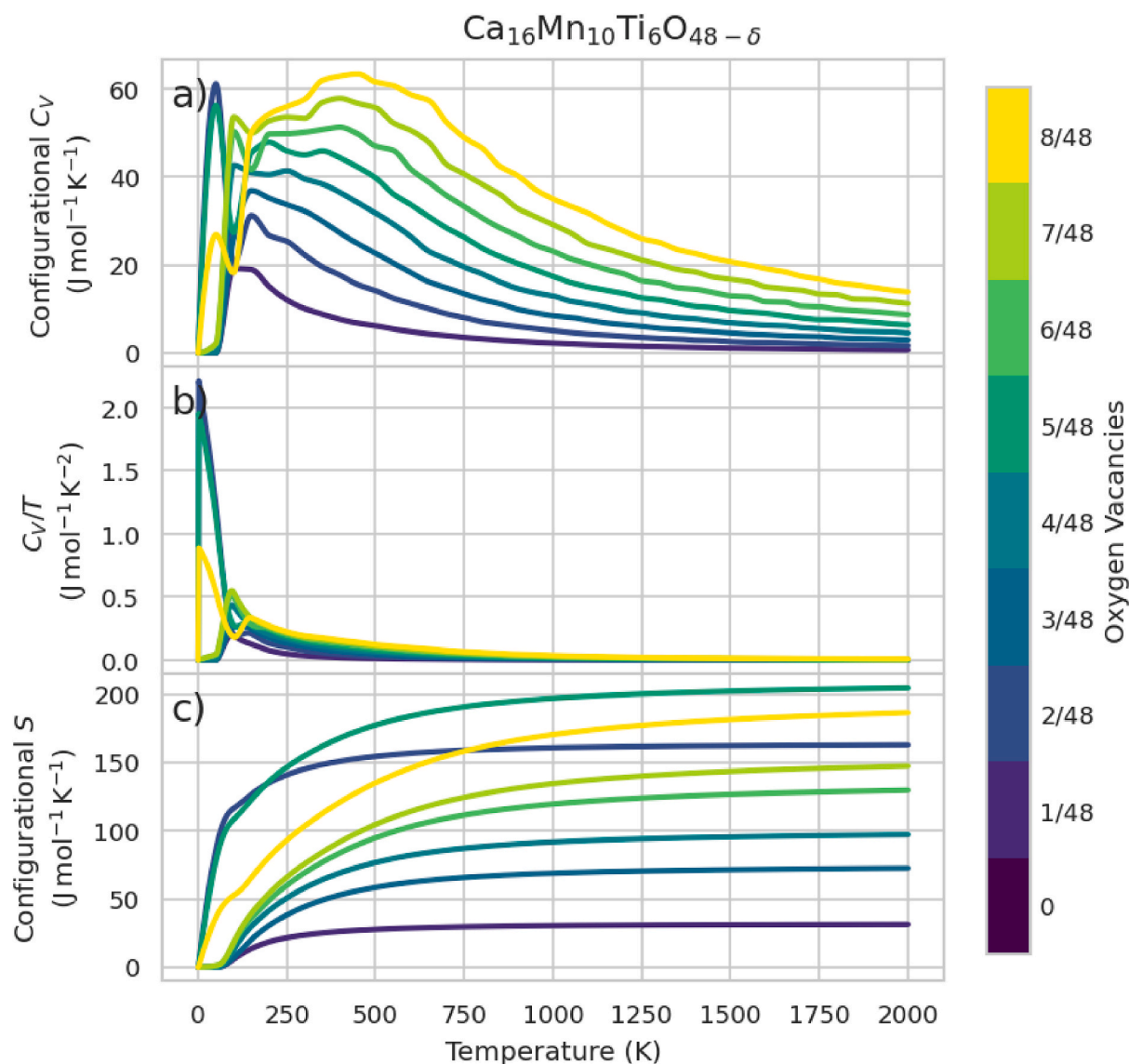


Fig. 7. Configurational thermodynamic properties for Ti-doped $\text{CaMnO}_{3-\delta}$ at different levels of oxygen vacancies. a) Configurational heat capacity, C_V^{conf} , as a function of temperature, showing peaks associated with order–disorder transitions. b) C_V^{conf}/T . c) Configurational entropy, S_{conf} , calculated by integrating C_V^{conf}/T .

can be found in the SI, [figures S93–S98](#). In addition, Si-doped systems were excluded due to computational difficulties associated with oxygen vacancy configurations, as discussed previously.

For all considered dopants (Fe, Sr, Ti, and Ce), the stoichiometric perovskite phase is stable under oxidizing conditions, i.e., low temperatures (~ 300 K) and high oxygen partial pressures ($p\text{O}_2 \approx 1$), see [Fig. 11](#) and [Fig. 12](#). With increasing temperature and decreasing $p\text{O}_2$, oxygen vacancy formation becomes thermodynamically favorable, leading to the stabilization of oxygen-deficient $\text{CaMnO}_{3-\delta}$ phases. This general behavior is consistent with the expected redox response of CaMnO_3 -based materials and supports their applicability in high-temperature environments such as CLC.

The nature of the reduction process, and especially the extent, differ significantly between dopants. Fe- and Sr-substituted systems exhibit progressive reduction across a broad range of temperatures and oxygen partial pressures while maintaining the perovskite structure. In particular, Fe-doped $\text{CaMnO}_{3-\delta}$ shows stepwise reduction through intermediate oxygen-deficient phases, while Sr-doped $\text{CaMnO}_{3-\delta}$ displays a similar behavior but with enhanced resistance to decomposition as it only occurs under strongly reducing conditions at very high temperatures (~ 1700 K). These characteristics indicate that both Fe and Sr

substitutions facilitate the formation of oxygen vacancies while preserving structural integrity, making them well-suited for redox cycling.

Ti- and Ce-doped systems exhibit a stronger preference for the fully oxidized perovskite phase. For Ti substitution, the onset of reduction shifts to higher temperatures and lower oxygen partial pressures than for Fe and Sr, indicating that oxygen vacancy formation is less favorable. This trend is even more pronounced for Ce doping, where the oxidized phase remains stable over a wider range of conditions. As a result, both Ti- and Ce-doped $\text{CaMnO}_{3-\delta}$ require more reducing environments to form oxygen vacancies, reflecting enhanced stabilization of the oxygen sublattice.

This distinction highlights a trade-off between reducibility and structural stability. While Fe and Sr promote oxygen vacancy formation and enable redox activity under moderate conditions, Ti and Ce increase resistance to reduction, thereby offering improved structural robustness during prolonged redox cycling. Consequently, the choice of dopant depends on the desired balance between oxygen release and long-term phase stability.

Overall, the phase stability analysis reveals clear differences in the redox behavior of the investigated dopants. Fe- and Sr-substituted systems exhibit broad stability regions for oxygen-deficient perovskite

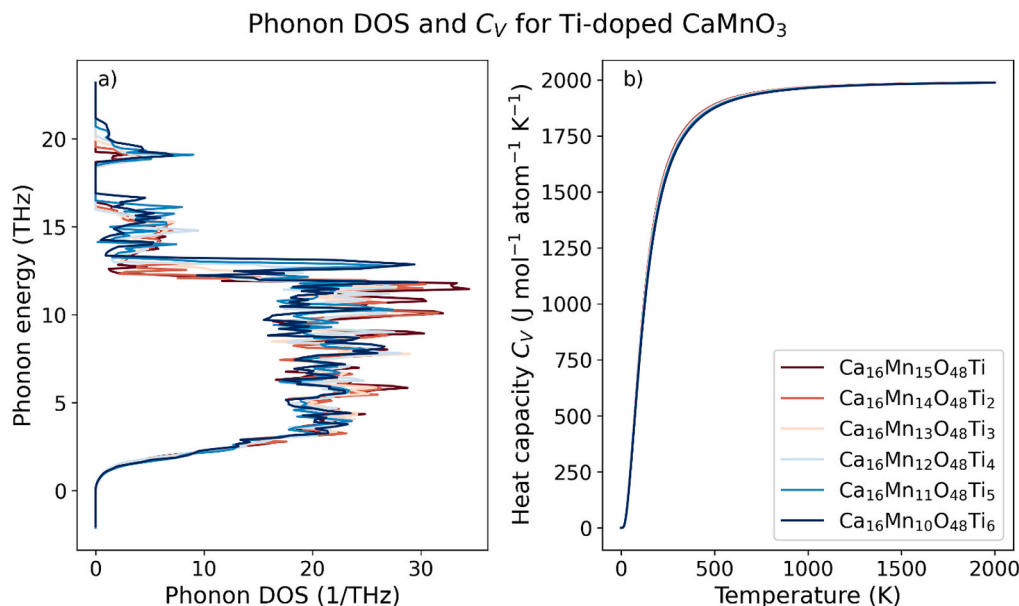


Fig. 8. a) Phonon density of states (DOS) and b) corresponding heat capacity C_V for Ti-doped CaMnO_3 ; the heat capacity has been scaled to match $\text{CaMn}_{1-x}\text{O}_3\text{Ti}_x$. The DOS reflects the distribution of vibrational modes that contribute to the thermal response, while the heat capacity illustrates the resulting temperature-dependent vibrational contribution to the thermodynamic properties.

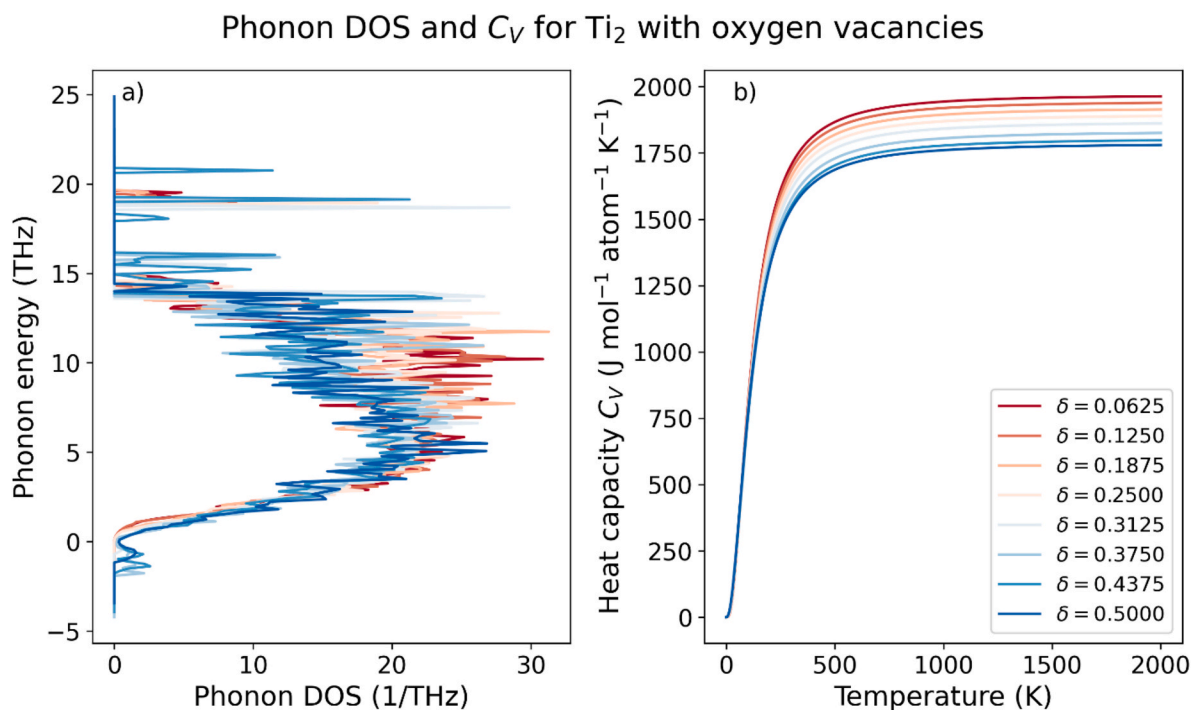


Fig. 9. a) Phonon density of states (DOS) and b) corresponding heat capacity C_V for Ti_2 with oxygen vacancies; the heat capacity has been scaled to match $\text{Ca}_{16}\text{Mn}_{14}\text{O}_{3-\delta}\text{Ti}_2$. The DOS reflects the distribution of vibrational modes that contribute to the thermal response, while the heat capacity illustrates the resulting temperature-dependent vibrational contribution to the thermodynamic properties.

phases, indicating that oxygen vacancies can form without destabilizing the lattice. In contrast, Ti and Ce substitution stabilize the fully oxidized phase and shift reduction to more extreme conditions. These results show that only a subset of dopants simultaneously supports structural stability and reversible reduction, both of which are required for oxygen-carrier applications.

3.5. Implications for CLC applications

The performance of oxygen carrier materials in CLC depends on their thermodynamic stability, oxygen release behavior, and ability to accommodate oxygen vacancies during redox cycling. An ideal oxygen carrier should exhibit sufficient structural stability to withstand repeated reduction–oxidation cycles while allowing oxygen to be released and reincorporated under realistic operating conditions.

The results presented above demonstrate that dopant substitution

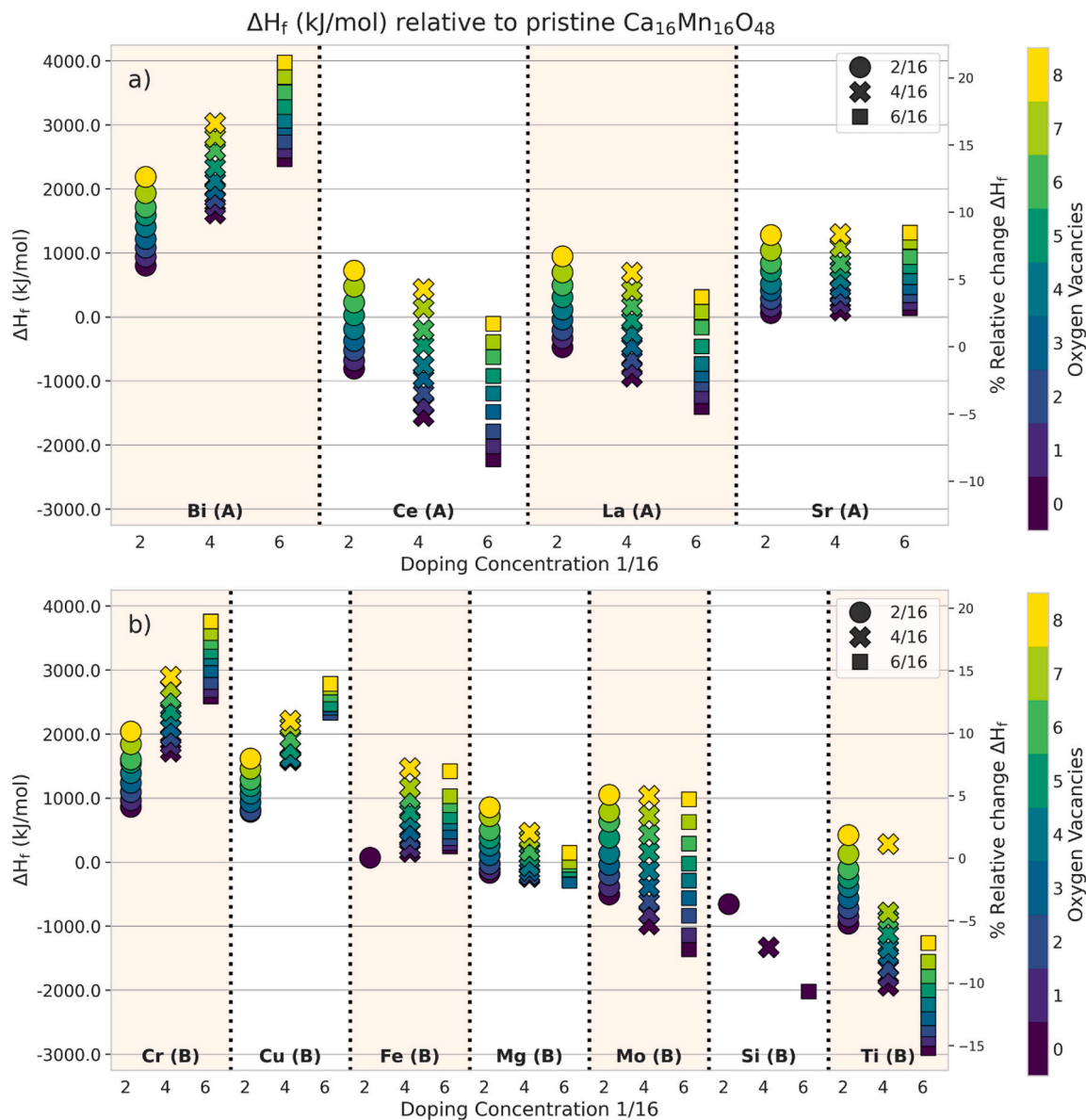


Fig. 10. Changes in relative formation enthalpies ($\Delta_f H^{298.15\text{K}}$) of CaMnO_3 with a) doped A-site and b) doped B-site.

significantly influences both the stability and vacancy formation behavior of CaMnO_3 , where the results are summarized in Table 2. Dopants such as Ce and Ti stabilize the perovskite structure by lowering the formation enthalpy, which may improve structural robustness during long-term redox cycling. These dopants also tend to increase the energetic cost associated with oxygen vacancy formation, which may limit the reducibility of the material.

Dopants such as Sr and Fe have a comparatively small effect on the formation enthalpy while facilitating the formation of oxygen vacancies. This behavior indicates that these dopants could enhance the redox activity of CaMnO_3 by enabling oxygen to be removed and reincorporated more readily. These characteristics are desirable for oxygen carrier materials operating under the high-temperature and variable oxygen partial pressure conditions typical of chemical-looping systems.

The phase stability analysis further supports these observations, as Sr- and Fe-doped CaMnO_3 exhibit stable perovskite phases through a wide range of temperatures and oxygen partial pressures. This indicates that these compositions provide a favorable balance between structural stability and oxygen reducibility. The oxygen-deficient compositions appearing in the phase diagrams provide a thermodynamic indication of

the accessible oxygen-release capacity, although the practical oxygen-transfer capacity also depends on reaction kinetics and cycling behavior. Oxygen-migration barriers and ionic conductivity were not calculated, and vacancy related enthalpy differences should therefore not be interpreted as a direct measure of oxygen mobility.

It is evident that dopant selection plays a critical role in tuning the thermodynamic properties of CaMnO_3 -based oxygen carriers. Dopants that facilitate oxygen vacancy formation while maintaining structural stability, such as Sr and Fe, are particularly promising for chemical-looping applications. These findings provide guidance for the design and optimization of perovskite oxygen carriers by balancing oxygen reducibility and phase stability. Future studies could investigate whether combinations of stability- and vacancy-promoting dopants provide a better balance between phase stability and reducibility. Although the calculated thermodynamic properties were benchmarked against available reference data, experimental validation would be valuable for confirming the predicted trends.

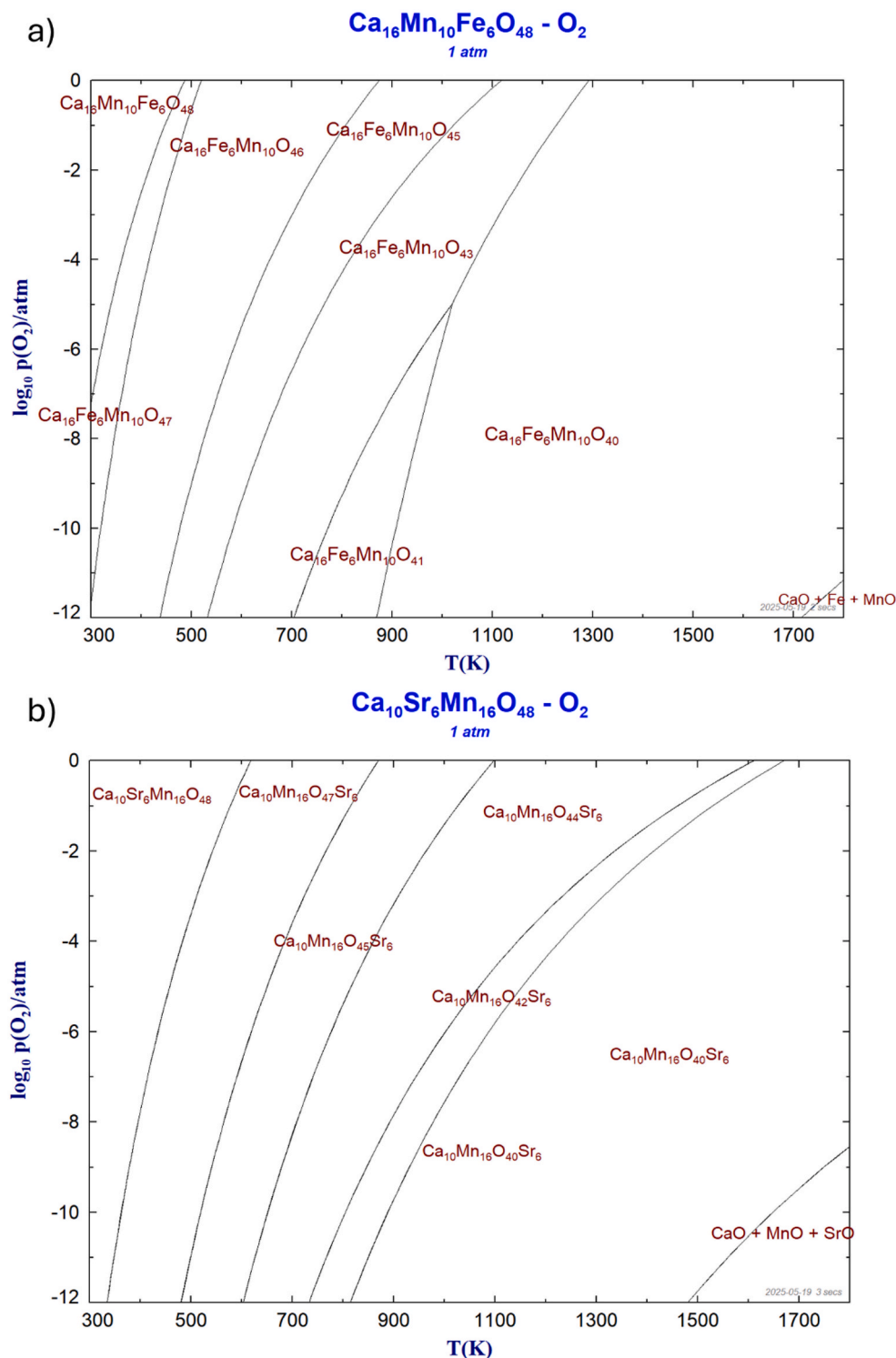


Fig. 11. Phase diagram of a) Fe and b) Sr doping of CaMnO_3 .

4. Conclusions

In this work, the thermodynamic properties and phase stability of doped $\text{CaMnO}_{3-\delta}$ were investigated using a computational framework combining machine-learning interatomic potentials, CEs, and thermodynamic modeling. The approach enables efficient exploration of dopant substitution and oxygen vacancy formation across a wide configurational space while retaining consistency with experimental reference data.

The results show that dopant substitution significantly affects the stability of the CaMnO_3 perovskite structure. Dopants such as Ce, Ti, La, Si, and Mo reduce the formation enthalpy and therefore stabilize the structure, whereas Bi, Cr, and Cu tend to destabilize the system. Sr, Fe, and Mg produce comparatively small changes in formation enthalpy. These enthalpy trends must be considered together with the phase-equilibrium results when assessing stability. For the investigated Mg concentrations, the equilibrium calculations favor heavily oxygen-deficient structures, while the fully oxygenated structures do not

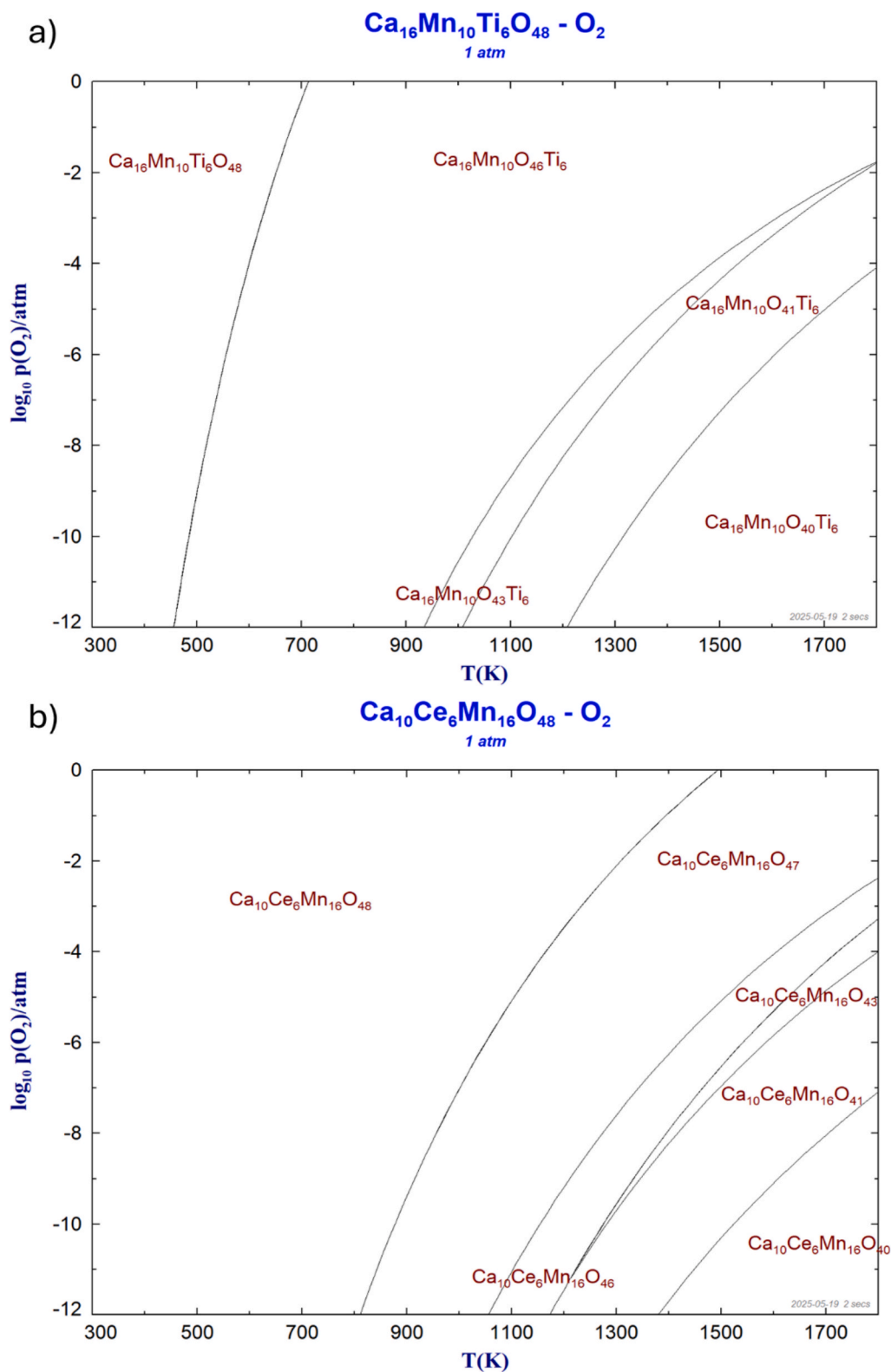


Fig. 12. Phase diagram of a) Ti and b) Ce doping of CaMnO_3 .

appear as stable phases within the investigated conditions.

The formation of oxygen vacancies depends strongly on which dopant is introduced. Sr- and Fe-doped CaMnO_3 show only a small increase in formation enthalpy when a vacancy is created, indicating that these systems readily accommodate oxygen vacancies. This suggests that such dopants improve the redox behavior of CaMnO_3 -based oxygen

carriers. Phase stability analysis further shows that several doped compositions remain stable over a wide range of temperatures and oxygen partial pressures relevant for CLC. In particular, the Sr- and Fe-doped systems provide a good balance, ensuring that the structure remains stable while still allowing oxygen vacancy formation. Ti- and Ce-doped systems, by comparison, exhibit enhanced phase stability but

Table 2

Summary of the calculated effects of A- and B-site substitution on the formation enthalpy, thermodynamic accommodation of oxygen vacancies, and phase stability of $\text{CaMnO}_{3-\delta}$.

Dopant	Site	$\Delta_f H$ effect	Vacancy accommodation	Phase stability	Experimental support
Ce	A	↓	Unfavorable	Oxidized	Reported [57]
Sr	A	≈	Favorable	Broad	Reported, CLOU studied [55]
La	A	↓	Intermediate	Restricted	Reported [62]
Bi	A	↑	Unfavorable	Restricted	Reported [59]
Ti	B	↓	Unfavorable	Oxidized	Reported, CLOU studied [11,12]
Fe	B	≈	Favorable	Broad	Reported, CLOU studied [13]
Si	B	↓*	n.d.	n.d.	Reported [61]
Cr	B	↑	Intermediate	Restricted	Reported [58]
Cu	B	↑	Favorable	Restricted	Reported [60]
Mo	B	↓	Unfavorable	Restricted	Reported [63]
Mg	B	≈	Favorable	Unstable	Mg-containing materials studied in CLC/CLOU, B-site incorporation unestablished [13]

Notation: ↓, ≈, and ↑ indicate decreased, limited change, and increased formation enthalpy relative to pristine CaMnO_3 , respectively. “Broad” denotes stability of oxygen-deficient perovskite phases over a comparatively wide range of conditions; “Oxidized” denotes preferential stability of the fully oxidized phase; and “Restricted” denotes stability only within limited temperature- $p\text{O}_2$ regions. “n.d.” means not determined. The experimental support column provide reference to if a phase has been experimentally reported in literature, and if CLC/CLOU experiments have been made with said phase. Mg is a special subject here where it has been extensively studied as a dopant in CLC/CLOU experiments, but never have been shown to incorporate into the B-site.

* Si-doped systems were excluded because a stable vacancy cluster-expansion model could not be obtained.

require more reducing conditions to form oxygen vacancies, indicating a trade-off between stability and reducibility, that may be advantageous in applications requiring complete fuel conversion.

Overall, the results highlight the critical role of dopant selection in tuning the thermodynamic behavior of CaMnO_3 -based oxygen carriers. These findings provide guidance for the design and optimization of perovskite materials with improved redox properties for CLC and related high-temperature energy applications.

CRediT authorship contribution statement

Jonatan Gastaldi: Writing – original draft, Visualization, Formal analysis, Conceptualization. **Alfred Juhlin Onbeck:** Writing – review & editing, Visualization, Investigation, Formal analysis, Conceptualization. **Joakim Brorsson:** Writing – review & editing, Conceptualization. **Anders Hellman:** Writing – review & editing, Supervision. **Tobias Mattisson:** Writing – review & editing, Supervision.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at <https://doi.org/10.1016/j.matdes.2026.117217>.

Data availability

Data will be made available on request.

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